



Synthesis, characterisation and catalytic performance of a mesoporous tungsten silicate: W-TUD-1



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ABSTRACT

Tungsten containing TUD-1 catalysts with Si/W ratios of 10–50 were synthesised by a two-step impregnation method and a direct one-step sol–gel method. The one-step method yielded finely dispersed catalytically active tungsten oxide nano-particles (<1 nm) (at Si/W ratio above 20), while the two-step method yielded both tungsten oxide nano-particles and bulk tungsten oxide. This was established using INAA, N₂ physisorption, powder XRD, Raman spectroscopy, TEM, diffuse reflectance UV–vis, FT-IR, H₂-TPR and NH₃-TPD analysis. Both types of catalyst preparation resulted in active acidic catalysts for the Prins cyclisation of citronellal. It was demonstrated that the finely dispersed tungsten oxide nano-particles were responsible for the catalytic activity.

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1. Introduction

The incorporation of metal oxides into the silica framework of mesoporous or microporous materials leads to a wide variety of catalytically active materials and has attracted extensive research interest. Depending on the chosen metal, these catalysts provide hydration/dehydration, redox or acid–base activity [1–7].

By variation of the synthesis method, different silica structures can be prepared [8]: MCM-41 [1,2,9], MCM-48 [3,10–12], SBA-15 [4,5,13–15] or TUD-1 [6,7] to name just a few. For the production of relatively large (in terms of molecular size) fine chemicals, mesoporous silicates are the catalyst materials of choice, because of their beneficial mass transfer properties. In this respect, TUD-1 is especially attractive, because of its high stability and straightforward, adjustable, environmentally benign synthesis [16,17].

TUD-1 has a mesoporous and amorphous sponge-like structure. It has been used as a carrier material for incipient wetness impregnation. In addition numerous metals i.e. Al, Ti, Zr, V, Cr, Mn, Fe, Co, Cu and Ga have been incorporated into its silica framework [16–18].

Tungsten is catalytically very active and its heteropoly acids have been employed for many purposes. To increase surface area

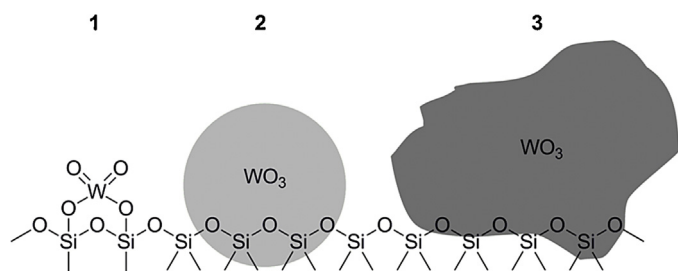
and accessibility of the tungsten it is desirable to incorporate it into or on mesoporous silicates. This is, however, not a trivial task since tungsten is considerably larger than silicon, with an ionic radius of 0.42 Å relative to 0.26 Å [19]. Consequently, relatively few tungsten containing mesoporous silicates are known to date [20]. Recently, a study was published where phosphotungstic acid, a heteropoly acid, was added to the synthesis mixture of TUD-1. This resulted in the inclusion of the heteropoly acid into the mesoporous TUD-1 matrix [21].

The incorporation (Scheme 1, 1) or fine dispersion of tungsten oxide nanoparticles (Scheme 1, 2) on the TUD-1 material, which is different from the inclusion of heteropoly acid, would be highly interesting because of its enhanced catalytic properties in acid catalysed reactions. In contrast, agglomeration of tungsten into bulk WO₃ (Scheme 1, 3) during the synthesis results in catalytically less active tungsten species.

