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Acid catalytic properties of reduced tungsten and niobium-tungsten oxides

Chaochao Yue [a], Xiaochun Zhu [a], Marcello Rigutto [b,1], Emiel Hensen [a,*]

[a] *Inorganic Materials Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands*
[b] *Shell Global Solutions International B.V., P.O. Box 38000, 1030 BN Amsterdam, The Netherlands*

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ABSTRACT

Tungsten oxide and mixed niobium–tungsten oxides were prepared by calcination of re-precipitated tungsten and niobium precursors. These materials were characterized by N_2 physisorption, XRD, XPS, UV–vis and UV Raman spectroscopy and H_2-TPR. With increasing calcination temperature the oxides were seen to transform from a mixture of h-WO_3 and HATB ($T < 400\,^\circ C$) to predominantly h-WO_3 ($400\,^\circ C < T < 470\,^\circ C$) and m-$WO_3$ ($T > 470\,^\circ C$). Ammonium ion and ammonia are essential to retain the hexagonal structure of the intermediate phase. The reducibility of the various samples was linked to their structure. In-situ XRD point to formation of β-W in the presence of Pd when the precursor was deeply reduced. When the precursor predominantly contained h-WO_3, $(NH_4)_{0.33-x}(H_3O)_yWO_{3-z}$ was obtained upon reduction of tungsten and mixed niobium–tungsten oxide materials. These exhibited good performance in the bifunctional hydroisomerization of *n*-alkanes, outperforming amorphous silica–alumina and tungstated zirconia catalysts.

1. Introduction

Acid-catalyzed hydrocarbon conversion processes are pivotal in modern oil refineries. For isomerization and alkylation purposes, acidic chlorinated aluminas as well as strong mineral acids such as $AlCl_3$, H_2SO_4, HF are employed. The use of these acids poses significant corrosion and environmental problems. Therefore, zeolites and amorphous silica–aluminas have been developed as heterogeneous acid catalysts, for instance for (hydro)cracking of heavy oil fractions. There continues to be interest in the development of new solid acid materials [1–3]. Tungsten-oxides comprise a class of solid acids, which have been investigated in detail in the last two decades [4–11]. Bulk WO_3 has low surface area with no apparent strong Brønsted acidity. It is generally assumed that the Brønsted acidity is associated with partial reduction of the WO_x surface. Protons compensate the delocalized charge induced by partial reduction of W^{6+} centers. The pseudo-metallic W_3O phase formed by high-temperature reduction of WO_3 has been argued to provide high and stable hydroisomerization selectivity in hexane reforming [12]. The addition of metals like Pt and Pd typically increases acidity in the presence of hydrogen [13,14]. Arata and co-workers reported on bulk mixed tungsten–niobium oxides containing strong Brønsted acid sites, which were argued to derive from substitution of W^{6+} with Nb^{5+} in the surface of WO_3 [15]. It has been mentioned that such mixed oxides display similar acid strength as layered $HNbWO_6$ and the catalytic performance in cumene cracking of these materials is higher than aluminosilicates [15,16]. Arata's group also reported about WO_x supported on ZrO_2 (WO_x/ZrO_2) [4,5]. Several structural models for the acid sites in tungstated zirconia have been discussed [6,17–21]. It is known that tungsten oxide supported on $ZrO_x(OH)_{4-2x}$ is more acidic than when supported on well-defined ZrO_2 crystallites [19]. Kiely and co-workers investigated the nanoscale structures present in supported WO_3/ZrO_2 and proposed that subnanometer WO_x incorporating some zirconium cations hold the acid sites with capable of catalyzing methanol dehydration [9]. For reduced tungstated zirconia, it has been proposed that Brønsted acid sites form in WO_3 clusters of intermediate size on zirconia [18]. Combined with Pt, these supported tungsten oxides are active and selective catalysts for the hydroisomerization of *n*-alkanes [22–24].

