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# LETTER

Silica supported copper nanoparticles prepared via Surface Organometallic Chemistry, active catalysts for the selective

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hydrogenation of 2,3-Dimethylbutadiene

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2,3-Dimethylbutadiene can be highly selectively hydrogenated into 2,3-Dimethyl-1-butene with a new catalyst based on silica supported copper nanoparticles (Cu-Nps) prepared via surface organometallic chemistry. Mesityl-copper was firmly grafted onto silica and the reduction of the resulting surface species under hydrogen at 350°C led to well-dispersed Cu-Nps. Prior to catalytic tests, the final catalysts as well as the intermediates were characterised by DRIFT, SS NMR, EPR, TEM, XRD and elemental analyses.

Branched  $C_6 \alpha$ -olefins are valuable intermediates within fine and petrochemical industry, in particular in the field of perfume synthesis and drop in fuel. For instance, 2,3-dimethyl-1-butene (DMB-1) is used in the preparation of fine chemicals such as aromatic musks, which are widely used in perfumery, household soaps and detergents.<sup>1,2</sup> For example Tonalide (1,1,3,4,4,6-hexamethyl-1,2,3,4 tetra-hydronaphthalene) is classically prepared by acid-catalysed cycloalkylation via Friedel–Crafts cyclisation of p-cymene with DMB-1.<sup>1</sup> Furthermore, branched hexanes are valuable additives for gasoline. Especially 2,3-dimethylbutenes (DMBs) after a simple hydrogenation to 2,3-dimethylbutane (DMBH) known to have a high research octane number (RON) of 103.5 and low RVP (Reid Vapour Pressure).<sup>3</sup> DMBs are generally prepared by dimerization of propylene on nickel catalysts. In particular, in  $\mathsf{Difasol}^{\mathsf{TM}}$  IFPEN process, a nickel salt is used in the presence of a bulky basic phosphine and an Al-alkylating agent.<sup>4</sup> However, this process is dependent on propylene, where the demand for such compound has incessantly risen in recent years, resulting in an important increase in its price.<sup>5</sup> Consequently, the development of new and less costly processes to obtain 2,3-DMBs and neohexene directly from other readily available feeds, are highly desirable. An alternative route is by selective hydrogenation of 2,3-dimethyl-1,3-butadiene (DMBD), which

can be easily obtained from the dehydratation of pinacol (Scheme 1).  $^{\rm 6}$ 



Scheme 1. Selective hydrogenation reaction of 2,3-dimethylbutadiene (DMBD) that can be obtained from pinacol to 2,3-dimethyl-1-butene (DMB-1)

The major challenge of this approach is to develop catalysts that are selective for the mono-hydrogenation of this substrate and that avoid the isomerization of DMB-1 into 2,3-Dimethyl-2-butene (DMB-2). Only few studies have exemplified the partial hydrogenation of DMBD in batch reactor in the presence of homogenous catalyst. However, the catalysts developed showed low activity toward DMB-1 formation.<sup>7-9</sup> Moreover, no example employing hetreogenous catalyst for this reaction has been reported in the literature. On the other hand, selective hydrogenation of 1,3-butadiene over supported monometallic and bimetallic nanoparticles based on Ni, Au, Ag, Cu and Pd carried on various oxide supports are largely studied.<sup>10-15</sup> Interestingly, supported Cu-Nps can partially hydrogenate both butadienes and alkynes derivatives into alkenes.<sup>16-19</sup> The metallic Nps are mainly obtained by either deposition-precipitation or incipient wetness impregnation and deposition of colloidal solution.

