Nanoengineered Core-Shell Structures Using Tubile Halloysite Clay

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ABSTRACT

Halloysite nanotubes are a versatile nanomaterial that can be used in a wide variety of applications. They have a unique structure which could be described as a flat material that consists of silica on one side and alumina on the other; this structure is rolled up in a way naturally forming an internal 10-15 nm lumen and interlayer spacing. This could lead to many potential applications for example incorporating halloysite as a template material or as a support structure. They are an inexpensive clay material that is available in large quantities (thousands of tons), so they may be practically used in industrial applications. In this work, they were used as a support structure for catalysts, gas sensors, as well as lithium sulfur batteries.

In catalysis it is essential to minimize aggregation of catalytic nanoparticles as aggregation leads to a reduction of surface area used for conducting chemical reactions. Support structures are used to minimize this aggregation. Halloysite nanotubes were used as a support structure to chemically attach two different catalytic metal nanoparticles: cobalt and ruthenium. There are a variety of techniques to synthesize catalytic nanoparticles onto/inside halloysite. To enhance inner-wall and lumen metal cluster formation for ruthenium, we intercalated the tube with furfuraldehyde and then converted it to tetradeutate ligands which have shown specific binding to Ru³⁺ ions from ethanol solution at elevated temperatures. One of the purposes of the ligands is to increase the amount of ruthenium loaded inside the halloysite. The other purpose is to firmly hold the
ruthenium inside the halloysite to prevent leakage of Ru. Metal particles of 2-5 nm diameters were formed both in the central lumen and in the interlayer spaces of the tube walls. This core-shell engineered catalyst was tested in hydrogenation of aromatics. Maximum turnover frequency (TOF) achieved was 17282 h⁻¹ in terms of hydrogen uptake per surface area of Ru-atoms. For halloysite-based ruthenium catalysts some metal leaching was observed after the 1st reaction cycle, which may be attributed to poorly retained nanoparticles located outside of the nanotubes, but these Ru-core-shell nanocatalysts were recycled up to ten times without loss of catalytic activity.

Halloysite was also used to load cobalt for catalytic purposes. Active cobalt mesocatalysts were prepared using four main methods: Wet impregnation of cobalt chloride into halloysite, adsorption of cobalt (II, III) oxide onto halloysite, and cobalt chloride linkage onto/into halloysite using azines as well as APTES. It turned out that the most efficient catalyst was the halloysite loaded with cobalt chloride using the azine acetone as a ligand with an R value (L/min x g(cat)) of three, which is higher than other previously made cobalt mesocatalysts which typically range from 0.9-2.9.

In addition to supporting metal catalytic nanoparticles, halloysite was used to load zirconia nanoparticles for gas sensor applications. We synthesized Y₂O₃-ZrO₂ on halloysite clay nanotubes, an example of an external metal oxide – internal ceramic core-shell system. This produced 5-10 nm diameter particles on the nanotubes. This system should limit the particle agglomeration at working temperatures of 500 ºC.

Halloysite nanotubes were also used as a nanoconfinement structure to load sulfur particles for increasing lithium-sulfur battery efficiency. The available nanoscale space in the lumen of halloysites nanotubes and between assembled halloysites clusters help
suppress the dissolution and migration of polysulfides in liquid electrolyte solution. The halloysite-sulfur cathode composite was incorporated into coin batteries, and the halloysite/sulfur composites successfully improve the cycling stability, retaining ~84% of the starting capacity for over 250 cycles.
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Author ___________________________

Date ____________________________
DEDICATION

This dissertation is dedicated to my parents who have encouraged and supported me every step of the way.
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CHAPTER 1

INTRODUCTION

Halloysite nanotubes are a versatile nanomaterial that can be used in a variety of different potential applications. Halloysite nanotubes are formed by 10-15 revolutions of kaolin aluminosilicate sheets and have diameters ranging between 50-60 nm, lumens in the range of 12-15 nm, and lengths within the 500-900 nm. It is an environmentally friendly, natural, and cheap tubule nanomaterial available in large quantities (thousands of tons). Halloysite surface is composed of SiO$_2$, and the tube’s interior is composed of Al$_2$O$_3$, which are oppositely (negative/positive) charged in the pH range of 3-9. Halloysite may be considered as an efficient, divalent, nano-adsorbent both for cations and anions. Halloysite can be modified and etched in order to produce a larger lumen for delivering a higher payload which can be useful in many different fields including drug delivery and corrosion mitigation. Nano-architectural modification of halloysite nanotubes includes modification of the outer surface, the inner lumen of halloysite, or a mixture of both according to the desired outcome. In this work, we used halloysite nanotubes as a support structure for catalytic nanoparticles, a confinement structure for lithium-sulfur batteries, as well as a template material for gas sensors.

For the goal of synthesizing nano-catalysts using halloysite nanotubes, protocols of similar work were modified accordingly. Previously, it has been proven that adsorption of metal ions on halloysite was used for synthesis of Fe, Ni, Pd, and Ag nanoparticles on
the tube surface, but catalysis was not tested. TiO$_2$ nanoparticles were bound to the nanotube surface though silane linkage. The first core-shell halloysite system consisting of silver nanorods and Cu-Ni nanoparticles was manufactured previously by Dr. Lvov and his former students in collaboration with NIST in Tsukuba. This system boosted the original exhaust gas catalytic efficiency at 400 °C by a factor of 50. However, the metal loading efficiency and the composite production yields were rather low (1 wt.%). There is no simple means of direct heavy metal ion penetration into the interlayer spacing of the aluminosilicate roll, and we have developed a special Schiff-base linker for this purpose. A potential intercalation can be confirmed with X-ray analysis by monitoring the 0.72-nm multilayer wall packing reflection. Halloysite tubes have a surface area of ca. 60 m$^2$/g, but enabling access to the interlayer space increases its adsorption capacity to 600-700 m$^2$/g, thus providing a larger space for formation of metal particles for efficient catalysis and allowing for loading of ten wt.% of metals. All our newly produced Ru and Co halloysite core-shell mesocatalysts have shown an essential increase in catalytic efficiency as compared with commercial Ru-, and Co- catalysts. These novel mesocatalysts were produced and tested in collaboration with the Russian State University for Oil and Gas, Moscow. Using similar, modified protocols, Y$_2$O$_3$-ZrO$_2$/halloysite core- clay shell systems were also prepared for future applications in gas sensors.

Another use of halloysite nanotubes is as a nanoconfinement structure for increasing efficiency of lithium sulfur batteries. Efficient and cost-effective battery systems are crucial to store and utilize clean and abundant alternative energy sources. Among different types of batteries, rechargeable lithium-sulfur batteries (Li-S) show
promising potential as a mobile energy supply because of their high energy storage capacity (a theoretical specific capacity of 1,673 mAh/g, or around five times that of existing lithium-ion batteries, LIBs). However, current Li-S batteries still suffer great technical challenges on their sulfur cathode, namely low conductivity, parasitic shuttle reactions induced by dissolution of lithium polysulfides \((\text{Li}_2\text{S}_x, 4 \leq x \leq 8)\), large volumetric expansion (~80%) upon lithiation, and self-discharge issues. The hollow nanotube of halloysites provides an appropriate size of lumen to confine sulfur nanoparticles while not too small to significantly impede the diffusion of \(\text{Li}^+\) ions. Their naturally assembled nanotube clusters create many nanoscale voids, which could divide electrolyte and solid-electrolyte interphases into isolated domains and add extra diffusion barrier to suppress the dissolution and migration of polysulfides when used in the cathode of Li-S batteries. Using halloysite in lithium sulfur batteries was performed in collaboration with Dr. Wang’s research group in the institute for micromanufacturing.

All these briefly describe developments are unified under our strategy of core-shell tubule clay nanosystems and will be described in details in this dissertation. The results of this dissertation are essentially a collection of publications which means this entire dissertation is a series of cooperative works, and I am grateful for the opportunity to collaborate with great scientists and with their help this work was accomplished.
CHAPTER 2

LITERATURE REVIEW

Our work is based on using halloysite clay nanotubes as template for design of metal-ceramic core-shell systems. The dissertation literature review was published in two book chapters with my co-authorship and cited in this chapter; I was the only graduate student so its content is used only in my dissertation.

2.1 Preview

2.1.1. Structural Characteristics of Halloysite

Halloysite is a natural inorganic silicate clay mineral with the formula $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4\cdot n\text{H}_2\text{O}$ ($n = 0, 2$), named after Belgian geologist Omalius d'Halloy who discovered the mineral. Berthier described the dominant form of the naturally occurring mineral, tubular halloysite, also known as the halloysite nanotube (HNT) [1]. This dioctahedral clay mineral has morphology of tubes with multilayer-walls, which was ascribed to the kaolin group. In contrast to other kaolin polytypes (like imogolite), halloysite is formed due to rolling of the kaolinite sheets in tubes with 0.5–2 μm length exposing silica containing a negative outer surface (tetrahedral silanol groups) and octahedral alumina-composed positive inner surface (lumen) with 10–30 nm diameters [2]. It also contains water molecules between the aluminosilicate layers (Figure 2-1, Figure 2-2).
The formation of the tubular structure is due to atomic-scaled stress in the unit layer originated from the mismatch in the larger tetrahedral sheet \((a = 5.02 \text{ Å}, b = 9.164 \text{ Å})\) and the smaller octahedral sheet \((a = 5.066 \text{ Å}, b = 8.655 \text{ Å})\) [3, 4]. The outer diameter of halloysite nanotubes is about 50-100 nm (depending on the clay deposit) with 15-20 aluminosilicate layers in the walls. The wall multilayer spacing varies from 1.0 to 0.7 nm depending on water content. When \(n = 2\) (the hydrated form of halloysite), one layer of water molecules is present between the multilayers, where the “10 Å” designation indicates the \(d_{001}\)-value of the layers. This form is named “halloysite-(10 Å)”. The dehydrated structure of halloysite (\(n = 0\)) may be obtained through the loss of the interlayer water molecules under mild heating and/or a vacuum environment and is called
“halloysite- (7 Å)” [5]. It is interesting to compare two types of clay nanotubes and carbon (CNT) (Table 2-1).

Table 2-1  Characteristics of Halloysite, Imogolite and Carbon Nanotubes [2]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>HNT</th>
<th>Imogolite</th>
<th>CNT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical formula</td>
<td>Al₂Si₃O₅(OH)₄</td>
<td>Al₂SiO₃(OH)₄</td>
<td>C</td>
</tr>
<tr>
<td>Length</td>
<td>0.5-2 μm</td>
<td>1-5 μm</td>
<td>1-5 μm</td>
</tr>
<tr>
<td>Outer diameter</td>
<td>50-100 nm</td>
<td>2-10 nm</td>
<td>2-10 nm</td>
</tr>
<tr>
<td>Inner diameter</td>
<td>10-30 nm</td>
<td>1-5 nm</td>
<td>1-3 nm</td>
</tr>
<tr>
<td>Biocompatibility</td>
<td>compatible</td>
<td>compatible</td>
<td>incompatible</td>
</tr>
<tr>
<td>Wettability</td>
<td>hydrophilic</td>
<td>hydrophilic</td>
<td>hydrophobic</td>
</tr>
<tr>
<td>Surface chemistry</td>
<td>outer SiO₂ inner Al(OH)₃</td>
<td>outer Al(OH)₃ inner SiO₂</td>
<td>Graphene planes on both sides</td>
</tr>
<tr>
<td>Surface charge at pH 3-9</td>
<td>Negative</td>
<td>Positive</td>
<td>Uncharged</td>
</tr>
<tr>
<td>Surface area, m²/g</td>
<td>60-150</td>
<td>300-400</td>
<td>15-250</td>
</tr>
</tbody>
</table>

According to Table 2-1, halloysite possesses a tubular porous structure from the meso (2–50 nm) to macro (~0.1 μm) sizes [2,6,7]. Due to the larger volume of its hydrophilic internal cavities, the lumens can be filled with chemicals and smaller nanoparticles. Besides, halloysite possesses different inside/outside chemistry (outer SiO₂, inner Al(OH)₃) with positive/negative charges of surfaces, which is a unique property allowing for its selective modification. In the past decade, natural halloysite having many advantages became a focus of many studies and patents leading to industrial applications. This is also supported by the low price and biocompatibility of this natural tubular clay mineral.
2.1.2. Occurrence of Tubular Halloysite

Halloysite is formed mainly from the wrapping of the 1:1 clay mineral layers driven by a mismatch in the oxygen-sharing tetrahedral and octahedral sheets in the 1:1 layer [3, 8]. The main geological occurrence of halloysite is in aluminosilicate rocks (gabbro, diabases, syenites, etc.), pedogenesis or hydrothermally altered ultramafic rocks, saprolites, soils, volcanic glass, and pumice [5, 9-11]. It is assumed that the formation of halloysite is related to Si-rich deposits. Halloysite was found to form in marine environments; they form on the seafloor due to hydro-thermal activity [12]. Also, neoformation of halloysite was described in the early stage of alteration of volcanic glass or rocks.

Natural halloysite often contains impurity phases and varies in morphology and porosity depending on deposits [14]. Generally, halloysite is accompanied by different types of associated minerals. The Dragon Mine halloysite deposit (Utah, USA), formed by the hydrothermal alteration of dolomite, is associated with kaolin, gibbsite, alunite, and quartz [15].

The crystallization conditions and geological occurrence of halloysite also have an effect on its morphology. Naturally occurring halloysite appears in varied morphologies, such as platy, spheroidal, and tubular. Generally, the latter is dominant. The crystallization from supersaturated solutions of volcanic glass and pumice lead to formation of nanoparticles with spheroidal morphology [5]; tubular morphology takes place when mineral is formed by the hydrothermal alteration of biotite [16], by the weathering of feldspar in granitic rocks [17], and by the topological alteration of platy kaolin [7, 13].
Halloysite is a low-cost clay mineral (few dollars per kilogram), but due to a specialized purification process the price could increase [18]. Its current global supply exceeds 40 thousands of tons per year, meaning that it could be widely used for industrial applications. Despite of the widespread occurrence of halloysite, the deposits of high purity halloysite are comparatively rare. The most well know are halloysite providers from USA, China, New Zealand/UK, Turkey, and Korea.

2.1.3. Physicochemical Properties

The specific surface area of halloysite is 60-70 m²/g, and it may be increased to 250-300 m²/g with alumina acid etching. Its external surface is composed of siloxane (Si-O-Si) groups while the inner lumen consists of aluminol (Al–OH) groups. Thus, halloysite is an aluminosilicate with Al–OH and Si–OH-edge groups. The wall multilayer spacing decreases from 1.0 to 0.7 nm during drying, and may be again widened with intercalation of small ions or organic compounds, like urea or furfural. The inner surface of halloysite can be selectively hydrophobized by sodium salts of carboxylic acids (sodium alkanoates) with different hydrophilic-lipophilic balance (C10 - C14). The resulting hybrid nanomaterials were found to absorb aliphatic and aromatic hydrocarbons from the gas and liquid phases. At the same time, the hydrophobization of the outer surface is carried out with compounds traditionally used for modification of hydroxyl silicon groups (organosilane grafting modification) [19].

It should be noted that halloysite undergoing ionization in aqueous media acquires opposite charges of inner and outer surfaces of tubes. This charge separation is preserved in water within a pH range from 3.0 to 8.5 and can be explained by comparing the negative and positive values for electrical ζ-potential of silica and alumina surfaces in
water. By inner adsorption of anionic compounds, the \( \zeta \)–potential of halloysite nanotubes can be changed from the initial \(-30\) mV to \(-80\) mV. Thus, tubular morphology and different inside/outside chemistry enables modification of halloysite nanotubes for its applications in different fields.

There are two main approaches for application of halloysite. The first one is as an additive to polymers to increase their mechanical stability and resistance to external impacts. The second one is caused by using the internal cavities of the mineral to introduce catalysts, corrosion inhibitors, flame retardants, drugs, etc. At the same time, the outer surface can be used to create compatibility of the nanotubes with media, providing good adhesivity or stable aqueous dispersibility. Halloysite formulations were previously suggested for different applications such as drug delivery and environmental remediation [20]. The reasonable biocompatibility of halloysite and its dispersibility in water, even in rather high concentrations leading to liquid crystalline phase formation were demonstrated. Thanks to its low toxicity, halloysite is a safe nanomaterial for biomedicine formulations which already found use in cosmetic and veterinary applications.

The most promising application of halloysite is a nanoscale support for the loading and sustained release of functional guests. The mesoporous structure of halloysite can be applied for immobilization of proteins such as serum albumin, catalase, laccase, glucose oxidase, lipase and hemoglobin [20, 21]. Halloysite also was used as a nanofiller for strengthening polymer/clay composites [22].

Halloysite is a prospective template for core-shell structured mesoporous nanocatalysts with tunable properties. Halloysite based catalysts are characterized by
high dispersion of active metal phase and enhanced temperature stability at 400-500°C. It provides surface availability of the supported metal nanoparticles for substrate molecules. The clay tubular structure with an empty lumen and different inside/outside chemistry allows for selective synthesis of new nanoarchitecturally designed hybrid materials with enhanced catalytic effects.

2.2. Synthesis of Core-Shell Metal-Ceramic Nanosystems

2.2.1. Selective Modification of Tubes (Inside/Outside)

Core-shell nanosystems have a core surrounded by another material, such as metal inside and ceramic outside or vice versa. In the case of halloysite based systems, there are several ways to produce core-shell structures (Figure 2-3). This work is a collaboration between our research group in Louisiana Tech and Russian Gubkin Oil and Gas University. Therefore, we give part of the results on this strategy in the literature review. Other results, published in three papers, will be presented in Chapters 4, 5, and 6 as our experimental results.

