Halloysite nanotubes as support for metal-based catalysts

M. Massaro,a C. G. Colletti,a G. Lazzara,b *S. Milioto,b R. Noto,a and S. Riela,a

Halloysite nanotubes (HNTs) are clay minerals with a hollow nanotubular structure. There is growing interest in these nanomaterials, due to their biocompatibility, potential applications and availability. The surface chemistry of HNTs is versatile for the targeted chemical modification of the inner lumen and outer surface. Functionalized halloysite constitutes a valuable support for metal nanoparticles, promoting catalytic applications with tunable properties. The peculiar tubular shape of HNTs favors the dispersion and surface availability of the supported metal nanoparticles that are active in the catalytic path. Moreover, the presence of an empty lumen opens new perspectives for the production of nanoarchitectures with synergistic catalytic effects, due to the increase in local concentrations and confinement. The main focus of this review is the research on modified halloysite nanotubes for the preparation of valuable supports for metal nanoparticles and their applications in catalytic processes.

1 Introduction

Since its introduction to the chemical industry by J. Roebuch in 1746, catalysis has played an important role in chemical research. Nowadays, approximately 85–90% of the products of the chemical industry are made in catalytic processes. In particular, due to disadvantages presented by the traditionally employed homogenous catalysts, much attention is devoted to the development of heterogeneous catalysts based on metal nanoparticles (NPs). The benefits of the use of metal-NPs as catalysts in the chemical industry are related to the increasing selectivity and activity of catalysts by controlling pore size and particle characteristics. Unfortunately, metal-nanoparticles have a tendency to agglomerate, forming large particles with low catalyst efficiency. To prevent the aggregation of metal-NPs...
during the catalyst’s synthesis process or a catalytic reaction, they are usually dispersed, but are preferably anchored to high surface-area and robust supports, so the reactant molecules can reach as many surface atoms of the metal as possible. When NPs are dispersed on high surface-area supports, their interactions with the support surfaces become important in determining their catalytic performances.\(^1\)

Many efforts have been devoted to the synthesis of various supports for metal nanoparticles based on silica, alumina, zeolites, organic polymers, dendrimers, fullerenes and so on.\(^2\)\(^,\)\(^3\)

Fullerene-ionic liquid and amorphous silica decorated with \(\text{C}_{60}\)-ionic liquid have been employed in order to immobilize PdNPs.\(^7\)\(^,\)\(^8\) These materials have been tested in the Heck and Suzuki couplings, showing high catalytic performances as well as high recyclability in both of the investigated reactions.

In recent years, the use of organic or inorganic nanotubular materials as catalyst supports has attracted much attention by reason of their exceptionally large surface area and peculiar tubular structure with an empty cavity. The metal-NPs can be generated \textit{in situ} within the limited space in nanotubes, and this strategy hinders the agglomeration of the catalyst.

More recently, Giacalone \textit{et al.} reported a heterogeneous palladium catalyst supported on single walled carbon nanotube-polyamidoamine dendrimers, and its efficiency in promoting C–C coupling reactions.\(^9\) The chemical functionalization of the tubular nanomaterial plays an important role in improving the dispersibility of the tubes and consequently their catalytic performance.

In the last 10 years, tubular halloysite clay has been considered an emerging nanomaterial, which has found application in several fields, especially in catalysis. Halloysite is particles and polymer/nanoparticle interactions. He is involved in several projects on halloysite clay nanotubes for drug delivery and conservation of Cultural Heritage. Lazzara has more than 90 publications in peer-reviewed international journals.

Giuseppe Lazzara received his Ph.D. in Chemistry from University of Palermo, Italy, in 2007. He conducted postdoctoral studies at the Chemistry Department, Lund University (Sweden). Lazzara became an associate professor in the Department of Physics and Chemistry, University of Palermo (Italy) in 2015. His research activities focus on smart nanomaterials, nanoparticles and polymer/nanoparticle interactions. He is involved in several projects on halloysite clay nanotubes for drug delivery and conservation of Cultural Heritage. Lazzara has more than 90 publications in peer-reviewed international journals.

Serena Rieła has been an Assistant Professor at the University of Palermo since 2002. She received her Ph.D. from the University of Bologna in 2000, under the supervision of Prof. D. Spinelli. She was post-doctoral researcher at the Organic Chemistry Department of the University of Palermo. She spent one year at University of California Los Angeles (UCLA) under the supervision of Prof. F. Stoddart and eight months at the University of Bordeaux 1 under the supervision of Prof. A. Castellan. Her current interests are focused on the chemical modification of halloysite nanotubes and their applications in catalysis, drug delivery, bioremediation, and so on. Rieła is the author of about 70 publications in peer-reviewed international journals.

Stefana Milioto received a Masters Degree in Chemistry at the University of Palermo in 1985. She defended her Ph.D. thesis in Chemical Sciences in 1989. She was Research Scientist (until 1998) and associate professor (until 2001) in Physical Chemistry. At present, she is a full Professor in Physical-Chemistry in the Department of Physics and Chemistry of the University of Palermo. Her scientific interests deal with the physico-chemical studies of eco-compatible nanostructures (self-assembled structures as well as solid nanoparticles) functionalized for application in the field of Cultural Heritage, drug delivery, and so on. She has more than 130 publications in peer-reviewed international journals.

Renato Noto obtained his chemistry degree from the University of Palermo in 1970. He has been a full Professor of Organic Chemistry since 1990. He began his research activity in the field of physical organic chemistry. Then, he became interested in the stereo-controlled synthesis of functionalyzed heterocyclic rings and studies on the inclusion equilibria of aromatic molecules in cyclodextrins. Recently he has turned his attention toward the behavior of organic salts as ionic liquids and/or gelators, and the use of functionalized halloysite nanotubes as catalytic systems or drug carrier systems. He is the author of more than 220 publications and five reviews.

F. Stoddart and eight months at the University of Bordeaux 1 under the supervision of Prof. A. Castellan. Her current interests are focused on the chemical modification of halloysite nanotubes and their applications in catalysis, drug delivery, bioremediation, and so on. Rieła is the author of about 70 publications in peer-reviewed international journals.

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a natural phyllosilicate with Al : Si ratio of 1 : 1, similar to the
platy kaolin. The origin of these two clay minerals is due to the
process known as “kaolinization”. Imperfections in the crystal
lattice of the halloysite, due to the interferences in the interlayer
of water molecules, cause a misfit between different alumi-
nowsilicate layers, which in turn causes the halloysite platelets to
roll up into a tubular form.

HNTs are widely deposited in soil in wet tropical and
subtropical regions, weathered rocks, and soil generated from
volcanic ashes. Very pure halloysite that possesses 90–98% of
tubular structure (HNTs) is available in abundance only in
France, Turkey, China, New Zealand and USA. Currently, the
HNTs price ranges from US $600 per ton for application in
fracking, to US $3000 per ton for fine chemical applications. In
addition, HNTs were found to be eco-compatible and non-toxic
nanomaterials. These features are also present in functional-
ized-HNTs.11,12

It easy to imagine that in the near future HNTs could replace
the much more expensive carbon nanotubes and in many cases,
HNTs could be used in high technological applications where
carbon nanotubes are just not suitable.