Surface Organometallic Chemistry (SOMC) is an established methodology that affords well-defined heterogeneous catalysts through the grafting of organometallic complexes on surface hydroxyls of classical supports such as alumina, silica, mesoporous silica, silica-alumina...<sup>20,21</sup> When the grafted organometallic complexes are treated under hydrogen, supported Nps can be obtained for late transition metals. However, for oxophilic elements such as group IV, V and VI, the stable M-O bond prevents agglomeration and hard conditions are usually required, and as a consequence, low control on the formed systems can be obtained with this

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Electronic Supplementary Information (ESI) available: Includes detailed information about catalysts preparations, catalysts and catalysts precursors characterisations (solution and solid state NMR, DRIFT, XRD) and catalysts selectivities. See DOI: 10.1039/x0xx00000x

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methodology. For late transition metals, Gates and co-workers reported the formation of rhodium Nps by reaction of silica supported diallylrhodium species  $[\equiv SiO-Rh(n^3-C_3H_5)_2]$ (obtained by the reaction of silica surface with  $[Rh(n^3-C_3H_5)_3]$ ) with hydrogen at room temperature, affording nanoparticles from 1 to 3 nm sizes.<sup>22</sup>

In this paper, copper nanoparticles supported on silica were prepared via Surface Organometallic Chemistry (SOMC) in two steps. This approach involves the grafting of mesitylcopper onto partly dehydroxylated silica. In fact, during the immobilization of the organometallic precursor, the silanol groups react with copper complexes resulting in a chemical bond between silica and copper with concomitant mesitylene release. The amount of copper loaded on the surface can be controlled by the surface density of the silanol groups, which depends on the dehydroxylation temperature. Thus, this strategy should provide a homogeneous distribution of the copper precursor, which in principle after the reduction of the supported copper moieties yields a narrow size distribution of the Nps. The obtained intermediates as well as the final catalysts were characterized, and their catalytic performances were evaluated in the selective hydrogenation of DMBD using a fixed bed flow reactor.

The grafting of mesitylcopper (1), mainly Cu<sub>4</sub> tetrameric clusters in toluene,<sup>23</sup> onto a non-porous silica dehydroxylated at 700°C, SiO<sub>2-700</sub>, was carried out in a glove-box at room temperature. The reaction is followed by IR (Fig. 1 (A)). After the grafting reaction, the isolated v(SiO-H) at 3747  $\text{cm}^{-1}$ completely disappeared and new bands appeared in the 3100-2850 cm<sup>-1</sup> as well as in the 1620-1400 cm<sup>-1</sup> ranges. These peaks are characteristic of aromatic and aliphatic v(C-H), v(C=C) and  $\delta$ (C–H) vibrations of the ligands of the surface chemisorbed Cu. <sup>1</sup>H MAS NMR spectrum of the resulting material shows signals at 2.2 ppm and 7.0 ppm respectively attributed to aliphatic  $CH_3$ and aromatic C-H protons of the mesityl ligand of copper (Fig1 (B)). Moreover, <sup>13</sup>C CP MAS NMR data highlighted in Fig.1 (C) shows signals at 18 ppm and 27 ppm, assigned to o-CH<sub>3</sub> and p- $CH_3$  correspondingly, likewise aromatic signals of o- $Csp^2$ , m-Csp<sup>2</sup> and p-Csp<sup>2</sup> were observed at 155, 125, 141 ppm, respectively. Furthermore, no EPR signal is observed, indicating that no Cu(II) is formed upon the grafting reaction.

Elemental analysis of this material showed the presence of 4.61 %<sub>wt</sub> and 5.51 %<sub>wt</sub> of Cu and C respectively (C/Cu = 6.3). On SiO<sub>2-700</sub>, monoatomic organometallics are usually grafted as monosiloxy (monopodal) complexes.<sup>24-26</sup> However the case of such a large cluster seems more complex. Indeed, in this case, almost all the surface silanols, ca. 220 µmol/g, have reacted according to IR, while only ca. 180 µmol/g of Cu<sub>4</sub> clusters are grafted. This strongly suggests that a mixture of mainly monopodal (about 80%) and bipodal (about 20%) tetranuclear species are formed (left part of Scheme 2). The reaction of the copper cluster with silanols was also characterized by a release of mesitylene, detected by GC/MS. A similar reactivity between a copper mesityl Cu<sub>4</sub> cluster and molecular  $\beta$ -diketiminato aluminum-monohydroxide, has been observed by Roesky et al..<sup>27</sup>



**Fig. 1** Characterizations of the surface complex resulting from the grafting of Mesitylcopper onto SiO<sub>2-700</sub>: (A) DRIFT spectra of a) silica dehydroxylated at 700 °C, b) After mesitylcopper grafting; (B) <sup>1</sup>H MAS NMR; (C) <sup>13</sup>C CPMAS NMR (peaks with an asterisk are spinning side bands).