The studies of the groups of Arata and Domen on tungsten-oxide based catalysts led us to study the structure, activation by calcination and reduction as well as the catalytic properties of bulk WO_3 samples. Bulk WO_3 was prepared by precipitation of an aqueous solution of ammonium metatungstate followed by calcination at different temperatures. A set of binary Nb–W oxides was prepared

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* Corresponding author. Tel.: +31 40 2475178.
E-mail addresses: marcello.rigutto@shell.com (M. Rigutto), E.J.M.Hensen@tue.nl (E. Hensen).

[1] Tel.: +31 20 6303221; fax: +31 20 6303110.

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in a similar manner a precursor containing Nb. XRD, UV–vis and Raman spectroscopy were used to follow the structural changes as a function of the calcination temperature. The reduction of these (mixed) oxides and their Pd-containing catalyst precursors were studied by TPR and XPS. The catalytic performance of the reduced samples was evaluated in the hydroisomerization of *n*-heptane and compared to zeolite, amorphous silica–alumina and WO_x/ZrO_2 reference catalysts.

2. Experimental methods

2.1. Preparation

An amount of 10 g of ammonium metatungstate hydrate (Sigma-Aldrich, 99.0%) was dissolved in 20 g water and stirred for 10 min at 70 °C. After slow evaporation of water at 70 °C, the powder was dried in an oven at 110 °C for 10 h. The dried powder was divided into several portions. Each portion was calcined in the air for 2 h at different temperatures, namely 380, 420, 450, 470 or 500 °C. The calcined samples were named WO_3-*T* with *T* denoting the calcination temperature. For comparison, mixed Nb-W oxides were also prepared at varying W/Nb ratios. For this purpose, solutions containing ammonium metatungstate hydrate and ammonium niobate oxalate hydrate in appropriate ratios were prepared and subjected to the slow evaporation procedure outlined above for the WO_3 precursor powder. The employed W/Nb ratios were between 5 and 120. The resulting powders were divided in two portions, one being calcined at 420 °C and the other at 450 °C for 2 h. These samples are denoted as NbW_x-420 and NbW_x-450 with *x* denoting W/Nb ratio.

To prepare Pd/WO_3 and Pd/NbW_x, an amount of 1.5 g of WO_3 or NbW_x powder was impregnated with 15 g of a solution of tetraamminepalladium nitrate (Sigma-Aldrich, 10 wt% in water) to reach a final Pd loading of 1.0 wt%. The excess solvent was evaporated and the final material was calcined at 300 °C for 2 h in air. These catalysts are denoted as Pd/WO_3-*T* (Pd/NbW_x-*T*).

Zirconia-supported WO_3 was prepared as described previously [14]. $ZrO_x(OH)_{4-2x}$ supports was first prepared by hydrolysis of 0.5 M $ZrOCl_2$ (Aldrich Chemicals, >98%) aqueous solutions fed at 500 cm^3 h^{-1} into a well-stirred vessel with a pH of 10 held constant by the controlled addition of 14 M NH_4OH. The precipitate was dried at 150 °C overnight after residual Cl^- ions were removed (<10 ppm) by thorough washing. The dried $ZrO_x(OH)_{4-2x}$ solids were impregnated to the point of incipient wetness with aqueous solutions of ammonium metatungstate of appropriate concentration. These samples were placed in shallow quartz boats, heated to the final oxidation temperature of 800 °C, and held isothermal for 3 h in dry air. Tungsten oxide loadings are reported as the weight percentage of WO_3 (4.5, 13.5 and 18 wt% WO_3) in the calcined samples. Samples are denoted as WZr(*x*) with *x* being the WO_3 loading. Pd loading was done in the same way as for the unsupported WO_3-*T* samples.