The global market for HNTs was approximately US $30 000
and this number is expected to rise dramatically to US $20
billion by 2022. The growing interest in HNT is reflected in the
increasing number of scientific publications and patents
observed in the last 20 years (Fig. 1a). There are several fields of
application for this smart nanomaterial, including drug trans-
port and delivery,16,17–19 environmental remediation,20–26 as a
filler in polymeric matrices,27–30 flame retardant31 and support
for catalysts13,23 (Fig. 1b).

This paper covers contributions in the last decade about the
use of halloysite nanotubes as a support for metal nanoparticles
and it provides information on several catalytic processes such
as oxidation, reduction, photodegradation, cross-coupling
reactions, as well as on the catalytic mechanism involved
(Fig. 1).

2 Structure and physico-chemical
properties of halloysite
From a chemical point of view, halloysite nanotubes with a
general formula of Al2Si2O5(OH)4/nH2O, are approximatively
40–60 nm in external diameter, 10–15 nm in the internal
diameter and 500–1500 nm in length, depending on the
extraction site and purification processes. Typically, HNTs have
10–15 aluminosilicate layer rolls. The presence of a monolayer
of water molecules in the interlayer space gives a basal distance
of 0.1 nm (n = 2); after dehydration, the basal distance becomes
0.07 nm in a completely non hydrated form (n = 0). The dehy-
dration is irreversible.32 HNTs consist of multiply rolled

Fig. 1 Comparison of (a) the annual number of scientific publications and patents related to the term “halloysite nanotubes”; (b) application fields of “halloysite nanotubes”; (c) reactions catalyzed by metal nanoparticles supported on “halloysite nanotubes”. The data reflect the past 20 years. (Data analysis of publications was done using the SciFinder Scholar search system with the term “halloysite nanotubes”, as on March 2017).
kaolinite sheets of octahedral gibbsite \( \text{Al(OH)}_3 \) and tetrahedral \( \text{SiO}_4 \). The different layers are linked to each other by hydrogen bonds formed between oxygen atoms of the tetrahedral sheet and inner-surface OH groups of the octahedral sheets (Fig. 2). The layers lead to the tubes having Si–O groups at the outer surface and Al–OH groups at the inner surface. They undergo ionization in aqueous media in the opposite way, generating a tube with inner and outer surfaces oppositely charged. This charge separation occurs in water within a wide pH range, from 3 to 8. Experimentally, the charge separation is predicted by comparing the negative and positive values for the electrical z-potential of silica and alumina surfaces in water, respectively (Fig. 3).

The different chemical compositions of the surfaces allows for selective loadings of positively charged molecules outside the nanotubes and negatively charged molecules inside the lumen that consists of the 10–15 vol% of the pristine tubes, or 30–40 vol% after etching with sulfuric acid. Therefore, chemical agents such as macromolecules, including drugs, DNA, proteins and other chemical active agents, e.g., for protective coating against corrosion, can be entrapped in the lumen. The empty lumen acts as a miniature container for processes that benefit from sustained release.

Besides drug immobilization in the inner lumen of the HNTs, some inorganic salts can be loaded and released from the halloysite lumen. Therefore, ammonium molybdate (\( \text{NH}_4\cdot6\text{MoO}_7\text{O}_{24} \)), potassium permanganate (\( \text{KMnO}_4 \)), sodium silicate (\( \text{Na}_2\text{SiO}_3 \)) and sodium chromate (\( \text{Na}_2\text{CrO}_4 \)) can be loaded into HNTs from their saturated solution in water via vacuum cycling. Complete release of the inorganic compounds from halloysite nanotubes is achieved within 1–2 hours.

The different charges on the surfaces are also exploited for the simultaneous interaction of an organic compound with both surfaces. In this context, a potential multi-pocket nano-container was obtained by combining halloysite nanotubes with cucurbit[8]uril. Abdullayev et al. exploited the loading of benzotriazole (corrosion inhibitor) and the obtained material was mixed into paint coatings in the amount of 2–10 wt%. Furthermore, the different inner and outer-compositions of halloysite facilitated different chemical reactions on each surface.

Modification of the halloysite outer surface can indeed improve clay dispersal in polymeric matrices or in solvents. Moreover, selective lumen modification via the covalent bonds of functional groups could open up new applications based on molecular recognition, such as molecular storage, molecular separation, catalysis and drug delivery.

The increasing interest in these nanomaterials could involve, in the long term, the release and accumulation of the nanoclay in the environment and could therefore cause damage to human health or plants; therefore, it is important to study the toxicity of halloysite nanotubes towards living organisms. Several recent studies reported the investigation of halloysite nanotoxicity in vitro, employing human cell cultures and microbial cells. The first example of a phytotoxic study on halloysite used as a support for palladium nanoparticles was reported, where each experiment performed showed that HNTs are safe materials, even at high concentration.

### 3 Support for metal nanoparticles

HNTs possess several advantages, including high stability, resistance against organic solvents, and ease of disposal or reusability.

In comparison to platy clays such as montmorillonite, kaolin and LAPONITE® that are stacked in larger crystallites, halloysite does not need exfoliation and thus has a large surface area without any additional material treatment. All these features
provide the metal nanoparticles supported on halloysite nanotubes with several advantages for their industrial application.

The most widely used method for supported metal nanoparticles involves the halloysite external surface modification with suitable functionality, able to interact with the metal salts, followed by reduction in order to obtain metal nanoparticles. Otherwise, it is possible to immobilize metal nanoparticles on the HNT surface by physical adsorption or self-assembly. In this context, Fe, Co, Ni and Pd were adsorbed on the halloysite surface, leading to hybrid nanomaterials. \(^{63,64}\) TiO\(_2\) nanoparticles were bound to the nanotube surface through silane linkage. \(^{64}\) Ag nanoparticles were successfully immobilized on halloysite by dispersing the nanomaterial in an aqueous solution of precursor AgNO\(_3\) and followed by a reduction reaction in the presence of reductants such as NaBH\(_4\) or polyols. \(^{65}\)

Since nanoparticles loaded into the HNT lumen are expected to be more stable than those supported on the external surface, it is interesting to design metal–halloysite hybrids where metal nanoparticles are located inside the tubes (Fig. 4). \(^{66}\) In this way, it is also possible avoid metal aggregation. Ouyang et al. reported the preparation of Ag NPs/HNTs composites under vacuum conditions. \(^{67}\) With this method, the solution of silver acetate fills the lumen of HNTs under vacuum and it is subsequently transformed to Ag NPs by a pyrolytic process.

