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Cu⁰-loaded organo-montmorillonite with improved affinity towards hydrogen-an insight in matrice-metal and non-contact hydrogen-metal interactions

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ABSTRACT

Copper-loaded organo-Montmorillonite showed improved affinity towards hydrogen under ambient conditions. Clay ion exchange with a propargyl-ended cation followed by thiol-yne coupling with thioglycerol resulted in porous structure with a 6 fold higher specific surface area, which dramatically decreased after copper incorporation. X-ray diffraction and photoelectron spectrometry, nuclear magnetic resonance (¹H and ¹³C) and CO₂-thermal programmed desorption revealed strong Sulfur:Cu⁰ and Oxygen:Cu⁰ interactions. This was explained in terms of structure compaction that 'trap' Cu⁰ nanoparticles 21 (CuNPs) and reduce their mobility. Transmission electron microscopy showed predominant 1.0-1.5 nm 22 CuNPs. Hydrogen capture appears to involve predominantly physical interaction, since differential scanning 23 calorimetry measurements gave low desorption heat and almost complete gas release between 20°C and 24 75°C. Possible hydrogen condensation within the compacted structure should hinder gas diffusion inside 25 CuNPs and prevent chemisorption. These results allow envisaging safe hydrogen storage with easy gas 26 release even at room temperature under vacuum. The reversible capture of hydrogen can be even more 27

attractive when using natural inorganic supports and commercial plant-deriving dendrimers judiciously 28 29 functionalized, even at the expense of porosity.

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Keywords: Copper; Nanoparticles; Thioglycerol; Montmorillonite; Hydrogen capture; Metal-organoclay.

1. INTRODUCTION

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 Nowadays, intensive research is being focused to promote clean technologies without carbon dioxide exhaust, and growing interest is now devoted to alternatives to fossil fuels, which have become major objectives¹. Hydrogen appears as a promising source of clean energy, being widely available in nature. However, for safety and efficiency reasons, hydrogen storage, more particularly in molecular form, still remains a challenge to be addressed. So far, several studies have been made in this regard ². H₂-containing materials are interesting hydrogen sources, but practical applications cannot be envisaged because hydrogen release requires energy-consuming processes 3,4 . The production of hydrogen from water also appears to be a more promising route, and an ample literature is now available in this regard. However, important challenges reside in avoiding thermal production processes and in developing effective storage methods.

A judicious approach involves a reversible capture of hydrogen by porous adsorbents under ambient 43 conditions via physical condensation with reduced formation of metal hydrides. This would allow easy gas 44 release without heating or pollutant emissions ^{5, 6}. Several adsorbents have already been evaluated, but, most 45 of them showed only low hydrogen uptakes under ambient temperature and pressure ⁷⁻⁹. Improvements in 46 this regard may be brought by the synthesis porous matrices with large specific surface areas hosting highly 47 dispersed metal particles (MP). The latter turn out to be an essential requirement for this goal, given their 48 high affinity towards hydrogen. The size distribution of MPs depends on the structure of the stabilizing 49

agent. Dendrimer-encapsulated nanoparticles (DENs)^{10, 11} and dendrimer-silica hybrid mesoporous materials 50 ¹², including sulfurated dendrimers ¹³, may offer several advantages towards this goal. 51

Hydrogen adsorption on MPs is known to generate metal hydrides, whose further decomposition to release 52 hydrogen requires chemical processes and energy consumption. A possible and original strategy to avoid or 53
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 reduce hydrogen chemisorption should consist in promoting non-contact hydrogen-MP interactions. Herein, we report an efficient route for the dispersion of copper nanoparticles (CuNPs) within the entanglement of a clay-supported dendrimer bearing metal-stabilizing groups such as sulfur and oxygen atoms (Scheme 1) 14 . Clay-based adsorbents are much more cost effective than nanostructured carbons and silicas, MOF, GOF, metal sulfides and many other sophisticated materials ^{9, 14}. The choice of Cu was based on many objective criteria, among which the relatively higher stability to oxidation and much lower toxicity as compared to other metal are the most important. Besides, Cu is much more cost effective than other metals such as palladium and platinum and other noble metals recognized for their higher affinity for hydrogen.

The synthesis of such materials was achieved by modifying Na⁺-montmorillonite with 4-(prop-2-ynyloxy)phenylammonium cation and further addition of thioglycerol groups through a photoactivated radicalmediated thiol-yne coupling (TYC). This reaction has emerged as a powerful "click" chemistry tools for obtaining advanced functional materials¹⁵⁻¹⁹. TYC reactions are usually carried out under UV irradiation in 65 the presence of potent photoinitiators, and are becoming increasingly employed in polymer chemistry and 66 material science ²⁰⁻²⁵. However, its applicability to clay minerals has not been systematically explored yet. 67

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Scheme 1

The resulting organoclay is expected to behave as host matrice for Cu⁰ nanoparticles (CuNPs) through the 69 grafted thioether groups, which are known to act as powerful ligands for MNPs²⁶. On one hand, Strong 70 thioether-Cu⁰ interactions should result in structure compaction that 'trap" CuNPs and reduce their mobility. 71 On the other hand, sufficiently high number of thioether groups is expected to entirely cover the external 72

surface of CuNPs, promoting non-contact hydrogen-Cu⁰ interaction. This may result in hydrogen 73 condensation around "covered" CuNPs, which should hinder gas diffusion inside CuNPs and prevent 74 chemisorption. When physical gas adsorption prevails, the size and number of CuNPs should play key roles 75 in tailoring optimum gas retention strength that allow both high hydrogen uptake and easy desorption 76
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 28 88 88 82 24 24 24 24 25 26 24 26 without or without low heating. This concept of truly reversible capture of hydrogen is similar to that already reported for carbon dioxide ²⁷⁻³¹. In other words, optimum interactions would be an essential requirement for high H₂ uptakes with easy regeneration. Therefore, physical and non-stoichiometric hydrogen condensation is a novelty in itself, which opens promising prospects for low cost clay-based adsorbents for storage purposes or at least for gas concentration from mixtures. 2. MATERIALS AND METHODS 2.1. General 88