Figure 2-3: Schematic illustration of possible core-shell halloysite based structures [1]
The first type core-shell structure composes of empty halloysite tubes with metal-containing shell. The second type is halloysite shell with metal loaded inside the lumen. The third type is multishell structures with metal both outside and inside the tube, sandwiched by the halloysite wall [23]. Due to the tubular structure, these aluminosilicate nanotubes could be a great carrier for nanoparticles of various compositions starting from zero state metals to metal oxides, halides, and chalcogenides. All kinds of catalytic centers could be produced on halloysite. Selective modification of the lumen results in core-shell structures with isometric particles or elongated rods captured in a space of 10–30 nm with 0.5 – 1 µm length. Such nanosystems possess improved catalytic, optical and magnetic properties. The first core-shell structures of halloysite were made by simple reduction with thermal decomposition of metal salts. For more sophisticated systems, a multistage synthesis is needed with halloysite surface pretreatment and followed by formation of metal nano-structures. The resulted materials are usually hybrids of ceramic tubule base, with 3-8 % metals selectively bound with organic ligands.

One of the common ways to modify halloysite surface is silanization. Usually APTES ((3-aminopropyl)triethoxysilane) is used to attach nanoparticles to halloysite surface. Silanization is a non-selective modification technique, which can take place both on the outer surface and inside tubes.

In [19], it was shown that the modification mechanism is strongly affected by the thermal pretreatments. While heating, the physically adsorbed water evaporates from halloysite surface. Heating to 400 °C helps to achieve condensation reaction of hydrolyzed APTES directly with hydroxyl groups on the internal wall, at the edge, and at defects of the external surface. The outer surface of halloysite is composed of nonreactive
siloxane (Si-O-Si) groups and chemically active Si-OH groups which exist only at the defect areas and the edge of the tubes. Vacuum ultraviolet radiation could be used to pretreat the nanotubes to generate more Si-OH groups on the external surface of halloysite and make silanization of external surface [24]. It was shown that pretreatment of halloysite with 30% hydrogen peroxide helps to essentially increase Zeta-potential of APTES modified tubes.

Various ligands capable of capturing metal ions are used to form shells made of nanoparticles. In this case, silanization could be also the first step for the surface modification. In [25], imine functionalization of halloysite through introduction of aminosilanes followed by condensation with salicylaldehyde was applied for the immobilization of CuI on halloysite. Polydopamine was also used to synthesize AgPd/PDA-HNT nanocatalysts [26]. It is widely believed that oxygen containing functionalities, hydroxyl groups, are necessary for binding metal ions, which thus help to control the sizes and distributions of the formed metal nanoparticles on the PDA-halloysite. Polydimethyl diallylammonium chloride (PDDA), a water soluble quaternary ammonium polyelectrolyte, was used as a reducing agent and stabilizer for fabricating nanostructured metals on halloysite to form Co-Cu catalysts [27]. Polyaniline (PANI) could form a coat on halloysite surface and capture nanoparticles. Therefore, conjugated PANI with wide band gap inorganic semiconductors in halloysite composites are interesting for optical, electronic, photocatalytic and photoelectric conversion applications [28].

A modification of the internal alumina surface is needed to produce the second type core-shell structures. As the inner surface of halloysite is positively charged, the
loading of positive metal ions is limited due to electrostatic repulsion. Selective inner modification is possible with negatively charged EDTA agents. This modifier could be easily loaded into the tube changing the positive lumen charge to slightly negative. It was used to load iron salt inside the nanotube; further heating resulted in iron nanorods shelled with halloysite [29]. A general approach is to modify inner lumen of halloysite with anionic short tail amphiphiles [30].

The selective modification was based on the ability of small molecules to intercalate into halloysite lumen [31]. At first, hydrazine hydrate was loaded inside the tubes. The second stage of the synthesis was to obtain various organic ligands capable of capturing metal ions. Selective surface modification makes it possible to obtain stabilized metal clusters inside of the halloysite lumen.

2.2.2. Quantum Dots

Quantum dots of various compositions are easily obtained using halloysite as a template for their stabilization [43]. As chalcogenides are negatively charged, they could be loaded inside halloysite as it is shown in Figure 2-4a. CdSe was synthesized hydrothermally using N₃H₄Se complex and cadmium nitrate in the presence of halloysite, it was found that CdSe nanoparticles formed mostly inside the tube.

APTES was successfully applied to graft quantum dots onto halloysite surfaces. Depending on the synthesis procedure, the population and the size of particles could be controlled. CdZnS quantum dots were formed both inside and outside the nanotube carrier modified with aminosilane (Figure 2-4b) [44]. Multishell structures could be achieved using azine ligands to stabilize CdS particles synthesized in-situ both on the outer surface and inside nanotubes (Figure 2-4c). These structures show high catalytic
activity in photocatalytic processes [45]. As the systems are very stable and a well dispersed in water they could be easily modified to form more active semiconducting systems using co-catalysts (Pt, Ru, MoS$_2$) or metal ions (Bi, Cr, Zr) [46]. Zinc sulfide nanoparticles were successfully deposited on the surface of natural halloysite nanotubes to produce ZnS/HNTs nanocomposites by the sol-gel method [47]. These nanosystems were used as fluorescent labels for biocells [42].

![Figure 2-4: Quantum dots stabilized on halloysite: CdSe inside the tube (a), CdZnS outside and inside the tube modified with APTES (b), CdS multishell structure (c) [45]](image)

Halloysite and graphene quantum dots offered a new strategy in the fabrication of eco-friendly electrode materials for high performance supercapacitor applications [48]. An environmentally friendly QD-HNT nanocomposite was fabricated in the presence of APTES to provide more charge storage sites as well as to allow for the fast charge transport for supercapacitor application. Morphological and surface analytical results show that 5−10 nm particles are homogeneously distributed on the surface of halloysite via amide linkage. In another approach, carbon dots were loaded into halloysite as “bullets into the gun nozzle” [49].

For the synthesis of nitrogen-doped carbon dots on halloysite, tartaric acid as carbon source and ethylenediamine (EDA) as nitrogen source were used [44]. The
halloysite-QDs hybrid material showed excellent photoluminescent properties with broad-range white light emission [50].

2.2.3. Alumina/Silica Ratio Optimization

To manipulate properties of halloysite, etching is widely used. Acid treatment results in selective alumina removal and alkaline treatment leads to predominantly silica surface decomposition. These two basic methods are applied in order to regulate the Al/Si ratio and to increase the surface area of halloysite from 60 to 300 m$^2$/g.

Alkali treatment offers benefits such as thinning the walls and increasing the density of hydroxyl groups on the surface [51]. Sodium hydroxide is a commonly used alkali. Concentration of alkali, time of reaction, and temperature strongly affect surface properties of halloysite. In extreme conditions, halloysite nanotubes turn to porous material and may lose its mechanical and structural characteristics [52].

Acid etching enlarges halloysite lumen and makes it more available for loading of active agents. Also the charge of lumen could be changed with acid treatment. Sulfuric, hydrochloric, and acetic acids have been used to widen the lumen [51]. Alumina removal from the nanotubes takes place in three steps: diffusion of hydrogen ions into the inner lumen, chemical reaction with alumina on the tube inner wall, and transport of the reaction products out of the lumen [53]. Sulfuric acid causes the most profound and rapid change in halloysite surface properties. This technique is particularly suitable for the preparation of catalysts due to an increase in surface area available for attaching the metals. Building alumina on halloysite by reaction of outer surface with aluminum precursors is another way to vary Al/Si ratio, which is significant for industrial applications.
2.3. Nanocontainer Concept and Functional Polymer Composites

2.3.1. Anticorrosion and Flame Retardant Composites

Doping 5% wt. of halloysite nanotubes into paint coatings provided sustained release of anticorrosion agents, resulting in longer term metal protection as well as 50-100% increase in the coating strength and adhesivity. Such enhanced coating is especially important for operations in extreme conditions (Figure 2-5). Comparative tests have shown an advantage of this coating technology for sea-water operations as compared with the existing coatings. Halloysite nanotubes can be loaded with anticorrosion inhibitors specific to steel, copper and aluminum. These nanoformulations can be used as powder additives to existing paints [53-57]. This green chemistry technology based on the natural nanoclay may be easily scaled up because this material is available in thousands of tons at a low price.

![Scheme of paint coating doped with the clay nanotubes loaded anticorrosion agents](image)

**Figure 2-5:** Scheme of paint coating doped with the clay nanotubes loaded anticorrosion agents [57]

Novel polymer coating composites containing 5% of clay nanotubes loaded with standard anticorrosion agents specific for steel, aluminum and copper (benzotriazolo, hydroxyquinoline, and dodecylamine) were developed. Encapsulation of these agents in clay tubes allow for longer anticorrosion protective function with enhanced action at the coating defects. Figure 2-6 demonstrates SEM images of bulk clay nanotubes, their
location in the paints layer and an efficiency of anticorrosion protection for steel and aluminum.

**Figure 2-6:** Image of clay nanotubes (A) and their location in paint (B); corrosion development on scratched painted metal samples after 9 months in simulated sea water (C-F): Steel: C-usual paint coating, and D-paint/halloysite composite loaded with dodecylamine. Aluminum 2024 alloy coated with transparent polyurethane paint: E-usual paint, and F-paint/halloysite composite loaded with benzotriazole [57].

Clay nanotubes were also tested as an additive to paint for enhanced flame-retardancy. Halloysite admixing at 4-8 wt.% enhances flame-retardancy of latex paint and does not change color, surface roughness, nor adhesion of paint to the substrate. For the nanocomposite coatings tested with a flame torch according to the ASTM E84 US standard, five wt.% halloysite doping was the best formulation exhibiting a two to three times reduction of flame spread and smoke development. Halloysite decomposition resulting in degradation and release of water molecules is believed to be a reason for the decreasing rate of combustion [57].

### 2.3.2. Drug Loading

Drug loading in halloysite nanotubes has previously been achieved. This knowledge is analogous to architectural core-shell design of halloysite metal and inorganic composites inside the tubes with consequent reduction reactions.

The biomedical studies on halloysite include its use for cancer cell isolation, bone implants, teeth fillers, cosmetics and controlled long lasting drug delivery [21, 58-61]. The first paper on halloysite as a nanocontainer, demonstrated 10-20 hours sustained
release of tetracycline, khellin and nicotinamide adenine dinucleotide (NAD) [8], and it was followed by multiple publications on halloysite pharmaceutical formulations [59, 61]. Many drugs were loaded at 5-15 wt.% into halloysite providing an extended release; for example: khellin, oxytetracyclin, gentamicin, ciprofloxacin, vancomycin, atorvastatin, metronidazole, dexamethasone, doxorubicin, furosemide, nifedipine, curcumin, resveratrol, and antiseptics - povidone iodine, amoxicillin, brilliant green and chlorhexidine [7].

Long lasting antibacterial halloysite spray was also created with special targeting for usage in hospitals and natural disaster sites. It is a simple and scalable formulation of clay nanotubes loaded with antibacterials (currently used cheap antiseptics: chlorhexidine, doxycycline, povidone iodine, amoxicillin and potassium clavulanate) [58]. Their colloidal formulations may be used as a spray of aqueous dispersion halloysite (Figure 2-7). The antiseptic loaded clay nanotubes may be additionally modified to enhance their surface charge making stable clay-water colloids. Antiseptic-halloysite added at five wt.% to latex spray paint may provide efficient antibacterial protection for one to two years.

**Figure 2-7:** Sustained release of (a) povidone iodine and (b) amoxicillin from halloysite nanotubes [2]
2.3.3. Halloysite Safety

Increasing use of halloysite urges the need to assess its toxicity towards living organisms. Overall, halloysite are considered non-hazardous to cultured human cells at least up to 0.5 mg/mL. The biocompatibility of this nanomaterial was supported through toxicity assessments from different human cell lines, like epithelial adenocarcinoma cells or dermal fibroblasts, to yeast, bacteria, algae, microworms and fish, as well as mice and rats. The toxicity of halloysite is typical for inorganics at higher concentrations, and much of the oxidative stress was attributed to the dissolution of Al$^{3+}$ ions in the gastric pH because alumina dissolves after long periods in acidic pH [53]. However, it was determined that daily oral consumption of one to two g of halloysite tablets was safe [62].

A pre-treatment etching of alumina in sulfuric acid solutions can be employed to remove up to 50% of the original Al content, without compromising the tubule structure, and ultimately reducing the liver toxicity. Efficient oral halloysite formulations for chickens and piglets removed dangerous mycotoxins (zearalenone, deoxynvalenol) present in grain feed. Recently, the potential inhalation exposure to halloysite was investigated in an industrial research laboratory. No significant exposure risk was found, but still cautions should be taken to the inhalation exposure to these clay nanotubes [63]. Halloysite is considered the biologically safest nanomaterial, based on comparisons of its toxicity with silica, montmorillonite, kaolin, bentonite, graphene and carbon nanotubes.

2.4. Halloysite Based Mesocatalysts

Many processes in chemical and pharmaceutical synthesis, such as hydrogenation, oxidation, reduction, isomerization and cross-coupling reactions are carried out, as a rule, in liquid medium at moderate temperatures (20-250 °C). Catalyst morphology, structure,
particle size distribution, and dispersion on the carrier surface are important parameters influencing the rate and selectivity of the reaction. Much attention is given to the development of heterogeneous nanosized catalysts. Obviously, the smaller the size of the nanoparticles, the higher the surface area, which is important for heterogeneous catalysis [64]. Unfortunately, due to the high surface free energy, metal-nanoparticles agglomerate to form large particles with low catalytic activity. To solve this problem, they are usually supported on high surface-area and robust supports. Thanks to tubular morphology and different inside/outside chemistry, halloysite nanotubes are prospective nanotemplates for core-shell structured mesoporous catalysts for hydrogenation, isomerization and oxidation catalysts, enabling the fast and practical synthesis of stable nanoparticles and preventing them from aggregation [64]. Catalytic metals can be incorporated on the nanotubes’ outer surface or in the inner lumens with selective metal binding. Non-selective coating of metal salts inside/outside the tubes can be performed also. These sandwich-like systems may contain different metals in the lumen and on the outer surface [65].

Another way to increase the specific surface area is incorporation of meso-phase nanostructured zeolites (ZSM-5), structured mesoporous silica oxides, or aluminosilicates HMS, MCM-41, SBA-15, SBA-16, etc. These materials have high surface area and large pore volume and are characterized by high hydrothermal and chemical stability. By varying alumina content, it is possible to control their acidity [64]. Nonetheless, due to its chemical inertness, in some cases halloysite nanoclays cannot be dispersed well nor can they reliably have uniformly distributed metal nanoparticles using the wetness impregnation method, due to the low accessibility of the inner surfaces [37, 65, 66]. To
solve this problem, modification of halloysite by various organic ligands, such as (APTES) [67, 68], schiff bases [32, 37] and polymers [19], possessing complex formation properties, were suggested. Moreover, selective modification via covalent bonds of functional groups could provide molecular recognition which is extremely important for catalysis. These organo-silica materials, impregnated by Pt, Ru or Pd nanoparticles, Fe, Mo or Cu complexes have been successfully applied in oxidation, hydrogenation and polymerization reactions [69].

This part deals with application of halloysite including modified halloysite hybrid materials as supports for oxidation, reduction, hydrogenation, and cross-coupling reactions catalysts. Additionally, it could be used in various petrochemical processes, such as hydrotreatment, catalytic cracking and isomerization.

2.4.1. Oxidation

Nanocatalysts, based both on natural and modified halloysite clays, have made use in gas-phase and high temperature oxidative reactions. Au-based catalysts are widely used for these reactions. They were found to be highly active in oxidation reactions under mild conditions. Au nanoparticles, supported on unmodified halloysite nanotubes (HNTs), were applied for oxidation of cyclohexene [70] and benzyl alcohol [71] by molecular oxygen. For cyclohexene, the reaction had a radical-chain mechanism; its rate and product distribution were significantly dependent on Au loading [70]. Maximum conversion was only 29% after 12 hours (80 °C, 0.4 MPa of O₂) with 2-cyclohexen-1-ol and 2-cyclohexen-1-one being formed as the main reaction products (maximum selectivities were 35% and 49% correspondingly). In the presence of Au/HNT catalyst, benzyl alcohol conversion reached about 77% with selectivity of benzaldehyde at 95%
after eight hours (110 °C, 1 atm. of O₂) [71]. Similar results were obtained in [72] where benzyl alcohol oxidation was carried out over Au nanoparticle-decorated halloysite nanotubes providing high benzaldehyde selectivity (above 90%). For one of the catalysts with halloysite loaded with Au, substrate conversion reached 99% after 45 min (100 °C, 1 MPa of O₂) [72]. The structure of the catalysts used in these works had a significant effect on their activity and selectivity. Thus, the oxidation of benzyl alcohol was carried out in the presence of well-dispersed catalyst, characterized by narrow particle size distribution for the loaded particles, with small particles (mean diameter 4.1 nm) being predominant [71].

High yields of 2-cyclohexen-1-one (99% conversion at 98% selectivity) were obtained in the presence of CuO nanoparticles, supported on unmodified halloysite, using tert-butylhydroperoxide (TBHP) as an oxidant [73]. The reaction appeared sensitive to the temperature applied: the optimum temperature was at 70 °C, with epoxycyclohexane being formed as a by-product in other cases. CuO/HNT catalyst was proved to be stable and metal-leaching resistant, maintaining high activity and selectivity with re-use. Recently, it was reported that Co²⁺ supported on halloysite was used for solvent-free oxidation of cyclohexene to allylic products with oxygen [74].

