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Metal-loaded polyol-montmorillonite with improved affinity towards hydrogen

N. Bouazizi ^{a,b,*}, D. Barrimo ^a, S. Nouisir ^a, R. Ben Slama ^b, T.C. Shiao ^a, R. Roy ^a,
A. Azzouz ^{a,**}

^a Nanoqam, Department of Chemistry, University of Quebec at Montreal, QC, H3C 3P8, Canada

^b Environment, Catalysis and Analysis Methods Laboratory, ENIG University of Gabes, Tunisia

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ABSTRACT

Metal-organoclays (MOC) were prepared through incorporation of Boltorn polyol dendrimer H30 in Na⁺-exchanged montmorillonite (NaMt), followed by in-situ dispersion of Cu⁰ and Pd⁰ nanoparticles (CuNPs and PdNPs). The organoclays displayed high CO₂ retention capacity (CRC) of 3.6–11.1 μmol/g, but metal incorporation induced a significant increase of hydrogen uptake up to 51.8–508.2 micromol/g at the expense of the CRC. Thermal programmed desorption and FT-IR investigations revealed strong interactions with CO₂ before metal incorporation. These interactions markedly depleted in the presence of CuNPs and PdNPs. This was regarded as a precise indicator of the appreciable metal stabilization within the organic entanglement, due to enhancements of –HO:Cu⁰ and –HO:Pd⁰ interactions at the expense of –HO:CO₂ carbonate-like association. The CO₂ and H₂ retention capacities (CRC and HRC, respectively) were found to strongly correlate to the number of OH groups of the dendritic moiety incorporated. Hydrogen retention appears to involve mainly physical interactions as supported by easy gas release between 20 °C and 75 °C or even at room temperature under vacuum. This demonstrates unequivocally the reversible capture of hydrogen. The increase of the hydrogen uptake with increasing contact time provides evidence of the occurrence of diffusion phenomena. This was not observed with CO₂ before metal incorporation, suggesting a structure compaction that improves metal stabilization. This opens new prospects for hydrogen storage via truly reversible capture on low cost clay materials and biodegradable hyperbranched macromolecules deriving from plants.

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1. Introduction

This last decade, hydrogen storage has become a major issue to be addressed as an alternative for clean technologies without fossil energy sources [1,2]. Hydrogen release from H₂-containing compounds has shown a series of shortcomings due to energy consumption [3,4]. A judicious strategy to use hydrogen as a sustainable energy source consists in designing sponge-like matrices that allow the reversible capture of hydrogen under ambient conditions via purely physical condensation [5–7]. This should be achieved without resorting to the use of harmful and hazardous metal hydrides [8]. Modified silicates [9], dendrimer-encapsulated nanoparticles (DENs) [10,11] and dendrimer-silica hybrid materials [12], including sulfated dendrimers [13,14] appear as promising candidates for this purpose.

In this regard, metal dispersion in dendrimer-modified clay is expected to provide Metal-Organoclays (MOC) with improved affinity towards hydrogen. In such materials, copper and palladium already showed interesting performances in the reversible capture of hydrogen in spite of their low specific surface area [7,14]. Clay minerals are widely available, low cost and recyclable layered materials that are largely employed for catalyst and adsorbent preparation. Such materials differ by their chemical compositions, more particularly their contents in silica, alumina and iron oxide. Their layered structure consists of more or less disordered stacks of elementary alternate sheets of silica and alumina, containing other isomorphously substituted atoms [15,16]. The most interesting clay mineral is undoubtedly montmorillonite (Mt),

* Corresponding author. Environment, Catalysis and Analysis Methods Laboratory, ENIG University of Gabes, Tunisia. Fax: +216 75 39 24 21.

** Corresponding author. Fax: +1 514 987 4054.

E-mail addresses: bouazizi.nabil@hotmail.fr (N. Bouazizi), azzouz.a@uqam.ca (A. Azzouz).

whose lamellar structure contains an octahedral alumina layer sandwiched between two tetrahedral silica layers, with aluminum (Al^{3+}) atoms partially substituted with iron (Fe^{2+}) and/or magnesium (Mg^{2+}) [17]. Numerous studies report significant improvements in the desired features of Mt-based nanocomposites such as mechanical properties [18], flame inhibition [19], gas barrier behavior [20], thermal stability [21], heat distortion temperature [22] and improved solvent resistance [23].

Some of our previous works [7,14] already demonstrated that chemical grafting of thioglycerol groups on clay surfaces produces effective host matrices for metal nanoparticles (MNPs), which, in turn, exhibited increased affinity towards hydrogen. This was explained in terms of structure compaction, which prevents metal aggregation and hinder hydrogen chemisorption on the metal surface. Nevertheless, the preparation of such matrices often requires sophisticated procedures. Nevertheless, some of these procedures such as “Click chemistry” and “Thio-lyne addition” are regarded as being fast and very convenient routes, given the unprecedented levels achieved by the surface affinity towards hydrogen. The mere attempt to use of a clay mineral for hydrogen storage purpose is a novelty in itself. To the best of our knowledge, no similar works have been published in this area so far.