In this study, commercially available HPLC grade solvents were used. Commercially available propargyl bromide solution (80% in toluene), 1-thioglycerol, and 2,2-dimethoxy-2-phenylacetophenone (DMPA) from Sigma Aldrich Canada LTD were used without further purification. Thiol-yne reaction was achieved under dry argon in a photometer cell from VWR North America (Cat. No 41400-064). Progress of the reactions was monitored by thin-layer chromatography using silica gel 60 F₂₅₄ coated plates (E. Merck). NMR spectra were recorded on Bruker Avance III HD 600 MHz spectrometer. Analysis and assignments were made using COSY and HSQC experiments. High-resolution mass spectra (HRMS) were recorded with a LC-MS-TOF spectrometer (6210 ESI-TOF, Agilent Technologies) in positive and/or negative electrospray mode by the analytical platform of UQAM.

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2.2. Preparation of N-[4-(Prop-2-vnvloxy) phenyl] acetamide (2) 96

Propargylation of 4-acetamidophenol 1 (10.00 g, 66.16 mmol, 1.0 equiv.) was carried out as previously 97 reported ^{32, 33}, using potassium carbonate (18.29 g, 132.32 mmol, 2.0 equiv.) and propargyl bromide solution 98 (80% in toluene, 6.93 mL, 1.2 equiv.) in dry acetone (100 mL). The reaction mixture was heated under reflux 99 on_J3 October 2017_Downlpaded by Ereie UpiwersitaetsBerlin.cm 13/10/2017 12-45:00. 6 8 2 9 9 5 70 00 00 00 00 00 00 00 00 00 00 for 3 h (Scheme 2). Details are provided as supporting information. The residue, obtained with a 90% yield, was purified by silica gel chromatography (DCM-MeOH 96:4), followed by solvent evaporation. The resulting propargylated compound 2 appeared as a white solid (11.27 g, 59.54 mmol, 90%). The latter was fully identified through ¹H NMR and ¹³C NMR (Fig. S1), and further used in the synthesis of compounds 3 and **4** through different procedures.

2.3. Preparation of N-(4-(2.3-bis(2.3-dihvdroxvpropvlthio) propoxv)phenvl)acetamide (3)

Propargyl ether 2 was then treated under photolytic TYC conditions with thioglycerol to produce compound 3. Thus, compound 2 (378 mg, 2.0 mmol, 1.0 equiv.), 1-thioglycerol (519 µL, 6.0 mmol, 3.0 equiv.) and 2,2dimethoxy-2-phenylacetophenone (DMPA, 5 mg, 0.02 mmol, 0.01 equiv.) were solubilized in THF/MeOH Published o (2:1, 3 mL) in a photometer cell. The resulting mixture was exposed to a 365 nm radiation for 15 min under continuous stirring at room temperature (Scheme 2). Compound 3 was purified by column chromatography, 111 then identified through ¹H NMR and ¹³C NMR (Fig. S2) and high resolution mass spectrometry (HRMS) 112 (Fig. S3). Compound 3 was not grafted on the clay mineral, but was only employed as a probe organic 113 matrice for assessing its intrinsic interactions with Cu^0 and Cu^{2+} through liquid phase NMR analysis. The 114 changes in chemical shifts were compared to those measured with Cu²⁺ cation used as the standard. For this 115 purpose, two mixtures of 50 mg compound 3 each were prepared: 1. with Cu^{+2} by dissolving 116 Cu(NO₃)₂.2.5H₂O (3 mg) in D₂O; 2. or with Cu⁰ by reacting a solution of Cu(NO₃)₂.2.5H₂O (20 mg, 9 117

Page 6 of 35

mmol) with NaBH₄ (3 mg, 9 mmol) in D₂O. The second mixture was stirred at room temperature for 6 h. 118 Both mixtures were analyzed through NMR (1 H-NMR for Cu $^{2+}$ only and 13 C-NMR for both Cu $^{2+}$ and Cu 0). 119 120

2.4. Preparation of 4-(Prop-2-ynyloxy) phenylammonium chloride (PPhA⁺Cl) (4)^{34 34} 121

12:45:00. De-N-acetylation of compound 2 under acidic conditions gave rise to the corresponding ammonium salt (4) 10201/21 with a 77% yield. For this purpose, a solution of HCl in MeOH (4M, 10 mL) was added into a solution of 52 piersitaetaBerlin and 25 compound 2 (1.89 g, 10.0 mmol, 1.0 equiv.) in ethanol (15 mL) and the mixture was stirred at 60°C for 3 h (Scheme 2). After cooling to room temperature, compound 4 was isolated by filtration, then washed with ethyl acetate (1.40 g, 7.7 mmol), and further fully identified through ¹H NMR and ¹³C NMR (Fig. S4). nlpaded by Ereie U 87 Details are provided as supporting information. Compound 4 was grafted via ion exchange on Na⁺exchanged Montmorillonite (NaMt), resulting in a propargyl-organo-Montmorillonite (Pg-Mt). The latter was further employed for the synthesis of Cu^0 -doped thioglycerol-organo-Montmorillonite (Cu/T-Mt) (Scheme 2).