In this paper we describe the nature of the tungsten particles derived from both incipient wetness impregnation of TUD-1 and a direct sol–gel synthesis of W-TUD-1. This is achieved by using several analysis methods like Instrumental Neutron Activation Analysis, nitrogen physisorption, XRD, Raman spectroscopy, Diffuse Reflectance UV–vis spectroscopy, TEM, H₂-TPR and NH₃-TPD. The acidic properties of the catalysts are tested in the industrially relevant Prins cyclisation of citronellal [6,7,22–24]. This acid catalysed reaction is part of commercial menthol synthesis [25–27].

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Scheme 1. Three types of tungsten on silica: (1) incorporated tungsten (isolated tungsten species) [20]; (2) WO_3 nano-particle (~ 1 nm); (3) bulk WO_3 particles (up to 100 nm).

Industrially it is catalysed by a homogeneous Lewis acid that cannot be recycled. A stable heterogeneous catalyst would therefore be highly desirable [6,7,22,23].

2. Materials and methods

2.1. Materials

Tetraethoxysilane (TEOS, Aldrich, 98%), triethanolamine (TEA, Acros, 97%), tetraethylammonium hydroxide (TEAOH, Aldrich, 35 wt% aqueous solution), tungstic acid (Aldrich, >99%), ammonium hydroxide (J.T. Baker, 25 wt% aqueous solution), tungsten(VI) ethoxide (Alfa Aesar), dry ethanol (Merck), dry *i*-propanol (Merck), *L*-citronellal (Janssen Chimica, 97%), dry toluene (sure seal, Aldrich).

2.2. Catalyst preparation

2.2.1. $\text{WO}_3/\text{TUD-1}$

TUD-1 was synthesised according to Heikkilä et al. [28], using 20.0 g tetraethoxysilane (TEOS, Aldrich, 98%), 14.8 g triethanolamine (TEA, Acros, 97%), 5.1 g demineralised H_2O and 20.1 g tetraethylammonium hydroxide (TEAOH, Aldrich, 35 wt% aqueous solution). The final molar gel composition was $\text{SiO}_2/\text{TEA}/\text{H}_2\text{O}/\text{TEAOH}$ (1:1:11:0.5). Three samples of $\text{WO}_3/\text{TUD-1}$ (10, 20 and 30 wt%) were prepared by incipient wetness impregnation of TUD-1 (pore volume = $0.897 \text{ cm}^3 \text{ g}^{-1}$) using solutions of appropriate amounts of tungstic acid (Aldrich) in aqueous ammonium hydroxide (J.T. Baker, 25 wt% aqueous solution). The material was dried overnight at 95°C and calcined at 600°C for 10 h with a temperature ramp of 1°C min^{-1} in a flow of dry air.

These materials are named $\text{WO}_3/\text{TUD-1}_x$, where x (10, 20 or 30) represents the wt% of WO_3 on the TUD-1 support.

2.2.2. W-TUD-1

A series of W-TUD-1 ($\text{Si}/\text{W} = 50, 40, 30, 20$ and 10) was synthesised using tungsten(VI) ethoxide ($\text{W}(\text{OEt})_6$, Alfa Aesar) as tungsten precursor. Initially, tungsten(VI) ethoxide was dissolved in a mixture of TEA, dry ethanol (8.0 g) and dry *i*-propanol (8.0 g) in a 250 mL polyethylene bottle. Under vigorous stirring 20.0 g TEOS (Aldrich, 98%) was slowly added with a dropping funnel. After stirring for 2–3 h a solution of TEAOH (20.1 g, Aldrich, 35 wt% aqueous solution) with additional demineralised H_2O was added dropwise and the vigorous stirring was continued for another 1–2 h. The amounts of $\text{W}(\text{OEt})_6$, TEA and demineralised H_2O were chosen so that the final molar gel composition was $\text{Si}/\text{W}/\text{TEA}/\text{H}_2\text{O}/\text{TEAOH}$ (1: n : $1 + 2n$: 11: 0.5). The resulting liquid was poured into a porcelain dish and aged at room temperature for at least 24 h. The resulting thickened gel was dried in an oven at 98°C for at least 12 h. The dried sample was ground and hydrothermally treated at 180°C for 5 h in a stainless steel Teflon-lined autoclave. Finally, calcination was performed at 600°C for 10 h with a temperature ramp of 1°C min^{-1} in a flow of dry air.

