Supporting information for:

Tight bifunctional hierarchical catalyst

Karen T. Højholt, Peter N. R. Vennestrøm, Ramchandra Tiruvalam and Pablo Beato

1. Experimental

All reagents were of reagent grade and used without any further purification: Sodium molybdate dihydrate (Na₂MoO₄·2H₂O, \geq 99.5 wt%, Sigma-Aldrich), nitric acid (HNO₃, 65 wt%, Sigma-Aldrich), cobalt(II) sulfate heptahydrate (CoSO₄·7H₂O, 99 wt%, Sigma-Aldrich), sodium peroxodisulfate (Na₂S₂O₈, \geq 99 wt%, Aldrich), sodium hydroxide (NaOH, 99 wt%, Riedel-de Häen), ammonium nitrate (NH₄NO₃, 99.5 wt%, Merck), ammonia (NH₃, 25 wt%, Fluka), toluene (C₇H₈, 99.7 wt%, Fluka), (3-aminopropyl)trimethoxysilane (APTMS, 97 wt%, Aldrich), hydrochloric acid (HCl, 37 wt%, Sigma-Aldrich).

1.1 Synthesis of Na₃[Co(OH)₆Mo₆O₁₈] ·8H₂O

Na₃[Co(OH)₆Mo₆O₁₈] was synthesised according to Nolan *et al.*¹ using the following procedure: First, 30.26 g Na₂MoO₄· 2H₂O was dissolved in 50 ml H₂O and acidified to pH 4.51 with HNO₃ (65 wt%). In another beaker 5.75 g CoSO₄· 7 H₂O was dissolved in 10 ml H₂O and then added to the molybdate solution under stirring. A solution of 7.53 g Na₂S₂O₈ dissolved in 8.8 ml H₂O was then added to the Co/Mo mixture as an oxidising agent. The obtained solution was heated to reflux until a dark turquoise solid precipitated. Upon further refluxing, the precipitate was redissolved and the original red colour of the solution returned. Following this, the solution gradually turned dark green, a color change indicating oxidation of the cobalt (II) to cobalt (III). Boiling was continued until evolution of oxygen ceased, by which time the solution became permanently dark turquoise. Finally the hot solution was filtered and the filtrate was left to precipitate dark green crystals upon cooling and consecutive evaporation of the solvent. The product is referred to as CoMo₆.

1.2 Synthesis of mesoporous ZSM-5

Hierarchical ZSM-5 was prepared by desilication of a commercially available ZSM-5 zeolite using a 0.3 M NaOH solution (33 ml per gram zeolite) for 30 min at 70 °C. The selective silicon leaching was stopped by quenching the solution in an ice-bath, and then washed three times with water by centrifugation. The desilicated ZSM-5 was dried over night at room temperature before further treatment. To obtain the ammonium form of the desilicated samples two consecutive ion exchanges were carried out using a 1.7 M NH₄NO₃/0.94 M NH₃ buffer solution with 10 ml solution per gram zeolite, at 80 °C under stirring for 2 hours. After each exchange, the NH₄-form of the zeolite was isolated by filtration, washed with water and dried in air at 110 °C. After the last ion exchange, the H-form of the desilicated zeolite was finally obtained by calcining the NH₄-form in air to 550°C for 3 h.

1.3 Anchoring CoMo₆ on mesoporous ZSM-5

The CoMo₆ clusters were anchored onto the mesopore surface of hierarchical ZSM-5 by first functionalising the surface with (3-aminopropyl)trimethoxysilane (APTMS): 4 g of mesoporous ZSM-5 were suspended in 160 ml toluene and heated to 65 °C, followed by the addition of 11 g APTMS. The suspension was stirred overnight, filtered and the obtained product washed with toluene and dried at room temperature. 2 g of functionalised mesoporous ZSM-5 were stirred over night in 150 ml 3 M HCl, filtered and left for drying at room temperature. The CoMo₆ Anderson ion

was finally attached to the mesoporous ZSM-5 zeolite by ion-exchange. The mesoporous ZSM-5 was added to a solution of 0.323 g Na₃[Co(OH)₆Mo₆O₁₈] in 60 ml H₂O (pH 4.2 adjusted with HNO₃, 65 wt%). After stirring for 12 hours, the solid was filtered of, washed with water and dried at room temperature. The product was named "CoMo₆-ZSM-5 (anchored)".

