

Metal Organo-Clays as potential adsorbents for hydrogen storage

Abdelkrim Azzouz,* Saadia Nousir, Nabil Bouazizi, René Roy

Nanoqam, Department of Chemistry, University of Quebec at Montreal,
P. O. Box 8888, Succ. Centre-ville, Montreal (QC), Canada, H3C3P8

ABSTRACT

Metal-Organo-Clays (MOC) were synthesized via the *in situ* formation of Cu(0) or Pd(0) nanoparticles (M-NPs) in montmorillonite-supported dendritic polyols. Among these, Boltorn™ dendrimers (H20, H30, H40) were incorporated via intercalation, while diethanolamine and 1-thioglycerol (Aldrich) were chemically grafted using (3-chloropropyl)triethoxysilane as silyl bridge precursor. Transmission electron microscopy revealed that the presence of sulfur atoms favors more homogenous M-NPs dispersion than nitrogen atoms. Thermal-programmed-desorption of carbon dioxide showed that the amount of retained CO₂ increases with the amount of incorporated OH groups. The latter were found to contribute to M-NPs stabilization within the dendrimer entanglement. Hydrogen retention tests revealed that M-NPs act as the main adsorption sites by promoting interaction with hydrogen. At normal pressure, hydrogen adsorption took place instantly at room temperature, and desorption was possible upon slight heating at 40-60°C. The results presented herein open new prospects for truly reversible hydrogen storage.

Keyword: dendrimers, metal nanoparticles, montmorillonite, hydrogen retention, metal-organoclays.

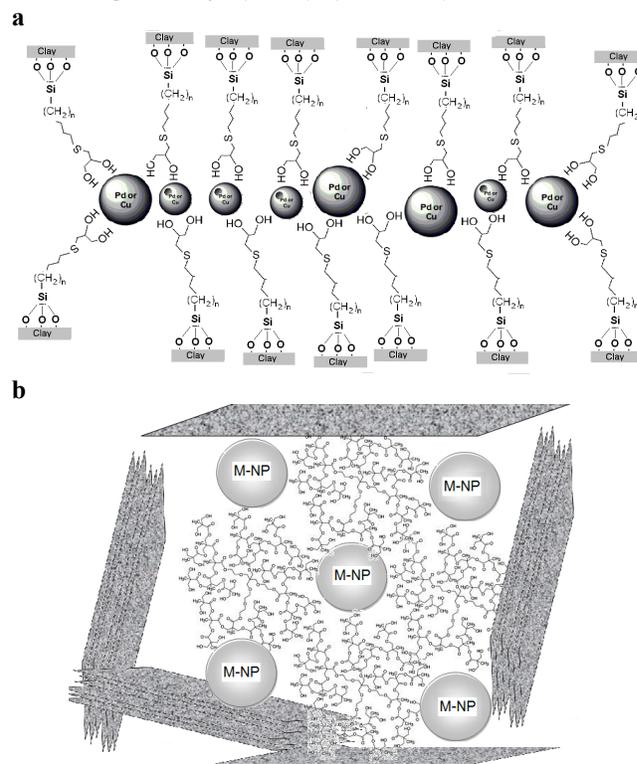
1. INTRODUCTION

Metals are known to exhibit affinity towards hydrogen, but unless highly dispersed, no appreciable adsorption capacity can be achieved. A promising alternative resides in the synthesis of sponge-like matrices capable of high hydrogen retention capacity (HRC) followed by easy desorption for regeneration with low or no heating. This concept was already developed for carbon dioxide retention on clay minerals intercalated by dendritic polyols, and was further envisaged for hydrogen capture by Si-based matrices [1]. The interest for such materials may grow when using available raw materials such as clay minerals.

Purely physical deposition of organic moieties often results in low specific surface area (SSA), but appears to promote higher M-NPs dispersion. Conversely, chemical grafting of organo-silane bridges is expected to generate higher SSA [2,3] but also unavoidable M-NPs concentration at the clay sheets edges. Up to now, a wide variety of materials have been tested in both chemical and physical hydrogen storage attempts [1]. However, the use

of clay minerals as inorganic supports for preparing H₂ adsorbents, more particularly montmorillonite for its 2-face surface, has never been envisaged so far.