Scheme 2 Grafting of tetrameric mesitylcopper (1) onto SiO<sub>2-700</sub> or SiO<sub>2-200</sub>.

Along the same prospect, mesitylcopper (1) was also grafted on silica dehydroxylated at 200 °C, SiO<sub>2-200</sub>, as previously described up above for (SiO $_{\rm 2-700}$ ). The DRIFT spectrum of SiO $_{\rm 2-200}$  showed in the v(O-H) stretching vibration region a band at 3741  $\text{cm}^{-1}$  for isolated silanols with a large shoulder centered at 3600 cm<sup>-1</sup> characteristic of bridged silanols<sup>28</sup> (Fig. S3 a)). After the grafting reaction, the 3741 cm<sup>-1</sup> band of isolated silanols almost completely disappeared and the band of the bridged silanols at 3624 cm<sup>-1</sup> increased in intensity (spectrum b Fig. S3), most probably due to an interaction of the residual surface silanols with the methyl and aromatic groups of the grafted complex in **2b**. Simultaneously v(C-H) and  $\delta(C-H)$ vibration bands characteristic of the ligands of the chemisorbed species appear. Moreover, no EPR signal was either observed after the grafting reaction of Cu(I) mesityl on SiO<sub>2-200</sub>, meaning that most likely the copper centers keep their Cu(I) oxidation state. Besides, the <sup>1</sup>H MAS NMR spectrum of the resulting material shows signals at 2.2 ppm and at 7.1 ppm attributed respectively to aliphatic  $CH_3$ and aromatic C-H protons of the mesityl ligand of copper (spectrum (A) in Fig. S4). Moreover, <sup>13</sup>C CP MAS NMR data show signals of the two o- $\underline{C}H_3$  and p- $\underline{C}H_3$  at 19 ppm and at 28 ppm respectively,

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likewise aromatic signals of o-Csp<sup>2</sup>, m-Csp<sup>2</sup> and p-Csp<sup>2</sup> at 154, 123 and 139 ppm, respectively (spectrum (B) in Fig. S4). Mass balance analysis of the material indicates a Cu and C content of 4.09 %wt and 2.61 %wt respectively (C/Cu = 3.4). These results may be interpreted by the formation of a 50/50 mixture of tetrameric Cu<sub>4</sub> cluster grafted respectively on two or three silanols with two or one remaining mesityl groups, as shown on the right part of Scheme 2.

The reduction of the grafted complexes on SiO<sub>2-700</sub> and SiO<sub>2-200</sub> under H<sub>2</sub>, at 350°C for 18h, gives dark-brown powders Cu@SiO<sub>2-700</sub> (**3a**) and Cu@SiO<sub>2-200</sub> (**3b**). The mechanism for Cu-Nps formation during the reduction is still not well understood in spite of many general proposed suggestions <sup>29, 30</sup>. The infrared spectrum on Fig.S5 and Fig. S6 show a depletion of the v(C–H) and  $\delta$ (C–H) bands, and the reappearance of the signal at 3747 cm<sup>-1</sup> characteristic of isolated silanols, due to the hydrogenolysis of Cu-O bonds and the formation of Cu-Nps.



Fig. 2 TEM micrographs and corresponding copper nanoparticles size distribution histograms for Cu@SiO<sub>2.700</sub>, **3a** (A) and Cu@SiO<sub>2.200</sub>, **3b** (B) catalysts.

TEM analyses performed on catalysts **3a** and **3b** showed highly dispersed copper particles (Fig. 2). For **3b**, smaller nano-particles sizes were obtained with a narrower distribution (maximum of the distribution at 1.9 nm, FWHM = 1.2 nm) than for **3a** (2.3 nm, FWHM = 1.4 nm). Despite the fact that the copper amounts grafted on both supports are very close, according to TEM, supported Cu-Nps are smaller on SiO<sub>2-200</sub> than on SiO<sub>2-200</sub> probably due to a better anchoring of the Cu<sub>4</sub> precursor on the SiO<sub>2-200</sub> surface. Moreover, XRD showed no peak that could be attributed to metallic copper on the diffractogram (Fig. S7). It can thus be stated that no or very few large copper particles (> 10 nm) are formed.