Scheme 2

2.5. Montmorillonite modification and CuNPs dispersion 133

Na-montmorillonite (NaMt), employed as inorganic support for the synthesis of Cu/T-Mt, was obtained from 134 the purification of an Aldrich bentonite having the following chemical composition: SiO_2 (66.45%), Al_2O_3 135 (22.28), Fe₂O₃ (3.85), MgO (2.58), Na₂O (2.33), CaO (1.34), K₂O (0.38), SO₃ (0.52), Ti (931 ppm), Sr (308 136 ppm), P (182 ppm) and Zr (165 ppm). Bentonite purification was achieved through full ion-exchange in a 2– 137 5M aqueous NaCl solutions at 80 °C for 3-4h and fractionation by repeated settlings in distilled water at 138 room temperature (RT), under ultrasound exposure, as described elsewhere ^{35, 36}. NaMt was then washed 139 with water, centrifuged, and repeatedly dialyzed overnight with distilled water in cellulose bags to remove 140

the residual excess of unreacted NaCl. Such a procedure resulted in an increase in the montmorillonite content from ca. 84% to approximately 96% and a decrease of the Si/Al mole ratio from 2.54 (bentonite) to 2.47 (NaMt), due to the elimination of dense silica phases such as quartz and cristoballite. This Si/Al value is close to the average value of 2.44 obtained through X-ray photoelectron Spectrometry (XPS) and Energy Dispersion X-ray fluorescence (EDS-XRF) measurements, as described further. The same analyses gave a cation exchange capacity (CEC) of 1.0 ± 0.05 meq.g⁻¹.

In a first step, propargylated montmorillonite (**Pg-Mt**) was prepared via cationic exchange of a NaMt suspension in deionized water with a solution of compound **4** in de-ionised water at 60°C for 24 h. The final product was filtered, repeatedly washed with water to remove the cation excess and then dried under vacuum at RT for 24h. In a second step, 250 mg of **Pg-Mt** was dispersed in a 3:1 vol. mixture of methanol and deionized water and mixed with dimethoxy-2-phenyl-acetophenone (0.2 eq) and then with 20 eq of thioglycerol. This mixture was stirred overnight at RT under UV radiation at 365nm, resulting in a thioglycerol-functionalized montmorillonite (or thioglycerol-organo-montmorillonite) denoted as **T-Mt**. The latter was recovered by centrifugation, repeatedly washed with de-ionised water and dried under vacuum at RT for 24h. T-Mt was further immersed in aqueous $Cu(NO_3)_2$. 2.5H₂O solution (0.9 mmol) at RT for 6 hours, using NaBH₄ (9 mmol) as the reducing agent. The organoclay suspension turned brown due to the formation of CuNPs. The resulting Cu^0 -doped T-Mt was denoted as Cu/T-Mt (**Scheme 2**).

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159 2.6. Characterization

160 Cu/T-Mt and its precursors were comparatively characterized using many techniques. NMR spectra were 161 recorded in DMSO and CDCl₃ solutions using a Brüker Avance III HD 300MHz spectrometer and different 162 solvents such as DMSO, water and CDCl₃ (δ 2.52, 3.41 and 7.27 respectively). T-Mt and Cu/T-Mt were 163 characterized through solid state ¹³C-MAS-NMR (Varian Inova MS600 NMR spectrometer, at 119.192

MHz. Transmission electron micrographs (TEM) of samples suspended in methanol and dried on holey 164 carbon-coated Ni grids were obtained by means of a JEOL JEM-2100F equipment, with an accelerating 165 voltage of 200 kV, coupled to an EDAX X-ray fluorimeter operating through energy dispersion (EDS-XRF). 166 The specific surface area (SSA), porosity and pore size distribution were measured by nitrogen adsorption-167
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 desorption isotherms at 77 K on samples previously dried and outgassed at 100-150°C using а Ouantachrome Autosorb equipment with an Autosorb automated gas system control. In this regard, calculations were achieved using BET and BJH models, respectively. Thermal gravimetric Analysis (TG and DTG) was performed by means of a Seiko TG\TDA-6200 thermal analyzer, under a 120 mL.min⁻¹ air stream and 5°C.min⁻¹ heating rate. Fourier transform Infrared spectra were recorded on a Model Nicolet 6700 FTIR instrument, operating in attenuated total reflectance (ATR) mode (Diamond ATR crystal) between 600 and 4000 cm⁻¹. Measurements by differential scanning calorimetry (DSC) were performed on a Mettler Toledo TGA-SDTA 851e, under dry nitrogen stream of 20 mL.min⁻¹ and heating rate of 5°C.min⁻¹.

X-ray photoelectron spectra (XPS) were recorded using a PHI 5600-ci instrument (Physical Electronics, Eden Prairie, MN, USA) and Al standard (1486.6 eV) as the anode for overflight spectra at 300 W. Highresolution spectra were recorded with Mg-Ka (1253.6 eV) at 150 W. The analyses were performed without charge compensation (neutralizer) at an angle of 45° with the analyzed surface (0.005 cm²). The synthesized 179 materials were also characterized through X-ray diffraction (XRD) using a Siemens D5000 equipment (Co-180 Kα at 1.7890°A). 181

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2.7. Measurements through thermal desorption analyses 183

CO₂ was used as a probe gas to assess the interactions of the terminal OH groups of the organic moiety 184 grafted with CuNPs. This is based on the high affinity of hydroxyls towards CO₂ and water ²⁷⁻³¹. On the one 185 hand, the appearance of competitive Cu:O- interactions may be detrimental for those occurring between 186

terminal OH groups and CO_2 and water, and may induce decreases in CO_2 and water retention capacities (CRC and WRC). On the other hand, the affinity towards hydrogen should be proportional to the number of CuNPs. Therefore, it is expected that, globally, higher hydrogen uptakes (HRC) will require highly dispersed CuNPs through Cu:O- interactions, i.e. low CRC and WRC.