These materials are named W-TUD-1_x , where x (10, 20, 30, 40 or 50) represents the Si/W ratio in the catalyst.

If the same synthesis was performed with $\text{W}(\text{OEt})_5$ or WCl_6 , the synthesis was not successful.

2.3. Catalyst characterisation

2.3.1. INAA

Elemental analysis for Si and W was established by Instrumental Neutron Activation Analysis (INAA) and was performed at the Reactor Institute Delft (RID). The sample was irradiated with neutrons (neutron flux of 1.6×10^{17} neutrons $\text{s}^{-1} \text{ cm}^{-2}$) in the Hoger Onderwijs Reactor. In this process, stable isotopes were converted into radioactive isotopes. These isotopes radiate gamma radiation which was measured with semi-conductor gamma-ray spectrometers equipped with a germanium semiconductor. The wavelength is specific for each element. The amount of each element was determined from the signal area of the sample and a calibration standard.

2.3.2. N_2 physisorption

Specific surface areas and pore characteristics of the materials were determined using the BET and BJH models from nitrogen sorption measurements on a Quantachrome Autosorb-6B at -196°C . Prior to the measurements, the samples were degassed overnight under vacuum at 350°C using a Quantachrome Autosorb degasser.

2.3.3. X-Ray diffraction

X-ray diffraction patterns of the W-TUD-1 samples were recorded on a Bruker-AXS D8 Advance diffractometer with $\text{Cu K}\alpha$ radiation, which was operated at 25 mA and 45 kV. The measuring step size was 0.0387° with a step time of 1 s^{-1} . The diffraction spectrum was taken over a range from 5° to $90^\circ 2\theta$.

X-ray diffraction patterns of the $\text{WO}_3/\text{TUD-1}$ samples were measured using a Bruker D8 Advance diffractometer with a Lynxeye detector and $\text{Cu K}\alpha$ radiation. Measuring range from 5° to $95^\circ 2\theta$ with a step size of 0.02° and a scan speed of 0.15 s^{-1} .

Low angle XRD spectra were obtained from a Bruker AXS D5000 with $\text{Cu K}\alpha$ radiation, which was operated at 36 mA and 36 kV. The measuring step size was 0.01° with a step time of 2 s^{-1} . The diffraction pattern was recorded over a range from 0.5° to $3.5^\circ 2\theta$.

2.3.4. FT-IR spectroscopy

The FT-IR spectra were measured on a Perkin Elmer Spectrum ONE instrument. A KBr wafer was prepared containing a particular amount of the calcined sample that allowed for a transmission of minimally 50% (<1 mg). The spectrum was taken over a range $450\text{--}4000 \text{ cm}^{-1}$ with a resolution of 1 cm^{-1} .

2.3.5. Raman spectroscopy

Raman analysis was performed using a Renishaw Ramascope System 2000 instrument linked to a Leica microscope. 20 mW Ar^+ laser (laser line of 514 nm) was used as excitation source. The backscattered light was filtered for Rayleigh scattering using a holographic notch filter. The spectrograph uses a grating to disperse the light over the detector, which recorded the Raman spectra with a resolution of 4 cm^{-1} . The beam position was determined by focusing on the magnified powder sample.

2.3.6. DR UV-vis spectroscopy

UV-vis spectra were obtained from a Perkin Elmer lambda 900 diffuse reflectance spectrometer with a SUPRASIL quartz glass sample holder, using BaSO_4 as reference. Measuring range from 190 to 600 nm with a scan speed of 2.5 nm s^{-1} .

The Kubelka–Munk relation was used to analyse the diffuse reflectance spectra, to determine the absorbance from the UV-vis

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