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Supported WO_x-based catalysts for methanol dehydration to dimethyl ether

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HIGHLIGHTS

- WO_x/TiO_2 are active and selective catalysts for methanol dehydration to DME.
- Stronger Lewis and Bronsted acid sites are formed upon increasing surface W density.
- Methanol dehydration rates increase with the strength of acid sites.

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ABSTRACT

TiO_2-supported WO_x solids with different W loadings (between 0.2 and 9.0 at. W nm^{-2}) were prepared by incipient wetness impregnation of TiO_2 with ammonium (para)tungstate aqueous solutions. The prepared materials were characterized in detail by inductively coupled plasma emission spectrometry (ICP-OES), N_2 adsorption-desorption isotherms, X-ray diffraction (XRD), temperature-programmed desorption of NH_3, X-ray photoelectron and Raman spectroscopy, and infrared spectroscopy using CO and pyridine as probe molecules. We have observed that the molecular structure of WO_x species and their acid features are markedly influenced by the W surface density. A relationship between catalytic performance in dimethyl ether formation *via* methanol dehydration and the acid properties is found.

1. Introduction

Dimethyl ether (DME) is used as spray propellant and as chemical intermediate for the production of dimethyl sulfate. In the last years, DME has been widely recognized also as a clean alternative fuel because of its more benign environmental features derived from the facts that DME does not form peroxides and considerably reduces NO_x emissions [1,2]. Moreover, DME can be obtained from a variety of sources, including biomass; therefore, a carbon neutral cycle concerning its production and use would be thus achieved. Another important advantage associated to the use of DME is related to the fact that the well-developed infrastructures for liquefied petroleum gas (LPG) could be utilized for DME with minor modifications. This is so because of the similar physical properties of DME and LPG [3]. Recently, direct utilization of DME or DME-derived H_2 for fuel cell applications has attracted considerable attention from researchers, in part because of the relatively simple transportation and handling compared to H_2 [4–6].

DME can be synthesized *via* acid-catalyzed methanol dehydration, or alternatively, from syngas (H_2/CO mixtures) using a bifunctional catalyst comprising a methanol synthesis component and an acid counterpart. The formation of DME from methanol requires a catalyst with optimum acid properties. Usually, strong acid sites favor secondary reactions that lead to undesired hydrocarbons and coke formation, which eventually causes catalyst deactivation. A myriad of acid solids have been previously used as catalysts for methanol dehydration reactions, including H-ZSM-5, H-mordenite, SAPOs, MCM-22, γ-Al_2O_3, etc. [7–13]. Zeolite materials tend to deactivate rapidly because their strong acid sites are responsible for the formation of significant amounts of undesired by-products (hydrocarbons and carbon deposits) [8,10–12]. On the other hand, γ-Al_2O_3, that possesses strong Lewis acid sites, exhibits lower methanol dehydration rates compared to zeolites, and this could be due to the preferential adsorption of generated H_2O molecules on the Lewis acid sites under the reaction conditions [8]. However, chemically modified alumina is reported to act as the industrial catalysts for DME synthesis from methanol (Topsøe DMK-10 catalyst, Cost Effective Topsøe DME Production Technology, www.topsoe.com).

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Previous reports have addressed the role of Brønsted and Lewis acid sites on methanol dehydration reactions [14–18]. It is commonly agreed that Brønsted acid sites of medium strength are required to obtain high reaction rates without causing relevant deactivation phenomena [8,19]. Therefore, it is very important to tune the acid sites strength through a detailed knowledge of the catalysts surface in order to improve the corresponding catalytic performance.

We explore here the use of supported tungsten oxides (WO_x) as solid acid catalysts for DME synthesis from methanol. These materials are very relevant materials in heterogeneous catalysis and are used for a large number of industrial reactions, such as *1*-butene metathesis [20,21], light alkane isomerization [22,23], isopropanol and propanol dehydration [24,25], and cyclopentene selective oxidation [26]. For many of these reactions, the acid properties of the supported tungsten oxides play a key role in their catalytic performance. Although supported WO_x catalysts are reported to be less active in methanol dehydration than conventional zeolite-type catalysts [27], they do not present strong acid sites, which could result in an extended life time of the catalyst. Furthermore, the presence of H_2O would not impact negatively on the catalytic performance. Therefore, supported WO_x could be suitable catalyst candidates for CH_3OH dehydration reactions.

Here, we report a detailed study on the use TiO_2-supported WO_x materials with a wide range of WO_x loadings (0–9 at. W nm^{-2}) to explore the effects of the specific WO_x molecular structures on their acid properties and catalytic performance in methanol dehydration reactions to form DME. We have found a relationship between methanol conversion rates and the presence of relatively strong Brønsted acid sites. Our results are consistent with previous reports [28] showing an increased in turnover frequency (TOF) values measured methanol dehydration with TiO_2-supported WO_x solids above monolayer surface coverage because of the higher activity of WO_3 nanoparticles as compared to that of surface WO_x species coordinated to the oxide support.