CO2 and water saturated samples of Cu/T-Mt and precursors were subject to thermal programmed desorption (TPD) in a tubular glass reactor coupled to Li840A dual CO₂\H₂O Gas Analyzer. The CO₂ and water retention capacity, denoted a CRC and WRC, respectively, were assessed as being the surface area described by each TPD pattern between the considered temperature ranges. For this purpose, each non-dehydrated sample (40mg, particle size of 0.05 to 0.1mm) was dried at 80-160°C for 1 h, then cooled down to 20 °C and saturated with dry CO₂ in static mode without nitrogen stream for accurate assessment of the CRC and WRC values, then the gas excess was evacuated by nitrogen stream (5 mL.min⁻¹) until no CO₂ was detected. The values of CRC and WRC were expressed in μ mol of desorbed gas per gram of adsorbent under 5 mL.min⁻¹ nitrogen stream and 5°C.min⁻¹ heating rate between 20 and 80 or 100°C depending on the limit of stability of each sample as given by thermal gravimetric results.

Similarly, samples previously saturated with dry hydrogen at RT and ambient air pressure were analyzed by H₂-TPD but using Q-S121 H₂ Gas detector. Hydrogen retention capacity (HRC) was also assessed through additional DSC and TGA measurements in dry helium, between 20 and 80 or 100 °C depending on the limit of stability of each sample as given by thermal gravimetric results.

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206 3. RESULTS AND DISCUSSION

207 3.1. Effects of clay modification

Propargyl incorporation via cation exchange in NaMt was supported by the appearance of a new absorption
band in the FTIR spectra of Pg-Mt (Fig. 1), i.e. at 818- 796 cm⁻¹ due to stretching vibrations of the primary

ammonium R-NH₃⁺ and C-N, at 1508 cm⁻¹ attributed to the aromatic C=C bonds and at 3296 cm⁻¹ assigned 210 to the \equiv C-H bond stretching. The latter totally disappeared as a result of thio-vne addition of the thioglycerol 211 groups. The decrease in intensity of the 3430-3450 cm⁻¹ band indicates depletion in the number of OH 212 stretching vibrations of sorbed water molecules and decay in the hydrophilic character. This is a special 213 feature of montmorillonite after incorporation of organic moieties ³⁷. This is in agreement with the significant decay in intensity of the 1650-1700 cm⁻¹ band, assigned to the H-O-H bending vibration of sorbed moisture.

Figure 1

on 13 October 2017, Downleaded by Rreie Universitate, Berlin on 13/10,2017 13,45:00. C 75 10 05 66 81 21 91 91 71 74,5:00. This band split in two sharp peaks upon functionalization with thioglycerol groups, and the hydrophilic character seems to be revived by the newly inserted OH groups. The broad absorption band around 3430-3450 cm⁻¹ should account for overlapped antisymmetric and symmetric stretching vibrations of H-bridged water ³⁸, while the shoulder observed around 3260 cm⁻¹ must be due to a bending mode of adsorbed water molecules. Nevertheless, this shoulder totally disappeared after CuNP incorporation, suggesting a new decay of the hydrophilic character. This must be due to an enhancement of competitive surface interaction with o paper o paper o HO:Cu⁰ interactions at the expense of water, as supported by the intensity depletion after CuNP incorporation for the band appearing at 3623-3626 cm⁻¹ assigned to OH stretching vibrations of structural 225 hydroxyl groups. 226

In the meantime, XRD analyses showed an increase in the d_{001} basal spacing of NaMt from 11.38 Å (2 θ = 227 8.51°) to 12.97 Å ($2\theta = 7.79^\circ$) (Fig. 2), reflecting an appreciable expansion of the interlayer space. The 228 marked sharpening of the d₀₀₁ XRD line indicates an improvement of the parallel arrangement of the clav 229 sheets and a uniform incorporation of the $PPhA^+$ cation within the interlayer space. 230

231

Figure 2

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Photocatalysed TYC addition of thioglycerol to the propargyl groups induced a much more pronounced

increase in the d_{001} value from 12.97 Å up to 18.06 Å. This suggests an additional structure expansion, in 233 agreement with the pronounced improvement of the specific surface area (SSA) from 54 to 296 m².g⁻¹ 234 (Table 1) and significant changes in micro (5-35 Å) and mesoporosity (35-200 nm) (Fig. S5). 235
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 Table 1 In contrast, CuNP incorporation induced an alteration of the parallel arrangement of the clay sheet and a decrease in the basal d_{001} spacing from 18.06 to 15.52 Å. The simultaneous decay of both the specific surface area from 296 to 70 m².g⁻¹ and pore volume from 1.363 cc.g⁻¹ to 0.142 cc.g⁻¹ indicate a structure compaction that agrees with previous data ^{14, 39}. This must be due to an enhancement of Cu⁰ interactions the S and O atoms of the organic moiety grafted. Unlike NaMt which showed appreciable thermal stability up to 400°C (*pattern 1*). TG analysis revealed new

thermal processes for its modified counterparts around 170-200°C with variable mass losses after clav modification by the organic cation (*pattern 2*) and thioglycerol groups (*pattern 3*), respectively (Fig. 3). This appears to be a thermal stability threshold, when thermal decomposition of the incorporated organic moieties should be triggered.