The silanol terminal groups located at the edges and the structure defects of clay sheets have great affinity towards the silyloxy groups of the organosilane moiety. They act as active sites for the chemical grafting of organic moieties through the formation of silyl bridges and alcohol by elimination upon slight heating [3]. Linking montmorillonite lamellae by silylated polyols would be an interesting option to trap and stabilize M-NPs, resulting in Metal-Organo-Clays (MOC) (Scheme 1).



Scheme 1. Structure of MOC matrices obtained by chemical grafting (a) and intercalation (b).

The latter are novel microporous matrices that can be synthesized via the *in-situ* formation and dispersion of Cu or Pd nanoparticles in montmorillonite-supported polyols. This concept has scarcely been tackled so far. The hydrogen uptake was correlated to the M-NPs size and CO₂ retention capacity through thermal programmed desorption investigations.

2. EXPERIMENTAL

2.1. MOC preparation and characterization

Na-exchanged montmorillonite (NaMt) was prepared by purification of commercial bentonite (Aldrich). Boltorn™ H20, H30 and H40 dendrimers (Perstorp, Sweden) were incorporated via mere intercalation. Diethanolamine and 1-thioglycerol (Aldrich) were chemically grafted using 3-chloro-propyl-triethoxysilane (3-CIPTES) as silyl bridge precursor. The resulting NaMt-S-N(OH)₂ and NaMt-S-S(OH)₂ samples were then immersed in a water-toluene mixture containing Pd(II)(OAc) or Cu(NO₃)₂ · 2.5H₂O at r.t for 2 hours in the presence of a reducing agent (NaBH₄) [4].

The resulting MOCs (Table 1) were characterized through ²⁹Si and ²⁹Al MAS-NMR (Varian Inova MS600 NMR spectrometer, at 119.192 MHz and 12.5 KHz ~~spinning rate~~). Nitrogen adsorption-desorption isotherms and BET calculations of the specific surface area (SSA) were performed on a Quantachrome device, with an Autosorb automated gas sorption system control. Thermal gravimetric analysis (TG and DTG) was performed by means of a TG/TDA6200 thermal analyzer (Seiko Instrument Inc.) under a 100 mL min⁻¹ nitrogen stream and a 5 °C min⁻¹ heating rate. Infrared spectra were recorded using a KBr IR cell and Fourier Transform Infrared spectroscopy equipment (Model IR 550, Magna Nicolet). Differential Scanning Calorimetry (DSC) was conducted on a Mettler Toledo TGA-SDTA851e, in dry nitrogen stream (20 mL min⁻¹) and heating rate of 5 °C min⁻¹.

2. 2. Adsorption-desorption tests

Thermal programmed desorption (TPD) was used to correlate changes in the retention capacity of CO₂ (**CRC**) and water (**WRC**) with the M-NPs incorporation and hydrogen uptake of the prepared MOCs (particle size of 0.05 - 0.1 mm). Each sample was dried in the TPD reactor under a 15 mL min⁻¹ nitrogen stream at 80°C for 40 min, cooled down to 20°C, and then contacted with dry CO₂ until saturation. The non-adsorbed CO₂ excess was evacuated by a nitrogen stream (1 mL min⁻¹) until no CO₂ was detected. TPD tests were run under a 1 mL min⁻¹ nitrogen stream at a 5 °C min⁻¹ heating rate between 20°C and 80°C.

Hydrogen adsorption tests were performed by contacting water-saturated or dry adsorbent with water-saturated or dry hydrogen at normal pressure (air) and ambient temperature. The amount of adsorbed hydrogen was assessed via triplicate measurements of volume decrease within a capillary glass tube with a 0.25 mm internal diameter.

3. RESULTS AND DISCUSSION

3.1. Effect of M-NPs dispersion

The formation of NaMt-O-Si-R bridges appears to involve exclusively silanol groups as revealed by ²⁹Si-NMR

at -67.71 ppm and the lack of corresponding resonance by ²⁹Al-NMR. X-ray diffraction showed no change in the d₀₀₁ basal spacing for silylated samples, but a slight increase up to 14-18 Å depending on the amount of physically intercalated dendritic polyols. Here, unlike intercalation, the silylation process seems to impede clay exfoliation, concentrating the organic moiety at the edges of compact clay lamella stacks. As a consequence, intercalated NaMt showed higher SSA (46 m²g⁻¹) than silylated counterparts (33 m²g⁻¹).

