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Synthesis, characterization, and catalytic function of novel highly dispersed tungsten oxide catalysts on mesoporous silica

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Abstract

The physical and chemical properties of tungsten oxide supported on SBA-15 mesoporous silica prepared by a controlled grafting process through atomic layer deposition (ALD) were studied using complementary characterization methods. X-ray diffraction, optical absorption, and transmission electron microscopy showed that tungsten oxide species are highly dispersed on SBA-15 surfaces, even at 30 wt% WO_x content (surface density, 1.33 WO_x/nm^2). ALD methods led to samples with much better thermal stability than those prepared via impregnation. Dehydration reactions of 2-butanol and methanol dehydration were used as probe reactions. Differences in reaction rates between the samples prepared by ALD and conventional impregnation may reflect the sintering resistance of catalysts prepared by ALD. Notably, temperature-programmed oxidation of spent catalysts showed that carbon formation was not responsible for the different dehydration rates in samples prepared by ALD and impregnation.

Keywords: Tungsten oxide; SBA–15; Methanol dehydration; 2-Butanol dehydration; DRS UV–vis; TEM; ^{1}H NMR; XRD; TPO

1. Introduction

Supported metal oxides are an important family of catalysts used in the petrochemical and refining industry. Catalytic reactions, such as ethylene polymerization, alkane oxidative dehydrogenation, alkene metathesis, and selective catalytic reduction of NO_x with ammonia, occur on supported metal oxides [1–7]. Many studies have addressed the structure and function of these catalytic materials, but the origins of their high activity remain the subject of active study. There is general consensus that active sites are of an acidic nature [8,9], but some studies suggest the possible involvement of redox cycles involving the reduction of metal oxide centers and radical-like intermediates [10].

Transition metal oxides with hexavalent and pentavalent cations have shown the highest activity for the aforementioned transformations. For some of these metal oxides, catalytic rates appear to be linked to the formation of strong Brønsted acid sites, which are stabilized by the effective delocalization of electron density in the conjugated base [11–13]. Among the transition metals with these characteristics, tungsten oxide gives the strongest Brønsted acid sites, either as bulk or supported oxides [14–18], but their structure and catalytic properties are strongly influenced by the support. Several studies have explored how interactions between support and tungsten oxide domains affect catalytic activity. Indeed, even for a given WO_x support system, WO_x domains exhibit a range of surface structures that depend strongly on synthetic protocols, such as the WO_x precursor and content, as well as on the thermal history of these materials [19–23].

Several reports have addressed the characterization of metal oxide-supported tungsten oxide species [16,24–27], and the specific nature of tungsten supported on ZrO_2 as acid cata-

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lysts for *o*-xylene isomerization [11–13] and butanol dehydration [28,29]. There are very few reports describing the use of mesoporous silica as a support for tungsten oxide species, however [30,31]. Zhang et al. described the synthesis of tungsten-containing MCM-41 with good dispersion, but segregated crystalline WO_3 was detected even after mild thermal treatments [32]. Briot et al. attempted to avoid crystalline phases by using oxoperoxometalate precursors that form at low pH in the presence of H_2O_2. The poor stability of these materials was evident from the extensive leaching of the tungsten species [33].

Here we report a novel method for grafting tungsten oxide species onto mesoporous silica (SBA-15) surfaces. This atomic layer deposition (ALD) method uses organic solvents and anhydrous conditions to control the deposition of tungsten oxide species onto the silica surface and to avoid the formation of WO_x oligomers prevalent in aqueous solutions at nearly neutral pH. The resulting improvements in dispersion and thermal stability of tungsten oxide species were confirmed using UV–vis light diffuse reflectance spectroscopy (DRS), X-ray diffraction (XRD), transmission electron microscopy (TEM), and magic-angle spinning (MAS) ^1H nuclear magnetic resonance (NMR). Methanol and 2-butanol dehydration were used as probe reactions. Temperature-programmed oxidation (TPO) and UV–vis spectra of spent samples were used to explore catalyst deactivation mechanisms and the effects of synthesis protocols on catalytic function.