2.2. Characterization

Powder X-ray diffraction (XRD) patterns were measured on a Bruker D4 Endeavor using Cu Kα radiation. Nitrogen sorption was measured on a Micromeritics Tristar 3000 system in static measurement mode. The samples were outgassed at 120 °C for 3 h prior to the sorption measurements. The Brunauer–Emmett–Teller (BET) equation was used to calculate the specific area from the adsorption data (p/p_0 = 0.05–0.25). Scanning electron microscopy (SEM) was performed using a Philips environmental scanning electron microscope FEIXL-30 ESEM FEG in high-vacuum mode at low voltage. TG profiles were measured on Mettler Toledo TGA/DSC STAR system using an O_2 flow of 40 mL/min and a protective N_2 flow of 20 mL/min. The powder was in an open alumina crucible and heated at a rate of 10 °C/min. UV Raman spectra was recorded with a Jobin–Yvon triple stage spectrometer with a spectral resolution of 2 cm^{-1}. The laser line at 325 nm of a Lexel 95-SHG laser was used as excitation source at an output of 10 mW. The power of the laser on the sample was about 2 mW. UV–vis spectra were recorded on a Shimadzu UV-2401 PC spectrometer in diffuse-reflectance mode using an integrating sphere (internal diameter 60 mm) and $BaSO_4$ was used as the reference. Temperature-programed reduction (TPR) experiments were carried out in a flow apparatus equipped with a fixed-bed reactor, a computer-controlled oven and a thermal conductivity detector. Prior to TPR, the catalyst was treated by a flowing mixture of 4 vol% O_2 in He at 30 °C. Then the sample was reduced in 4 vol% H_2 in N_2 at a flow rate of 8 ml/min, while heating from room temperature to 800 °C at a ramp rate of 10 °C/min and keeping for 60 min at 800 °C. The H_2 signal was calibrated using a CuO/SiO_2 reference catalyst.

X-ray Photoelectron Spectroscopy (XPS) was done on a Kratos AXIS Ultra spectrometer, equipped with a monochromatic Al Kα X-ray source and a delay-line detector (DLD). Spectra were obtained using an aluminum anode (Al Kα = 1486.6 eV) operating at 150 W, with survey scans at constant pass energy of 160 eV and region scans at a constant pass energy of 40 eV. The background pressure was 2×10^{-9} mbar. XP spectra were fitted with the CASA-XPS software. Quasi-in situ XPS measurements were performed after reduction of the samples in a tubular stainless reactor. The samples were heated at a rate of 10 °C/min from room temperature to 440 °C in a flow of H_2 at 35 bar. After cooling to room temperature, closing valves at the in- and outlet of the reactor prevented interaction with air. The samples for XPS measurements were then prepared in an Ar-flushed glove box.

2.3. Catalytic activity measurements

The acidity of the WO_3-based samples was evaluated from catalytic activity measurements in the hydroconversion of *n*-heptane. For this purpose, the oxides were first loaded with Pd. The resulting materials were calcined at 300 °C. Prior to testing, the catalysts were reduced at 440 °C at 35 bar in flowing hydrogen. Hydroconversion of *n*-heptane was carried out at 35 bar at a H_2/hydrocarbon ratio of 24 mol/mol. The reaction temperature was lowered from 440 °C till 200 °C at a rate of 0.2 °C/min. The conversion of *n*-heptane involves its dehydrogenation catalyzed by the noble metal, isomerization or β-scission by strong Brønsted acid sites and hydrogenation of the *i*-olefins to *i*-paraffins. The activity of the catalyst is expressed as the temperature at which a hydrocarbon conversion of 40% was achieved. From the temperature required to obtain 40% conversion, relative values for the rate constant *k* for two catalysts at a reference temperature T_{ref} can be determined using the expression

$$\ln(k_1/k_2) = E_{act,1}/R_g(1/T_{40,1} - 1/T_{ref}) - E_{act,2}/R_g(1/T_{40,2} - 1/T_{ref}) \quad (1)$$

or, if we choose the second catalyst as the reference $T_{ref} = T_{40,2}$

$$\ln(k/k_{ref}) = E_{act}/R_g(1/T_{40} - 1/T_{40,ref}) \quad (2)$$

in which E_{act} is the activation energy (J/mol) and R_g the gas constant (J/mol K). Here we choose Pd/WO_3-380 as the reference catalyst.

3. Results and discussion

Solid tungsten oxide powders were prepared by dissolving ammonium metatungstate (AMT), $(NH_4)_6[H_2W_{12}O_{40}]\cdot 4H_2O$, followed by slow evaporation of water, precipitation and calcination at temperatures in the 380–500 °C range. The XRD patterns of the