In another work, Ag nanoparticles were loaded into the HNT lumen by exploiting the different charges between the external surface and the inner one. This method considers the electrostatic interactions between N-acetyl-l-cysteine-modified Ag NPs and the positively charged HNT lumen. The Ag NPs loaded in the lumen of HNTs possess excellent structural stability due to the irreversible electrostatic interaction. \(^{68}\)

Similarly, Cu–Ni NPs were loaded into the halloysite internal surface by means of a ligand-assisted reduction of Cu\(^{2+}\) and Ni\(^{2+}\)-cations, followed by annealing. Specifically, Cu–Ni NPs were encapsulated in the HNT lumen by co-reduction of CuCl\(_2\) and NiCl\(_2\) in aqueous ethanol. In order to better disperse the cationic metals ions onto the alumina surface, sodium citrate was used as a cation-delivery ligand, exploiting, also in this case, electrostatic interactions. The cations were finally converted to the required Cu–Ni NPs by treatment with hydrazine at 80 °C. \(^{69}\)

A different strategy to fill the HNT lumen with CuO was reported, where inorganic reverse micelles were developed using alkyltrimethylammonium bromide surfactants adsorbed at the outer HNTs surface. The as-prepared reverse inorganic micelles generated water-in-oil emulsions, and copper sulphate aqueous solution was entrapped in the lumen. After calcination, uniform CuO distribution in the HNTs lumen was observed. \(^{69}\)

### 3.1 Oxidation reactions

Amines, alkenes, alkanes, alcohols and aromatic compounds were found to be able to undergo conversion to the corresponding oxygenated chemicals catalyzed by metal-based nanocomposites. Among the metal supported catalysts, gold nanoparticles have attracted more and more attention since this metal possesses unique catalytic properties under mild conditions. \(^{70,71}\)

Gold nanoparticles were successfully loaded on halloysite \(^{72}\) and the obtained Au/HNTs hybrid showed high catalytic activity for the solvent-free aerobic oxidation of benzyl alcohol. \(^{73}\)

\(\alpha,\beta\)-Unsaturated ketones are very important intermediates in organic synthesis and over the years, they have found broad applications in many fields, such as chemosensors for metal ions, \(^{74}\) building blocks and products of pharmaceutical interest \(^{75}\) and intermediates of many natural products and bioactive compounds. \(^{76}\) \(\alpha,\beta\)-Unsaturated compounds are easily obtained by the allylic oxidation of cyclohexene that represents the most promising starting material for this kind of reaction. Thus, finding the optimal oxidation conditions is a challenging task. CuO nanoparticles were successful loaded on halloysite nanotubes and employed for oxidation of cyclohexene to 2-cyclohexene-1-one. \(^{77}\) Catalytic studies revealed that pristine halloysite showed no activity in the oxidation of cyclohexene. The CuO nanoparticles exhibited a higher selective oxidation performance, achieving an 84% maximum conversion and 82% maximum selectivity for 2-cyclohexene-1-one at 70 °C. In contrast, for the CuO/HNTs catalysts, at 70 °C, the conversion of cyclohexene and selectivity of the target product of 2-cyclohexene-1-one were remarkably increased to the maximum values of 99% and 98%, respectively, exhibiting 15% higher

![Fig. 4](image-url)  
**Fig. 4** Schematic representation of the synthesis of Ru nanoparticles inside the HNT lumen. Reproduced from ref. 66 with permission from Taylor and Francis Online.

![Fig. 5](image-url)  
**Fig. 5** Catalytic activities of HNTs, nano–CuO and nano–CuO/HNTs catalysts as a function of reaction temperature. Adapted from ref. 77 with permission from Elsevier.
values than those of the CuO nanoparticles (Fig. 5). Furthermore, recyclability studies showed that the synthesized nanocatalyst retains its catalytic activity at least for three cycles, maintaining the stabilizing conversion and excellent selectivity. Carrillo and Carriazo,\textsuperscript{78} reported the synthesis of Co and/or Cu oxides supported on halloysite nanotubes as effective catalysts for the total oxidation of toluene, the most used VOC for industrial purpose. The supported catalysts, using Cu and/or Co oxides as the active phase, showed elevated activity for the complete combustion of toluene at moderate temperatures. Among the monometallic catalysts, the cobalt catalyst showed better performance than copper catalyst. A cooperative effect was observed between the copper and cobalt oxides, and Cu/Co molar ratios of 1 : 1 and 1 : 2 showed the highest catalytic activity in the studied reaction.

The epoxidation of alkenes is among the most studied oxidation reactions because the resultant epoxides are essential precursors in the synthesis of perfumes, epoxy resins and plasticizers. Therefore, finding the best catalyst for these types of reactions is crucial.\textsuperscript{79,80} A number of soluble Mo complexes with different ligands have been synthesized and used as homogeneous catalysts for the epoxidation of various alkenes.\textsuperscript{81} Ma et al.\textsuperscript{82} reported, for the first time, the synthesis of Mo catalysts on modified HNTs supports and tested the different nanomaterials obtained as catalyst in the epoxidation of a wide range of alkenes (Fig. 6). It was found that this catalyst efficiently converted cyclic, linear, and aromatic alkenes to their corresponding epoxides. It showed that carbocyclic alkenes were efficiently converted into the corresponding epoxides with high conversion and TOF (Table 1, entries 1 and 2). However, oxidation of aromatic and linear alkenes required longer reaction times and higher reaction temperatures than carbocyclic alkenes (entries 3–7). Also, in this case, recycling studies showed that the catalyst can be efficiently used for at least eight cycles without loss of catalytic activity.

Ruthenium nanoparticles were successfully immobilized on HNTs support by means of different procedures in order to enhance the catalytic performances of the metal. In particular, two different methods were evaluated. One method involves the immobilization of RuCl\textsubscript{3} by wet impregnation and the subsequent metal reduction at 450 °C\textsuperscript{83} whereas, the other method takes into account the immobilization of preformed Ru nanoparticles by polyol reduction.\textsuperscript{84} The HNTs-supported Ru nanoparticles were applied to the preferential oxidation of CO in a H\textsubscript{2}-rich atmosphere (PROX). The catalytic performances of the two catalysts were evaluated as a percentage of CO conversion and CO\textsubscript{2} selectivity. The authors found that in the PROX reaction, the second catalyst presented significantly higher CO conversion and CO\textsubscript{2} selectivity than the counterpart obtained by traditional wet impregnation. This is explained by the different sizes of the Ru nanoparticles dispersed on HNTs after the two different methods. Indeed, small-

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**Table 1**  Epoxidation of various alkenes with TBHP catalyzed by HNTs–Mo\textsuperscript{a,82}