Bimetallic CuCo nanoparticles, supported on unmodified halloysite, were also applied for exhaustive oxidation of toluene to carbon dioxide by molecular oxygen (1 atm. of O₂, 200-400 °C) under continuous-flow conditions [75]. Herein Cu₁Co₁/HNT and Cu₁Co₂/HNT catalysts were the most active. Though these catalysts were significantly inferior to conventional Pt/γ-Al₂O₃ in their activity, they showed high stability both at re-use and at prolonged time-on-stream regimes in the studied temperature range.
Bimetallic Au–Ag and Pt–Ag halloysite-based nanocatalysts are also used for oxidation reactions [76]. Au–Ag and Pt–Ag bimetallic nanocages were fabricated by loading on natural halloysite nanotubes (HNTs) via galvanic exchange based on Ag/HNT. As it turned out these systems are more active in oxidation of o-phenylenediamine compared with monometallic Au/HNT and Pt/HNT catalysts. The authors underline that HNT incorporation enhanced the thermal stability for every system, whether monometallic Ag nanoparticles, bimetallic Au–Ag or Pt–Ag nanocages. Halloysite etching was also used to enhance metal loading of silver. After etching, silver was loaded into halloysite using aqueous silver acetate solution heated at 300 °C in order to decompose it into metal.

Preliminary stabilization of Ru nanoparticles by poly(N-vinylpyrrolidone) (PVP) before the immobilization in halloysite nanotubes was applied [19]. The use of hydrophilic polymer, being able to form hydrogen bonds with silanol groups, located on the halloysite surface, allowed forming well dispersed particles with narrow size distribution. The catalysts obtained were studied in the oxidation of CO to CO₂ in reductive atmosphere. Activity and selectivity of these catalysts were dependent on both synthesis conditions and the temperature applied. Preliminary reduction of the catalysts synthesized were found to enhance their activity and extended operating temperature range.

Fe [77] and Mo complexes [78] supported on modified halloysite nanotubes, allowed to selectively epoxidize both cyclic and linear alkenes. Fe catalysts were in the form of a complex with anionic porphyrin, containing SO₃⁻ groups, easily forming hydrogen bonds, while the immobilization process was performed by the hydrothermal
method, using pre-calcinated (so called “meta”) halloysite as a support. To synthesize Mo catalyst, APTES-modified halloysite, treated with salicylic aldehyde, was applied. Both Fe and Mo catalysts gave conversions and selectivities of 80-100% and 90-99% correspondingly. Herein, Fe-Por/HNT nanocomposite, combined with PhIO as an oxidant, gave an epoxide yield of 85% after one hour at room temperature, which is highly efficient when compared to other homogeneous molecular catalysts [77]. In the case of Mo-salen/HNT catalyst, with tert-butylhydroperoxide (THBP) as an oxidant, both temperature and reaction time were dependent on size and shape of the substrate (longer linear alkenes and styrene required higher temperatures and longer reaction time for effective reaction proceeding) [78], that could be attributed to the substrate-selective properties of halloysite nanotubes. Herein both Fe and Mo nanocomposite catalysts were recycled several times without significant loss of their activity and selectivity [69].

Mo-salen supported on surface-modified halloysite nanotubes were used for efficient epoxidation of alkenes including linear, cyclic, and aromatic alkenes [79]. The catalysts were prepared using a facile chemical halloysite surface modification by 3-aminopropyltrimethoxysilane (APTMS) and [3-(2-aminoethyl)aminopropyl] trimethoxysilane (AAPTMS) followed by MoO(O\textsubscript{2})\textsubscript{2}(DMF)\textsubscript{2} immobilization. These catalysts were shown to provide efficient conversion of carbocyclic alkenes to the corresponding epoxides with high TOFs, while oxidation of aromatic and linear alkenes required longer reaction times and higher reaction temperature. The authors postulated that the salen structure in contrast to other ligands, such as the N atom as a single ligand provide immobilization of MoO(O\textsubscript{2})\textsubscript{2}(DMF)\textsubscript{2} improving the conversion and efficiency of alkene epoxidation by several times without significant loss of catalytic activity.
2.4.2. Reduction

For catalytic activity testing of halloysite-supported metal nanoparticles in aqueous solution, the reduction of 4-nitrophenol is perhaps the most common model reaction. Au and Ag, incorporated into the inner halloysite lumen as nanorods, were chosen as the active metal phase, with Fe₃O₄ coating on the external surface of halloysite nanotube [40, 80]. Both Au and Ag nanoparticles, supported on HNT/Fe₃O₄ composite, demonstrated excellent catalytic activity in the reduction of 4-nitrophenol by NaBH₄ in water medium, as well as the high stability and good resistance to metal leaching at recycling (Figure 2-8). While the latter can be easily explained in terms of the carrier’s magnetic nature, facilitating the recovery and reuse of catalysts [40], and the former was attributed to the featured halloysite structure [80]. Namely, electron-deficient 4-nitrophenol molecules adsorb at first on the electron-rich halloysite surface, coated with Fe₃O₄, and then diffuse to the active metal phase through the HNT pores, forming surface complexes. These complexes undergo later metal-catalyzed reduction, forming the product, 4-aminophenol, that finally desorbs from the support. Herein the electron-rich amino group, contained in the product molecule, may afford desorption of the latter from the electron-rich halloysite surface.
Ag and Au nanoparticles, incorporated into halloysite nanotubes (HNT), modified with (3-aminopropyl)triethoxysilane (APTES), were successfully applied for catalytic reduction of 4-nitrophenol [67]. The process was carried out at room temperature in water medium, using NaBH₄ as a reducing agent. The catalysts were stable, recyclable, and superior to many other systems, such as common Ag/C [81], Ag/Fe₃O₄ [82, 83], Au/Fe₃O₄ [84, 85] or homogeneous Au/PAMAM dendrimer catalysts [86]. Also, it was found that the in situ synthesized Ag/APTES-HNT nanoparticles were more active than both Au and Ag nanoparticles. Analogously Pt nanoparticles, supported on APTES modified halloysite, were successfully applied for the reduction of potassium hexacyanoferrate (III) to potassium hexacyanoferrate (II) [68].

The superparamagnetic coaxial gold/halloysite nanotube/Fe₃O₄ nanocomposites (Au/HNTs/Fe₃O₄) were suggested for reduction of 4-nitrophenol in the presence of NaBH₄ at room temperature [40]. Due to the difference in inside/outside surface charges, selective decoration of the inner lumen and the external wall of halloysite nanotubes was carried out using KAuCl₄, FeCl₃·6H₂O and FeCl₂·4H₂O as metal sources. Au nanorods

**Figure 2-8:** Reduction of 4-nitrophenol in the presence of Ag/HNTs/Fe₃O₄ catalyst [1]
were selectively generated within the lumen of HNTs, while Fe$_3$O$_4$ nanoparticles uniformly deposited on the external wall. Being easily recovered, co-produced catalysts showed high catalytic activity for at least three cycles.

A simple and facile method to prepare Ag nanoparticles loaded in the lumen of halloysite nanotubes was proposed (Figure 2-9) [87]. Herein, N-acetyl-L-cysteine modified silver nanoparticles with negative charges spontaneously and stably resided in the lumen of halloysite via electrostatic interactions, resulting in particle with size of 2.6 nm uniformly distributed in the lumen, which is beneficial to the mass transfer for the catalytic reaction.

![Figure 2-9: Scheme of NAC-modified Ag NPs formation in the lumen of halloysite nanotubes (a), TEM images of HNTs (b), Ag/HNTs (c-e). [87]](image)

The small size of Ag nanoparticles and incompact dispersion in halloysite nanotubes provide larger specific surface areas and a more active center, and thus leading to high catalytic efficiency in reduction of 4-nitrophenol to 4-aminophenol in the presence of NaBH$_4$. Analogously, silver nanoparticles supported on halloysite nanotubes via the in situ reduction of AgNO$_3$ by polyol were used for the catalytic reduction of 4-nitrophenol with NaBH$_4$ in alkaline aqueous solutions [88].
For reduction of nitroaromatic compounds, AuPd bimetallic nanocatalysts using halloysite nanotubes were proposed [89]. Herein, the catalysts were obtained by coating of halloysite nanotubes with magnetite Fe₃O₄ particles through a one-pot solvothermal synthesis method followed by alloying by AuPd nanoparticles. The catalytic activities of the nanocatalysts toward the reduction reaction of 4-nitrophenol and its derivative were investigated in the presence of NaBH₄ as a reductant in aqueous media. The catalysts were found to demonstrate high activity with nitroanilines at room temperature (Table 2-2).

**Table 2-2**  Catalysts at Room Temperature

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Time, min</th>
<th>Conversion, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>p-nitroaniline</td>
<td>8</td>
<td>99</td>
</tr>
<tr>
<td>2</td>
<td>m-nitroaniline</td>
<td>6</td>
<td>99</td>
</tr>
<tr>
<td>3</td>
<td>o-nitroaniline</td>
<td>5</td>
<td>99</td>
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<td>4</td>
<td>2,4 nitroaniline</td>
<td>7</td>
<td>99</td>
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<tr>
<td>5</td>
<td>m-nitrotoluene</td>
<td>68</td>
<td>81</td>
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<td>6</td>
<td>o-nitrotoluene</td>
<td>76</td>
<td>75</td>
</tr>
<tr>
<td>7</td>
<td>2,4-dinitrotoluene</td>
<td>82</td>
<td>79</td>
</tr>
</tbody>
</table>

The high catalytic activity of the catalytic system is ascribed to synergetic effects between Pd and Au. The authors underlined, that HNT/Fe₃O₄/Au₄₀Pd₆₀ catalysts can be easily separated from the reaction system with the help of an external magnet and reused several cycles without significant loss of the activity.

**2.4.3. Cross-Coupling**

C–C bond formation is one of the most important reactions for the synthesis of biaryls, constituting the basic skeleton of many complex molecules. Pd-catalyzed cross-coupling reactions between aryl halides and arylboronic acids, alkenes or aryl-tin
compounds are the most valuable and effective synthetic routes to prepare various styrenes and biaryls [69]. To obtain effective cross-coupling catalysts, various amino modified halloysites have been already applied. In particular, catalysts, containing so-called supported ionic liquid phase (SILP), were developed [92, 93]. One of the proposed synthetic routes suggests preliminary modification of halloysite nanotubes by 3-mercaptopropyl trimethoxysilane followed by Michael addition of octylvinylimidazolium bromide, both under microwave irradiation [92]. The second is primary coating of halloysite surface with 3-azidopropyl trimethoxysilane, which interacts then with terminal alkyne compounds, forming cationic triazolium salts (Figure 2-10) [93].

![Chemical Reaction Diagram]

**Figure 2-10**: The synthesis of Pd/HNT-SILP catalyst for Suzuki cross-coupling reaction, modified from [93]

Both modified halloysite supports were impregnated with Pd nanoparticles and tested in Suzuki cross-coupling reactions, using microwave irradiation. It was found that conversions of 95-99% were achievable already within ten minutes at 120 °C in water-ethanol medium, with K₂CO₃ as a base [92, 93]. Herein the reaction yields were
dependent on the nature of both halide and substituent as well as the latter’s position compared to the former in the aryl halide molecule [92]. Thus, the highest yields (> 99%) were observed for para-substituted aryl bromides. Replacement of para-substituted substrates by those of meta-substituted substrates resulted in decrease of conversion to 80%. Analogous effect was also seen for aryl bromides with nitrogenous substituent in para-position instead of oxygenate. The use of aryl chloride instead of aryl bromide as a substrate led to sharp decrease in the reaction yield down to 33%. Both imidazolium- and triazolium modified halloysite-based catalysts were successfully recycled several times without Pd leaching [93, 94].

The interesting approach is described in [95] where for the Suzuki and Heck C-C bond formation under microwave irradiation, Pd nanocatalysts stabilized by thiol functionalized halloysite nanotubes and highly cross-linked imidazolium salts were used. The hybrid materials were synthesized by the in situ radical polymerization of the bis-vinylimidazolium salt with thiol functionalized halloysite. The microwave assisted Suzuki reaction has been tested on a set of substituted aryl bromides having either electron-donating or electron-withdrawing groups and phenyl boronic acid at 120 °C in alcohol-water media. Heck C-C cross-coupling 4-iodoanisole with methyl acrylate was chosen as a model. The reaction was carried out at 120 °C using DMF as solvent with trimethylamine (TEA) as the base both via traditional heating and microwave irradiation. The nanoclay indeed, with its specific surface area and tunable surface properties, allows a good dispersion of the dicationic salt and consequently better stabilization of palladium nanoparticles providing the almost quantitative conversions with excellent isolated yields.
Another way to synthesize Pd-containing halloysite-based catalyst for Suzuki cross-coupling reactions was suggested by the authors of [96]. Halloysite nanotubes here, before Pd nanoparticles were impregnated, had been modified with poly(N-isopropylacrylamide) (PNIPAAM), changing its secondary structure and hydrophobic properties at 32 °C, while lower critical solution temperature (LCST) has been achieved. Grafting the polymer on the APTES coated halloysite surface was carried out at the temperature above LCST, under microwave conditions, while Pd deposition was performed at room temperature. The catalyst obtained appeared as thermo-sensitive, giving low conversions (< 20%) at ambient temperature below (25 °C) and high (95-99%) at temperatures above 50-120 °C, with TOF values up to 37500 h⁻¹ [96]. Herein the maximum conversions (95-99%) were observed for substrates with electron withdrawing substituents, located in para-position to the halogen, under all other conditions being equal. In spite of the absence of the visible metal leaching, the catalyst synthesized revealed tendency to lose activity upon recycling. The phenomenon observed was explained in terms of so-called “release and catch” mechanism [97], according to which soluble palladium species were formed and took part in the reaction process; after the reaction completed they were redeposited back onto the halloysite surface, showing no leaching as a result.

2.4.4. Petrochemistry and Oil Refining

Hydrocracking (HC) and hydrodesulfurization (HDS) processes in the presence of various mono- and bimetallic catalysts, supported on saponite and montmorillonite clays, were investigated [98-101]. The halloysite-based catalysts were useful in hydrocracking processes [102]. Due to halloysite internal cavity, there are no sterical hindrances for
bulky molecules adsorption and further cracking inside tubes. Moreover, increasing of halloysite inner porosity can be obtained by acid etching. These mesoporous-based core-shell catalysts containing Ni and Co oxides are highly active in hydrocracking of the heavy oil residue obtained from vacuum distillation of the Azerbaijan crude oils at 450 °C and 1–4 MPa hydrogen pressure. The total yield of the fuels varied at 52–57% range depending on hydrogen pressure.

The authors of [103] studied the alkylation of toluene with tret-butanol over acid-modified bentonite and HY zeolite catalysts in a continuous flow, fixed-bed tubular micro-reactor. The toluene conversion proceeded more effectively in the presence of acid-modified bentonite that was attributed to larger pore diameter and smaller micropore surface area of the latter as well as to higher ratio of total Lewis acid centers to total those of Brönsted. The maximum selectivity on 4-tert-butyltoluene was observed to be 82% at conversion of 47% at 180 °C within four hours.

Ni-containing halloysite based catalysts obtained by calcination of natural halloysite were used for the production of syngas using methane and CO$_2$ [104]. Testing of catalysts was carried out in quartz tube fixed-bed continuous reactor at atmospheric pressure and temperature of 700 °C. For halloysite calcined at 1000 °C supported Ni catalyst, the conversion of CH$_4$ and CO$_2$ reached 75 and 40%, respectively with comparable CO and H$_2$ selectivity. The authors underlined high coke and Ni sintering resistance of these catalysts compared with the supported Ni catalyst on traditional silica alumina.

The numbers of research reports are devoted to catalytic cracking using halloysite-based catalysts [105, 106]. Thus, catalytic cracking of vegetable oils with
vacuum gasoil was performed using commercial high alumina zeolite FCC catalyst and halloysite nanotubes as a catalyst at the temperature range of 480–540 °C and mass hourly space velocity of 20.9 ± 0.3 h⁻¹ [105]. It was shown, that performance of the cracking catalyst in terms of gasoline yield and coke formation was significantly improved upon addition of halloysite, providing skeletal isomerization within halloysite pores and increasing the yield of the branched hydrocarbons in produced gasoline and hence octane rating. The activity of the halloysite-based catalysts is reasonably well compared to commercial mesoporous zeolite catalysts, giving 46.5% gasoline yield and 2.5% coke at 63% conversion of heavy vacuum gasoil. In other work, the authors showed that the utilization of halloysite nanotubes along with high silica Y-zeolite was very efficient in increasing the gasoline yield and lowering the coke formation during catalytic cracking of the vacuum gasoil and cottonseed oil [106]. The octane rating was also increased due to hydrocarbon skeletal isomerization for halloysite-based catalyst.

The Ni-Mo catalysts supported on halloysite treated with mineral acids (chlorine and sulfuric) can be used for hydroconversion (isomerization and cracking) of n-decane [107]. Acid treatment on the 1:1 clay mineral (halloysite) considerably improved its surface area and acidity, without significantly compromising the nanotubular structure and macro- or meso-porosity of the starting mineral. The modifications allowed obtaining catalysts with high mesoporosity, which are active in the hydroconversion reaction of n-decane (100% conversion at temperatures below 300 °C).

The better catalytic performance was achieved for supports treated with H₂SO₄ due to the improved mesoporosity and acidic properties, which in turn favor the dispersion of the hydrogenating phases (Ni-Mo), and enhance both the reactivity and
molecular transport. The treating of halloysitic supports with H$_2$SO$_4$ led to the increase in wider pores (with a radius of 245 Å), and this in turn increased the selectivity of bulky isomers such as ethyl-octanes and methyl-nonanes, compared to the obtained catalysts.

Another interesting approach for design of halloysite-based isomerization catalysts is growing of zeolites, mesoporous structured silica oxides or aluminosilicates on a halloysite template, producing a novel architectural system with stronger mechanical properties and ability for loading of the clay nanotubes containing reactive metal nanoparticles [108]. Thus, the Pt-containing ZSM-5 armed with halloysite nanotubes-based catalyst was used for isomerization of the xylene reforming fraction at the temperature range of 360-440 °C under hydrogen pressure, inhibiting side reactions, reducing the intensity of coke formation and increasing the rate of isomerization. The H$_2$:raw materials molar ratio was 5, and the mass hourly space velocity – 1 h$^{-1}$.