Below 120°C, a single mass loss of ca. 10 % at 95-115°C due to dehydration was registered. TPD measurements at temperatures of up to 80°C did not affect MOCs' thermal stability even after repetitive adsorption desorption cycles.

TEM observations revealed uniformly dispersed pseudo-spherical Cu and Pd M-NPs, with average particle sizes of 2-6 nm for intercalated MOCs (Fig. 1). Apparently bulkier M-NPs were observed for Pd-NaMt-H40 (Fig. 2-a), but restricted to the clay edge structure where the silyl bridges are supposedly more concentrated (Fig. 2).

It is worth noticing that on PdNaMt-S-S-(OH)₂ and PdNaMt-S-N-(OH)₂ and copper-based counterparts, each M-NP appeared as a dark core coated by a thick shell that prevents from aggregation with other neighboring particles into bulkier metal clusters. The overall particle size was of ca. 5-15 nm, but the estimated diameter of the dark core was of ca. 4-8 nm. The coating layer of 1-7 nm was identified as being organic compounds by energy dispersion analysis, confirming thereby its role in M-NPs stabilization.

Additional evidence of M-NPs stabilization within the dendrimer entanglement was provided by FTIR analysis. The shifts of the 2920 and 2850 cm⁻¹ band, assigned to the asymmetric and symmetric stretch of the CH₂ groups to lower wavenumbers indicates a compaction of organic chains around M-NPs in the MOC structures.

The O-H symmetric stretching vibration frequency at 3445-3450 cm⁻¹ also shifted to lower frequency, resulting in a much broader band of 3425-3420 cm⁻¹ upon M-NP incorporation. The reason of this broadening must be due to an enhancement of interaction occurring between OH groups, presumably through the formation of hydrogen bonds between the next-neighboring organic species.

The shift of the 1650-1550 cm⁻¹, band towards lower wavenumber registered after the incorporation of M-NPs. indicated that water and C=O groups, if any, were also involved in interactions with metal surface. Besides, the C-O stretching vibration frequency also shifted from 1150-1120 cm⁻¹ to lower frequency after M-NP insertion. This confirms the dendrimer binding to M-NPs through interaction with the oxygen atoms of the OH groups and hydrogen bonds between neighboring organic species.

XPS studies already showed that in dry media metal-ROH interactions take place via attractive force between oxygen atoms and metal particles [5]. This must be due to the higher affinity of thiol groups towards metal [6], which involves strong chemical interactions with M-NPs, mostly at the expense of the interactions with hydrogen and water.