<table>
<thead>
<tr>
<th>Entry</th>
<th>Alkene</th>
<th>( t ) (h)</th>
<th>Solvent</th>
<th>( T ) (°C)</th>
<th>Conversion\textsuperscript{b} (%)</th>
<th>Selectivity (%)</th>
<th>TOF (h\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>4</td>
<td>CH(_2)Cl(_2)</td>
<td>40</td>
<td>95</td>
<td>96</td>
<td>23.75</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>4</td>
<td>CH(_2)Cl(_2)</td>
<td>40</td>
<td>&gt;99</td>
<td>98</td>
<td>25.0</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>6</td>
<td>CH(_2)CN</td>
<td>80</td>
<td>87</td>
<td>90</td>
<td>25.50</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>6</td>
<td>CH(_2)CN</td>
<td>80</td>
<td>89</td>
<td>91</td>
<td>14.83</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>6</td>
<td>CH(_2)CN</td>
<td>80</td>
<td>83</td>
<td>90</td>
<td>13.83</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>8</td>
<td>CH(_2)CN</td>
<td>80</td>
<td>80</td>
<td>93</td>
<td>10.0</td>
</tr>
<tr>
<td>7</td>
<td></td>
<td>12</td>
<td>Toluene</td>
<td>110</td>
<td>91</td>
<td>99</td>
<td>7.58</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Reaction conditions: alkene (2.5 mmol), TBHP (5 mmol), HNT–Mo (60 mg), solvent (8 mL). \textsuperscript{b} Determined by gas chromatography.
sized and uniformly dispersed Ru nanoparticles were obtained by polyol reduction that favored the PROX reaction (Fig. 7). Nakagaki et al. reported the successful immobilization of the anionic iron(III)porphyrin [Fe(TDFSPP)] (FePor) on precalcinated halloysite (meta-HNTs) (Fig. 8). The catalytic activity of the Fe-Por/ meta-HNTs was evaluated in the heterogeneous oxidation of several substrates (namely cyclooctene, cyclohexane, or n-heptane) using iodosylbenzene as oxidizing agent. Good catalytic results and appreciable turnover numbers were achieved in comparison with the non-supported porphyrin. The high yield and turnover number achieved in the case of cyclooctene oxidation (Table 2) suggest that the FePor binds to the surface of the support, and that the catalytic site remains accessible to the reactants. The contact between the species involved in the oxidation reaction is thus facilitated, favoring the generation of the active catalytic species and product formation. Recycling tests highlighted that the heterogeneous catalytic system can be recovered and reused without significant leaching of porphyrin (Table 2, entry 3).

### 3.2 Catalytic photodegradation

Water pollution is a critical environmental problem facing humans worldwide. The hazardous effluents are usually discharged from industries such as those involving textiles, paper, rubber, plastics, leather, pharmaceuticals and cosmetics. In this context, photocatalysis, which is based on the in situ generation of highly reactive transitory species (i.e., $\cdot$OH, $\cdot$O$_2$) for the mineralization of pollutants (dyes or drugs) into CO$_2$ and H$_2$O, has been proved to be a desirable method, for application in the degradation of wastewater, with ambient operating conditions, low costs, and high efficiency.

For its versatile features, halloysite has been a promising support for the assembly of nanoarchitectures for pollutant photodegradation. Recently, a number of studies on the photodegradation of dyes or antibiotics in aqueous solution, mediated by metal nanoparticles supported on natural or modified HNTs, have been reported (Table 3).

Zheng et al. reported the synthesis of TiO$_2$–HNTs nanocomposites by deposition of anatase TiO$_2$ on the surface of HNTs with calcination treatment. The new materials were employed for photodegradation of methylene blue. As expected, the TiO$_2$ supported on HNTs exhibited efficient photocatalytic activity in the decomposition of methylene blue, compared to pristine HNTs.

Liu et al. studied the effects of HNTs on the visible-light photocatalytic ability of electrospun carbon doped TiO$_2$/HNTs nanofibers (Fig. 9). The photocatalytic performances of the nanocomposite were studied using methylene blue as the dye

### Table 2  Cyclooctenoxide yields achieved in the oxidation of cyclooctene by PhIO catalyzed by Fe-Por and Fe-meta-HNTs

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Cycle</th>
<th>Yield (%)</th>
<th>TON$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Fe-Por-meta-HNTs</td>
<td>1</td>
<td>85</td>
<td>38.7</td>
</tr>
<tr>
<td>2</td>
<td>Fe-Por-meta-HNTs</td>
<td>2</td>
<td>85</td>
<td>38.7</td>
</tr>
<tr>
<td>3</td>
<td>Fe-Por-meta-HNTs</td>
<td>3</td>
<td>85</td>
<td>38.7</td>
</tr>
<tr>
<td>4</td>
<td>Fe(TDFSPP)</td>
<td>1</td>
<td>85</td>
<td>5</td>
</tr>
<tr>
<td>5</td>
<td>None</td>
<td>1</td>
<td>10</td>
<td>0.1</td>
</tr>
<tr>
<td>6</td>
<td>meta Halloysite</td>
<td>1</td>
<td>30</td>
<td>&lt;0.01</td>
</tr>
</tbody>
</table>


### Table 3  Semiconductor metal-based photocatalysts supported on halloysite nanotubes, used for pollutant removal

<table>
<thead>
<tr>
<th>Metal NPs</th>
<th>Supporting method</th>
<th>Pollutant</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeO$_2$/AgBr</td>
<td>Microwave</td>
<td>Methyl orange</td>
<td>87</td>
</tr>
<tr>
<td>CdS</td>
<td>Hydrothermal</td>
<td>Tetracyline</td>
<td>88</td>
</tr>
<tr>
<td>AgNPs</td>
<td>Electrostatic immobilization</td>
<td>Methylene blue</td>
<td>89</td>
</tr>
<tr>
<td>ZnO</td>
<td>Calcination</td>
<td>Tetracyline</td>
<td>90</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>Impregnation</td>
<td>Rhodamine B</td>
<td>91</td>
</tr>
<tr>
<td>Au–Ni/Fe$_3$O$_4$</td>
<td>Impregnation</td>
<td>Congo red</td>
<td>92</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>Impregnation</td>
<td>Methylene blue</td>
<td>94–96</td>
</tr>
<tr>
<td>ZnO or TiO$_2$</td>
<td>Deposition</td>
<td>Methylene blue</td>
<td>97</td>
</tr>
<tr>
<td>LaFeO$_3$</td>
<td>Sol–gel</td>
<td>Chlortetracycline</td>
<td>98</td>
</tr>
</tbody>
</table>

Fig. 7  TEM images of RuNPs supported on HNTs. Reproduced from ref. 84 with permission from The American Chemical Society.

Fig. 8  Schematic representation of Fe-Por immobilization on meta-HNTs.
model. The obtained results showed that the visible light photocatalytic efficiency of the nanofiber was greatly reinforced with a moderate HNTs doping amount of 8%, far greater than that of commercial anatase TiO₂.

The synthesis of Ag nanoparticles supported on halloysite nanotubes for photocatalytic decomposition of dyes, was reported by Du et al. The catalyst was used for the degradation of methylene blue using tea polyphenols as reductant. The obtained results showed a good catalytic activity and high removal capacity of the materials; indeed, within 60 min, nearly 90% of dye had been decomposed photocatalytically (Fig. 10b).

Similarly, Ni et al. supported CeO₂/AgBr on HNTs by a microwave mediated method. The authors found that the synergistic effect of CeO₂ and AgBr greatly promoted the photocatalytic activity and the introduction of AgBr species was useful for extending the spectral response from the UV to the visible region.

Li et al. reported the immobilization of LaFeO₃, one of the most important perovskite-type semiconductors, on HNTs surface via a facile sol-gel method (Fig. 11). The catalytic performances towards the degradation of antibiotics were evaluated under visible light using chlortetracycline as the drug model. The decomposition studies revealed that pristine halloysite possessed no photocatalytic activity, whereas after irradiation of chlortetracycline in the presence of the pure LaFeO₃, the 74% of drug was degraded within 90 min. On the contrary, the degradation rate increases up to 87% when LaFeO₃/HNTs were used as catalyst. Furthermore, the doping of the catalyst with Ce nanoparticles, significantly increased the conversion up to 99%, indicating that the nanocomposite has remarkable photocatalytic activity. This latter aspect could be attributed to the Ce doping, which increases the visible light absorption, as well as the contribution of HNTs support.