Pt-containing ZSM-5/Hal-based catalysts, having high substrate selectivity, are highly active in m-xylene and ethylbenzene isomerization providing 40% and 82% conversion at 440 °C, respectively. The maximum p- xylene selectivity (81%) is achieved at 380 °C, thanks to micro-mesoporous structure of the support but decreases to 50% when the temperature is increased. The authors underlined that a significant amount of benzene and toluene (37% at 440 °C) is present in the reaction products due to ethyl benzene and xylene dealkylation. The ethylbenzene and m-xylene conversion at 440 °C over Pt/ZSM-5/Hal catalyst were 82 and 37%, respectively while the ethylbenzene conversion was 65%.

Ag nanoparticles, stabilized by n-butylamine and immobilized in the halloysite nanotubes, were reported to catalyze the polymerization of alkysilane, C$_{18}$H$_{37}$SiH$_3$ [109].
This catalyst demonstrated high polymerization activity, forming superhydrophobic silanol/siloxane composite microspheres. Similar results were obtained in the literature [109]. The modification of halloysite with vinyltrimethoxysilane (VTMS) and silicon chloride (SiCl$_4$) was applied to obtain the Ziegler–Natta catalysts for in situ polymerization of propylene [110]. Cu-containing halloysite nanoclays, modified by polyamine ligands on its external surface, were applied for methyl methacrylate (MMA) polymerization [111]. Herein aminosilane might act both as a ligand for CuBr and as a base co-catalyst for the heterogeneous MMA polymerization.

SO$_3$H-functionalized halloysite, combined with Cr$_{3+}$ ions as an active phase, was applied for one-pot cellulose conversion into 5-hydroxymethylfurfural in the ionic liquid medium ([EMIM]Cl) [112]. The maximum yield was 41% at 120 °C within 120 min. Nonetheless, this catalyst, in spite of its moderate activity, was easily recycled without significant loss of activity.

2.5. Separation Processes

2.5.1. Halloysite-Based Adsorbents

Due to the presence of both positively and negatively charged surfaces, halloysite nanotubes are versatile adsorbent particles. Direct use of halloysite as adsorbent is not very fruitful, however, because of its relatively low surface area (about 40 to 65 m$^2$/g). Fortunately, this drawback can be overcome by etching or modification of halloysite, enlarging its surface area or grafting onto its surface moieties having the affinity to the adsorbates of interest. Halloysite-based adsorbents were studied by a number of research groups over the past several decades, and the results were summarized in the exhaustive recent review [113].
Pristine halloysite nanotubes were used for adsorption studies with model adsorbents (dyes) [114-118], but also with benzene [119], and ciprofloxacin antibiotic [120]. Etching of the halloysite nanotubes with concentrated acids or, even better, consecutive alkali and acid treatment, sharply increases the surface area of clay nanotubes. This increase comes at the expense of number of active centers (aluminol groups in the case of acid etching), so the maximum adsorption capacity is not necessarily increasing much. Still, interesting results were obtained not only for the model dyes [113, 121], but also for the prometryn herbicide [122].

The modification of halloysite with cyclodextrine leads to only modest adsorption capacity towards rhodamine B [2], but when the cationic compounds such as cetyltrimethylammonium bromide or aminosilanes are grafted onto the halloysite surface, the obtained composites can be employed for the efficient Cr(VI) removal from wastewater [123, 124]. Clay nanotubes can be rendered ferromagnetic by modification with iron oxide particles (most often, Fe₃O₄). Magnetic nanoparticles do not significantly increase the adsorption capacity, but serve for better recycling of the adsorbent. Such adsorbents were used for the adsorption of methyl violet [125, 126] and arsenates [127]. The most promising halloysite-based composites include both magnetic nanoparticles and modifiers for the efficient adsorption of target adsorbates. These ternary composites successfully purify water from dangerous inorganic pollutants both in cationic [128] and in anionic forms [128-130].
We selected results of the adsorption studies and divided them into groups: ‘pristine’ [114-120], ‘etched’ [113, 121, 122], ‘modified’ [2, 123, 124], ‘magnetic’ [125-127], and ‘modified magnetic’ [128-130]. The dependence of adsorption capacity from BET surface area is shown in Figure 2-11. As one can see in Figure 2-11, the best results are provided by ternary halloysite-Fe$_3$O$_4$-carbon or the ternary system- HNT-Fe$_3$O$_4$-PEO-chitosan nanofibers. The optimization of magnetic and adsorption properties will open the way for the versatile adsorbents capable of removing cationic and anionic pollutants.

2.5.2. Halloysite-Doped Membranes

Often catalysis is accomplished with separation membranes; this is why we also described here the formation of membranes containing halloysite nanotubes. Separation of mixtures of water and hydrophobic components (oils) is a problem of global
importance due to the increasing volumes of industrial wastewater contaminated with hydrocarbons and frequent oil spill accidents. Traditional methods are not effective in the treatment of water contaminated with micro-sized droplets of emulsified oil, especially in the presence of surfactants. Membrane is promising for water purification due to the small size and simplicity of devices used, low energy consumption and environmental safety. Ultrafiltration membranes are capable of separating emulsions with micro-sized particles, but their effectiveness is significantly reduced when oil drops are deposited on the membrane surface and in its pores.

An ultrafiltration membrane based on polyethersulfone containing halloysite nanotubes with the addition of copper ions Cu$^{2+}$ was obtained by the phase inversion method [131]. The SEM, AFM data showed that the addition of halloysite did not affect the microstructure of the polymer membrane. Cu$^{2+}$-HNTs played the role of an antibacterial agent and were obtained by chemically modified HNTs with silanes and subsequent interaction with copper chloride. The membranes were characterized by SEM, AFM, TEM, contact angle and mechanical measurements. Modification with halloysite made it possible to obtain a hybrid membrane with higher hydrophilicity and mechanical strength. The addition of 3% Cu$^{2+}$-HNTs resulted in a 64% increase in pure water flux compared to a sample without clay nanotubes. The hybrid membrane has good antibacterial properties with respect to both Gram-negative bacteria (Escherichia coli) and Gram-positive bacteria (Staphylococcus aureus), which can be used to control bacterial fouling in wastewater treatment.

A similar approach to modifying an ultrafiltration membrane was proposed [132]. A polyethersulfone membrane with improved anti-fouling properties was prepared by
phase inversion and incorporating dextran grafted onto halloysite nanotubes (HNTs-Dextran). The modification of halloysite with dextran was confirmed by FTIR, TGA, and TEM. The nanohybrid membrane with the addition of HNTs-Dextran had an increased hydrophilicity, higher flux and antifouling properties compared to the unmodified polyethersulfone membrane.

A novel ultrafiltration membrane based on the poly(vinylidene fluoride) polymer matrix (PVDF) and the halloysite nanotubes modified by APTES was described [133]. The APTES-HNT/PVDF composite membrane showed a higher pure-water flux and lower contact angle values compared to the PVDF polymer membrane and the HNTs/PVDF membrane. The separation of four oil/water emulsions using the obtained membranes was also studied. The rejection ratio of oil for the sample APTES-HNT/PVDF was more than 90%. The APTES-HNT/PVDF nanocomposite membrane retained the ability to effectively separate mixtures of water and oil after three cycles of use. The introduction of modified halloysite into the polymer mat plays an important role in increasing the efficiency of the composite membrane by enhancing its hydrophilicity. The modification of HNTs with APTES contributes to a more uniform distribution of nanotubes in the polymer matrix and improves the ability of the composite membrane to separate mixtures of water and oil by reducing free surface energy.

In recent years, the use of graphene oxide (GO) to fabricate a membrane material for wastewater treatment has been studied widely. GO has a high specific surface area and flexibility, however membranes based on it usually have a low water flux due to the small distance between adjacent sheets of carbon atoms. In recent papers, HNTs [134] and dopamine-modified HNTs (D-HNTs) [135] have been proposed to solve this
Composite superoleophobic membranes were obtained, in which halloysite is intercalated between GO layers using vacuum filtration. The presence of aluminosilicate nanotubes made it possible not only to enhance water flux, but also to improve its surface morphology and structure. It was shown that the wettability of the membrane can be further improved by the addition of ethylenediamine. The resulting membranes were successfully used for the simultaneous removal of oil impurities and dyes from wastewater. The samples exhibited good rejection ratio, high water flux, and excellent anti-oil-fouling property.

The separation of emulsions in wastewater in a high-temperature and corrosive environment is a big challenge for membrane systems based on polymers. Recently, a new composite membrane with a hierarchical structure, having a high thermal and chemical stability, was proposed. The membrane consists of HNTs intercalated into a graphene oxide coating on a porous nanofibrillar matrix of poly(arylene ether nitrile) (PEN) [136]. The membrane is obtained by the controlled assembly of HNTs intercalated into GO (skin layer) on the surface of electrospun PEN nanofibrous mats (substrate) and further polydopamine coating. The structure is shown in Figure 2-12. This structure of membrane provides super-hydrophilic properties of the skin layer and underwater super-oleophobic nature.
Samples showed a high preferential rejection ratio (more than 99.0%) and a remarkable antifouling performance for various oil/water emulsions. The presence of filtration channels in the surface layer due to the intercalation of halloysite, the porous structure and high wettability can increase the permeate flux of the composite membranes to 1130.56 L/m²·h. The membrane retains its effectiveness under high-temperature conditions (90 °C), in an acidic and basic solutions (pH = 1-14), and therefore is promising for the purification of wastewater in harsh environments.

As another example, a highly oriented layer of halloysite on polyacrylonitrile microporous membrane was prepared via a facile evaporation-induced method. It resulted in a well aligned tubular clay cover film providing additional nanopore barrier for better filtration performance (Figure 2-13). The well-ordered nanotube coating allowed for the excellent dye rejection (98% for Reactive Black-5) with high salt permeation (87% for...
aqueous NaCl); therefore, these membranes were suitable for dye purification or concentration. These well-aligned nanotubes’ composite membranes also showed excellent fouling resistance against dye accumulation and bovine serum albumin adsorption as compared to the pristine polyacrylonitrile or membrane coated with disordered halloysite layer [137-141]. Our research goals included incorporating ZrO2 halloysite composites organized in layers.

![SEM images of membrane surface and cross-section for oriented halloysite coating layer (a-f)](image)

**Figure 2-13:** SEM images of membrane surface and cross-section for oriented halloysite coating layer (a-f) [137]

### 2.6. Halloysite Composites for Sensing Applications

#### 2.6.1. Composites for Electrochemical Sensing

Halloysite nanotubes provide the positively and negatively charged surfaces for the site-selective modification with charged molecules. Moreover, the selective modification affects the zeta potential of halloysite nanotubes, opening the way to the self-assembly of highly charged nanotubes into well-organized micropatterns [142]. The self-assembly behavior stems from the high aspect ratio of halloysite nanotubes, which
stipulates the tendency of nanotubes to form nematic or columnar phases in water
dispersions [143]. This phenomenon can be employed for the creation of nanostructured
surfaces for electrochemical, adsorptive, or optical detection of analytes of interest.

Halloysite itself, like other aluminosilicate materials, usually acts as an inert
carrier for the active species in electrochemical experiments [144]. However, it can be
easily modified with metal nanoparticles, magnetic nanoparticles, or analyte-responsive
polymers for the selective sensing of numerous chemicals, including those of interest for
biomedical studies.

Clay nanotubes decorated with metal nanoparticles can be readily used as the
modifier for the sensing electrode system. Nanoparticles or complexes of noble metals,
such as palladium, ruthenium, or rhodium, serve as the direct electrochemical or
electrochemiluminescent active particles, and the nanostructured surface of
halloysite-modified electrode helps to disperse the nanoparticles and provide sufficient
electrochemical activity with low loading of precious metal. Also, the decoration of
halloysite with gold or silver nanoparticles can enhance surface plasmon resonance
properties.

The modification of the working electrode with noble metals can be promoted
with halloysite nanotubes as carrier. For the electrochemical sensing, the chemically inert
glassy carbon electrode is often the substrate of choice. The modification can be done by
direct drop-casting of mixture of halloysite and rhodium nanoparticles stabilized with
suitable zwitter-ionic surfactant [145], or by the preliminary assembling of halloysite
with metal nanoparticles formed inside the lumen [146]. The charged noble metal
complexes, such as Ru(bpy)$_3^{2+}$, are easily loaded onto the halloysite via the cation
exchange, and the formed composites could be immobilized by the impregnation in the polydopamine film on the electrode surface [147] (Figure 2-14).

![Figure 2-14](image)

**Figure 2-14:** Schemes of electrochemical halloysite-based sensors assembled with mixture of halloysite and nanoparticles (A), halloysite decorated with nanoparticles (B), and halloysite with nanoparticles formed inside the lumen (C) [1]

Gold or silver nanoparticles are promising components of electrochemical sensors due to their electrocatalytic activity. Gold nanoparticles grafted onto the outer surface of halloysite nanotubes *via* APTES express the electrocatalytic activity sufficient for the detection of $10^{-6}$ M hydrogen peroxide, and improve the sensitivity of electrochemiluminescent halloysite–Ru(bpy)$_3^{2+}$ complexes [148]. Silver nanoparticles synthesized onto the APTES-modified halloysite were employed for the enzymatic glucose sensor, providing the support and electron transfer for the immobilized glucose oxidase [149].
2.6.2. Fluorescent Sensing Composites

Fluorescent markers are especially useful for biomedical studies, where they can show the colocalization of important cellular features, including the 3D-resolved position of either cell surface receptors or intracellular organelles. There are various small fluorescent markers available for the selective contrasting of organelles of interest (DAPI for nuclei, dye-grafted phalloidin for the cytoskeleton, etc.), but the fluorescent nanotubes enable the important feature often desired for the biomedical studies: the opportunity not only to attach to living cells, but at the same time to deliver certain chemicals to cells. This feature, would serve for the programmed apoptosis of cells we prefer to kill (such as cancer cells) or to modify their behavior (i.e., to stimulate the secretion of hormones), thus combining the contrasting of cells with therapy and leading to theranostics approach (therapy + diagnostics). Halloysite nanotubes, otherwise biologically inactive, offer safer vehicle for the drug delivery comparing to stem cells [150].

As most water-soluble fluorescent dyes have charged functional groups, they can be simply attached to halloysite nanotubes by ion-exchange procedures. However, dyes immobilized by this way are inherently prone to desorption, which is highly undesirable for the composites intended for theranostics use. In order to mitigate the possible dye desorption, one may incorporate the dye into the silica shell synthesized onto the halloysite nanotubes [151], or immobilize the rare-earth fluorescent moieties by multicarboxyl polymers grafted to halloysite by surface-initiated atom transfer radical polymerization [152], but these approaches render the nanotubes inaccessible for loading, which complicates their theranostics use.
An alternative option is to employ not the water-soluble fluorescent dyes, but fluorescent particles immobilized onto the halloysite surface. The most promising candidates to fulfill this concept are quantum dots—tiny semiconductor nanoparticles, exhibiting size-dependent fluorescent properties. Interestingly enough, cadmium chalcogenide quantum dots can be synthesized in presence of modified halloysite nanotubes that serve as stabilizing agent. Amine groups grafted onto the halloysite nanotubes with APTES or azine moieties grafted by hydrazine-furfural treatment coordinate forming cadmium chalcogenide particles, thus preventing their aggregation [43, 44] (Figure 2-15). It should be noted, however, that the widely studied cadmium chalcogenide quantum dots are potentially toxic if accumulated within human body, and have to be replaced with safer alternatives.

**Figure 2-15:** Synthesis of fluorescent halloysite-QD composites (A); TEM image of the halloysite/Cd$_{1-x}$Zn$_x$S composite (B); confocal image of the halloysite-CdS composite well-dispersed on glass slide and excited by 405 nm laser (C). Bars, 100 nm (B), 200 μm (C). [2]

Recently, the heavy-metal-free halloysite-based fluorescent composites were produced. These composites contain carbon quantum dots (CQD)—small carbon
nanoparticles derived from organic precursors via pyrolysis or microwave heating. The halloysite–CQD composites were obtained by microwave digestion of ethylenediamine in presence of tartaric acid-coupled APTES-modified halloysite. In the resulting composites, nitrogen-doped CQD are covalently immobilized on the halloysite surface [50]. The simplicity of the synthesis procedure, however, does not offer the control over the uniformity of CQD, leading to the broad size distribution and, therefore, to the broad fluorescence spectra (white emission) of the obtained markers. The dedicated synthesis of CQD from citric acid and ethylenediamine provides better control over the particle size, and the obtained CQD exhibit emission in the blue-green spectral range with near-UV excitation. Simultaneous grafting of these CQD and biotin onto the PEG-NH₂-modified halloysite with subsequent quercetin adsorption leads to the theranostic composites [153].