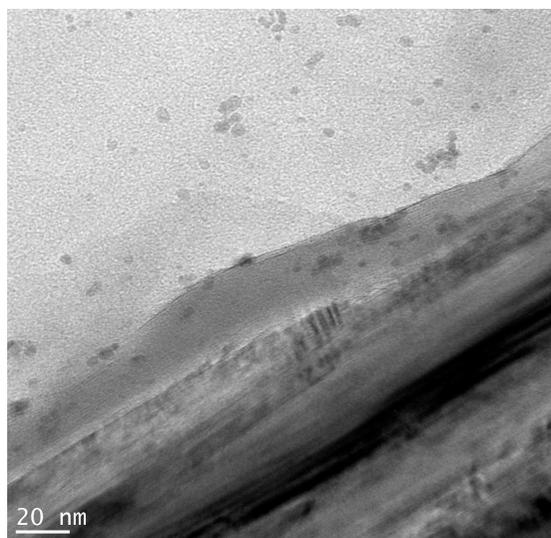


Fig. 1 : Transmission electron micrographs of PdNaMt-H40

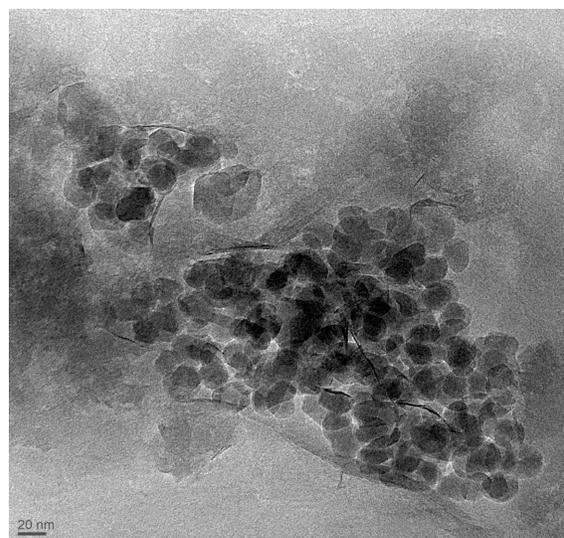


Fig. 2 : Transmission electron micrographs of PdNaMt-S-S(OH)₂-1

Table 1. MOC features before and after mnp incorporation

Sample	Preparation procedure	SSA (m ² .g ⁻¹)	CRC ^b (mmol/g)	WRC ^b (10 ⁻⁶ μmol/g)
NaMt	Purification of a crude bentonite	50	0.327	4.26
PdNaMt-H30	Pd dispersion on NaMt-supported H30	46	-	-
PdNaMt-H40	Pd dispersion on NaMt-supported H40	-	-	-
NaMt-S-N(OH) ₂ -1 (3:1 wt) ^c	Chemical grafting of diethanolamine	27	0.283	3.98
NaMt-S-S(OH) ₂ -1 (3:1 wt) ^c	Chemical grafting of thioalcohol	-	0.130	5.34
NaMt-S-S(OH) ₂ -3 (1:1 wt)		18	0.234	4.59
PdNaMt-S-N(OH) ₂ -1	Pd dispersion dispersion using Pd(II)OAc)	33	0.068	4.09
PdNaMt-S-S(OH) ₂ -1	after chemical grafting of diethanolamine		0.096	5.30
CuNaMt-S-S(OH) ₂ -3	Cu dispersion using (Cu(NO ₃) ₂ .2.5H ₂ O)	19	0.086	4.33
	after chemical grafting of thioalcohol			

^a Specific surface area (SSA). ^b The CRC et WRC (μmol.g⁻¹) were assessed through TPD measurement between 20°C and 80°C at a nitrogen stream of 15 mL/min, after contacting until saturation 45 mg of dry adsorbent with 200 mL CO₂. ^c NaMt-S-N(OH)₂ and NaMt-S-S(OH)₂ were synthesized using NaMt and the silylating agent in a 3:1 or 1:1 wt proportion ratio.

3.2. Affinity towards CO₂

Preliminary TPD measurements gave CRC values of 0.283 mmol/g for NaMt-S-N(OH)₂ and 0.130-0.234 mmol/g for NaMt-S-S(OH)₂ (**Table 1**). In the meantime, the WRC values reached values of 3.98-5.88.10⁻⁶ and 4.59-5.34.10⁻⁶ micromol/g, respectively. Here, it is worth mentioning that no significant CRC and WRC changes were registered.

This must be due to a possible ‘‘shading effect’’ of the organophilic character of the incorporated species. This is

expected to attenuate the affinity of the OH groups towards CO₂ and their hydrophilic character.

Further incorporation of Cu-NPs and Pd-NPs was found to reduce considerably the affinity towards CO₂. This provides clear evidence of the high affinity of the OH groups towards M-NPs at the expense of CO₂. After Pd and Cu dispersion within the entanglement of the clay-supported polyol, the CRC decay dramatically dropped down to 0.068-0.096 mmol/g (PdNaMt-S-N(OH)₂) and 0.086 mmol/g (CuNaMt-S-S(OH)₂), but no noticeable change in the moisture content.

This decay in the affinity towards CO₂ is explained in terms of enhancement of OH-metal interaction, and depletion of the number of free OH groups available for CO₂ adsorption. In other words, once “bridged” to metal M-NPs, the OH groups cannot interact with the surrounding CO₂ molecules.

The moisture content decreased dramatically but only for NaMt-S-N-(OH)₂ samples. This confirms once again that M-NPs insertion reduces the number of accessible OH groups for interaction with CO₂ and water molecules. NaMt-S-S-(OH)₂ samples behaved differently, presumably due to the low hydrophilic character of the S atoms.