For similar purposes, graphitic carbon nitride (g-C₃N₄), which possesses high thermal and chemical stability and suitable band gap, was combined with halloysite and ZnO via a facile calcination method (Fig. 12).
The visible light photocatalytic tests, toward an antibiotic model such as tetracycline, show that the g-C3N4–ZnO/HNTs nanocomposites possess much higher photocatalytic activity than those of either individual ZnO or C3N4, and ZnO/HNTs for drug degradation under visible light irradiation. Furthermore, the immobilization of the photocatalyst on the halloysite support provides an enhancement in the catalyst stability.

In the last examples, it is worth noting the peculiar electron-transfer process of the nanocomposites, based on metal supported on halloysite, due to the synergistic effect between the tubular support and metals. In fact, the hollow nanotubular structure of halloysite with high specific surface areas and considerable adsorption ability, makes the diffusion of reactants into the photocatalyst easier and improves the light adsorption by scattering. Besides, the surface chemical structures of rolling silica tetrahedral layers and alumina octahedral layers with a higher conduction band edge in halloysite, may modulate interfacial electron transfer dynamics, thus increasing the physical separation of injected electrons and decreasing the charge recombination reactions. Therefore, the enhancement of the charge migration at the nano-interface causes an improvement in the photocatalytic performance.

Tsouﬁs et al., reported a novel and facile synthetic approach involving a modiﬁed wet-impregnation method for the in situ synthesis of small, magnetic nanoparticles at the surface of natural halloysite nanotubes (HNTs-magnetite) (Fig. 13). This nanomaterial was employed for the ﬁrst time for the catalytic decomposition of pentachlorophenol in solution at room temperature. The HNTs-magnetite composite exhibited much higher catalytic efﬁciency and kinetics, compared to free unsupported magnetite NPs synthesized by alternative synthetic routes (e.g. co-precipitation method). Furthermore, by means of recycling tests, it was demonstrated that the nanocomposite can be easily separated, cleaned and reused for multiple catalytic cycles without any signiﬁcant loss in its catalytic activity.

A photocatalyst based on HNTs was prepared by Huo et al., by combining CdS with the nanotubes by the hydrothermal synthesis method. The main drawback of using CdS nanoparticles as catalysts is their aggregation. To solve this, there has been great interest in the preparation of supported CdS catalysts and several nanomaterials have already been used, such as carbon nanotubes and graphene supported composites. The supports can indeed effectively block the agglomeration, and the stability of the CdS photocatalyst can be simultaneously improved by using supported technology; however, the high cost and complex preparation process (as for carbon nanotubes) limited its application in supported materials. Thanks to the special chemical characteristics of HNT and its natural availability and low cost, the HNT/CdS hybrids seem to be very promising. In addition, the presence of hydroxyl groups on the HNT surfaces allows CdS nanoparticles to directly grow on the surfaces, and the resulting complex photocatalyst of CdS/HNTs is very stable. This material was used as the core for fabricating a novel thermal-responsive surface molecularly imprinted photocatalyst, where the shell was created by introducing a thermo-responsive polymer such as PNIPAAM. The imprinted polymer layer provides the photocatalyst with molecular recognition ability to form the selective photodegradation of the target pollutant and, thanks to this, it might be used for the treatment of antibiotics from wastewater.

### 3.3 Reduction reactions
The catalytic reduction of 4-nitrophenol is perhaps the most often used reaction to test the catalytic activity of metal
nanoparticles in aqueous solution. The interest in this reaction is mainly due to the fact that 4-nitrophenol is a common reactant in pharmaceuticals and can be a hazardous by-product that is inhibitory and toxic in nature, whereas 4-aminophenol is used for black-and-white film and the production of acetyaminophen. In addition, the reaction can be easily monitored by UV-vis spectroscopy and the determination of the apparent rate constant \( k_{\text{app}} \) from the slope of the linear correlation of \( \ln(A/A_0) \) with time \( t \) is straightforward.\(^{104}\)

Wang \textit{et al.}\(^{105}\) reported the synthesis of a novel super-paramagnetic coaxial gold/halloysite nanotube/Fe\(_3\)O\(_4\) (Au/HNTs/Fe\(_3\)O\(_4\)) nanocomposite, by the selective modification of the inner lumen and external wall of HNTs. In particular, in the HNTs lumen Au nanorods were firstly immobilized after Fe\(_3\)O\(_4\) nanoparticles were deposited on the external surface via the electrostatic assembly. The so-obtained Au/HNTs/Fe\(_3\)O\(_4\) material was tested as a catalyst in the reduction of 4-nitrophenol, exhibiting excellent catalytic activity. In addition, recycling tests highlighted that the material, thanks to its magnetic nature, can be easily recovered and used for at least three cycles.

Similarly, Wang \textit{et al.}\(^{106}\) described the synthesis of super-paramagnetic sandwich-structured silver/halloysite nanotube/Fe\(_3\)O\(_4\) (Ag/HNTs/Fe\(_3\)O\(_4\)) nanocomposites. As reported above, the Ag/HNTs/Fe\(_3\)O\(_4\) nanocomposites were fabricated by the selective modification of the lumen of HNTs with silver nanorods and the external wall with Fe\(_3\)O\(_4\) nanoparticles and it was successfully tested as a catalyst in the reduction of 4-NP into 4-AP. The authors showed the importance of halloysite as a support for the metal nanoparticles. Indeed, they hypothesized that the reactant molecules are firstly adsorbed on the surface of the supports, and then diffuse to the active sites through the pores of the HNTs to form the surface complex. Subsequently, the complex is catalyzed to generate the products, and the products finally desorb from the support. Furthermore, the amino group of Ag/HNTs/Fe\(_3\)O\(_4\) can contribute to desorption of the products from the catalyst to maintain adsorption sites toward the reactants in the next recycling reduction (Fig. 14).

Recently, the selective modification of the halloysite inner lumen has become attractive in metal-based catalysis. The formation of specific Al–O–C bonds on the HNTs inner lumen ensures the localization of the metal nanoparticles on the exposed aluminol functionalized surfaces, allowing the control of the environment of the future catalytic reactions. This strategy was employed by Dedzo \textit{et al.} to obtain an efficient catalyst for the reduction of 4-nitrophenol by functionalizing the inner lumen with an ionic liquid, which was used as immobilizing agent for palladium nanoparticles.\(^{107}\)

Selective hydrogenation of \(\alpha,\beta\)-unsaturated aldehydes to unsaturated alcohols is of great significance for producing various fine chemicals, pharmaceutical intermediates and for scientific insight into catalyst design. The selective hydrogenation of cinnamaldehyde to cinnamyl alcohol is a representative of such a class of reactions. Many published research efforts have applied Pt catalysts for the selective hydrogenation of cinnamaldehyde to cinnamyl alcohol. Zhang \textit{et al.}\(^{108}\) reported an easy approach to obtaining roughened surfaces on halloysite nanotubes through etching the wall of HNTs in a molten-salt system. The authors used this nanomaterial to immobilize Pt nanoparticles via a one-step hydrothermal reduction (Pt@RHNTs). The catalytic performances of the catalyst towards cinnamaldehyde reduction were investigated and the obtained results showed that Pt@RHNTs possess higher catalytic activity towards cinnamaldehyde hydrogenation.