2.6.3. SERS-Active Halloysite-Based Composites for Sensing

Surface-enhanced Raman scattering is an enormous (10⁴–10¹⁴ times) increase of Raman scattering by molecules adsorbed at the nanostructured metal surface [154]. Halloysite nanotubes form thin organized layers on the suitable supports, providing roughness at the 50 nm to several micrometer scale. Such nanostructured surfaces may be treated with hydrophobizing agents like alkylsilanes, providing the peculiar superhydrophobic substrates, promising for sensing applications [155]. The nanostructuring of the plasmonic interface with halloysite nanotubes also improves the sensitivity of SPR sensors [156]. Hence, it is not surprising that this nanostructuring can be employed for the construction of SERS substrates through various strategies (Figure 2-16).
Figure 2-16: Strategy for the construction of SERS halloysite-based substrates: synthesis of gold nanoparticles in situ (A), decoration of halloysite with pre-synthesized nanoparticles (B), formation of thin metal film on halloysite by sputtering (C) [1]

In the first report of SERS-active halloysite substrate, the role of nanostructuring is questionable, because the substrate was constructed by polyphenol-assisted in situ synthesis of gold nanoparticles on the amino-grafted halloysite, and thus consisted of disordered nanoparticle-covered nanotubes [154]. The SERS activity of the substrate was rather low, with barely recognizable spectrum of $10^{-6}$ M rhodamine 6G registered, though with more common substrates this model analyte is detectable down to $10^{-9}$ M. A similar approach with the separately synthesized polyethylenimine-stabilized gold nanoparticles led to similar results with rather high detection limit of 4-aminothiophenol of about $10^{-6}$ M [157]. It was shown that the reduction of gold could be carried on until the whole surface of halloysite is covered with thin metal shell, thus providing the tunable plasmon substrates with resonance wavelengths in the range of 600–800 nm [33]. The fabrication of the continuous metal layer by vacuum sputtering onto the halloysite substrate indeed provides the SERS-active substrates, albeit with even lower activity ($10^{-3}$ M 4-mercaptobenzoic acid) [158]. Despite the various approaches tested, so far there are no
highly active SERS substrates created using the nanostructuring properties of halloysite nanotubes.

2.7. Safety and Practicality

Many works are devoted to the study of halloysite nanotubes as a nanocontainer for encapsulating and controlled release of various materials (dyes, biocides, drugs, corrosion inhibitors). Considerably, less attention was paid to the toxicity of halloysite and their influence on the natural environment. This topic is very important in the context of the possible practical application of halloysite and its derived materials in industry. Nanomaterials can be cytotoxic due to oxidative stress, interaction with protein and DNA molecules, and physical destruction of the cell structure. The factors that determine the toxicity of nanomaterials in relation to the cells of living organisms include their concentration, size, specific surface, particle shape as well as electrochemical and biochemical surface properties.

Bacteria are the simplest model organisms for which the effect of halloysite, as an environmental stressor, has been investigated. The cytotoxicity of halloysite to bacterial cells of Escherichia coli in a wide range of concentrations (0.01 - 1.0 mg/mL) was studied [159]. It was found that the halloysite without surface modification demonstrated the highest level of cytotoxicity, which the authors associated with damage of cell membranes as a result of direct contact of HNTs and / or the production of reactive oxygen species (ROS). The surface modification of halloysite with amino groups slightly reduced cytotoxicity. Surface modification of halloysite makes it possible to control the cytotoxic properties of HNTs.
In addition to bacterial cells, the toxicity of HNTs were studied in vitro with respect to the human epithelial adenocarcinoma cell line (HeLa) and human breast cancer cell line (MCF-7) [160]. Halloysite demonstrated a high biocompatibility and low cytotoxicity towards to the cell cultures. When the concentration is less than 75 μg/mL, the toxic effect was absent. According to the results of visualization of the halloysite uptake by cells using confocal microscopy, it was found that HNTs are located in the vicinity of cell nuclei.

The compatibility and toxicity of HNTs to blood cells for biomedical applications has been evaluated in vitro [161]. It was shown that HNTs can easily be incorporated into living cells and form agglomerates around the nucleus region. HNTs do not cause hemolysis. In addition, the presence of halloysite in the blood leads to a decrease in plasma recalcification time, which indicates the presence of procoagulant activity of halloysite with citrate plasma. Thus, HNTs shows good compatibility with blood cells at low concentrations (<50 μg/mL).

The cytotoxic effects of Fe₃O₄ nanoparticles and the nanocomposite HNT/Fe₃O₄ are determined for Gram-negative bacteria Escherichia coli and Gram-negative bacteria Bacillus subtilis, as well as for Vero cell lines and human lung cancerous (A-549) [162]. It was shown that the nanocomposite with halloysite is less toxic to the bacterial cell than the iron oxide nanoparticles. The lesser toxicity is explained by the smaller value of the zeta potential of the nanocomposite (-33.2 mV), the larger particle size (308 ± 52.5 nm) and the increased hydrophilicity of the nanocomposite (contact angle 12 ± 1.5 °). At the same time, HNT/Fe₃O₄ nanocomposite showed more cytotoxicity than Fe₃O₄ nanoparticles on A-549 cell lines.
Toxicity of halloysite was determined in vivo using the soil nematode *Caenorhabditis elegans* [7, 163]. It was concluded that halloysite nanotubes do not adversely affect nematodes and therefore are safe for *Caenorhabditis elegans* at a concentration up to one mg/mL, which is approximately 1000 times higher than the possible concentrations of halloysite in the soil contamination.

Another in vivo study, conducted using the protozoan model organism *Parametium caudatum*, confirmed that halloysite is the most biocompatible compared to other nanoclays (montmorillonite, bentonite, kaolin) and especially compared to relatively toxic graphene oxide [164]. An enhanced dark field microscopy and fluorescence microscopy were employed to observe the uptake of the HNTs by the protozoans. Figure 2-17 shows microscopy images of *P. caudatum* and halloysite ingestion. As one can see from Figure 2-17 (c, d) after ingestion, clay nanoparticles are transferred into the food vacuoles of *P. caudatum*. The safe concentration of halloysite for one of the most common fresh water ciliate protist *P. caudatum* was ten mg/ml, which is ten times higher than the concentration that is considered safe for cell cultures (about one mg/mL).
However, in vivo studies in mice showed that, at high concentrations (> 50 mg/kg), orally administered halloysite causes growth inhibition and oxidative stress in the liver and lungs, as well as an inflammatory process in the lungs, probably due to the accumulation of aluminum cations Al$^{3+}$ [62]. Mice treated with low doses of halloysite nanotubes (less than five mg/kg body weight) showed no signs of oxidative stress or other toxicity problems. Moreover, mice that were given low doses of HNTs with food showed higher growth rates.

The biocompatibility and biodegradability of the materials obtained was investigated using cells (in vitro) and rats (in vivo). Adding HNTs has been shown to significantly improve the mechanical stability and wettability of biopolymer scaffolds, without impairing cell growth and development. In vivo study has shown that there is
good internalization and subsequent formation of blood vessels at the site of implantation of polymer-halloysite composites [163].

High biocompatibility and low toxicity of halloysite is confirmed [165]. It was shown that HNTs modified using the surfactant, stearyldimethylbenzylammonium chloride, can be used as an effective treatment for piglets in case of poisoning with mycotoxin zearalenone. The toxicity effects of HNTs against model human cell lines (in vitro) and zebrafish embryos and larvae (in vivo) were investigated [166]. Halloysite at a concentration of <200 μg/mL is characterized by good biocompatibility and does not induce apoptosis in HUVEC and MCF-7 cells. The survival rate of zebrafish embryos and larvae remained almost unchanged at different developmental stages (24, 48, 72, 96, and 120 hours past fertilization) when processed with different concentrations of nanotubes (0.25 - 10 mg/m). Halloysite accumulated mainly in the gastrointestinal tract of the zebrafish larvae after ingestion. The results indicate a comparative environmental safety of the use of halloysite. The potential exposure to inhalation of halloysite was also investigated [63]. No significant risk was found for mice. However, inhalation exposure to halloysite nanotubes must be followed by precautions due to the very limited amount of toxicological data.

Nanotubes are excellent candidates for fabrication of nanoarchitectonic drug delivery vehicles due to their structural and chemical properties. Carbon nanotubes (CNTs) are theoretically useful in a variety of medical applications; however, there are many concerns on their possible toxicity. Loaded CNTs can be used for vaccine treatment, gene therapy, and cancer treatment due to their efficient penetration into cells. CNT composites are prospective materials that can be used as tissue scaffolds and
artificial implants. They have been used as electro-reactive components in model biosensors, but no real medical applications were reported. There may be exceptional cases where biocompatibility of halloysite facilitates its use in a number of biomedical applications. The mechanisms of cellular internalization of nanotubes have been briefly overviewed, although there is still need for additional studies.

2.8. Conclusions and Prospects

Halloysite is a prospective nanotemplate for core-shell hybrid functional materials with tunable properties. The tubular structure of ca. 50 nm diameter has an empty lumen and different inside/outside chemistry allowing selective surface modification of halloysite, which opens possibilities to create new metal/organic/ceramic hybrid materials architecturally designed for synergistic effects of the components. A development of new functionalizations will lead to more efficient (10-20 wt.%) loading of metal materials inside and outside the nanotubes. New core-shell structures could be obtained using different metals on inner/outer surfaces; such multifunctional nano-engineered objects open new opportunities to extend the applications of halloysite in catalysis, medical and biological fields, photosensitive materials, and gas sensors. Novel polymer coating composites with clay nanotubes loaded with anticorrosion agents specific for steel, aluminum and copper, allow for a longer protection. In flame retardant polymeric composites, halloysite thermo decomposition resulting in degradation and release of water molecules may be a reason for the decreasing rate of combustion.

Halloysite nanoclays are good materials for design of mesocatalysts for petrochemical synthesis. Combined with active metal clusters, halloysite-based core-shell catalysts have proved efficiency in oxidation, reduction, hydrogenation, cross-coupling
and polymerization reactions. Hollow cavities in halloysite are able to provide substrate selectivity and may act as nanoconfined reactors. Selective modification of halloysite inner/outer surface by organic ligands may improve particle dispersion, and as a consequence, enhance catalysis. A development of catalytic nanoreactors with bifunctional properties on the inside/outside tube surfaces, self-assembly of halloysite with other silicates and zeolite systems are promising for new synergistic catalysts for petrochemical synthesis and oil refining.

Versatile self-organizing behavior of high aspect ratio halloysite nanotubes is already employed for the development of sensing systems. Particularly, development of highly active SERS halloysite-based substrates is an interesting problem. The fluorescent theranostic halloysite composites are promising for biomedical and cancer research. The synthesis of halloysite-quantum dot composites gives narrow fluorescence response with suitable excitation, required for the multilabel cell imaging.

*In vitro and in vivo* studies conducted using various cells and organisms demonstrate a high biocompatibility of halloysite. This nanoclay is more environment-friendly and characterized by a higher biological compatibility as compared to other clays (i.e., kaolin, montmorillonite, bentonite) and has significantly lower toxicity than graphene and carbon nanotubes. Low toxicity of halloysite to bacteria, ciliates, soil nematodes, mice, chicken, piglets and fish is proved. The future applications of halloysite include use for cancer cell isolation, bone implants, teeth fillers, cosmetics and topical long lasting drug delivery. Availability of halloysite in thousands of tons ensures rapid scale up of its formulations for commercial use in industry.
Perhaps the main advantage of carbon nanotubes over halloysite is that they are conductive and in turn can theoretically be used in electrical applications. However, halloysite are more advantageous overall for several reasons. First, carbon nanotubes are very toxic so there are environmental concerns with their potential application. Also, they are exponentially more expensive than halloysite which makes them less practical in large scale industrial applications. Another disadvantage of CNTs is the fact that there are several types such as SWCNTs and MWCNTs with highly different properties, and until this day there is no efficient and practical way to synthesize a specific type for a specific application. This brings up another point, which is the fact that that they typically have to be synthesized as opposed to halloysite which is naturally available. Halloysite are very inexpensive, natural, nontoxic, and can be modified in many different ways for various applications. As a result, we have pursued the route of halloysite core-shell nanoarchitecture.

In Chapters 4, 5, and 6 we will use modified protocols discussed in the literature review to synthesize halloysite core-shell structures for mesocatalysis, gas sensors, as well as lithium-sulfur batteries. For catalytic applications, Ru and Co were loaded onto/inside halloysite nanotubes with particle sizes ranging from 5-10nm using various techniques. A loading of 5-10 wt % of non-aggregated metal nanoparticles was achieved, and our collaborators in Russia carried out the catalytic testing proving the enhanced catalytic efficiency of these mesocatalysts over similar commercial catalysts. In some cases, the catalytic activities of our Ru-mesocatalysts were twice as high as the commercial counterparts using the same metals. In Chapter 6, we used halloysite nanotubes for loading sulfur to achieve a more efficient and practical version of lithium
sulfur batteries by using inexpensive nanoclay to reduce polysulfide dissolution. This improved the cycle life of the energy dense lithium-sulfur batteries. This is another example exploiting the halloysite nano-architectural approach to develop novel engineering solutions.
CHAPTER 3

INSTRUMENTATION

3.1 Zeta-Potential Analyzer

A ζ-Plus Microelectrophoretic instrument (Brookhaven Instruments, Co.) was used to measure the surface charge of halloysite nanotubes. The instrument was calibrated using a standard sample from the manufacturer. For each measurement of the sample, 20 μL of the sample was diluted up to 1.8 mL by DI water. The ζ-potential was measured in ranges of 200 mV to -200 Mv (Figure 3-1).

Figure 3-1: Zeta potential analyzer (ζ-Plus Microelectrophoretic instrument)
3.2 Scanning Electron Microscope

Scanning Electron Microscope Hitachi S 4800 FE was used for morphology of pristine halloysite nanotubes as well modified halloysite. Samples were suspended in water and dried in oven on a silicon wafer. Samples were then typically sputtered with gold or palladium at ten mA for 60 seconds before imaging to improve conductivity and enhance the image quality (Figure 3-2).

![Scanning Electron Microscope](image)

**Figure 3-2:** Scanning electron microscope (Hitachi S 4800 FE)

3.3 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) was used to determine the loading efficiency of the amount coated of compound on or in halloysite clay nanotubes. Halloysite and its composites with any other compound were heated to a temperature of up to 600°C to determine the quantity of each component in the prepared composites. A heating rate of
ten °C per minute was used for the analysis. The organic content in a composite is only from the loaded/coated compound and thus the weight loss by thermal degradation corresponds to the compound of interest (Figure 3-3).

![Figure 3-3: Thermogravimetric analysis](image)

3.4 Surface Area Analyzer

Nitrogen adsorption isotherms of halloysites were obtained at liquid N₂ temperature on a Quantachrome Instruments NOVA 2200 surface area analyzer. Samples were degassed at 300 °C for three hours prior to analysis. The total surface area was calculated according to the Brunauer–Emmett–Teller (BET) method. The pore volume and size distribution were obtained by the Barrett–Joyner–Halenda (BJH) analysis of the desorption branch of the isotherm.
Figure 3-4: Surface area analyzer (Quantachrome Instruments NOVA 2200)

3.5 Other Supporting Instruments

Branson 1510 ultrasonic water bath (Branson Ultrasonics, U.S.A.) and bench top vortex (VWR, U.S.A.) were used to wash loaded samples as well as disperse aggregated halloysite and halloysite composites. It was also used as a mechanism for enhancing chemical reactions. Centrifuge 5804R (Eppendorf, Germany) with rotor FA-45-30-11 (30 x 2 mL tubes) and 5417C (Eppendorff, Germany) with rotor FA-45-24-11 were used to separate washed material from waste products (supernatant).
CHAPTER 4

USING HALLOYSITE NANOTUBES FOR LOADING CATALYTIC RUTHENIUM NANOPARTICLES

4.1 Preview

This experimental chapter focuses on our paper “Formation of Metal Clusters in Halloysite Clay Nanotubes,” in which I am the only graduate student coauthor, allowing me to include it in this dissertation. I would like to acknowledge again our collaborators in Gubkin University for their contributions. Techniques in chemical and nanoengineering were used to synthesize precisely modified structures. Previous related work includes architectural metal nanostructures allowing for fine-tuning particle size, shape and location that were based on a one-step reduction of metal salts bound to an interface of block copolymer dendrites and amphiphile ensembles. Three to five nm diameter Pt, Au, Pd, and their bi-metallic composites were used to form highly porous dendritic mesostructures [167]. Extending this strategy, we synthesized Ru nanoparticles inside clay nanotubes.

We found that furfuraldehyde shows good intercalation abilities allowing for further formation of organic ligands for metal ions inside the nanotubes. This procedure of halloysite modification with furfuraldehyde based Schiff bases significantly enhances an intercalative loading of metal ions both into the lumen and also into interlayer space of the nanotubes.
A simple method of metal ion inclusion from solutions based on ligand-functionalized halloysite nanotubes (ligand-HNTs) is suggested. Subsequent reduction reactions resulted in formation of metal particles in the tube’s interior. Further freeing the ligands allowed for repetition of the nanoparticle formation process, resulting in efficient adsorption of metal ions. Elongated heavy metal particles of 3-4 nm diameter were formed both on the inner lumen surface and in the interlayer slit-like pockets of the halloysite walls.

4.2 Experimental

4.2.1 Materials and Reagents

Halloysite clay was supplied by Applied Minerals Inc., USA. Furfuraldehyde, silver acetate, RuCl3 and other chemicals were purchased from Sigma-Aldrich. Field emission scanning electron microscope, (SEM-Hitachi) and transmission electron microscope (TEM, JEM-2100, JEOL) were used for imaging metal-ceramic core-shell structures. X-ray diffractometer (Bruker-D8) was used to analyze the halloysite multilayer wall packing spacing. Local elemental analysis was carried out with energy dispersive X-ray analysis (JEM-2100, JEOL). Halloysite surface potential in aqueous dispersion was measured with a zeta potential analyzer (ZetaPlus, Brookhaven Instruments Corp). Furfuraldehyde loading efficiency was estimated with thermogravimetrical analysis (TGA Q50, TA Instruments) under nitrogen flow of 25 cm3 / min for the sample and ten cm3 / min for the balance. The explored temperature interval ranged between 25 and 900 °C and the heating rate was ten °C / min.
4.2.2 Preparations of Halloysite Loaded with Organic Ligand (Schiff-base)

Halloysite (1g) was mixed with furfuraldehyde (20 mL); the suspension was dispersed ultrasonically for 30 min and centrifuged to remove the chemical excess. Then hydrazine hydrate (20 mL) was added to the furfuraldehyde loaded halloysite and the mixture was stirred for 30 min under 70 ºC to form Schiff bases (Figure 4-1). The modified halloysite underwent extensive washing / centrifugation with ethanol to remove Schiff bases from the halloysite nanotubes’ outer surfaces.