247

Figure 3

For this reason, the temperature range for further TPD measurements was restricted to less than 100°C. 248 Preliminary tests revealed no changes in the CO₂-TPD profiles after repeated adsorption-desorption cycles as 249 long as temperature is maintained within this temperature range. The latter is sufficiently wide to detect 250 unequivocally thermal dehydration processes. In agreement with our previous statement, Pg-Mt (pattern 2) 251 and Cu/T-Mt (pattern 4) displayed very much weaker hydrophilic character, with a mass loss of ca. 1% at ca. 252 90-100°C, as compared to T-Mt (pattern 3) with mass loss of ca. 16% at 70°C. 253

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3.2. XPS evidence for CuNP stabilization 255

XPS analysis of T-Mt revealed changes in the pattern shape after CuNP incorporation (Fig. S6). The binding 256 energy of S_{2p} and O_{1s} electrons shifted from 164.19 eV to 163.39 eV and from 532.22 eV to 531.42 eV, 257 respectively (Tables 2, S1-S2). This accounts for an attenuation of the binding energy and enhanced electron 258 13€2:00. mobility around S and O atoms due to interactions with next-neighboring CuNPs. Given the magnitude of
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 <t the changes measured for the binding energy, these interactions must be sufficiently strong to produce a compaction of the organic entanglement around CuNPs, as already reported ¹⁴.

Table 2

No detectable shifts in the binding energy were noticed for carbon atoms belonging to the organic mojety. and both Si and Al atoms of the clay surface. This suggests that CuNP interactions with the carbon atoms of the organic moiety, the silanol and aluminol groups, if any, should only have minor contributions, and, subsequently, that CuNP stabilization involves mainly S-Cu⁰ and O-Cu⁰ interactions.

Figure 4

Evidence of the presence of Cu^0 was provided by the main XPS peaks at 936 eV (Cu- $2p_{3/2}$) and 956 eV (Cu- $2p_{1/2}$), which were unequivocally identified through their area ratio around 0.5 (Fig. 4). This agrees with the weak but clear signal at 919 eV, which accounts for a LMM spectrum of Cu⁰. Slight shoulders difficult to 270 discriminate around these values 40 and weak satellite signals of Cu²⁺ between 945 and 950 eV indicate that 271 the amounts of Cu²⁺ and other oxidation states, if any, should be negligible. This must be due to the capacity 272 of alkyl sulfides to prevent copper oxidation⁴¹. The peak broadness suggests a diffuse dispersion of the 273 electron density around S atoms of the thioglycerol groups, seemingly a common feature for other -C-S: 274 metal systems ⁴²⁻⁴⁴. This may slightly influence the electron density on next-neighboring carbon atoms, and 275 deeper insights through ¹³C-NMR would be useful in this regard. 276

3.3. NMR evidence for CuNP stabilization. 278

CuNP stabilization was supported by ¹³C-NMR of non-grafted organic compound **3** in aqueous media before 279 (A) and after incorporation of Cu^{2+} cations (B) or CuNPs (C) (Fig. 5). Fluctuations of the chemical shifts and 280 peak splitting were noticed for carbons neighboring S, O, and N atoms of T-Mt after CuNP incorporation 281 13:45:00. **28**:55:00. (Carbons d, i, j, k, l, m, n, and o) (Table S3). The decrease in intensity of these carbons (except d) was 13/10/2017 1 88 accompanied by the appearance of many smaller peaks. This corresponds to a chemical shift dispersion due to the appearance of anisotropy, a special feature of rigid structures.

Figure 5

The most significant changes in the chemical shifts were observed for carbon **h** (from δ 44.8-44.7 to 48.5-48.9 ppm) and *i* (from δ 34.0 to -38.0-38.1 ppm). Carbons *i* and *m* also showed noticeable increases in the chemical shifts, as a result of the presence of electron-donor (Cu^0) in their vicinity. This suggests a shielding enhancement due to a synergistic effect of both neighboring S and O atoms. More pronounced changes were registered after incorporation of Cu⁰, presumably due to a higher affinity towards thioglycerol as compared to Cu²⁺ cations. The latter appeared to rather favor interaction with S and O atoms neighboring carbon g, as supported by the appreciable shielding of protons a and g (Table S4, Fig. S7). The slight decreases in 293 chemical shift of carbon d from δ 155 to 154.5 ppm, and to a lesser extent of carbon n and k from δ 70.4-70.8 to 70.0-70-5 ppm indicate a de-shielding effect, presumably due to electron attraction by N atoms. This 294 can be explained by the higher electronegativity of oxygen (3.44) and nitrogen (3.04) as compared to carbon 295 (2.55) and sulfur (2.58). 296

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3.4. CuNP Dispersion 298

A first overview of TEM images of Cu/T-Mt showed the preponderant formation of CuNPs with particle size 299 not exceeding 5-6 nm (Fig. S8). A close-up on a particle edge revealed well-ordered organo-clay stacks of 300

parallel lamellae (Fig. 6), in agreement with the XRD data. The linear arrangement of CuNPs indicates an 301 interlayer incorporation of copper. Interestingly, much smaller CuNPs with fairly uniform dispersion were 302 observed between the organoclay lamellae as compared to the external surface of the clay sheet stacks. Most 303 CuNPs (ca. 90%) have an average size below 3.0 nm, including 39% of 1.0-1.5 nm particles and 14% of 304 subnanometric particles (Fig. 7).