Recycling tests performed on the catalyst that was used for at least five cycles showed that the conversion and selectivity for cinnamyl alcohol over Pt@RHNTs decreased slightly, but maintained a high level, above 90% and 80%, respectively (Fig. 15).

Zhang \textit{et al.}\(^{109}\) reported a mild \textit{in situ} deposition method at room temperature to prepare novel nano-sized MnO\(_x\)/HNTs catalysts (Fig. 16). The so-obtained catalysts were used for the selective catalytic reduction of NO\(_x\) with NH\(_3\) in a wide temperature range. Compared with other MnO\(_x\) supported catalysts, the MnO\(_x\)/HNTs showed the highest catalytic activity at low temperature, achieving a NO conversion of 95% at 100 °C at a space velocity of 36 000 h\(^{-1}\).

Yang \textit{et al.}\(^{110}\) immobilized Pd nanoparticles on HNTs modified with APTES in order to obtain the HNTs-NH\(_2\)/Pd

Fig. 14 Proposed mechanism for the catalytic reduction of 4-NP with the Ag/HNTs/Fe\(_3\)O\(_4\) nanocomposite. Adapted from ref. 106 with permission from Royal Society of Chemistry.

Fig. 15 (a) Conversion and selectivity of Pt@HNTs and Pt@RHNTs for cinnamyl alcohol as a function of reaction time; (b) recyclablility of the Pt@RHNTs. Reproduced from ref. 108 with permission from The Royal Society of Chemistry.
nanocatalyst. This nanomaterial exhibited excellent catalytic activity in the hydrogenation of styrene to ethylbenzene. The introduction of the silane moiety on the external surface of the halloysite improves the catalytic activity of the material if compared to similar catalysts obtained in the presence of pristine HNTs (HNTs/Pd) (Fig. 17). This behavior was explained considering Pd nanoparticles with smaller size, compared to the nanoparticles deposited on pristine halloysite.

3.4 Cross coupling reactions

Carbon–carbon bond formation is one of the most important reactions for the synthesis of biaryls, which are an important class of organic compounds since they constitute the basic skeleton of many complex molecules, such as drugs, advanced materials and natural products. The palladium-catalyzed Suzuki–Miyaura cross-coupling reaction of aryl halides with arylboronic acids is one of the most valuable synthetic routes for the preparation of symmetric and asymmetric biaryls.

For this purpose, halloysite was recently modified by attaching an ionic liquid moiety to its external surface, to obtain the so-called supported ionic liquid phase (SILP) for palladium nanoparticles. The covalent grafting of ionic liquids on the HNTs external surface was achieved in two synthetic steps: (i) the halloysite was modified with 3-mercaptopropyl trimethoxysilane to obtain an HNTs-SH scaffold; (ii) anchorage of octyl vinylimidazolium halide on HNTs-SH by a thiol−ene reaction. Both reactions were carried out under microwave irradiation (MW), which allowed high loading efficiency and reduction of reaction time and, since they were performed in solvent-free conditions, ensured that the overall process met the standards of Green Chemistry. Subsequently, palladium nanoparticles (PdNPs) were immobilized on this material to obtain the HNTs-SILP/Pd catalyst (Scheme 1). This new catalyst was successful employed in the Suzuki cross-coupling reactions.

Fig. 16  Schematic illustration of the synthetic process of the in situ deposition method. Reproduced from ref. 109 with permission from Elsevier.

Fig. 17  Catalytic properties of the samples. The change in concentration of styrene and ethylbenzene with the progression of the reaction. Reproduced from ref. 110 with permission from The Nature Publishing Group.

Scheme 1  Schematic representation of the synthesis of HNTs-SILP/Pd catalyst.
between phenylboronic acid and several aryl halides (Table 4). Recycling tests highlighted that the halloysite catalyst retained its catalytic activity for at least five cycles without Pd leaching.

First and second generations of environmentally friendly halloysite-triazolium salt catalysts were prepared. The first was based on halloysite modified with a triazolium salt, whereas, the second was a dicationic triazolium material, which was synthetized by click reactions of a diyne derivate in the presence of previously synthetized 3-azidopropyl-modified halloysite. In this way, a high loaded triazolium salt framework (ca. 25 wt%) was obtained and it permitted the immobilization of palladium at high loading after the exchange of halogen ions with tetrachloropalladate ions in toluene, and reduction with sodium borohydride (Scheme 2).

Table 4  Suzuki cross-coupling reaction of phenylboronic acid with various halides under optimized reaction conditions under microwave irradiation\textsuperscript{a,113}

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Product</th>
<th>Conversion\textsuperscript{b} (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Br-CHO</td>
<td>CHO-CHO</td>
<td>&gt;99</td>
</tr>
<tr>
<td>2</td>
<td>Br-COCO\textsubscript{2}H\textsubscript{3}</td>
<td>COOCH\textsubscript{3}</td>
<td>80</td>
</tr>
<tr>
<td>3</td>
<td>Br-OCO\textsubscript{2}H\textsubscript{3}</td>
<td>C\textsubscript{6}H\textsubscript{5}-CHO</td>
<td>&gt;99</td>
</tr>
<tr>
<td>4</td>
<td>Br-\textsubscript{2}NH\textsubscript{2}</td>
<td>-NH\textsubscript{2}</td>
<td>78</td>
</tr>
<tr>
<td>5</td>
<td>Br-OCO\textsubscript{2}H\textsubscript{3}</td>
<td>CHO-NH\textsubscript{2}</td>
<td>95</td>
</tr>
<tr>
<td>6</td>
<td>Br-COO\textsubscript{2}H\textsubscript{3}</td>
<td>OCH\textsubscript{3}</td>
<td>&gt;99</td>
</tr>
<tr>
<td>7</td>
<td>Cl-COO\textsubscript{2}H\textsubscript{3}</td>
<td>CHO-CHO</td>
<td>33</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Reaction conditions: aryl halide (1.01 mmol), phenylboronic acid (1 mmol), K\textsubscript{2}CO\textsubscript{3} (1.12 mmol), solvent (1.2 mL), HNT-IL/Pd (1 mol%).

\textsuperscript{b} Calculated by \textsuperscript{1}H-NMR.

The catalytic performances were tested in the Suzuki reaction under MW. The obtained results show that the first generation catalyst was not stable as highlighted from recyclability tests. On the contrary, the dicationic triazolium catalyst was employed successfully in the Suzuki cross coupling for the synthesis of several biaryls, working only with water as solvent. Recycling tests highlighted that the catalyst retains its catalytic activity for at least five cycles without Pd leaching (Fig. 18).