4.2.3 Synthesis of Intercalated Ru-Nanoparticles

Halloysite with Schiff base molecules (1 g) was dispersed ultrasonically in RuCl₃ ethanol solution (0.05 M) to obtain a homogenous suspension and refluxed for 30 min under stirring to form an Ru Schiff base complex. The nanotubes were repeatedly washed/centrifuged to remove excess RuCl₃. Then NaBH₄ was added for the Ru³⁺ reduction reaction. After the reaction and degassing were completed, the modified halloysite was centrifuged and washed with water. We demonstrated three approaches in selective nanoconfined metal synthesis: 1) on the tube outer-surface, 2) in the tube central lumen, and 3) clusters bound through Schiff base reaction for formation of metal particles in the slit-like gap defects within the tube multilayer walls. This is the most interesting strategy because the area of potential metal adsorption is enhanced by a factor of ten.

4.2.4 Organic Linkage Assisted Metal Clusters Formation

To enhance metal loading into the clay nanotubes, formation of an organic linkage was employed. First, clay nanotubes were loaded with furfuraldehyde. A high furfuraldehyde loading of five wt. % was shown with TGA analysis data but zeta potential was not changed (-32mV). These small organic molecules were then
transformed into tetradequate ligand (Schiff base) capable of binding metal cations through reaction with hydrazine hydrate. The reaction scheme is shown in Figure 4-1. The tetradequate Schiff base is devoid of any ionizable protons and serves as neutral ligand forming cationic complexes [168]. Proposed structure of the Ru-complex is also shown in the scheme. Differential scanning calorimetric (DSC) analysis proved the formation of the Schiff base inside the nanotubes. Characteristic phase transition at 115 °C for pure Schiff base is similar to its complex with halloysite.

**Figure 4-1:** Formation of Schiff base from furfuraldehyde and hydrazine hydrate and proposed structure of the Ru-complex [169]

Such modified clay nanotubes were exposed to a solution of RuCl₃ for 30 min. The mixture was then heated to 80 °C for formation of the metal complex and treated with NaBH₄ for metal ion reduction. The TEM images show a dense tube intercalation with Ru nanoparticles (Figure 4-2). These nanoparticles coated internal voids of the tubes
including the larger central lumen, as well as multiple slit-like defects formed from folds in the tube wall multilayers. Contrary to the first two approaches, these nanoparticles have an elongated shape of 3-4 nm cross-section diameter and are oriented parallel to the tube axis.

**Figure 4-2:** Transmission electron microscopy (TEM) of halloysite nanotubes intercalated with Ru nanoparticles bound though Schiff bases [169]

Location of the metal nanoparticles along slit-like defects in the tube multilayer wall is in accordance with TEM imaging of slit-like pockets in the halloysite tubes. These folding packing defects appeared during halloysite drying accompanied with collapse of multilayer spacing from 1.0 to 0.7 nm which separate the monolithic hydrated wall to dehydrated blocks with slits [13]. Interestingly, the position of X-ray diffraction
reflections corresponding to 0.72 nm spacing in the tube walls did not change after Ru cluster intercalation indicating that the nanoparticles are located only in the wall slit-voids.

From high resolution TEM images in Figure 4-2, we obtained the Ru lattice spacing of 0.205 ± 0.05 nm corresponding to the (101) plane of the hexagonal close packed (hcp) structure. This is similar to the crystal structure observed with three nm diameter Ru particles [16] and corresponds to the Ru-bulk lattice. 2-4 nm hcp Ru crystals generated a higher CO oxidation activity in comparison with face-centered cubic Ru nanoparticles, but for larger crystals catalytic efficiency decrease was observed [169-170]. It is remarkable, that the yield of metal-modified tubes was very high as well as metal loading (Table 4-1). This demonstrates a great advantage of this ligand-based method as compared with spontaneous loading of metal complexes into the tubes’ lumens. Results of the energy dispersive X-ray analysis of the sample in Fig. 4-2a are summarized in Table 4-1. The measured Ru percentage depended on the selected spot on the sample and varied from six to ten wt. %. The strong Cu K signal originated from the copper sample support.

Table 4-1  Results of Elemental Analysis of Ru-Halloysite Core-Shell Structures. Total Mass of 100 % Does Not Include Copper Which Is Not Part of the Nanotubes

<table>
<thead>
<tr>
<th>Element</th>
<th>Energy (keV)</th>
<th>Mass (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O K</td>
<td>0.525</td>
<td>40.6</td>
</tr>
<tr>
<td>Al K</td>
<td>1.486</td>
<td>13.8</td>
</tr>
<tr>
<td>Si K</td>
<td>1.739</td>
<td>33.7</td>
</tr>
<tr>
<td>Fe K</td>
<td>6.398</td>
<td>1.2</td>
</tr>
<tr>
<td>Cu K</td>
<td>8.04</td>
<td>----</td>
</tr>
<tr>
<td>Ru L</td>
<td>2.558</td>
<td>10.7</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>100</td>
</tr>
</tbody>
</table>
4.3 Catalytic Activity of Ru-Halloysite Systems

These Ru-halloysite core-shell mesocatalysts were tested in hydrogenation of phenol in aqueous phase and demonstrated high catalytic efficiency (2–times higher than commercially available Ru-catalysts). A high catalytic activity in phenol hydrogenation was due to optimization of Ru-content, its distribution on the nanotubes, the particle sizes, and metal-valence. Maximum turnover frequency (TOF) achieved was 17282 h\(^{-1}\) in terms of hydrogen uptake per surface Ru-atoms. The TEM image of Ru-halloysite clay nanotubes and particle size distribution (scale bar 100 nm) are given in Figure 4-3.

The most active were the catalysts with ca two nm particles encased inside the clay tubes; these formulations used furfural and hydrazine hydrate to modify the initial nanoclay carrier. The rate and yield of reaction were strongly dependent on the clay to catalyst ratio and the substrate structure: decrease in ruthenium loading and replacement of phenol with cresol led to a significant downfall in the conversion. For halloysite-based ruthenium catalysts some metal leaching was observed after the 1\(^{st}\) reaction cycle, which may be attributed to poorly retained nanoparticles located outside of the nanotubes, but further these Ru-core-shell nanocatalysts were recycled up to ten times without loss of activity.
Figure 4-3: a,b) TEM image of Ru-halloysite clay nanotubes and particle size distribution (scale bar 100 nm). C,d) Plot of phenol conversion vs. catalyst loading (a) and PhOH/Ru molar ratio (b) in the presence of Ru. (80 °C, 3 MPa of H₂, 3 h., m(PhOH) = m(H₂O))

4.4 Conclusions

To enhance inner wall and lumen metal cluster formation, we intercalated the tube with furfuraldehyde and then converted it to tetradeinate ligands which have shown
specific binding to Ru$^{3+}$ ions from ethanol solution at elevated temperatures. Therefore, a simple method of metal ions exclusion from solutions based on ligand-functionalized halloysite nanotubes (ligand-HNTs) was suggested. The reduction of the sample with NaBH$_4$ and cooling the halloysite composite resulted in formation of metal particles in the nanotube interior and freeing the ligands which allowed for repetition of the process and further enrichment of the tubes with metal up to nine wt.%. Metal particles of 2-5 nm diameters were formed both in the central lumen and in the interlayer spaces of the tube walls. Similar binding results were obtained for other heavy metal ions (Ag, Rh, Pt, Co). Halloysite, our nanotemplate of choice, is inexpensive and available in large quantities (thousands of tons) in the form of clay. It is a safe, green nanomaterial [3, 18-19] promising easy scale up capabilities for industrial applications as a mesoporous carrier for metal nanocatalysts.
CHAPTER 5

HALLOYSITE NANOTUBES AS A SUPPORT STRUCTURE FOR LOADING COBALT AND ZIRCONIA NANOPARTICLES

5.1 Preview

_halloysite nanotubes were also used to load cobalt for various catalytic reactions. Hydrolysis of sodium borohydride is a promising reaction with possible practical implementation as a source of hydrogen fuel. Sodium borohydride has significant advantages such as high energy density, relatively low cost, and high stability [171]. This reaction is catalyzed well by noble metals: among the VIII group metals, the highest activity is expected for rhodium and ruthenium, and the lowest activity – for palladium. But because of their high cost, many investigations were made to improve the economic feasibility of this process. A promising way to increase the activity of cobalt and noble metal-based systems is to find the appropriate carrier for metal nanoparticles. Various supports were used to stabilize metal particles, like carbon, graphene, carbon nanotubes, and clays [172-173]. Here we present cobalt based mesoporous catalysts for hydrogen evolution with enhanced activity. We use cobalt instead of platinum due to its low cost and high activity. We will compare different halloysite-cobalt catalysts preparation methods using the surface modification of halloysite with silane or azines and comparing them to pristine halloysite with metal salt wet impregnation. Results of this work were
published in a different paper where I was the only graduate student coauthor and I would like to acknowledge Prof. A. Glotov, Dr. Anna Stavitskaya and other collaborators for their contributions.

5.2 Experimental Details

All the reactants used were purchased from Sigma-Aldrich: cobalt (II) chloride hexahydrate, ≥97 % (CoCl2*6H2O), furfural, ≥98 % FCC FG, Acetone Laboratory Reagent ≥99.5 %, 2,3butanedione 97 %, hydrazine hydrate solution 78-82 %, sodium borohydride powder ≥98.0 %, sodium hydroxide reagent grade ≥98 % pellets (anhydrous), Halloysite clay powder with 1.3 mL/g pore volume and cobalt(II,III) oxide powder < 50 nm particle size, 99.5 % trace metals were also from Sigma-Aldrich.

5.2.1 Wet Impregnation of Cobalt Chloride into Halloysite (Co-1/Hall)

The cobalt chloride hydrate (0.8 g) was added to the 20 ml of acetone to obtain cobalt chloride solution. Halloysite (one g) was mixed with three ml of cobalt chloride solution and sonicated for ten minutes and dried under 50°C for 60 min. The procedure was repeated five times until the cobalt chloride solution was fully added to the halloysite. Then the sample was put in the muffle furnace at 70°C for 24 hours. The obtained powder was blue-grey and was named as Co-1/Hall.

5.2.2 Pre-formed Cobalt (II,III) Oxide Nanoparticle Adsorption onto Halloysite (Co-2/Hall)

Halloysite and cobalt (II,III) oxide nanoparticles were mixed at 8:1 ratio and DI water was added. The sample was sonicated until a saturated solution was formed. The sample was then heated to 80°C and stirred for three hours with cover to prevent evaporation. The heating was terminated and the sample was left to stir overnight with
the cover. The cover was then removed and the sample was left under stirring until dry. The obtained powder was dark grey and named Co-2/Hall.

5.2.3 Cobalt Chloride Linkage onto/into Halloysite Using Azines (Co-3(a,b,c)/Hall)

To obtain halloysite modified with various azines through the intermolecular condensation reaction with hydrazine the following procedure was performed. One g of the halloysite was firstly dispersed in the ultrasonic bath with 20 ml of hydrazine hydrate for 15 minutes at 30°C. The mixture was further centrifuged at 8000 rpm for four minutes to remove the excess of hydrazine hydrate. Then 40 ml of the second component (acetone (a)/furfural (b)/butane-2,3-dione (c)) was gradually added to the sediment and held in the ultrasonic bath at 50°C for 30 minutes. After reaction the mixture was centrifuged at 8000 rpm for three minutes followed by washing with ethanol and re-centrifugation with the same parameters. Halloysite modified with azine using (a), (b) or (c) compound was called 3a-Hall, 3b-Hall, and 3c-Hall. To prepare the catalysts, 0.8 g of cobalt chloride hydrate was first dispersed in ethanol to reach a homogeneous solution and then added to the modified halloysite to react in the ultrasonic bath for 30 minutes and to form a chelate-metal complex. After the last step, samples were put in the muffle furnace at 70°C for 24 hours. Using this scheme, the following systems were made: Co-3a/Hall (blue-grey powder), Co3b/Hall (green powder), Co-3c/Hall (violet powder).

5.2.4 Cobalt Chloride Linkage into Halloysite Using APTES (Co-4/Hall)

First halloysite modified with APTES was obtained. One g of halloysite was dispersed in 80 ml of ethanol and stirred for one hour to obtain homogeneous dispersion. Then 0.2 ml of APTES was dissolved in 20 ml of ethanol and mixed with halloysite dispersion. The mixture was stirred at 60°C for 124 hours to obtain halloysite grafted
with APTES. The solid was separated using centrifuge, washed with ethanol several times and dried at 60°C for 24 hours. Modified halloysite was then covered with cobalt chloride: 0.8 g of CoCl$_2$*6H$_2$O was first dispersed in ethanol to reach a homogeneous solution and then added to the modified halloysite to react in the ultrasonic bath for 30 minutes. Sample was put in the muffle furnace at 70°C for 24 hours.

5.2.5. Catalyst Characterization

Obtained catalysts were characterized by elemental analysis that was carried out using the ARL ADVANT’X X-ray fluorescence spectrometer with an X-ray tube with a rhodium anode operated at 50 kV. Data was processed using QuantAS software. To study the morphology of the samples a transmission electron microscope (JEM-2100, JEOL, Japan) was used.

XRD analysis of the samples was performed by the Bruker D8 Advance diffractometer, equipped with a nickel β-filter and system of controlled slitters for monochromatization (λ[CuKα] = 1.54 Å) and position-sensitive LynxEye detector, in the angle specter 4-80° with a 0.02° step at the 2θ angle. Obtained XRD data was then compared to the theoretical XRD patterns. Dependence of the background noise from the 2θ angle was modeled using the Chebyshev polynomial series up to the fifth order. For taking in the attendance equipment specialties, a method of fundamental parameters, obtained in the advance from the lanthanum boride (LaB6) sample, was used. The particles size was determined with an LVol-IB method (volume averaged column height calculated from the integral breadth) [173]. All the calculations were made with TOPAS software [Coelho, TOPAS 4.2, Bruker AXS GmbH, Karlsruhe, Germany, 2009].
5.2.6 Catalytic Activity of Halloysite Based Cobalt Catalysts in the Hydrolysis of NaBH₄

To evaluate the efficiency of produced catalysts the convenient proportion of sodium borohydride and sodium hydroxide was chosen according to the literature [174-177], and preliminary studies. The water solution of ten wt % NaBH₄ with 2.5 wt % of NaOH was used as a standard test mixture. Fifty mg of catalyst was put into a 50 mL three-necked flask with a magnetic stirrer, fixated into a thermostatic (298º K) water bath. The flask was connected to a 1000 ml gas burette and magnetic stirrer was set to the approximately 800 rpm. Then 20 ml of standard test mixture was added immediately after its preparation. Hydrogen generation rate (L/min×g(cat)) was estimated via water displacement method.

5.3 Results

It is well known that cobalt catalysts are very efficient in solid borohydride hydrolysis reactions especially when deposited on various carriers like graphene, carbon nanotubes, etc. In this work, for the first time, halloysite based cobalt catalysts are reported as catalysts for NaBH₄ hydrolysis reaction. To prepare efficient catalyst, several preparation techniques were performed including wet impregnation and a ligand-assisted method that was partly described in other works [166-170].

5.3.1 Characterization of Halloysite Based Cobalt Catalysts

Figure 5-1 shows the morphology of pristine halloysite (a) and cobalt-containing catalysts prepared using different methods. Figure 5-1b shows the Co-I/Hall catalyst made by wet impregnation, it could be seen that uniformed nanoparticles are formed within the tubes due to partial decomposition of cobalt chloride after drying. The
elemental analysis of the sample showed 8.9 wt % of cobalt loaded on halloysite, which is about 56 % of the initial concentration of cobalt in the stock solution. Such loading efficiency is not high if compared to other works [175-178]. Nevertheless, this method was used to compare halloysite with previously reported NaBH4 decomposition catalysts based on other carriers (Table 5-1).

Figure 5-1c shows the catalysts formed by halloysite and adsorbed pre-formed nanoparticles of cobalt oxide (Co-2/Hall), as one can see the particles are larger in sizes and are not uniformly distributed on the surface. The cobalt concentration in this material reached 16 wt. % This preparation method is also simple but due to the low interaction of halloysite and nanoparticles, such materials could lose their activity.

Figure 5-1d shows the morphology of Co-3a/Hall catalyst after the first hydrolysis reaction cycle. That means the cobalt chloride complex was reduced to form Co-B. Ligand-assisted method of cobalt salt loading using azines was used to enhance cobalt loading efficiency. The cobalt concentration in the Co-3a/Hall sample reached 16.4 wt % which is 2-times higher than in the case of the wet impregnation technique. It is clearly shown that the cobalt was loaded inside the mesoporous lumen of halloysite as well as outside the tubes.
Table 5-1 shows some properties of cobalt containing mesoporous nanoclay catalysts. Surface area of catalysts Co-1/Hall and Co-2/Hall is close to that of pristine halloysite (47 m²/g). This could be an evidence of metal adsorption on the outer surface (not clogging the lumen). Loading of halloysite with ligand linked cobalt reduces the surface area. The largest decrease from 47 to 14 m²/g is observed in the case of furfural ligand. This could be due to loading of ligand inside halloysite lumen followed by the metal complex formation. Average pore diameter of all the samples is 45 ± 3 Å showing that nano pores are preserved after organic ligands loading. The surface area and average pore diameter of ligand-halloysite systems are the highest for azine Co3a/Hall. Co-4/Hall catalyst prepared with standard modification technique using APTES shows low cobalt loading efficiency as compared to other catalysts (Figure 5-2).
Table 5-1: Physico-Chemical Properties of Halloysite Based Cobalt Catalysts

<table>
<thead>
<tr>
<th>Name</th>
<th>Complexation agent initial structure</th>
<th>Cobalt content, wt %, ±1%</th>
<th>BET surface area, m²/g, ±2%</th>
<th>BJH Adsorption average pore diameter (4V/A), Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-1/Hall None</td>
<td>8.9</td>
<td>41</td>
<td>44</td>
<td></td>
</tr>
<tr>
<td>Co-2/Hall None</td>
<td>16</td>
<td>43</td>
<td>41</td>
<td></td>
</tr>
<tr>
<td>Co-3a/Hall</td>
<td>16.4</td>
<td>28</td>
<td>58</td>
<td></td>
</tr>
<tr>
<td>Co-3b/Hall</td>
<td>16.9</td>
<td>14</td>
<td>47</td>
<td></td>
</tr>
<tr>
<td>Co-3c/Hall</td>
<td>15.6</td>
<td>27</td>
<td>43</td>
<td></td>
</tr>
<tr>
<td>Co-4/Hall</td>
<td>5.7</td>
<td>23</td>
<td>43</td>
<td></td>
</tr>
</tbody>
</table>

Figure 5-2: The scheme of cobalt chloride linkage onto/into halloysite using azines [167]

Previously we also showed that the nature of chelating agent plays a role in catalyst structure and activity [20]. Here azines made of hydrazine hydrate and acetone/furfural/butane-2,3-dione were used as metal-complex formation agents for Co-3a/Hall, Co-3b/Hall and Co-3c/Hall preparation, respectively. Chelating ligand composition is shown in Table 5-1 together with the cobalt loading efficiency, BET
surface area and average pore diameter. Characterization of these catalysts using FT-IR, XRD and TGA/DSC showed that Co-3a/Hall and Co-3c/Hall are close but their catalytic activity is different.