Figure 6

Figure 7

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 Such a high dispersion of CuNPs must be due to a combination of a "cementing" effect of the organic mojety around CuNPs and a "sandwiching" effect of organic chains belonging to two neighboring clay sheets sharing common CuNPs. This ought to reduce the mobility of both the organic branches inserted and CuNPs, conferring a certain rigidity that prevents entrapped CuNPs from re-aggregating. Repeated CO₂ or hydrogen adsorption-desorption cycles between 20 and 80°C produced no change in the TPD profiles and, subsequently, no CuNPs re-aggregation. This finding agrees with the appearance of anisotropy, and reinforce the concept of structure compaction.

A close-up on Cu^0 particle (Fig. S9) showed a d₁₁₁ spacing of 2.1 nm, a special feature of the face-centered cubic symmetry of copper (fcc), which appears to be maintained even at subnanometric scale. XPS analysis 316 (Table 2) gave a C atom concentration of 27.85 %, before Cu⁰ incorporation, i.e. 1.09 mmol organic moiety 317 per gram dry NaMt. This value is close to the measured CEC (1.0 meq.g⁻¹), and indicates full exchange of 318 Na^+ with the *PPhA^+* cation. The calculations accuracy is supported by the fact that the measured C/S atom 319 ratio is in the same magnitude order as the molecule formula of the inserted organic compound. 320

Given the Cu⁰ compactness factor of 0.74 due its fcc symmetry, the measured Cu⁰/S atom ratio of 1.63 (Cu⁰ 321 content of 57 mg.g⁻¹ or 0.9 mmol.g⁻¹), which is in the same magnitude as that obtained through EDS-XRF 322 measurements on spots of uniform CuNP dispersion (Fig. S10). This accounts for ca. one 0.5 nm particle 323

 $(4.70 \text{ Cu}^{0} \text{ atoms})$ per ca. 3 sulfur atoms, or one 1 nm particle (37.6 Cu⁰ atoms) per 23 sulfur atoms or one 1.5 324 nm particle (126.9 Cu⁰ atoms) per 78 sulfur atoms. Consequently, there exists a strong correlation between 325 the structure compaction and metal dispersion and stabilization. Higher Cu⁰/S atom ratios were noticed at the 326 edges and external surface of the clay sheet stacks, i.e. when no sandwiching effect is involved. It results that 327 bulky CuNPs are surrounded by less thioglycerol groups than those entrapped within the interlayer space.

3.5. Cu^{0} : OH interaction assessment through CO₂-TPD

Given the affinity of OH groups towards both CO₂ and metals, Cu⁰ incorporation is expected to reduce the CO₂ retention capacity (CRC). This detrimental effect is regarded as a precise indicator of the enhancement of competitive -HO:Cu⁰ interaction at the expense of -HO:CO₂ carbonate-like association ²⁷⁻³¹. Preliminary tests revealed that carbon dioxide adsorbs spontaneously at ambient temperature and pressure. As a general feature. TPD measurements within the thermal stability range showed that CO₂ can be released by slight heating starting from ca. 45°C (Fig. 8). As, expected, T-Mt displayed increasingly higher amount of desorbed CO₂ (*pattern 1*) and water (*pattern 2*), and, subsequently, increased affinity towards CO₂ and hydrophilic character as compared to its metal-loaded counterpart (*patterns 3* and *4*, respectively)^{14, 27-31}.

Figure 8

T-Mt showed higher CRC (279.5 µmol.g⁻¹) than Cu/T-Mt (94.1 µmol.g⁻¹) between 20 and 100 °C (**Table 1**). 340 This cannot be explained only by decreases in the specific surface area from 296 to 76 m².g⁻¹ and of pore 341 volume from 1.363 to 0.142 cc.g⁻¹, since porosity decrease was already found to play a minor role ^{14, 27-31}. 342 This must be due mainly to an accentuation of Cu⁰-Oxygen interactions in Cu/T-Mt at the expense of [-343 HO:CO₂] carbonate-like associations in T-Mt. CuNP incorporation also induced a suppression of CO₂ 344 physical adsorption, as supported by the increase in the desorption heat from 0.70 to 24.7 kcal.mol⁻¹. 345

3.6. Affinity toward hydrogen and non-contact hydrogen-metal interaction 347

Combined TG-DSC measurements revealed a higher mass loss of 13.1 mmol.g⁻¹ for Cu/T-Mt versus 3.53 348 mmol.g⁻¹ for T-Mt, taken as the reference. This accounts for a hydrogen retention capacity (HRC) of 9.54 349 mmol.g⁻¹ or a surface affinity factor (SAF) of 126 μ mol.m⁻², which is in the same magnitude order as other 350 Cu-loaded organoclays³⁹. This SAF value suggests a non-stoichiometrical amount of captured hydrogen, given the relatively low amount of incorporated Cu⁰. This performance is ca. eight times lower than that reported for MIOMs¹⁴, but still remains higher than those reported for lanthanum-based MOFs⁴⁵ or many sophisticated adsorbents reported in the literature under similar conditions ^{9, 46-48}.