2. Experimental

2.1. Catalyst synthesis

Mesoporous SBA-15 silica was prepared using a previously reported protocol [34]. The resulting BET surface area after treatment in air at 773 K for 4 h was ~860 m^2/g, and the average pore size was ~7 nm using the N_2 adsorption method. This sample was suspended in anhydrous toluene (Aldrich, 99.8%) and refluxed for 3 h in a N_2 atmosphere to remove physisorbed water. Tungsten precursor solutions were prepared by dissolving a given amount of WCl_6 (Aldrich, 99.9%) in ~150 cm^3 of toluene at ambient temperature and then adding 20 cm^3 ethanol (Aldrich, anhydrous). The solution was then refluxed in N_2 until a wet pH paper strip indicated that HCl was no longer present in the nitrogen effluent. The suspension containing dehydrated mesoporous silica in toluene was added to the tungsten precursor solution after the latter was cooled to ambient temperature, and the mixture was refluxed overnight in N_2. The reaction mixture was cooled, filtered, and washed with toluene several times until optical absorption analysis of the washing solvent indicated that tungsten precursors were no longer present. The solids were then dried in ambient air at 393 K for 0.5 h. This sample is designated as "as-synthesized." The amount of WCl_6 added was varied to give 0.33–2.66 WO_x/nm^2 surface density on SBA-15. We assume that three Si–OH groups on SBA-15 react with each WCl_6, which corresponds to a full monolayer at ~30 wt% WO_3, or 1.33 WO_x/nm^2. The density of Si–OH groups on the mesoporous silica has been estimated as 4.0 Si–OH/nm^2 [35]. Samples with 25% (0.33 WO_x/nm^2), 50% (0.66 WO_x/nm^2), 75% (1.00 WO_x/nm^2), and 100% (1.33 WO_x/nm^2) monolayer coverage were prepared. As-synthesized WO_x/SBA-15 silica samples were treated in flowing dry air (Airgas, zero grade, 1.7 $cm^3\,s^{-1}\,g_{cat}^{-1}$) at 673 and 773 K for 2 h. An additional sample with 200% (2.67 WO_x/nm^2) monolayer coverage was prepared by repeating the ALD process described above on a 1.33-WO_x/nm^2 sample after calcination. Two other samples were prepared by incipient wetness impregnation (RI) of SBA-15 with aqueous solutions of ammonium metatungstate (Aldrich, 99.99%) to give 1.00 and 1.33 WO_x/nm^2 surface densities. These samples were also treated for 3 h at 673 K in flowing dry air. After calcination, all catalysts obtained by ALD were analyzed by Fourier transform infrared spectroscopy to ensure that no organic residues remained on the samples.

2.2. XRD

XRD data were collected with a Philips PW3040/00 X'Pert MPD system equipped with a Cu source ($\lambda = 1.5406$ Å), a vertical Θ–Θ goniometer (220 mm radius), and focusing optics (Bragg–Brentano geometry). The in situ experiments were performed using a heated stage equipped with an Anton Paar HTK 1200 oven. The samples were mounted within an alumina cavity-type holder (18 mm diameter) for analysis. Diffraction data were analyzed using JADE (Materials Data, Livermore, CA) and the Powder Diffraction File database (2003 Release, International Center for Diffraction Data, Newtown Square, PA).

2.3. TEM

TEM micrographs were obtained using a JEOL 2010 high-resolution analytical electron microscope operating at 200 kV. An energy-dispersive X-ray (EDX) analyzer was used for elemental analysis. Samples were dispersed using 2-propanol (Aldrich, 99.5%) onto a carbon-coated copper grid.

2.4. ^1H NMR

Solid-state ^1H NMR spectra were measured using a Varian/Chemagnetics CMX Infinity 300 MHz NMR device equipped with a Varian/Chemagnetics 7.5 mm HX MAS probe, operating at a spectral frequency of 299.98 MHz. All spectra were externally referenced to tetramethylorthosilicate at 0 ppm and were obtained using a 1-s recycle delay and a 5-kHz spinning rate.

2.5. UV–vis spectroscopy

UV–vis spectra were measured in diffuse reflectance mode using a Varian Cary 5G UV–vis–NIR spectrophotometer with an internal integration sphere. Powder samples were placed within a quartz cell, and spectra were measured in the region of 200–800 nm after drying ex situ at 343 K. A halon white (PTFE) reflectance standard was used for background subtraction unless otherwise indicated. Spent catalysts were first treated in flowing air (Airgas, zero grade) at 673 K to remove