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Porous Catalysts

One-Pot Aerosol Route to MoO_3-SiO_2-Al_2O_3 Catalysts with Ordered Super Microporosity and High Olefin Metathesis Activity**

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The cross-metathesis of light olefins is a crucial reaction that allows the regulation of olefin feedstock as a function of the market demand.[1] Currently, the production of high-demand propene from the cross-metathesis of butene and ethene is of particular interest.[2] While industrial processes are today in operation with modest performance and/or high catalyst cost, the challenging development of robust, cheap, and very active heterogeneous catalysts will boost the sector, thus allowing a more rational use of light hydrocarbon at the refineries.

MoO_3 supported on silica–alumina is recognized as a highly active metathesis catalyst.[3] It is typically prepared in two steps by the deposition of a Mo precursor on a preformed aluminosilicate support.[4] However, this method suffers from several severe limitations, as discussed recently[4d] (such as inhomogeneity and genesis of inactive species). Some of these limitations can be overcome with adapted impregnation methods.[4c,e] Recently, attractive one-step preparation methods were also proposed (non-hydrolytic sol–gel[5] and flame-spray pyrolysis[6]). Conventional hydrolytic sol–gels are widely used in the preparation of various porous mixed oxides.[7] The method relies on the consecutive hydrolysis and condensation of alkoxide precursors generating a gel by the formation of oxo bridges. The reactivity of most metal precursors however differs from the reactivity of silicon alkoxides. This, even in the presence of templating agents, hinders the preparation of truly homogeneous MoSiAl mixed oxides with controlled structure and texture. One elegant way to overcome this difficulty is to speed up the kinetics by spraying and fast-drying an aerosol of the precursor solution in the presence of a structuring agent.[8] As the silica matrix builds fast around the self-assembled organic template it quenches the Al and Mo precursors, leading to a truly molecular dispersion within the nanostructured solid.

Herein, an aqueous solution of tetraethyl orthosilicate and ethanol is sprayed in the presence of a block copolymer (Brij58), $AlCl_3$, and $12\,MoO_3{\cdot}H_3PO_4{\cdot}x\,H_2O$ (Keggin heteropolyacid) or $MoCl_5$. The aerosol is dried in a tubular furnace and the recovered solid is then calcined to remove the surfactant and release the organized porosity.

Thermogravimetric analyses in dry air were performed to determine the calcination temperature needed to eliminate the surfactant (Supporting Information, Figure S1). The combustion of Brij58 is complete at around 500 °C, with main weight-loss peaks at 240 °C, 310 °C, and 410 °C. After calcination at 550 °C, the surfactant was effectively removed from the catalyst, as demonstrated by thermal gravimetric analysis (TGA) and IR spectroscopy (Supporting Information, Figures S1 and S2).

In the aerosol process, every nonvolatile species added in the sprayed solution are systematically found in the final solid sample. The composition of the catalysts can thus easily be controlled by adjusting the amount of precursors. The experimental composition, as verified by ICP-AES, is very close to the nominal one: MoO_3 (10.0 wt %):Al_2O_3 (5.7 wt %):SiO_2 (84.0 wt %):P_2O_5 (0.4 wt %).

Aerosol MoO_3-SiO_2-Al_2O_3 catalysts consist of perfectly spherical particles with variable diameter (Figure 1 A,B). Their shape is linked to the preparation process: spherical particles are produced after the evaporation of water and ethanol contained in spherical aerosol droplets. The smallest particles are found in the 30–50 nm range and the largest reach 3 μm. This polydispersity is intrinsic to the aerosol mode of production.[8b] All particles present the same regularly organized porosity. At high magnification, the pore size can be visualized and estimated to 1.8–2.0 nm. This is correlated to the templating effect of the surfactant forming micelles, around which silica condensation occurs.

The nanoscale organization of the solid was confirmed by small-angle X-ray scattering (SAXS) already in the dried solid. After calcination, the scattering ring becomes even more resolved and accounts for a repetition unit of about 4.6 nm (Figure 1 C). Combined with the average pore-size diameter, this SAXS analysis allows estimating (by difference) a wall thickness of about 2.7 nm.