3.3. Affinity towards hydrogen

All adsorbents showed affinity towards hydrogen, as supported by DSC measurements, which revealed a significant increase in the desorption heat up to more than 200 kcal mol⁻¹ for hydrogen-saturated MOCs (Fig. 3). This was a common feature of all other copper-MOC samples.

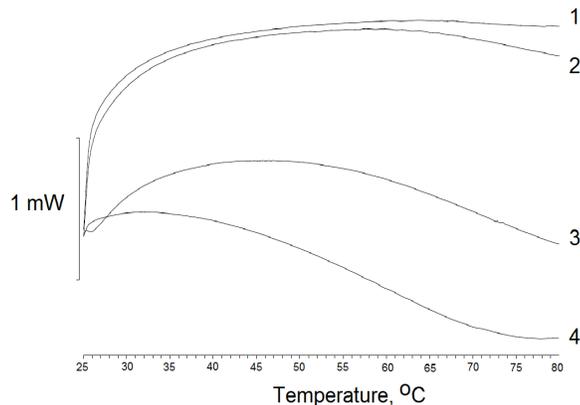


Fig. 3. DSC patterns for fresh PdNaMt-S-S(OH)₂-1 (1) and PdNaMt-S-N(OH)₂-2 (2) and hydrogen-saturated PdNaMt-S-N(OH)₂-2 (3) and hydrogen-saturated PdNaMt-S-S(OH)₂-1 (4).

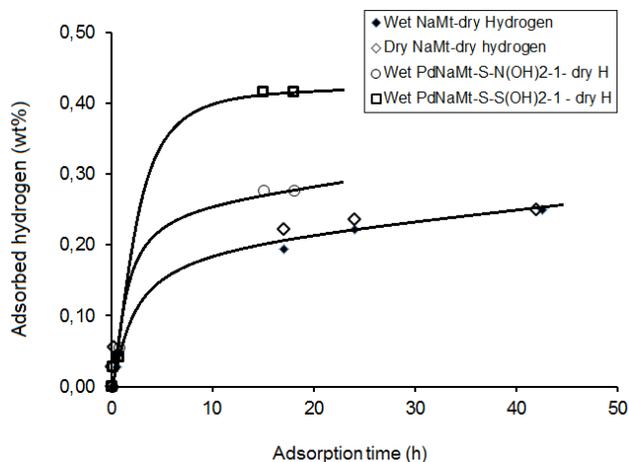


Fig. 4. Evolution in time of the hydrogen retention capacity

As compared to the starting NaMt sample, chemical grafting of dendritic species combined with M-NPs dispersion and stabilization turned out to be a judicious method to produce hydrogen uptake of up to 0.45wt% and beyond, even at ambient temperature and pressure (Fig. 4).

The fact that the maximum hydrogen uptake was obtained only after 10-20 h of contact time is explained in terms of diffusion hindrance. Increases in porosity and specific surface area are expected to produce significant improvement. Investigations are still in progress in this regard. It clearly appears that sulfur atoms induced higher affinity towards hydrogen, as supported by the higher hydrogen uptake of PdNaMt-S-S(OH)₂ (0.43wt%) as compared to its N-based counterpart (0.28wt%).

4. CONCLUSION

Chemical grafting of OH groups and incorporation of polyol dendrimers produced metal-organoclays with affinity towards hydrogen. The latter was found to adsorb H₂ at room temperature, and higher amounts were retained in the presence of sulfur atoms. Hydrogen uptakes of 0.45 wt% were obtained at normal pressure, which allows envisaging higher uptakes under higher pressure. The higher affinity of NaMt-S-S(OH)₂ towards CO₂ and water are attributed to the presence of sulfur atoms in the polyol structure. The adsorbent regeneration can be easily achieved upon slight heating at 40-60°C. The results presented herein open new prospects for truly reversible hydrogen storage.

Acknowledgments: This work was supported by a grant from MDEIE-FQRNT to R.R. and A.A. We are thankful to Perstorp (Sweden) for generous supply of the BoltornTM polyols. R. R. also acknowledges financial support from the Natural Sciences and Engineering Research Council of Canada (NSERC) for a CRC grant.

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