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 This beneficial effect of CuNP incorporation can be explained by the increased affinity to metal towards hydrogen, but it paradoxically contrasts with the attenuation of the hydrogen retention strength reflected by a gas release starting from room temperature and a decrease in the desorption heat from 72.5 to 44.0 kcal.mol⁻ ¹. A possible explanation should consist in the partial suppression of chemical absorption of hydrogen, presumably due to structure compaction. This is expected to hinder hydrogen diffusion towards CuNPs, reducing the direct contact of hydrogen with the metal. Even after reaching the metal surface, hydrogen should adsorb spontaneously on the metal surface ⁴⁹, giving rise to a first layer of metal hydride that act as a barrier that impede further hydrogen diffusion inside the metal ⁵⁰. This is in agreement with previous data, 362 which revealed that for short adsorption times, much higher linearity was noticed with a pseudo-second-363 order kinetic model, which supposes the occurrence of chemical processes ⁵¹. This indicates that hydrogen 364 chemisorption onto the MNPs, if any, should take place only in a quick initial step, i.e. as long as MNPs do 365 not contain adsorbed or absorbed hydrogen. The loss in linearity noticed for longer impregnation times of 366 the adsorbent by hydrogen suggests a consecutive physical adsorption of higher and nonstoichiometric 367 amounts of hydrogen. This was supported by intraparticle diffusion kinetics attempts, which revealed a 368 multi-step hydrogen adsorption. Many attempts with even more porous structures reported in the literature ⁴⁵⁻ 369

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^{48, 52-55} could not afford such a performance at ambient temperature and pressure, and without modifying
 irreversibly the CuNP structure.

Figure 9

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The shift of the slight bump in the DSC profile (**Fig. 9**) from 60- 70°C for T-Mt (*pattern 3*) up to ca. 90°C for Cu/T-Mt (*pattern 4*) once contacted with hydrogen is a clear evidence that CuNPs are responsible of the affinity improvements towards hydrogen. The fact that most hydrogen desorbs at temperature not exceeding 80-90°C suggests a predominantly physical adsorption, most likely in the form of a multilayer and nonstoichiometrical condensation of hydrogen in the organic entanglement surrounding CuNPs, as already been reported elsewhere ¹⁴. Repeated hydrogen adsorption-desorption cycles between 20 and 80°C produced no change in the adsorption profiles. Three successive adsorption tests on dry Cu/T-Mt performed at room temperature by contacting

Repeated hydrogen adsorption-desorption cycles between 20 and 80°C produced no change in the adsorption profiles. Three successive adsorption tests on dry Cu/T-Mt performed at room temperature by contacting Cu/T-Mt with dry hydrogen gave almost similar adsorption profiles (**Fig. S11**). Test 1 was achieved with the as-synthesized Cu/T-Mt after air drying at 30°C in sealed enclosure containing dry nitrogen and NaOH pills. Tests 2 and 3 were carried out after thermal regeneration up to 80°C without rehydration and re-saturation with dry hydrogen in sealed enclosure. Both tests gave lower surface affinity factor than the fresh sample (Test 1). As already stated in the manuscript, a ca. 15-20% loss in the surface affinity factor was noticed after test 1 and regeneration at 80°C. Investigations are still in progress for achieving more tests.

Hydrogen capture through physical condensation does not necessarily require highly porous structure but rather optimum hydrogen-matrice interactions. The latter should be sufficiently strong to retain high and non-stoichiometric gas amount but also sufficiently weak to allow easy release upon strong stream of the carrier gas. Some dendrimers and derivatives ^{10, 11, 13, 56-58} may fulfill these requirements in dry media if judiciously functionalized and combined with suitable inorganic supports, even at the expense of porosity. These findings open new prospects for natural or commercial compounds deriving from vegetal sources. 393

4. CONCLUSION 394

The results obtained allow concluding that truly reversible capture of hydrogen is possible on copper-loaded 395 organoclay at ambient conditions. High metal dispersion and stabilization through simultaneous interactions 396 7_{AD}0wnlogded by Ereie Universitates Berlincon 13/102017 12;45:00. 70 00 66 66 66 66 of sulfur and oxygen atoms belonging to the organic moiety with Cu⁰ nanoparticles were found to produce a compact matrix that reduces Cu⁰ nanoparticles mobility and impedes their aggregation. Such a structure favors physical condensation of hydrogen at the expense of chemisorption by hindering gas diffusion towards the metal surface. Non-contact metal-hydrogen interaction can explain the low desorption heats measured and almost complete release up to 80°C or under vacuum at lower temperature. Optimum metal loading and density of the organic chains with tunable strength of the chelating sites are essential requirements for achieving truly reversible and effective hydrogen storage. This finding is of great importance, because it allows envisaging safe hydrogen storage without energy constraints by eco-friendly Published on A3 October 201 20 900 500 500 500 matrices, with promising prospects for clay materials and biomass-deriving sulfureted polyglycerols. Further work is being focused on other metal nanoparticles, and data will be published in due course.

ACKNOWLEDGEMENTS 408

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FIGURES CAPTIONS

Scheme 1. Structure of copper-doped T-Mt (Cu/T-Mt). 505

Scheme 2. Synthetic strategy for the synthesis of compounds 3 and 4 and of Cu/T-Mt.

Fig. 1. FTIR spectra evolution after NaMt modifications. 1. NaMt; 2. Pg-Mt; 3. T-Mt; 4. Cu/T-Mt. The samples were preserved under wet air (20% moisture) analyzed without previous dehydration.

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 Fig. 2. XRD spectra evolution after NaMt modifications. 1. NaMt; 2. Pg-Mt; 3. T-Mt; 4. Cu/T-Mt. The samples were preserved under wet air (20% moisture) analyzed without previous dehydration.

Fig. 3. TGA patterns evolution after NaMt modifications. 1. NaMt; 2. Pg-Mt; 3. T-Mt, 4. Cu/T-Mt. These TG patterns were recorded with samples previously dried overnight at room temperature.