Nitrogen physisorption measurements confirm the supermicroporous structure of the catalyst (Figure 1 D). Isotherms are reversible, with a well-defined progressive uptake at low relative pressure ($p/p_0 = 0.05$–0.30) characteristic of super-

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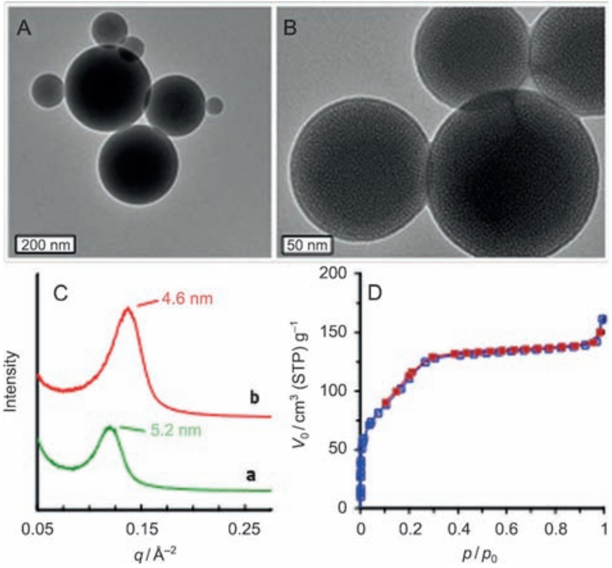

Figure 1. A, B) High-resolution (HR) TEM images of the calcined MoO_3-SiO_2-Al_2O_3 aerosol catalyst. C) SAXS plot for the a) dried catalyst and b) calcined catalyst. Right: N_2-adsorption (□) and desorption (■) isotherms.

microporous systems (pores at the limit between the micro and meso ranges) measured by the BJH equation at 1.9–2.0 nm.[9] The BET specific surface area reaches 480 $m^2 g^{-1}$ (with $C_{BET} = 76$) and the pore volume is 0.23 $cm^3 g^{-1}$. No other micropore is observed by t-plot analysis.

NMR spectroscopy (Figure 2) shows that Al atoms are stabilized in tetrahedral (54 ppm) and octahedral (0 ppm) coordination.[10] Five-fold coordinated species (ca. 30 ppm) are also observed, as is often found in amorphous silica–aluminas.[10] Importantly, no mixed Mo-Al oxide phase is detected in the dried sample. This observation contrasts with the case of MoO_3/SiO_2-Al_2O_3 catalysts prepared by wet impregnation (WI) of silica–alumina with ammonium heptamolybdate (AHM), in which the formation of the Anderson-type heteropolyanion, $[Al(OH)_6Mo_6O_{18}]^{3-}$ (abbreviated to $\{AlMo_6\}$) is systematically encountered (sharp peak at 14 ppm).[4d] The presence of $\{AlMo_6\}$ leads, after calcination, to MoO_3 crystals (detectable in XRD) and dehydrated $Al_2(MoO_4)_3$ (sharp NMR peak at −14 ppm).[4a,b] In our case, after calcination, X-ray diffraction attests that the samples are totally amorphous, meaning that no bulky MoO_3 crystals were formed. Molybdates species are thus undoubtedly well-dispersed in the silica–alumina matrix, as attested by EDX mapping of Mo element (Supporting Information, Figure S3).

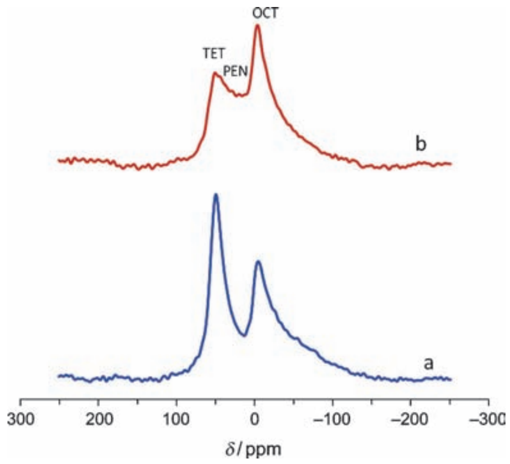

Figure 2. ^{27}Al MAS-NMR spectra of the catalyst a) before calcination and b) after calcination. Octahedral, pentahedral and tetrahedral species are indicated as OCT, PEN, and TET, respectively.

^{31}P NMR (Supporting Information, Figure S4) of the dried catalyst shows a sharp peak at −3.5 ppm, attributed to P atoms in the Keggin structure,[11] and another broad but weak peak at about −21 ppm, attributed to condensed polyphosphates and/or aluminophosphates.[12] The Keggin heteropolyanion is thus partly disrupted during the aerosol synthesis. After calcination, the −21 ppm signal increases and only trace of Keggin-type P are preserved.

The catalyst was tested in the cross-metathesis of ethene and butene to propene, and exhibited outstanding activity (up to 32 $mmol\,g^{-1}h^{-1}$). In Figure 3, it is compared to reference supported MoO_3 catalysts described in previous studies[3c,4e] and re-tested herein. The specific activity is 2–3 times higher, as compared to silica–alumina-supported Mo oxide catalysts prepared by wet impregnation with AHM, which are themselves much more active than catalysts based on pure silica or pure alumina. At high loading (20 wt% MoO_3) and with a catalyst developed with an optimized impregnation method employing oxalic acid as an additive,[4e] we reached a maximum cross-metathesis activity of 15 $mmol\,g^{-1}h^{-1}$. Bao et al. reported Mo/Hβ-Al_2O_3 catalysts that reach 12 $mmol\,g^{-1}h^{-1}$ at most, while working at higher temperatures and higher pressures.[4a,13]