Figure 5-3 demonstrates the IR-spectra of pristine halloysite, halloysite after azine made from hydrazine and furfural formation (3b-Hall) and after CoCl$_2$-azine complex formation (Co3b/Hall). The graphs clearly show characteristic halloysite peaks. All samples show the bands at 3696 and 3620 cm$^{-1}$, assigned to two OH-stretching bands being linked to two Al atoms and the single Al$_2$OH-bending at 909 cm$^{-1}$. 3548 cm$^{-1}$ is corresponds to the O-H stretching vibration of Si-OH. The band observed at 909 cm$^{-1}$ is caused by the O–H deformation of inner-surface hydroxyl groups. 790 and 745 cm$^{-1}$ can be assigned to O–H translation vibrations of halloysite O–H units. Peaks at 655 and 520 cm$^{-1}$ are vibrations of Si-O-Al in plane bending mode. 1001 and 1028 cm$^{-1}$ are responsible for Si-O stretching band and in-plane Si-O-Si deformation. 1638 cm$^{-1}$ peak corresponds to strongly adsorbed water molecules. 1120 cm$^{-1}$ peak is assigned to apical Si-O stretching vibrations [171,172].
Figure 5-3: IR-spectra of halloysite (a), halloysite modified with azine (3b-Hall) (b), halloysite based cobalt catalyst (Co-3b/Hall) (c) [171].

The decrease of 1001 cm\(^{-1}\) peak especially well observed on Co-3b/Hall spectra and Co-3a/Hall (Figure 5-3) is an evidence of Si-O bonds rupture, probably due to formation of Si-N bonds with N\(_2\)H\(_4\). After azine formation on halloysite surface a few low abundant peaks appeared on the spectra including: 3360 cm\(^{-1}\) associated with N-H stretching vibration, 1610 cm\(^{-1}\) that referred to C=N bond in open chain and increased absorbance in range of 1700-1150 cm\(^{-1}\). After Co-complexation new peaks were observed: 3290, 3230 cm\(^{-1}\) corresponded to C-H stretching, 1570 cm\(^{-1}\) correspondent to C=N associated bond could be formed due to complex formation with a nitrogen atom. Peak at 1165 cm\(^{-1}\) could be C-O-C stretching.

XRD analysis of halloysite and halloysite based cobalt catalysts prepared using modification of carrier with azine was performed (Figure 5-4).
Figure 5-4: XRD of pristine halloysite (a) and halloysite based cobalt catalysts Co-3a/Hall (b), Co3b/Hall(c). (* halloysite nanotubes, + CoCl₂, and v CoOₓ) [167]

It is seen that cobalt structures co-exist with halloysite providing more intensive Bragg picks due to its higher electron density and better crystalline ordering thus resulting in very sharp lines. Halloysite peaks at 2θ=11.7, 20, 34.9, 62.3° [28] are preserved but scaled down in graphs b and c of Co-3a/Hall and Co-3b/Hall. The peaks indicative for CoCl₂ (2θ=16.1°, 32.4°, 39.4°), CoOOH (2θ=20.8°) and various oxides forms CoOₓ (2θ=33.0°, 37.9°, 42.3°), detecting similar cobalt-containing structures.

From XRD it was assumed that concurrently to the main process of small cobalt particle formation, large clusters were formed as well due to partial aggregation, as shown in the Figure 5-4. These clusters are distinctly seen through the XRD analysis. In the case of ketazine, the average size of the super cluster, calculated by the LVol-IB method, was 89 nm, while usage of furfural-based ligand led to the reduction of the average super cluster size to 32 nm. More peaks with a wider and less intensive specific average surrounding the peak were detected in the Co-3b/Hall sample: 2θ=32.5° and 41.4°
The smaller clusters size in the case of furfural containing azine indicates that it is a better complexation and stabilization agent although its activity is lower than in case of ketazine. The possible explanation could be the sensitivity of NaBH₄ hydrolysis reaction to impurities. Probably, chemical and steric activity of the ligands in samples Co-3b/Hall and Co-3c/Hall inhibit the reaction and reduce total process efficiency. Ketazine was used as a ligand in Co3a/Hall which means it could be hydrolyzed back to the hydrazine and acetone, which hydrogenate to the isopropyl and may promote the reaction. IR spectra of Co-3a/Hall before and after reaction (Figure 5-5) shows that C=N and C-H bonds vibrations disappear from the spectra. Ketazine was found to be a good chelating agent for cobalt particle immobilization on halloysite surface, simple in preparation and the one that may promote the targeted reaction.

**Figure 5-5:** IR-spectra of halloysite based cobalt catalyst Co-3a/Hall (a) and Co-3a/Hall after first reaction cycle [167]
More information could be obtained from simultaneous TGA and DSC analysis (Figure 5-6). Halloysite is characterized by three main thermal event: dehydration at 105°C, dehydroxylation at 478°C and nanotubes deformation at 1000°C. The chosen analysis mode shows two stages: at 100°C and 478°C. At the first thermal transition corresponding to water boiling of about 4.5% of weight was lost and on the second stage ca. 13.4% of weight was lost (both stages are endothermic) (Figure 5-6a).

Figure 5-6: Simultaneous TGA and DSC analysis of pristine halloysite, Co-3a,b/Hall and Co-4/Hall catalysts [167]

Cobalt catalysts prepared using halloysite modified with APTES (Co-4/Hall) show the same thermal events: dehydration and dehydroxylation (Figure 5-6b). After the first thermal event at 105°C 1.5%, 1.8% of weight was lost at temperature of 120°C and 212°C correspondent to desorption of APTES as its boiling temperature is 217 °C. Physically adsorbed silane desorbs completely before 300 °C with additional weight loss. A thermal decomposition of grafted silane gives weight loss of about 4%.
5.3.2 Catalytic Efficiency

The hydrogen production dynamics of the reaction using azine stabilized halloysite-cobalt catalysts Co-3a/Hall, Co-3b/Hall and Co-3c/Hall are shown on Figure 5-7b. It can be seen that activity of the catalysts varies greatly depending on the ligand used. The efficiency of the catalysts decreases from Co-3a/Hall to Co-3c/Hall, hydrogen generation rate equals 3, 1.9 and 1.3 L/min×g(cat), respectively. Since loading efficiency of ligands is similar and varies from 15.6 to 16.9 the cobalt content is not the only parameter that influences the reaction kinetics. Ketazine was the best catalyst ligand for hydrogen evolution from NaBH4. Though Co-3a/Hall and Co-3c/Hall catalysts are quite similar in physico-chemical properties, their catalytic activity changes greatly. This could due to the decomposition of ketazine during the reaction with formation of promoting species. In the case of butane-2,3-dione the ligand is stable and may inhibit the reaction because of high sensitivity of the hydrolysis to impurities.

![Figure 5-7: Influence of catalysts preparation methods (a) and chelating agent (b) on hydrogen generation rate](image)

Figure 5-7: Influence of catalysts preparation methods (a) and chelating agent (b) on hydrogen generation rate [167]

Figure 5-8 shows that after first reaction cycle all the halloysite catalysts lose 50-70 % of their activity. The best sample was Co-3a/Hall which generated 0.9 L/min×g(cat)
during the second reaction cycle. Catalytic activity of azine-stabilized catalyst in second reaction cycles becomes closer to it but remains much higher that catalysts prepared with other methods. APTES grafting is less efficient for production of cobalt catalysts active in NaBH₄ hydrolysis reaction.

![Bar graph showing catalytic activity of cobalt catalysts in recycling cycles](image)

**Figure 5-8**: Halloysite based cobalt catalysts recycling cycles in the reaction of NaBH₄ hydrolysis [167]

To prove the potential of halloysite as a carrier for cobalt catalysts we decided to compare it to other reported catalysts. As all the materials reported in the Table 5-2 are mostly in the form of cobalt borides (Co-B) we also decided to show the data of the first reaction cycle as a reduction procedure when the Co-1/Hall and Co-3a/Hall become Co-B-1/Hall and Co-B-3a/Hall, respectively. Although we think that this cycle should not be considered as a reduction but a production cycle.
**Table 5-2**  Comparison of Cobalt-Containing Catalytic Systems Activity in the Reaction of Hydrolysis of NaBH₄ [167]

<table>
<thead>
<tr>
<th>Name</th>
<th>Co, wt %</th>
<th>t, C</th>
<th>NaBH₄, wt %</th>
<th>NaOH, wt %</th>
<th>R, L/min×g(cat)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-1/Hall</td>
<td>8.9</td>
<td>20</td>
<td>10</td>
<td>2.5</td>
<td>1.8</td>
</tr>
<tr>
<td>Co-3a/Hall</td>
<td>16.4</td>
<td>20</td>
<td>10</td>
<td>2.5</td>
<td>3.0</td>
</tr>
<tr>
<td>Co-B-1/Hall (after first cycle)</td>
<td>8.9</td>
<td>20</td>
<td>10</td>
<td>2.5</td>
<td>0.4</td>
</tr>
<tr>
<td>Co-B-3a/Hall (after first cycle)</td>
<td>16.4</td>
<td>20</td>
<td>10</td>
<td>2.5</td>
<td>0.9</td>
</tr>
<tr>
<td>Electrodeposited Co–P</td>
<td>85.0</td>
<td>30</td>
<td>10</td>
<td>1.0</td>
<td>2.1</td>
</tr>
<tr>
<td>Graphene-Co</td>
<td>12.0</td>
<td>20</td>
<td>20</td>
<td>0</td>
<td>1.2</td>
</tr>
<tr>
<td>Co-MWCNT</td>
<td>17.0</td>
<td>20</td>
<td>20</td>
<td>3.0</td>
<td>0.9</td>
</tr>
<tr>
<td>Co–P nanotube arrays</td>
<td>94.4</td>
<td>30</td>
<td>10</td>
<td>2.0</td>
<td>2.9</td>
</tr>
<tr>
<td>Co-Zn-B/GP</td>
<td>86.0</td>
<td>30</td>
<td>3</td>
<td>5.0</td>
<td>2.2</td>
</tr>
<tr>
<td>Co–B–TiO₂</td>
<td>69.8</td>
<td>25</td>
<td>1.5</td>
<td>5.0</td>
<td>2.0</td>
</tr>
</tbody>
</table>

From Table 5-2 one can see that indeed the efficiency (R, L/min×g(cat)) of the catalysts reported earlier and R of pristine halloysite based cobalt catalysts are comparable or even higher. This fact proves that halloysite is an appropriate template for the reactions that take place in dispersive form, requires liquid permeability, and result in gas formation. Also economic feasibility of the proposed carrier is much higher than in the case of expensive artificial templates and more complicated synthesis schemes.
Consequently, further implementation of halloysite nanotubes in industrial processes can reduce the costs and simplify catalyst production and development [174-183].

5.4 Nano-Architectural Metal-Ceramic Composites for Scale Integrated Gas Sensors

We have modified previous techniques for loading catalysts on halloysite, in order to also load zirconia for gas sensor applications. Composite nano/micro materials can provide a means to tailor gas sensor components for higher efficiency. Our project will employ abundantly available aluminosilicate clay nanotubes, which we pioneered for materials research We will design core-shell mesoporous systems with enriched alumina components and location of ZrO2 nanoparticles selectively inside or outside of this tubes. With this we will drastically increase porosity of alumina-zirconia composites (shifting from micro to nanoscale), which assumingly will allow for higher impedance-metric response of such material in gas sensors. We will optimize design of our nanosystems for the highest NO /CO sensor efficiency.

Solid state electrochemical gas sensors are highly reliable devices that provide selective and accurate monitoring of harmful emissions. These sensors are favored over other gas analysis techniques, such as mass spectroscopy and gas chromatography, as they tend to have a compact size, simplistic design, and provide real-time analysis [178]. Typically, the sensor electrolyte is zirconia as it is mechanically and chemically stable under both reducing and oxidizing gas conditions; and, the high ionic conductivity contributes to the sensing response. For decades, these sensors have proven effective for monitoring automotive emissions (i.e., NO, NO2, CO and CO2) resulting from traditional fuels. As cleaner and alternative fuels such as H2 and natural gas transition into
automotive and other industries, zirconia electrolyte sensors remain critical for verifying
gas constituents in the exhaust, monitoring the release of unconsumed fuel, regulating
engine operation, and enabling early leak detection to avoid hazardous conditions.

Studies on zirconia electrolyte sensors indicate increased gas sensitivity and
accuracy in the sensor response when operated via the impedancemetric method.
Furthermore, studies indicate modifying the microstructure of sensor components (i.e.,
the electrolyte and electrodes) can help to limit undesirable reactions, thereby, enabling
greater detection of target gases at substantially lower gas concentrations. This is
beneficial for early leak detection, monitoring clean diesel emissions, and air quality
control. Recent impedancemetric sensor studies have found the porous microstructure of
the electrolyte significantly influences sensor sensitivity to the analyte gas [184].
Identifying a suitable electrolyte porosity typically involves taking into account the
pathways required for gas diffusion along with the necessary reaction sites at the
electrode/electrolyte interface. Increasing the concentration of reaction sites promotes gas
sensing reactions, but also has the counter effect of constricting gas diffusion pathways
causing a slow sensor response. Practical sensors must demonstrate high sensitivity and
accuracy, as well as a rapid response [185].

5.5. Procedure

Various experiments were performed and the following procedure gave the best
results: 18 mg of Y2O3 was dissolved in 1M HCl with ethanol to increase solubility. The
solution was stirred for two nights. 0.3g ZrOCl2*H2O was dissolved in 100mL H2O, then
0.5g HNTs was added and the mixture was sonicated for 30 min, followed by stirring for
two nights. The two mixtures were put in autoclave and heated to 160°C for 24 hours. The mixture was washed with water twice then dried at 80°C overnight.

5.6. Results

There was a high yield of HNTs coated with yttria-stabilized zirconia nanoparticles. The size of the nanoparticles varies (10-50nm). The shape of the nanoparticles varies as well but the overall shape is spherical, and aggregates of small, relatively spherical particles form the larger irregular shapes.

Figure 5-9: SEM images of zirconia nanoparticles loaded on halloysite nanotubes
5.7 Conclusions

Cobalt mesocatalysts were synthesized using four methods: Wet impregnation of cobalt chloride into halloysite, adsorption of cobalt (II,III) oxide onto halloysite, and cobalt chloride linkage onto/into halloysite using azines as well as APTES. The most efficient catalyst was the halloysite loaded with cobalt chloride using the azine acetone as a ligand with an R value (L/min x g(cat)) of three. This is a higher loading than other previously made cobalt mesocatalysts which ranged from 0.9-2.9.

Halloysite was also used to load zirconia nanoparticles for gas sensor applications. We synthesized Y_2O_3-ZrO_2 on halloysite clay nanotubes, an example of an external metal oxide – internal ceramic core-shell system. This produced 5-10 nm diameter particles on the nanotubes. This system could potentially limit particle agglomeration at working temperatures of 500 °C.
CHAPTER 6

SULFUR NANOCONFINEMENT USING HALLOYSITE NANOTUBES FOR INCREASED LITHIUM-SULFUR BATTERY EFFICIENCY

This chapter is a collaborative work with Dr. Wang’s research team in the Institute for Micromanufacturing, and it was submitted for publication by Y. Pei, Y. Wang, Y. Darrat, A-Y. Chang, Y. Lvov, and S. Wang, to J. Power Sources. The title is “Confining Sulfur Particles in Clay Nanotubes with Improved Cathode Performance of Lithium-Sulfur Batteries.”

6.1. Preview

Not only can halloysite be used as a nanocontainer for catalysts, it also can be used to confine sulfur particles for enhanced lithium-sulfur battery efficiency. We have synthesized a novel cathode material consisting of halloysite nanotubes containing sulfur particles to improve cycling stability of lithium sulfur batteries.