1.4 Preparation of reference material

The impregnated reference catalyst was prepared via successive incipient wetness impregnation of the mesoporous ZSM-5 (0.518 g) with aqueous solutions of 2.923g (NH₄)Mo₇O₂₄·4H₂O (AHM) and 0.7844g Co(H₂O)₆(NO₃)₂ in 25ml water. After drying overnight at room temperature, the sample was calcined at 500 °C for 3 hours.

1.5 Model activity test

Catalytic testing was performed in a fixed bed reactor charged with 300 mg catalyst in the fraction 600-850 μ m. To achieve a steady flow the catalyst was mixed with Ballotini glass balls (150-250 μ m) until a final volume of 1 ml was obtained. Prior to catalytic test the catalyst was sulfidized in a flow of 2.5 % dimethyldisulfide (DMDS) dissolved in *n*-heptane at 350 °C and 50 bar for 4 hours. Helium was used as a carrier gas with a flow of 250 Nml/min.

After 4 hours of sulfidation the feed was changed to a model oil feed containing 3 %

dibenzothiophene (DBT), 0.5 % indole, 1 % naphtalene, 2.5 % dimethyldisulfide (DMDS), 0.5 % *n*-nonane, the rest being *n*-heptane solvent.. The catalytic reaction was also performed at 350 °C, 50 bar using helium as a carrier gas with a flow of 250 Nml/min. The employed feed rate of oil was 0.3 ml/min and the total WHSV was 68 h^{-1} . The products from the reaction were analysed by an on-line GC equipped with a FID using n-nonane as an internal standard. The reaction was allowed to stabilize over 4 hours in order to obtain steady state conditions after changing to the oil feed prior to catalytic measurements. Afterwards eight GC analyses of the product stream were made with 1 hour intervals.

The activity was determined as a pseudo first order rate constant, k which is calculated on the basis of the 8 measured conversions of DBT. The rate constant k was calculated using the equation for the first order rate law (Eq. 6.1) and the correlation between residence time t and *WHSV*:

$$ln\left(\frac{\begin{bmatrix} DBT \end{bmatrix}}{\begin{bmatrix} DBT \end{bmatrix}_{0}}\right) = -kt \Leftrightarrow ln\left(\frac{\begin{bmatrix} DBT \end{bmatrix}_{0} - conv. \cdot \begin{bmatrix} DBT \end{bmatrix}_{0}}{\begin{bmatrix} DBT \end{bmatrix}_{0}}\right) = -kt \Leftrightarrow ln(1 - conv.) = -kt$$

where [*DBT*] is the concentration of DBT at time t, [*DBT*]₀ is the concentration of DBT at time t = 0 and *conv*. is the fractional conversion of DBT.

At steady state conditions the catalyst produces a product stream of steady composition. The time t in the first order kinetic equation is therefore the residence time of the feed in the reactor. This residence time is equal to the reciprocal Weight Hourly Space Velocity (WHSV) defined as:

$$WHSV = \frac{flow \times feed \ density}{catalyst \ mass}$$

and thus get:

 $k = -WHSV \cdot ln(1 - conv.)$

2. Characterisations

2.1 XRPD

The obtained XRPD pattern for the $CoMo_6$ precursor compound is shown in Figure 1 together with the XRPD patterns for ZSM-5 before and after desilication.



Figure S1: XRPD patterns of a) Na₃[Co(OH)₆Mo₆O₁₈]·8H₂O and b) ZSM-5 before and after desilication

As seen in Figure S1a the prepared $Na_3[Co(OH)_6Mo_6O_{18}]\cdot 8H_2O$ is a crystalline material with the desired phase¹. The XRPD patterns for ZSM-5 before and after desilicated (Figure 1b) show that the MFI structure is preserved after the formation of mesopores².

2.2 SEM

Figure S2 gives representative SEM images of the parent and desilicated ZSM-5 samples.