Although various supports such as carbon, polymers and modified SiO\textsubscript{2} have been utilized to develop heterogeneous Pd catalytic systems,\textsuperscript{4} most of them needed either a higher reaction time, up to 19 h, or an organic solvent, such as ethanol, or DMF to achieve comparable catalytic activities\textsuperscript{115} to the dicationic triazolium catalyst. These differences highlight the importance of using halloysite as a support for metal nanoparticles.

Another type of catalyst, particularly a thermo-responsive one, was obtained by filling PNIPAAM hydrogel with different amounts of halloysite (Fig. 19).\textsuperscript{116} The obtained PNIPAAM/HNTs hydrogels were used for the immobilization of palladium nanoparticles and their catalytic performances were tested in the Suzuki reaction. The results show that the Pd-anchored PNIPAAM/HNTs catalysts demonstrated excellent catalytic activities for various Suzuki reactions in water at 70 °C.

To the best of our knowledge, to date, there is only one example of direct chemically grafted stimuli-responsive PNIPAAM on the external surface of HNTs in literature.\textsuperscript{117} In this case, the material was used for PdNPs immobilization and tested in the Suzuki reaction under microwave irradiation.
The presence of palladium species in the structure of the HNTs-PNIPAAM/PdNPs catalyst was confirmed by energy dispersive X-ray spectroscopy (EDS) and SEM analysis (Fig. 20a). The EDS experiment was useful in determining that the palladium loading of the catalytic system was 1.3 wt%, as confirmed by ICP-OES analysis. EDS measurements further confirmed the successful functionalization, highlighting the presence of sulfur in the structure of the nanomaterial derived from the covalently grafted polymer.

TEM investigations (Fig. 20b and c) showed that the Pd nanoparticles were mainly immobilized on the surface of the support and also anchored to the interlayer of HNTs, having spherical morphologies with diameters of about 5.5 \( \pm \) 1.0 nm. It was demonstrated that this kind of new catalyst works well in water, under microwave irradiation at a temperature above the low critical solution temperature (LCST). At room temperature, the PNIPAAM chains adopt an extended conformation forming a hydrophilic nanoenvironment; therefore, the Suzuki reaction, with hydrophobic substrates, such as 4-bromoacetophenone, is unsatisfactory and the yields are low. Above the LCST the PNIPAAM chains collapse to form a dense layer covering the HNTs surface; the grafted PNIPAAM brushes

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The presence of palladium species in the structure of the HNTs-PNIPAAM/PdNPs catalyst was confirmed by energy dispersive X-ray spectroscopy (EDS) and SEM analysis (Fig. 20a).

Table 5  Suzuki cross-coupling reaction of phenylboronic acid with various aryl halides under optimized reaction conditions under microwave irradiation\textsuperscript{117}

<table>
<thead>
<tr>
<th>Entry</th>
<th>Ar-X</th>
<th>Conversion\textsuperscript{a} (%)</th>
<th>TON\textsuperscript{b}</th>
<th>TOF\textsuperscript{c} (h\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4-Bromoacetophenone &gt;99</td>
<td>6250</td>
<td>39 063</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>4-Iodoanisole              85</td>
<td>5312</td>
<td>33 200</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>4-Bromobenzaldehyde        94</td>
<td>5875</td>
<td>36 719</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>4-Bromoanisole             85</td>
<td>5313</td>
<td>33 206</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>3-Bromobenzaldehyde        82</td>
<td>5125</td>
<td>32 031</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>3-Bromoanisole             64</td>
<td>4000</td>
<td>25 000</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>4-Iodoacetophenone         94</td>
<td>5875</td>
<td>36 719</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>2-Iodotoluene              73</td>
<td>4563</td>
<td>28 519</td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a} Determined by \textsuperscript{1}H-NMR. \textsuperscript{b} Turnover number (TON) calculated as moles of substrate converted/moles of palladium. \textsuperscript{c} Turnover frequency (TOF) calculated as TON/hours.
become hydrophobic, facilitating the mass-transfer of hydrophobic substrates and promoting the cross coupling process. As a result, the authors observed higher conversions at temperatures above the LCST.

The good catalytic activity was also demonstrated by the low amount of catalyst employed (just 0.016 mol%, 2.34 mg) and high TON and TOF values (Table 5).

A comparison of the performance of the HNT–PNIPAAM/Pd catalyst with other supported Pd nanoparticle catalysts developed for Suzuki cross coupling reactions is worth considering. Several studies have reported Pd nanoparticles stabilized by hybrid polymeric materials used as catalysts in Suzuki reactions. Among them, Pd nanoparticles have been stabilized by polyvinyl pyrrolidone (PVP), polystyrene-polyethylene oxide and poly(amido-amine) dendrimers as well as other polymers. However, some nanocatalysts have shown limited catalytic activity, such as lower product yields, using low catalyst loadings, no recyclability and low TON and TOF values. On the basis of these examples, it can be concluded that the current HNT–PNIPAAM/Pd material provides highly stable and efficient catalysts for cross coupling reactions as compared to other Pd nanoparticles stabilized by polymeric molecules.

### 3.5 Miscellaneous

Ag nanoparticles were successfully supported on halloysite by soaking halloysite nanotubes in ethanolic solutions of AgNO₃ and butylamine, where butylamine acted as a reductant (Fig. 21). The new catalyst was employed in the polymerization of an alkylsilane, C₁₈H₃₇SiH₃. Wang et al. demonstrated that Ag supported on HNTs exhibited high polymerization activity and formed superhydrophobic silanol/siloxane composite microspheres. The superhydrophobic properties of the obtained polymerization products greatly promote their practical application to surface cleaning.

HNTs were employed as supports for the heterogeneous atom transfer polymerization of methyl methacrylate (MMA) into poly (methylmethacrylate) using CuBr as catalyst. Pristine halloysite was modified by grafting silane groups on its external surface. The silane so anchored can act as a ligand for CuBr as well as catalyst for the heterogeneous polymerization of MMA (Fig. 22).

Poly(4-vinylpyridine) (P-4VP) brushes of different lengths were grafted onto halloysite nanotubes by surface-initiated atom transfer radical polymerization (SI-ATRP) and methyl-tetroxorhenium(VII) (CH₃ReO₃, MTO) was immobilized onto HNTs through P-4VP brushes to catalyze the epoxidation of soybean oil. Traditionally, MTO was immobilized on mesoporous MCM-41 functionalized by pyrazolpyridine or zeolite, but in all these cases, MTO loading is limited by the amount of ligands. In this context, functionalized halloysite is a good material for MTO loading and in addition, it has regular open-ended pores with a larger pore radius than that of zeolites and therefore, HNT is more suitable to act as a support for catalysts for the epoxidation of viscous liquids.