The catalytic performances of both materials were evaluated for the hydrogenation of 2,3-dimethylbutadiene (DMBD) in a continuous flow reactor at 75°C under atmospheric pressure and compared to Cu-Nps supported on silica prepared through incipient wetness impregnation (Cu@SiO<sub>2-wi</sub>). Surprisingly, **3a** and **3b**  presented a much more important activity compared to the catalyst prepared by a more classical method (Fig. 3).

The conversion of DMBD in the presence of Cu@SiO<sub>2-200</sub>, **3b**, slowly decreased with time from 75% to 50% after 20 h (curve a in Fig. 3). For Cu@SiO<sub>2-700</sub>, the conversion drops drastically from 45% to 18% during the first hour of reaction and then decreases smoothly to 13% after 10 h (curve b) in Fig. 3). In the presence of Cu@SiO<sub>2-wi</sub>, the conversion is solely around 15% at the beginning of the catalytic reaction and then falls very near zero after 1 h. Remarkably, the analysis of the hydrogenated products shows a high selectivity towards DMB-1, around 89% and about 10 % towards DMB-2 for both SOMC-prepared catalysts, Cu@SiO<sub>2-200</sub> and Cu@SiO<sub>2-700</sub> (Fig. S8 (A) and (B)). Concomitantly, only traces of fully hydrogenated DMBH are observed. The DMB-1/DMB-2 ratio is much higher than predicted by thermodynamic at 75°C (9 instead of 0.35).<sup>31</sup>



Fig. 3 Catalytic activities for hydrogenation of DMBD over a) Cu@SiO<sub>2-200</sub>, 3b; b) Cu@SiO<sub>2-700</sub>, 3a and c) Cu@SiO<sub>2-wi</sub>

In conclusion, Mesitylcopper Cu(I) clusters could be firmly grafted via SOMC onto non-porous silica supports dehydroxylated either at 700 °C (SiO<sub>2-700</sub>) or 200 °C (SiO<sub>2-200</sub>). The resulting materials were characterized by DRIFT, elemental chemical analysis, ESR and solidstate MAS NMR (<sup>1</sup>H, <sup>13</sup>C). These surface species were further reduced under hydrogen at 350°C and led to supported Cu-Nps, with a size of ca. 2.3 nm onto SiO<sub>2-700</sub> and 1.9 nm onto SiO<sub>2-200</sub>. according to TEM. These new materials were then successfully used to selectively hydrogenate DMBD into DMB-1. With a DMBD conversion of up to 75%, a selectivity into DMB-1 of up to 90 % was reached while that into 2,3-Dimethyl-2-butene (DMB-2) was less than 10% and just traces of fully hydrogenated 2,3-dimethylbutane (DMBH) were observed. Besides, these catalysts presented a good stability with time on stream. Further investigations will be conducted in order to explain the better activity of SOMC-prepared Cu catalysts compared to more classical catalysts.

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## Experimental

### I General

All experiments (mesitylcopper synthesis, grafting reactions) were performed under moisture and oxygen free argon using either standard Schlenk or glove-box techniques, with carefully dried and degassed solvents. Aerosil<sup>®</sup> silica was wet with

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#### Letter

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water and compacted, calcined and dehydroxylated for 16 h at two different temperatures, 200°C and 700°C that led to two different supports, denoted as SiO<sub>2-200</sub> and SiO<sub>2-700</sub> respectively. Elemental analyses were performed by the Mikroanalytisches Labor Pascher; Remagen, Germany. <sup>1</sup>H and <sup>13</sup>C solution NMR were performed on an AC-300 spectrometer (<sup>1</sup>H 300 MHz, <sup>13</sup>C 75 MHz). <sup>13</sup>C CP MAS solid state NMR spectra were collected on a Bruker avance 500 NMR spectrometer. Diffuse reflectance Fourier-transformed infrared (DRIFT) spectra were recorded on a Nicolet 6700-FT spectrometer using a cell equipped with CaF<sub>2</sub> windows. Powder X-ray diffraction (XRD) patterns were carried on a Siemens Bruker AXS D-500 instrument using Cu Ka1 radiation in bragg-bretano reflecting geometry. Transmission electron microscopy (TEM) observations were carried out on Philips CM120 instrument with an acceleration voltage up to 120kV.