Figure S2:Representative SEM images of ZSM-5 before (a) and after desilication (b, c)

The parent ZSM-5 sample consists of particles in the range of ~ 0.5-3 µm, Figure 2, and the shape is more oval-like than the typical coffin-shaped zeolites. From the SEM images of the desilicated sample the particles appear sponge-like, typically for mesoporous zeolites, but retain more or less their original size. Some particles are fragmented, probably as a result of the desilication.

2.3 N₂ Physisorption

The pore volumes and surface areas calculated from the N_2 physisorption measurements are listed in Table S1. Figure 3 shows the physisorption isotherms given by the parent and desilicated ZSM-5 samples and the pore size distributions derived from the desorption isotherm.

	area ^a [m ² /g]	area ^b [m ² /g]	surface area [m ² /g]	volume ^b [cm³/g]	volume ^c [cm ³ /g]
Parent ZSM-5	430	48	382	0.17	0.26
Desilicated	521	221	300	0.13	1.07

Table 6.1: Surface areas and pore volumes of the parent and desilicated zeolite samples

^a Calculated using the BET method, ^b determined using the t-plot method and ^c volume adsorbed at P/P₀=0.99



Figure S3 N₂ adsorption-desorption isotherms (a) and corresponding pore size distribution (b) of the parent and desilicated ZSM-5 zeolites. The pore size distributions are obtained from the desorption branch of the isotherm using the BJH method

The isotherm from the desilicated sample in Figure S3a exhibits a hysteresis typical for mesoporous materials. The sample can therefore be classified as a hierarchical zeolite. Contrary, the isotherm of the parent sample does not contain any significant amount of hysteresis and displays an isotherm typical for solely microporous materials. Figure S3b shows the pore size distributions, including the artefacts at 2 and 4 nm due to the well known quasi-phase transition of N_2 and forced closure of the hysteresis loop, respectively. For the desilicated sample pore size distribution is spread over the mesopore and macropore region, centred at 27 nm. Table S1 quantitatively reveals the large increase in total pore volume and external surface area upon the desilication treatment calculated from the isotherms. It is noteworthy to mention that the large increase in mesopore volume and external surface area only occurs at a small expense of the micropore volume and surface area. This indicates that most of the intrinsic properties of the ZSM-5 zeolite are preserved after the treatment.

2.4 TEM

Samples for examination by transmission electron microscopy (TEM) were prepared by dispersing the catalyst powder in high purity ethanol, then allowing a drop of the suspension to evaporate on a holey carbon film supported by a 300 mesh copper TEM grid. Samples were then analysed in a Philips CM200 microscope operating at 200kV. Phase contrast images were obtained under very low electron dose conditions (Spot size 6 and gun lens 6 with a 50 μ m C2) aperture to minimize electron beam damage to the zeolite structure. The TEM images were acquired and subsequently

processed in Gatan Digital Micrograph with a 3 pixel cross mask median filter to minimize x-ray noise. Representative TEM images are shown in figure S4 and S5.



Figure S4: Representative TEM images of the spent catalyst whose precursor contained anchored CoMo₆ clusters



Figure S5: Representative TEM images of the spent catalyst whose precursor contained anchored CoMo₆ clusters

Throughout the sample, MoS_2 slabs are present both as single and double sheets. The MoS_2 slabs are primarily located in the mesopores since they are too large to fit into the micropore system of the zeolite. The MoS_2 slabs are estimated to 2-3 nm. To further explore the location of the MoS_2 inside the zeolite particles TEM tomography is planned as future work.

In selected areas small round particles of homogeneous size distribution at around 1 nm were observed, especially apparent in Figure S5c. XRPD of the spent catalyst did only detect crystalline ZSM-5 together with an undefined amorphous phase. This could be due to the very small particles size of both the undefined particles and MoS_2 slabs. Most likely the small particles are due to not or only partially sulfided CoMo phase.

¹ A.L. Nolan, C.C. Allen, R.C. Burns, D.C. Craig, G.A. Lawrance, Aust. J. Chem., 1998, **51**, 825

² Website of the International Zeolite Association: http://www.iza-structure.org/databases/ (1st of June 2011)