2-Bromoisobutyryl bromide was chosen as the initiator of SI-ATRP and was anchored by reacting with hydroxyl groups of HNTs. The coordination between N in pyridine rings and MTO, allowed the authors to obtain a novel heterogeneous catalyst with different loadings of MTO for the epoxidation of soybean oil. The results obtained are listed in Table 6, which show that for the different synthesized catalysts, the conversion and yields of homogeneous MTO are significantly greater than that of P-4VP–HNTs–MTO. On the other hand, this result does not consider the difference in active sites between homogeneous and heterogeneous catalysts. Taking into account the last parameters, the authors were able to calculate TOF values; the TOF gap between homogeneous MTO and P-4VP–HNTs–MTO is not so enormous. As MTO loading increased, TOF of P-4VP–
HNTs–MTO increased and selectivity remained at 100%. This indicates that higher MTO loading is essential for obtaining high yield, and no ring-opening reaction occurred during epoxidation.

Zhang et al.\textsuperscript{125} functionalized the halloysite surface by means of the grafting of –SO\textsubscript{3}H and Cr(III) in order to obtain an innovative catalyst for the one-pot transformation of cellulose into 5-hydroxymethylfurfural. The authors carried out the one-pot conversion of cellulose over HNTs–SO\textsubscript{3}H–Cr(III) in a liquid ionic medium such as [EMIM]Cl and they found a maximum yield of 41.2% of conversion at 120 °C within 120 min. In addition, the prepared catalysts could be easily recycled without significant loss in activity.

Li et al.\textsuperscript{126} reported the synthesis of novel Co\textsubscript{3}O\textsubscript{4} nanoparticles supported on halloysite for the Fischer–Tropsch reaction. Compared with other inorganic supports for Co nanoparticles, such as SBA-15,\textsuperscript{127} halloysite possesses at least two advantages when used as support: (i) it has a regular nanometer scale tubular morphology, allowing penetration of cobalt ions into the matrix and (ii) it has a versatile mesoporous structure, high surface area, as well as low cost. The cobalt nanoparticles were immobilized by two different methods, namely the double-solvent and wet impregnation methods. Compared with the catalyst prepared by wet impregnation, the catalyst prepared by the double-solvent method prevents Co\textsubscript{3}O\textsubscript{4} particles from migration and agglomeration, due to size-induced effects, thus showing higher CO conversion and C\textsubscript{5+} selectivity for Fischer–Tropsch synthesis.

In another work, Co nanoparticles were immobilized, via a one-pot solvothermal method, on halloysite previously modified with 3-aminopropyltrimethoxysilane (APTES).\textsuperscript{128} The obtained nanocomposites were employed as catalyst to generate H\textsubscript{2} from NaBH\textsubscript{4} hydrolysis in aqueous medium. Comparison of the catalytic performances of the nanocomposite with those of pure Co showed significant enhancement. In addition, the catalyst can be removed from the reaction medium by means of a magnet, and reused, for the same reaction, at least for four cycles without loss in its catalytic activity.

Prstine halloysite derived from silica–alumina composite oxides (SA-H) through calcination at diverse temperatures was used as a support for Ni nanoparticles.\textsuperscript{129} It was obtained as an efficient catalyst for the steam-CO\textsubscript{2} dual reforming of methane for the production of synthesis gas.

Wang et al.\textsuperscript{130} reported the preparation of FeNi alloy nanoparticles (FeNi and BFeNi) supported on natural halloysite nanotubes and the obtained catalyst was successfully applied to the catalytic decomposition of toxic phosphine (PH\textsubscript{3}) to yellow phosphorus and hydrogen. The good catalytic performance can be explained by the proposed mechanism; after the adsorption of PH\textsubscript{3} on the surface of the catalysts, it was activated by Ni and could therefore dissociate H atoms forming the [PH\textsubscript{2}] species. The electron-rich [PH\textsubscript{3}] species can “spill over” to the [Fe\textsuperscript{III}–O] species in Fe\textsubscript{2}O\textsubscript{3}, which have unoccupied electronic orbitals on the HNT supports; one electron is then transferred from [\textsuperscript{3}P\textsuperscript{H\textsubscript{2}}] to[Fe\textsuperscript{III}–O] to form the reduced [Fe\textsuperscript{III}–O] and [\textsuperscript{3}P\textsuperscript{H\textsubscript{2}}]. When the reduced [Fe\textsuperscript{II}–O] meets the adsorbed H on nickel centers, the electron in the reduced [Fe\textsuperscript{II}–O] can be immediately transferred to H and form an activated [\textsuperscript{3}P]. The [Fe\textsuperscript{II}–O] itself returns to being [Fe\textsuperscript{III}–O]. Subsequent reactions with [\textsuperscript{3}P\textsuperscript{H\textsubscript{2}}] and [\textsuperscript{3}P\textsuperscript{H}–] result in the stepwise reduction to form [P\textsubscript{4}], containing three unpaired electrons, and then these species easily recombine into the stabilized P\textsubscript{4}, namely yellow phosphorus. Meanwhile, the formed activated [\textsuperscript{3}P] radicals may collide with each other and form hydrogen (Fig. 23).

### 4 Conclusions and perspectives

Halloysite nanotubes are natural aluminosilicate clay with a hollow tubular structure. HNTs have a peculiar surface chemistry, being constituted by siloxane surface and aluminol groups in the inner lumen.

Halloysite with external surface modifications is used as a valuable support for metal nanoparticles and the obtained nanoarchitectures were tested in different catalytic applications.

Introducing the proper anchor moieties between the clay nanotubes and the active metallic nanoparticles is strategic to controlling the catalytic efficacy and tuning the performance under specific stimuli.

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**Table 6** Catalytic activity and selectivity of different catalytic systems\textsuperscript{133}

<table>
<thead>
<tr>
<th>Catalytic system</th>
<th>Conversion (%)</th>
<th>Yield (%)</th>
<th>Selectivity (C/Y) (%)</th>
<th>TOF\textsuperscript{a} (h\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>MTO/H\textsubscript{2}O\textsubscript{2}</td>
<td>100</td>
<td>98</td>
<td>98</td>
<td>23</td>
</tr>
<tr>
<td>P-4VP–HNTs–MTO 1/2H\textsubscript{2}O\textsubscript{2}</td>
<td>8.13</td>
<td>8.13</td>
<td>100</td>
<td>8</td>
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<tr>
<td>P-4VP–HNTs–MTO 2/2H\textsubscript{2}O\textsubscript{2}</td>
<td>10.77</td>
<td>10.77</td>
<td>100</td>
<td>10</td>
</tr>
<tr>
<td>P-4VP–HNTs–MTO 3/2H\textsubscript{2}O\textsubscript{2}</td>
<td>17.88</td>
<td>17.88</td>
<td>100</td>
<td>16</td>
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</tbody>
</table>

\textsuperscript{a} TOF, turnover frequency, which is calculated by the following expression: [epoxide]/[catalyst] × time (h\textsuperscript{-1}).

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*Fig. 23* Hypothesized mechanism of catalytic PH\textsubscript{3} decomposition on FeNi/HNTs nanoparticles. Reproduced from ref. 130 with permission from Elsevier.
Thanks to the presence of a hollow cavity, they can be used for local concentration control, due to the confinement effect. The peculiar surface chemistry of HNTs is strategic in this context. The literature reports clearly outline a path, following which the clay nanotubes can open up to sophisticated nanoarchitectures working simultaneously as support and nanocontainer with catalytic activity.

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Notes and references