#### II Preparation of CuMes@SiO<sub>2-700</sub>, CuMes@SiO<sub>2-200</sub>, CuO@SiO<sub>2-wi</sub>

#### II.2.1. Grafting of mesitylcopper on silica 700:

Mesitylcopper was synthesized according to previously described methods.<sup>23,32-33</sup> A solution of 219 mg of mesitylcopper (1.2 mmol, 6 equiv) in 15 ml of toluene was added to 800 mg of  $SiO_{2-700}$  (0.250 mmol/g - 0.75 OH/nm<sup>2</sup>). After stirring the suspension overnight at room temperature, the solid was filtrated and washed 5 times with 2 ml toluene and then 4 times with 2 ml pentane to remove the excess. The filtrate solutions were combined and analyzed by GC in order to quantify the amount of mesitylene released. The yellow material was dried under high vacuum (10<sup>-5</sup> mbar).

#### II.2.2. Grafting of mesitylcopper onto silica 200:

In order to obtain a similar Cu loading on SiO<sub>2-200</sub> (0.830 mmol/g - 2.5 OH/nm<sup>2</sup>), while the concentration of the surface OH anchoring sites is much higher than on SiO<sub>2-700</sub>, a solution of 105 mg of mesitylcopper (*ca.* 4.6 wt% Cu /SiO<sub>2-200</sub>, limited amount of Cu, unsaturated solid, colorless resulting solution) dissolved in 15 ml toluene was added to 800 mg of SiO<sub>2-200</sub>. The preparation was then conducted as above. The powders were stored in a glovebox.

#### II.2.3. Preparation of CuO on silica by wet impregnation:

This catalyst was prepared as reported in the literature from copper (II) nitrate trihydrate (Cu(NO<sub>3</sub>)<sub>2</sub>.  $3H_2O$ ) and 1g of Aerosil<sup>®</sup> silica.<sup>34</sup> The suspension was stirred in the Erlenmeyer flask until the water has evaporated to the atmosphere. The powder was then recovered and calcined under air in a muffle oven at 500 °C overnight.

#### II.2.4. Formation of Cu nano-particles by reduction:

Prior to catalytic tests, supported copper materials were reduced under hydrogen in a continuous-flow reactor with a flow of mixed gases of H<sub>2</sub>, 4.6 mL/min and Ar, 15.0 mL/min for 18 h at 350°C. This led to CuMes@SiO<sub>2-700</sub>, CuMes@SiO<sub>2-200</sub>, CuO@SiO<sub>2-wi</sub> catalysts.

#### III. Catalytic test (hydrogenation of 2,3-dimethylbutadiene):

In a continuous-flow reactor, a flow of 15 ml/min H<sub>2</sub> enclosing 10% of 1,2-dimethylbutadiene (v.p. 100 mbar at 10°C), was sent through the catalyst (amount of material containing 2.3 mg of Cu). The temperature was maintained at 75°C. Every 17 min, an automatically withdrawn amount was injected in the GC (Column: KCl/Al<sub>2</sub>O<sub>3</sub>, 50 m x 0.32 mm x 0.25  $\mu$ m).

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# **Table of Content**

Mesitylcopper reacts with silica surface to give Cu(I) supported clusters. They were reduced as nanoparticles, Cu-NPs, under  $H_2$  at 350°C. These materials allow the selective hydrogenation of 2,3 dimethylbutadiene into 2,3 dimethyl-1-butene. Catalysts and precursors were characterised by DRIFT, SS NMR, EPR, TEM, XRD and elemental analyses.