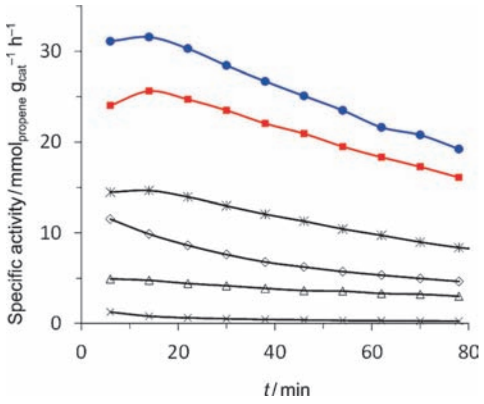

Figure 3. Metathesis specific activity of the aerosol-synthesized catalyst (●), and another aerosol-synthesized catalyst obtained with $MoCl_5$ as a Mo source (■). Reference catalysts prepared by wet impregnation: (×) MoO_3 (6 wt%)/SiO_2,[3c] (△) MoO_3 (10 wt%)/Al_2O_3, (◇) MoO_3 (6 wt%)/SiO_2-Al_2O_3,[3c] and (*) MoO_3 (20 wt%)/SiO_2-Al_2O_3 prepared by an optimized wet impregnation.[4e]

The remarkable activity of the new catalyst can be attributed to its high surface area and to the good dispersion of active Mo centers. The templating effect of the surfactant is the key to obtain a material with high surface area. The pores are large enough to allow the facile diffusion of reactants and products. The dispersion of Mo atoms in the matrix is excellent. It was shown recently that highly dispersed MoO_x species, presumably isolated molybdates, are the active metathesis centers.[6] Furthermore, MoO_3 crystals and $Al_2(MoO_4)_3$, both of which are deleterious for the metathesis activity,[4b,d] are absent in the aerosol catalyst. This aerosol catalyst combines all of the positive factors identified earlier for exhibiting high metathesis activity.

The preparation, characterization, and evaluation have been repeated and showed excellent reproducibility (less than 10% deviation in activity with catalysts from two different synthesis batches). Moreover, the same preparation procedure was applied replacing the Keggin precursor by molybdenum chloride. All observations made above concerning composition, texture, structure, absence of crystallinity, and Al environment were identical. As shown in Figure 3, the activity was slightly lower, though still remarkably high. The direct aerosol synthesis, known to be versatile and easily up-scalable to industrial production, is shown herein to be particularly successful in the synthesis of highly active porous MoO_3-SiO_2-Al_2O_3 metathesis catalysts.

Experimental Section

Solution A: Tetraethyl orthosilicate (10.96 g) was hydrolyzed under stirring overnight in an aqueous solution (20 g, pH 2, HCl 0.02 M) in the presence of $AlCl_3\cdot 6H_2O$ (1.06 g). The desired amount of Mo precursor was added either at the beginning (Keggin heteropolyacid, $H_3PMo_{12}O_{40}$) or at the end ($MoCl_5$) of this hydrolysis step. Solution B: Brij58 (3.88 g) was dissolved in ethanol (45 g) and water (8 g) and left under magnetic stirring for one night. Solutions A and B are then put together and sprayed with a 6-Jet 9306A atomizer from TSI with an air pressure of 30 psi and the aerosol was dried by passing through a tubular quartz tube heated at 450 °C. The recovered powder was stored for one night at 70 °C and then calcined under static air at 550 °C for 8 h.

Elementary analysis was carried out by ICP-AES. N_2 physisorption measurements were made on a BelSorb apparatus. SSA was determined by the BET method in the 0.05–0.30 p/p_0 range. Pore volume is determined by the amount of N_2 adsorbed at $p/p_0 = 0.98$. Wide-angle X-ray diffraction measurements were realized with a Bruker d8 facility. SAXS was performed on a Rigaku SMAX3000. High-resolution transmission electron microscopy was carried out with a Tecnaï Twin Spirit G2 (120 kV). A Brucker Avance III 300 apparatus was used to record the magic-angle spinning (MAS) NMR spectra of ^{27}Al and ^{31}P.

Metathesis activity was measured at 40 °C with 200 mg of pressed and sieved catalyst after 2 h activation at 550 °C in a N_2 atmosphere. Equimolar flows of ethene and 2-butene were fed (total flow of 8 mL min^{-1} including 0.8 mL min^{-1} of N_2 as internal standard). Reactor and analytic facilities are described in reference [6]. Specific activity is the number of moles of propene produced per gram of catalyst and per hour. 2-Butenes and ethene were converted into propene with about 99% selectivity. The standard deviation for activity measurements was less than 3% in relative terms.

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