Fig. 4. XPS spectra of Cu/T-Mt. The weak Cu^{2+} satellite signal around 945-950 eV and the broad $Cu_{2p3/2}$ correspond to a very weak contribution of other oxidation states. The weak but clear signal at 919 eV in the 516 small binding energy shift region accounts for a LMM spectrum of Cu⁰. 517

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Fig. 5. ¹³C NMR spectra of compound 3 before (A) and after incorporation of Cu²⁺ cations (B) or CuNP (C) 519 in D₂O (20 mg sample-in 0,4 mL solvent). These samples previously dried overnight at room temperature. 520

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Fig. 6. TEM images of CuNPs. Linear arrangement of black stains is a precise indicator of an interlayer of 522 smaller size NPs not exceeding 2 nm, as compared to CuNP dispersed on the functionalized external surface. 523

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Fig. 7. Distribution of CuNPs entrapped between T-Mt lamellae as determined using the Image-J software. A 526 proportion of 90% of ca. 200 particles numbered displayed a diameter lower than 2 nm, and 14 % were 527 found to be subnanometric particles.

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 Fig. 8. TPD patterns for CO₂ and water: 1. CO₂-TPD of T-Mt, 2. H₂O-TPD of T-Mt, 3. CO₂-TPD of Cu/T-Mt, 4. H₂O-TPD of Cu/T-Mt. These TPD patterns were recorded under nitrogen stream of 5 ml.min-¹ after impregnating 45 mg adsorbent overnight with 200 mL of CO₂ at room temperature in dynamic regime under a 5 mL.min⁻¹ dry nitrogen stream, followed by a purge under similar conditions. These samples were not previously dried.

Fig. 9. DSC patterns of CO₂ saturated T-Mt (1) and Cu/T-Mt (2) and H₂-saturated T-Mt (3). Cu/T-Mt (4) at a heating rate of 5 °C.min⁻¹ under a dry nitrogen stream of 20 ml.min⁻¹. For DSC measurements. The different adsorbents were previously saturated by dry pure H₂ overnight in static mod. without carrier gas at ambient 539 temperature and pressure.

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Tables

Table 1. Features of modified supports before and after incorporation of CuNPs 548

SAMPLE	Preparation procedure	Specific surface area $(m^2.g^{-1})^a$	Pore Volume (cc.g ⁻¹) ^b	d ₀₀₁ (A°)	CRC^{c} $\mu mol.g^{-}$
NaMt	Aldrich bentonite purification	54	-	11.38	-
Pg-Mt	Ion Exchange with PBA ^b	22	0.171	12.97	-
Thioglycerol-organo- montmorillonite (T-Mt)	Thiol-yne reaction	296	1.363	18.06	279.5
Cu/T-Mt	Cu ^o NP dispersion using (Cu(NO ₃) ₂ 2.5 H ₂ O)	76	0.142	15.52	94.1

^a The specific surface area was determined through nitrogen adsorption-desorption isotherms and BET calculation model;

^b The pore volume was determined through nitrogen adsorption-desorption isotherms and BJH calculation model;

^c TPD measurements of CO₂ retention capacities (CRC were carried out between 20 and 100°C under a 5mL.min⁻

¹ nitrogen stream, after static saturation of 40 mg of samples with 200 ml of dry CO_2 at 20°C;

^d The ion exchange process was carried out by NaMt impregnation in aqueous solution of 4-(Prop-2 ynyloxy)phenylammonium cation (PPhA⁺).

12:45:00.	NaMt	Aldrich bentonite purification	54
0/2017	Pg-Mt	Ion Exchange with PBA ^t	22
lin on 13/1	Thioglycerol-organo- montmorillonite (T-Mt)	Thiol-yne reaction	296
sitaet Berl	Cu/T-Mt	Cu ^o NP dispersion using (Cu(NO ₃) ₂ 2.5 H ₂ O)	76
Ctober 10, 12, 12, 12, 12, 12, 12, 12, 12, 12, 12	 ^a The specific surface area calculation model; ^b The pore volume was determi ^c TPD measurements of CO₂ re ¹ nitrogen stream, after static sa ^d The ion exchange process ynyloxy)phenylammonium cati 	was determined through nit ned through nitrogen adsorpti- tention capacities (CRC were aturation of 40 mg of samples was carried out by NaMt ion (PPhA ⁺).	rogen adsorption-dea on-desorption isother carried out between 2 with 200 ml of dry C t impregnation in a
б <u>т</u> 10 10 10	Table 2. Binding energies in com	ipound 3 before and after C	unp incorporation.
lished	Before	CuNP incorporation	After CuNP i
Pub	Electron type Binding en	ergy	Binding energy

	Before CuNP incorporation		After CuNP incorporation	
Electron type	Binding energy (eV)	Atom %	Binding energy (eV)	Atom %
O-1s	532.22	40.52	531.42	30.85
C-1s	285.00	27.85	285.00	24.40
S-2p	164.19	2.19	163.39	1.15
Si-2p	102.59	22.24	102.59	12.12
Al-2p	75.39	7.20	75.39	29.60
Cu-2p	-	0	932.24	1.87

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Schemes

564 **Scheme 1**



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572 Scheme 2

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581 Figure 1





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Cu^o-loaded organo-montmorillonite with improved affinity towards hydrogenan insight in matrice-metal and non-contact hydrogen-metal interactions

Radia Sennour, et al..... and Abdelkrim Azzouz*

Graphical abstract



Thioglycerol-functionalized organo-montmorillonite with highly stabilized Cu^0 nanoparticles was found to favor the reversible capture of hydrogen at ambient conditions. This compacted structure promotes physical hydrogen adsorption in the form of multilayer condensation at the expense of chemosorption. Similar adsorbents can be manufactured starting from low cost clay materials and biomass-deriving polyglycerols.