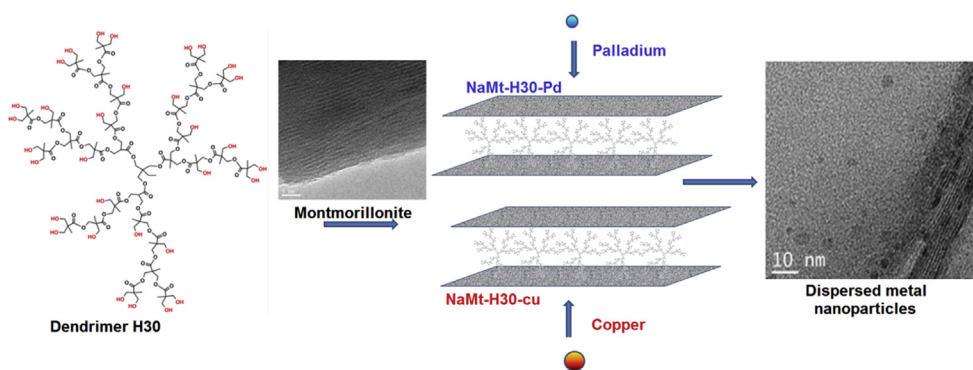
A judicious compromise between optimal surface affinity and low cost synthesis procedure can be achieved by incorporating organic moiety in the lamellar clay structure through mere physical insertion upon impregnation in aqueous solutions. That is why the present work was undertaken. For this purpose, commercially available bentonite previously purified into a sodium form montmorillonite (NaMt), then modified through the incorporation of Boltorn dendrimer H30 and further incorporation of palladium (Pd^0) and copper (Cu^0) as metallic nanoparticles (MNPs) (Scheme 1).

The choice of dendrimer H30 is justified by its availability and its optimum feature that offers high number of hydroxyl groups with minimum structure collapse in dry media, at least for low dendrimer loading [24]. This is expected to induce affinity towards hydrogen, given the strong tendency of hydrogen to dissolve in metal. Truly reversible capture of hydrogen on organoclay-supported MNPs obtained through purely physical insertion of the organic moiety is a new concept that has scarcely been tackled up today. Comparison with the starting material is expected to provide valuable data to explain the role of the organic moiety in improving both the metal dispersion and surface affinity towards hydrogen.

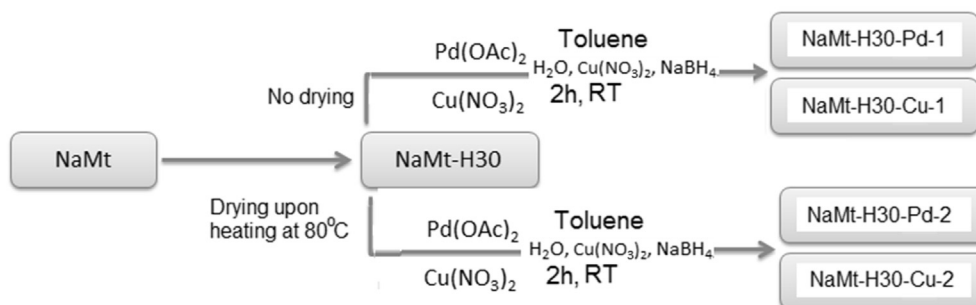
2. Experimental

2.1. Bentonite purification and activation

Crude bentonite (Aldrich) with a 2.48 Si/Al mole ratio, was purified and ion-exchanged into a Montmorillonite (NaMt) with a 2.43 Si/Al mole ratio, by removing dense silica phases and other impurities according a procedure fully described elsewhere [25]. Further, purely physical intercalation was achieved by dendrimer incorporation in a proportion of 1 wt.% of the amount of dry clay mineral. For this purpose, 200 mg of NaMt powder samples were impregnated, overnight at room temperature under vigorous stirring, with 25 mL aqueous solutions containing well determined amounts of H30. The resulting organo-montmorillonite (NaMt-H30) was further separated by filtration, repeatedly rinsed with water and dried at 80 °C for 6 h. Aqueous solutions of $\text{Cu}(\text{NO}_3)_2$ and $\text{Pd}(\text{OAc})_2$ (0.9 mmol) were used as precursors for the incorporation of copper (Cu^0) and palladium (Pd^0) nanoparticles (CuNPs and PdNPs). This was achieved in toluene (99.5%, $d = 0.865 \text{ g mL}^{-1}$) as the solvent in the presence of NaBH_4 (9 mmol) as the reducing agent (Scheme 2). The mixture turned brown after 2 h



Scheme 1. Procedures for the preparation of NaMt-H30-Cu and NaMt-H30-Pd.



Scheme 2. Detailed procedures for the preparation of some adsorbants at room temperature (RT).

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