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Comparison of the conventional impregnation method using ammonium heptamolybdate with a simple route to silica-supported molybdenum(VI) materials

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Abstract

Silica-supported molybdenum oxide materials have been prepared by using the ability of molybdenum oxoperoxo complexes to interact with the surface hydroxyl groups of the support, which after calcination, have a highly dispersed MoO_x/SiO_2 structure, and lead to leach-resistant catalysts; with a polyoxo precursor, $(NH_4)_6[Mo_7O_{24}] \cdot 4H_2O$, there is a formation of MoO_3 clusters and a weaker MoO_3/SiO_2 interaction.

Keywords: Epoxidation; Molybdenum; Mesoporous materials; H_2O_2

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1. Introduction

The field of application of nanotechnology for the development of catalysts for "Green Chemistry" is likely to grow rapidly during the next decade [1,2]. Surprisingly, there has been little work in which MCM-41, SBA-*n*, etc. have been exploited as replacability for classical industrial supports such as silicas, aluminas, silica-aluminas, etc. Are the catalytic performances of mesoporous materials superior to those of analogues obtained by transposition or conventionally prepared? Obviously, many problems concerning the catalytic target processes have to be considered [3] particularly economic factors related to: (i) the use of expensive inorganic complexes such as metal and/or silicon alkoxides and surfactants, (ii) lengthy hydrothermal syntheses, (iii) template removal, (iv) poor attrition strength for industrial-scale reactors, etc.

From studies on systems of aqueous $[MoO_4]^{2-}$ or $[Mo_7O_{24}]^{6-}$ solutions and silicas, it is well known that molybdenum(VI) uptake by silica is relatively low over the entire pH range, except for a small increase at pH ≈ 2 or lower, owing to the formation of $[SiMo_{12}O_{40}]^{4-}$ ions, which commonly desorb into solution [4–6]. Silanols such as R_3SiOH, $R_2Si(OH)_2$ and $RSi(OH)_3$ are easily prepared and used in synthesis. The isolation of mono- or dimeric oxoperoxo compounds: $[Ph_3SiOMO(O_2)_2]^-$,$[Ph_2SiO_2\{M_2O_2(\mu\text{-}O_2)_2(O_2)_2\}]^{2-}$ and of $[\{Ph_2SiOMO(O_2)_2\}_2(\mu\text{-}O)]^{2-}$, where $M = Mo$ or W [7,8], led us to think that molybdenum (or tungsten) oxoperoxo species may be more suitable than $[MoO_4]^{2-}$ or $[Mo_7O_{24}]^{6-}$ anions for preparing heterogeneous-Mo (or W) silica-supported catalysts.

In a preceding paper [9], a simple and low-cost synthesis route was proposed to develop highly dispersed molybdenum(VI)-silica-based materials, via the so-called "oxoperoxo route" with transient formation of low nuclearity

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moieties such as ≡Si–O–Mo(OH)$(O_2)_2$. The η^2-peroxo ligands are good leaving groups; they were decomposed during thermal treatments to give oxo groups with a nearly regular distribution of the surface species such as "(≡Si–O)$_2$–Mo(O)$_2$" [10]. We showed, once a catalytic reaction has been proven using mesoporous materials (MCM-41, SBA-15), it can be developed on cheaper silica-based supports. In this note, for the first time, this "oxoperoxo route" is compared with the "traditional route" involving ammonium heptamolydate, $(NH_4)_6[Mo_7O_{24}] \cdot 4H_2O$. The reported detailed characterization of the materials by Raman, TEM and EDX and catalysis tests shows the interest of these techniques for checking such materials.

2. Experimental

Before impregnation, SiO_2 (beads or precipitated silica) were calcined in air (180 cm^3 min^{-1}, 1 K min^{-1}) from ambient to 820 K (samples maintained at the final temperature for 6 h). Oxoperoxo route: wet impregnation was performed by suspending 0.950 g of the silica in a peroxidic solution of Mo(VI) initially prepared by mixing 0.060 g MoO_3, 3 mL H_2O and 0.5 mL H_2O_2 30 wt.% (entries 1, 2; Table 1) or 0.135 g MoO_3, 3 mL H_2O and 3 mL H_2O_2 30 wt.% (entry 3), stirred 30 min at 333 K in both cases, to generate the peroxo complexes. The suspension was stirred for 4 h at room temperature. The yellow solid was filtered off on a fritted glass disk, as such quickly dried over P_4O_{10}, then calcined in air (150 cm^3 min^{-1}, 1 K min^{-1}) from ambient to 820 K. The solid (MoO_x/SiO_2) is maintained at the final temperature for 6 h to favor the anchoring of molybdenum(VI) by "≡Si–O–Mo" bonds.