Battery systems are crucial to store and utilize clean and abundant alternate energy from wind, ocean, and solar power; it is also crucial to ensure they are efficient and cost-effective [186-190]. Rechargeable lithium-sulfur batteries (Li-S) have a high energy storage capacity (a theoretical specific capacity of 1,673 mAh/g, which is five times that of existing lithium-ion batteries, LIBs) [190]. However, there are drawbacks.
Li-S batteries are currently not practical because of the sulfur cathode because of the following reasons: low conductivity cathode degradation. Cathode degradation happens due to parasitic shuttle reactions induced by dissolution of lithium polysulfides (Li$_2$S$_x$, $4 \leq x \leq 8$), large volumetric expansion (~80%) upon lithiation, and self-discharging [190-194]. In the past decade, scientists have been trying to figure out how to mitigate these issues for example by utilizing sulfur/carbon composites to increase sulfur cathode conductivity [194-195] and incorporating additional layers [191-195] and porous structures [196-203] to slow down or lock intermediate polysulfides and prevent them from migrating away from the cathode (shuttle effect). However, the presence of large grain sulfur particles in these materials aggregate which reduces reactive surface area. It also restricts the diffusion of Li$^+$ ions and transformation kinetics between sulfur and lithium sulfur (Li$_2$S). In order to decrease these effects, some pioneer scientists found that sulfur nanoparticles adhered to a conductive carbon host in monodispersed status are effective to achieve almost theoretical discharge performance [204-206]. It also shown that even a slight increase of the size of sulfur nanoparticles causes nearly 25% loss of the initial capacity when sulfur nanoparticles of five nm are replaced by 40 nm ones [205]. Sulfur species naturally change in dimensions and migrate away from their support structures during long-term cycling. The unsolved polysulfide shuttle effect and deposition issue of Li$_2$S when alternating between charge and discharge cycles further worsen the electrical contact issue within the sulfur cathode, especially at high current rates. Our goal was to maintain the dimensions of sulfur nanoparticles with efficient sulfur utilization.
Since halloysite has a rolled-up tubular nanostructure, an inner nanotube diameter of 15-20 nm, a gap between neighboring roll layers of 7-10Å, and an average length of 0.5-2 µm, it was our nanomaterial of choice for solving the typical problems of lithium sulfur batteries [206-207]. This is done by incorporating sulfur within the halloysite lumen and interlayer spacings to prevent sulfur expansion upon lithiation as well as mitigating lithium polysulfide dissolution into the electrolyte. It was also previously shown that addition of 5-10 wt % of halloysite to polyethylene oxide based electrolytes increased ionic Li\(^+\) conductivity for LiTFSI, giving \(\Omega \sim 1.5 \times 10^{-4}\) S/cm, while also increasing tensile strength \(\sigma = 50-60\) MPa [37-38].

The halloysite lumen has an appropriate size to confine sulfur nanoparticles while not too small to significantly impede the diffusion of Li\(^+\) ions (Figure 6-1b). Halloysite nanotube clusters have nanoscale spaces which could divide electrolyte and solid-electrolyte interphases as well as provide an extra diffusion barrier minimizing dissolution and migration of polysulfides. (Figure 6-1c). To increase sulfur loading percentage, halloysites are first etched by sulfuric acid to increase the volume of the inner lumen. Prior to serving as the host of sulfur particles, a conductive carbon skin is coated on the surface of halloysites nanotubes through a hydrothermal method using glucose as the precursor. Sulfur is further introduced by wet impregnation with sulfur nanoparticles initially dissolved in either toluene or ethylene diamine (EDA). These nonpolar solvents were used since sulfur is nonpolar. The sulfur and carbon loaded halloysite is then mixed with other cathode additives and assembled into coin batteries to analyze the electrochemical performance.
6.2. Experimental Details

6.2.1. Materials and Reagents

Halloysites nanotubes were supplied by Applied Minerals Inc., NY. The dimensions are length of 300-600 nm, external diameter of 50-60 nm and inner lumen diameter of 10-15 nm. Sucrose, sulfur, ethylene diamine (EDA), toluene, N,N-dimethylformamide (DMF, 99.8%), bis(trifluoromethane-sulfonyl)imide (LiTFSI), LiNO₃, lithium hexafluorophosphate (LiPF₆, 99.99%), 1,3-Dioxanes (DOL) and Dimethoxyethane (DME, with DOL: DME, 1:1 by vol.%), were purchased from Sigma-Aldrich (St Louis, MO). Aluminum foil (250 μm thick), microporous polypropylene membrane (25 μm thick) separator, and coin cells were purchased from MTI Corporation.
(Richmond, CA). All chemicals and materials were used without further purification or treatment unless specified.

6.2.2. Halloysite Preparation

Aggregated halloysite clusters were first grinded in mortar and filtered to remove debris. The fine halloysite nanotubes were then treated with sulfuric acid (0.5-3 M) at 50-90 °C for 4-8 hours as described in [40]. The acid etched samples were washed until pH of supernatant was almost neutral, then dried in oven. A carbon layer was introduced onto the nanotube surface through a glucose hydrothermal treatment. Briefly, halloysites are loaded into a glucose aqueous solution (1.0 wt%) and hydrothermally treated at 160°C for four hours in a Teflon-lined autoclave. The samples were then dried followed by calcination in a quartz tube reactor at 800°C for three hours at a heating rate of 3°C/min under N₂ gas flow protection. The calcination process removes hydrogen producing pure carbon, making the sample conductive. The purpose of the N₂ maintain an inert atmosphere to prevent unwanted side reactions such as oxidation.

6.2.3. Sulfur Loading in Halloysites

Sulfur was loaded into halloysite nanotubes by wet impregnation. Sulfur powder was first dissolved in EDA or toluene to form a saturated sulfur solution. The etched, carbon coated halloysite was then mixed with a sulfur solution and incubated with stirring for six hours with a halloysite/sulfur ratio of 1:4. After vacuum drying overnight, the powder was further moved in a quartz tube furnace. The conditions were 180°C at a heating rate of 5°C/min in N₂ atmosphere. The HNTs/sulfur samples were held there for another two hours after reaching the desired temperature to evaporate solvent and evenly
coat the sulfur within the composites. Thermogravimetric analysis was used to calculate the actual sulfur mass in the obtained HNTs/sulfur composites.

6.2.4. Material Characterization

Scanning electron microscopy (SEM) images were taken using a Hitachi S-4800 instrument. All samples (excluding halloysites with only carbon skin) were sputter coated with gold to reduce the potential charging effect. Energy-dispersive X-ray spectroscopy (EDX) was conducted by a TEAM EDS analysis system installed on the SEM at 15 kV.

Nitrogen adsorption isotherms of halloysites were obtained at liquid N2 temperature on a Quantachrome Instruments NOVA 2200 surface area analyzer. Samples were degassed at 300 °C for three hours before measurements were taken. The total surface area was calculated according to the Brunauer–Emmett–Teller (BET) method. The pore volume and size distribution were obtained by the Barrett–Joyner–Halenda (BJH) analysis of the desorption branch of the isotherm.

X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance X-ray diffractometer using Cu Kα radiation at room temperature at 40 kV and 40 mA. Data was collected with the 2θ range of 6–60° at a step size of 0.02°.

Thermo-gravimetric analysis (TGA) was done to monitor the weight loss of composite samples using a TGA 2050 Thermogravimetric Analyzer (TA Instruments, Inc). The thermal scanning was performed from 30 to 400 °C at a ramp rate of 10 °C min⁻¹ in air environment.

6.2.5. Battery Performance Tests

The ratios of components in the cathode material was 80 wt% of HNTs/sulfur, ten wt% of super P carbon black, and ten wt% of polyvinylidene fluoride (PVdF) binder
in N-methyl-2-pyrrolidone (NMP). The mixture was then spread on flat aluminum foil surface and dried in a vacuum oven at 120 °C for 12 hours to completely remove solvent. The dried samples were cut into discs and moved to a glove box under an inert argon atmosphere.

The electrolyte was prepared by dissolving 1M bis(trifluoromethanesulfonyl)imide (LiTFSI) and 0.1M LiNO₃ in a mixture of 1,3-Dioxanes (DOL) and Dimethoxyethane (DME, with DOL: DME, 1:1 by vol.%) a microporous polypropylene membrane (25 µm thick) was used as the separator. The CR2032 coin cells were assembled with the HNTs/sulfur composites as the cathode and a lithium disc as the anode in an argon-filled glove box. Their electrochemical performance was evaluated by galvanostatic charge/discharge cycling under different current rates. A voltage range of 1.8 and 2.8 V versus Li+/Li was used in charge and discharge tests with the specific capacity calculated based on the actual mass of sulfur content measured by TGA prior to assembly with a typical load of ~2-10 mg. Electrochemical impedance spectroscopy (EIS) measurements were conducted on Autolab PGSTAT302N electrochemical workstation (Metrohm, Switzerland). The ac perturbation signal was set at ten mV with a frequency range of 10⁻¹ -10⁵ Hz.

6.3. Results and Conclusions

6.3.1. Etched Halloysites Nanotubes

The specific surface area of pristine halloysite sample was of 34.2 m²/g, a pore volume of 0.15 cm³/g, and an average pore size of 19.4 nm, calculated based on N₂ BET desorption isotherm (Figure 6-2). To expand the lumen space and shorten the nanotube length, halloysites were etched with H₂SO₄ to remove some layers of aluminoxane inner
rolls. The appropriate lumen size of halloysite and uniform lumen size distribution make them favorable sulfur confinement hosts for battery applications.

![Graph](image.png)

**Figure 6-2:** (a) BET surface texture property and (b) pore size measurement of halloysite nanotubes

### 6.3.2. Sulfur Loading in Halloysite Nanotubes

Sulfur was loaded into halloysites in the same way (wet impregnation) for both untreated and acid etched halloysites. Elemental sulfur was initially dissolved in an appropriate solvent and quickly mixed with halloysite powders for six hours. In this way, sulfur is introduced both in the inner central lumen and on the external surface of halloysites nanotubes (Figures 6-3a & 6-3b). For sulfur loaded inside the lumen space of halloysites, the size of the loaded sulfur particles loaded within the lumen vary from several nanometers to around the diameter of lumen due to the space restriction, as shown in Figure 6-3b. The TEM image in Figure 4b is a unique one because it shows directly loaded sulfur particles occupying approximately a half of the lumen volume, which may be estimated as ca. ten wt % loading respective to the total tube’s mass. It is assumed that the majority of sulfur loading is on the external surface.
Figure 6-3: (a) SEM, (b) TEM, and (c) EDS element mapping images of sulfur-loaded carbon/halloysite composites. In panel c, subpanel c(i) is a SE image of carbon/halloysite composites location done for element mapping analysis and subpanel c(ii-vi) are x-ray images for carbon, oxygen, silicon, aluminum, and sulfur elements, respectively.

The free sulfur nanoparticles located outside halloysites reach 30 nm or larger, since the lumen is not involved in restricting the size. Annealing was performed to help disperse sulfur coating uniformly on the host surface. EDS elemental mapping images in low magnification show sulfur evenly dispersed on the composite (Figure 6-3c). This is important to avoid large aggregates which decrease overall battery efficiency. The annealing process also helps to adhere the sulfur to the halloysite surface, as well as forming clusters of halloysite. This leads to neighboring halloysites assembling into large clusters which create many nanoscale voids in between them (Figure 6-1c). These nanovoids slow down the dissolution of lithium polysulfides via diffusion restrictions.
The XRD spectrum show the characteristic peaks for sulfur and halloysite in the halloysite/sulfur composite sample (Figure 6-4a). Strong sulfur peaks can be seen which indicate high sulfur loading on halloysites. As shown in Figure 6-4b, for untreated halloysites nanotubes, sulfur loading weight percentage is 7.6% and 30%, respectively when sulfur/toluene and sulfur/EDA solution is used as the sulfur loading media, respectively. Due to the hydrated halloysite surface, more sulfur loading with a sulfur/EDA solution than that with a sulfur/toluene solution is probably attributed to two different effects. One is the strong hydrophilicity of halloysite surface and the affinitive interactions of amine groups of EDA and hydroxyl groups of halloysites. Capillary forces pull in the sulfur/EDA solution deep within the nanotubes to have more sulfur uptake dosage. The other reason is the acidic lumen surface. The majority of the lumen is comprised of Aluminum. So many acidic sites are there which have a high affinity for sulfur within the loaded sulfur-EDA complex precursor solution [28]. This is also a contributing factor to the small size of the sulfur that is loaded. The etching process also increases the surface area and pore volume of halloysite nanotubes. As a result, the sulfur loading capacity of etched halloysites is increased. It shows in Figure 6-4b that the loading dosage of sulfur in etched halloysites reaches 62 ± 5 wt % and 75 ± 5 % for the sulfur/toluene and sulfur/EDA solution loading media respectively. The maximum loading volume within the lumen of halloysite is ten wt. %, so the rest will be loaded on the surface of the nanotubes. The sulfur/EDA solution performed better than the sulfur/toluene solution in terms of sulfur impregnation into/onto halloysite. Therefore, sulfur was loaded into etched halloysites nanotubes samples from EDA solution unless otherwise specified.
Figure 6-4: (a) XRD spectra of the composites with spectra of pristine halloysite and pristine sulfur for comparison; (b) TGA of halloysite loaded with sulfur using various sulfur solutions: (I, ii) sulfur in toluene and (iii, iv) sulfur in ethylene diamine; (i, iii) halloysite nanotubes without H₂SO₄ etching and (ii, iv) with H₂SO₄ etching

6.3.3. Battery Testing Performance

HNTs/sulfur composites cathode was analyzed galvanostatic charge/discharge experiments. This is to show the electrochemical performance. Figure 6-5a shows the effect of different current rates on the specific capacity of the coin battery using the synthesized composite cathode. Its specific capacity for both charge and discharge steps shows good preservation of the cathode for the next 50 cycles.

Figure 6-5: Different current rates of coin battery using the synthesized composite cathode
Unlike largely matched charge and discharge capacity at small current rates (0.1C and 0.5C), elevated current rates (1C and 2C) cause obvious capacity differences between discharge and charge steps with a coulombic efficiency dropped to 92-94%. High charge/discharge rates cause migration issues of Li\(^+\) ions inside nanotubes. Nonetheless, the charge and discharge capacity at the same current rate sustain with only minor variations, indicating the lithiation or delithiation situations in the composites are similar during short-term cycling. The HNTs/sulfur composites also exhibited long-term cycling. For over 250 cycles, the capacity of the composite cathode retains 84% of 657 mAh g\(^{-1}\) and nearly 100% of the coulombic efficiency (Figure 6-5b). These satisfactory electrochemical results suggest that the halloysite nanotube template serves its purpose as an effective nanoconfinement material for lithium sulfur batteries.

6.3.4. Conclusions

The core-shell methodology was applied to lithium sulfur batteries to enhance their efficiency. The purpose of these composites was to confine and disperse highly loaded sulfur nanoparticles. The nanoscale spaces in the lumen of halloysites nanotubes confine the sulfur, and the nanoscale voids in between assembled halloysites clusters also help suppress the dissolution and migration of polysulfides in liquid electrolyte solution. The sulfur loading in the composites could reach as high as 80 wt\%, after treatment processes such as etching to enlarge the lumen of halloysite. The HNTs/sulfur composites were incorporated into coin batteries and successfully improve the cycling stability, retaining ~84% of the starting capacity for over 250 cycles.
CHAPTER 7

CONCLUSIONS

7.1. Core-Shell Mesocatalysts-Ru

There are a variety of techniques to synthesize catalytic nanoparticles onto/inside halloysite. To enhance inner-wall and lumen metal cluster formation, we intercalated the tube with furfuraldehyde and then converted it to tetradeutate ligands. Therefore, a simple method of linking metal particles using ligand-functionalized halloysite nanotubes (ligand-HNTs) was suggested. The reduction of the sample with NaBH₄ and cooling the halloysite composite resulted in formation of metal particles in the nanotube interior and freeing the ligands which allowed for repetition of the process and further enrichment of the tubes with metal up to nine wt.%. These Ru-halloysite core-shell mesocatalysts were tested in hydrogenation of phenol in aqueous phase and demonstrated high catalytic efficiency (2–times higher than commercially available Ru-catalysts). A high catalytic activity in phenol hydrogenation was due to optimization of Ru-content, its distribution on the nanotubes, the particle sizes, and metal-valence. A high maximum turnover frequency (TOF) was achieved (17282 h⁻¹) in terms of hydrogen uptake per surface Ru-atoms.
7.2. Core-Shell Mesocatalysts-Co

Halloysite were used as a nanostructure template to also load cobalt particles. Samples were prepared using four main methods: Wet impregnation of cobalt chloride into halloysite, adsorption of cobalt (II,III) oxide onto halloysite, and cobalt chloride linkage onto/into halloysite using azines as well as APTES. The most efficient catalyst was the halloysite loaded with cobalt chloride using the azine acetone as a ligand with an R value (L/min x g(cat)) of three, which is higher than other previously made cobalt mesocatalysts which typically range from 0.9-2.9.

7.3. Y$_2$O$_3$-ZrO$_2$ Core-Clay Shell Systems for Gas Sensors

In addition to supporting metal catalytic nanoparticles, halloysite was used to load zirconia nanoparticles for gas sensor applications. Yttria stabilized zirconia particles (Y$_2$O$_3$-ZrO$_2$) on halloysite clay nanotubes were produced via hydrothermal synthesis. This produced 5-10 nm diameter particles on the nanotubes providing a large surface area in terms of active zirconia for potential use in gas sensor applications.

7.4. Sulfur-Halloysite Core-Shell System for Li-Battery

Halloysite nanotubes were also used as a nanoconfinement structure to load sulfur particles for increasing lithium-sulfur battery efficiency. The available nanoscale space in the lumen of halloysites nanotubes and between assembled halloysites clusters also help suppress the dissolution and migration of polysulfides in liquid electrolyte solution. Through appropriate treatment, the sulfur loading in the composites could reach as high as 80 wt %. When assembled as the cathode of Li-S batteries, the halloysite/sulfur composites successfully improve the cycling stability, retaining ~84% of the starting
capacity for over 250 cycles. The migration difference of Li$^+$ ions outwards and into the hollow nanostructure of halloysites depends on the length of nanotubes during the discharge step and only those with small aspect ratios show good sulfur utilization and no obvious capacity fading at intermediate current rates.
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