2. Experimental

2.1. Preparation of catalysts

A series of TiO_2-supported WO_x catalysts (0.2–9.0 at. W nm^{-2}) was prepared by incipient wetness impregnation. Previously, the support (TiO_2, 53 m^2 g^{-1}, 80% anatase, 20% rutile) was treated in ambient air at 823 K for 4 h. Then, an aqueous solution of ammonium paratungstate ($(NH_4)_6H_2W_{12}O_{40}$) was added dropwise to TiO_2. Several successive impregnations were needed because of the limited solubility of $(NH_4)_6H_2W_{12}O_{40}$ in H_2O (~0.1 g cm^{-3}). Subsequently, the solids were dried at 393 K overnight, and finally treated in ambient air at 773 K for 4 h. The latter temperature was selected from the thermogravimetric analysis in air (not shown). The solids are referred here as xW/TiO_2, where x represents the tungsten surface density (at. W nm^{-2}).

2.2. Characterization techniques

The elemental composition of the solids was determined by inductively coupled plasma emission spectrometry (ICP-OES) using a Perkin-Elmer Optima 3300DV apparatus.

Brunauer–Emmett–Teller (BET) surface areas were determined from N_2 adsorption-desorption isotherms at 77 K collected on a Micromeritics ASAP 2010 apparatus. Prior to the physisorption measurements, all samples were outgassed at 413 K for 16 h.

X-ray diffraction (XRD) patterns (2θ = 15–90°) of powder samples in the scan mode (0.04°, 20 s) were recorded with a Seiffert 3000 X'Pert X-ray diffractometer using the Cu Kα radiation.

The molecular structure of the supported WO_x was determined by Raman spectroscopy. A Renishaw Raman Microscope spectrometer, equipped with a laser beam emitting at 532 nm (100 mW output power) was used to collect the Raman spectra. The photons scattered by the sample were dispersed by an 1800 lines/mm grating monochromator and simultaneously collected on a CCD camera; the collection optic was set at 50 × objective. The spectral resolution was 1 cm^{-1}. Samples were *in situ* dehydrated (10 vol.% O_2/N_2, 723 K, 1 h) before collecting the Raman spectra.

X-ray photoelectron spectra (XPS) of samples were obtained with a VG Escalab 200R spectrometer equipped with a hemispherical electron analyzer using a Mg Kα ($h\nu$ = 1253.6 eV) X-ray source. The XPS data were signal average for at least 200 scans and were taken in intervals of 0.1 eV. The charging effects were corrected using C 1s core level as a reference (284.6 eV). High-resolution spectral envelopes were obtained by curve fitting synthetic peak components using the XPS peak software. The raw data were used with no preliminary smoothing. The curve fitting was performed with Newton's iteration method and 200 iterations. Symmetric Gaussian–Lorentzian product functions were used to approximate the line shapes of the fitting components. Chi-squared minimum values were used to mathematically ensure and obtain the optimized fitting parameters.

A Micromeritics TPR/TPD 2900 instrument was used to measure NH_3 temperature-programmed desorption (TPD) profiles. The sample (~50 mg) was introduced into a quartz microreactor and pretreated with He at 493 K for 1 h. Next, the temperature was decreased to 393 K and a 5 vol.% NH_3/He mixture (50 cm^3 min^{-1}) was flowed for 0.5 h. Physisorbed NH_3 was removed by flowing He (393 K, 0.5 h). TPD profiles were recorded upon heating the sample in He (50 cm^3 min^{-1}) from 393 to 1243 K at a heating rate of 15 K min^{-1}.

Fourier Transform Infrared (FTIR) spectra were recorded with a Nicolet Nexus instrument, using conventional IR cells connected to a gas handling system, under static conditions. Experimentally, pressed disks of pure solid powders (~20 mg) were thermally treated within the IR cell at 573 K under vacuum (0.01 Pa) for 1 h. CO adsorption (0.13 kPa) experiments were performed at 133 K, and spectra were recorded in the range 133–278 K while outgassing. Pyridine (0.4 kPa) was introduced at 298 K, and spectra were recorded after evacuation at increasing temperatures (298–573 K).

2.3. Methanol dehydration catalytic activity

Methanol conversion to DME was measured in a fixed bed reactor. The catalytic bed was prepared by diluting the catalyst (0.5 g, 0.25–0.30 mm) with SiC (2.0 g, 0.25–0.30 mm) to avoid the formation of temperature gradients during the reaction. The reaction was performed with CH_3OH/N_2 mixtures (6.1 kPa CH_3OH; 6.9 mmol CH_3OH h^{-1} g_{cat}^{-1} space velocity) at 573 K. Reactants and products were analyzed *on line* with a gas chromatograph (Varian CP-3800) equipped with a packed column (Carboxen-1000, 4.6 m × 0.32 cm) connected to a thermal conductivity detector to measure the inorganic gases (H_2, N_2, CO and CO_2), and a capillary column (SPB-5, 60 m × 0.53 mm) connected to a flame ionization detector to analyze the organic compounds (CH_3OH, DME, hydrocarbons).

3. Results and discussion

3.1. Characterization techniques

The chemical composition of all xW/TiO_2 samples determined by ICP-OES is shown in Table 1. A good agreement is found between nominal and actual tungsten loading values. BET surface

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