Polyoxo route: 0.058 g of $(NH_4)_6[Mo_7O_{24}] \cdot 4H_2O$ (entry 4) or 0.098 g (entry 5) was dissolved in 3 mL H_2O under stirring at 333 K. After cooling at room temperature 0.600 g (entry 4) or 0.950 g (entry 5) of the precipitated silica is added to the solution and stirred 4 h, the rest of the synthesis being identical to that for MoO_x/SiO_2. Samples synthesized according to the polyoxo route are denoted MoO_3/SiO_2.

The silica is mainly prepared by precipitation (pH < 7) from a sodium silicate solution. This is followed by agglomeration of silica particles in more or less loose aggregates in aqueous medium (sol). The precipitate is recovered, washed with distilled water and dried. See Rhône-Poulenc Pat. FR 871 5275, 4 Nov. 1987.

Raman spectra were recorded on a Kaiser Hololab 5000 R (excitation line, 785 nm; power source, 5–20 mW; 2–100 scans; 10 s per scan; 0.3 cm^{-1} resolution). Elemental analyses were carried out at the Service Central d'Analyse (CNRS/Lyon) by inductive coupling plasma atomic emission spectroscopy (ICP-AES) after alkaline fusion with $Li_2B_4O_7$. Diffuse reflectance IR spectra (resolution: 2 cm^{-1}) were taken on a Fourier transform apparatus (Bruker Vector 22) equipped with a Harrick diffuse reflection attachment. Adsorption and desorption isotherms for nitrogen were obtained at 77 K using a Micromeritics ASAP 2010. The samples were outgassed at 393 K and 0.1 Pa for 12 h before measurements. Transmission electron microscopy (TEM) and energy dispersive X-ray analysis (EDX) were performed using a JEOL JEM 2010 transmission electron microscope operating at 200 kV, equipped with a PGT Imix-PC system. The X-rays (Si Kα at 1.74 keV and Mo Kα at 17.48 keV) emitted from the surface (spot beam analysis) were collected in the 0–20 keV range. Data do not include oxygen. Catalysis experiments were performed at room temperature (18–20 °C); olefin (6–10 mmol) in 7 mL of pentane, catalyst (Mo/olefin = 1/100 mol/mol), 1.5 mL of 10% anhydrous t-BuOOH in decane (9 mmol of oxidant added with vigorous stirring) were placed in a home-made reactor avoiding direct contact between the catalyst and the magnetic stirring bar. The progress of the reaction was monitored by GC and the products were analysed after 24 h and quenching with MnO_2.

3. Results and discussion

Precipitated silica or beads (BET specific surface area ≃ 143–223 m^2 g^{-1}) and yellow molybdenum oxoperoxo species (mainly $[MoO(O_2)_2(H_2O)_2]$ and $[\{MoO(O_2)_2(H_2O)\}_2(\mu\text{-}O)]^{2-}$) interact in aqueous acidic medium to form fairly stable surface oxoperoxo species (Fig. 1), with a characteristic IR band $\tilde{\nu}_{O-O}$ near 870 cm^{-1} ($\tilde{\nu}_{O-O}$ is usually expected to be at 830–885 cm^{-1}) [11]. In Table 1 are presented the physicochemical characterizations of pre-cat-

Table 1
Textural properties of MoO_x/SiO_2 or MoO_3/SiO_2 pre-catalysts (calcined samples after wet impregnation and drying)

Entry	Samples	Synthesis route	S_{BET}[a] (m^2 g^{-1})	Pore volume (cm^3 g^{-1})	Mo (wt.%)	Si (wt.%)	Si/Mo (mol/mol)
1	MoO_x/SiO_2 (beads)	Oxoperoxo	217 (219)[b]	1.09 (1.21)[b]	1.8	44.1	84 (50)[c]
2	MoO_x/SiO_2 (crushed beads)	Oxoperoxo	223 (223)[b]	1.10 (1.10)[b]	1.8	44.1	84 (50)[c]
3	MoO_x/SiO_2 (precipitated)[d]	Oxoperoxo	103 (143)[b]	0.65 (0.84)[b]	5.5	40.1	25 (25)[c]
4	MoO_3/SiO_2 (precipitated)[d]	Polyoxo[e]	123 (143)[b]	0.80 (0.84)[b]	0.65	43.5	230 (33)[c]
5	MoO_3/SiO_2 (precipitated)[d]	Polyoxo[e]	120 (143)[b]	0.80 (0.84)[b]	2.3	41.5	61.5 (28)[c]

[a] Calculated with the BET model (±5 m^2 g^{-1}).

[b] The corresponding values for the bare (unused) supports studied.

[c] Expected ratio of starting products.

[d] Precipitated hydroxylated silica: the density of silanol groups is about 2 or 3 Si–OH/nm^2.

[e] Conventional impregnation method with $(NH_4)_6[Mo_7O_{24}] \cdot 4H_2O$ (Section 2).