Nature of surface sites of $V_2O_5-TiO_2/SO_4^{2-}$ catalysts and reactivity in selective oxidation of methanol to dimethoxymethane

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ABSTRACT

The selective oxidation of methanol to dimethoxymethane (DMM) over sulfated vanadia–titania catalysts, prepared by co-precipitation and calcined at different temperatures, was studied in the 393–473 K interval under steady state conditions. The catalysts were characterized by X-ray diffraction (XRD), Brunauer–Emmett–Teller isotherms (BET), inductively coupled plasma optical emission spectroscopy (ICP-OES), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR), and Raman spectroscopy. The redox and acidic properties were examined using temperature programmed reduction (TPR), isopropanol probe reaction, ammonia adsorption calorimetry, and pyridine adsorption FTIR techniques. As evidenced by pyridine adsorption FTIR, some Brönsted acid sites transformed to Lewis sites upon removal of sulfate species by washing the samples with deionized water. A high sulfur content increased the number of Brönsted acid sites but reduced their strength. The best catalyst revealed the presence of amorphous polymeric VO_x species with terminal V=O bonds, and both redox and Brönsted acid sites, resulting from an adequate balance between the calcination temperature and the sulfate concentration. These are the key parameters for optimizing the DMM production.

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1. Introduction

Dimethoxymethane (DMM) is especially interesting for industrial applications [1–4], since it is suitable as fuel additive with a high chemical stability, as solvent in the perfume industry and as reagent in organic syntheses. Industrially, DMM is produced by a two-stage process: methanol oxidation to formaldehyde on silver and ferric molybdate catalysts and dehydrative condensation of the formaldehyde with methanol in the presence of liquid and solid acids [3,4]. Thus, a one-stage heterogeneous reaction process has economical and environmental benefits in the production of DMM, where three methanol molecules are incorporated into one DMM molecule $(3CH_3OH + 1/2O_2 \rightarrow CH_2(OCH_3)_2 + 2H_2O)$. It has been reported in the literature that DMM can be also synthesized by the direct oxidation of methanol on crystalline $SbRe_2O_6$ [5], Re/γ-Fe_2O_3 [6], heteropolyacids [7], RuO_x/SiO_2 [8], Cu–ZSM-5 [9], and V_2O_5/TiO_2–$Ti(SO_4)_2$ [10].

Irrespective to the catalytic system, all the studies suggest a dual mechanism involving redox and acidic sites (Brönsted in case of Keggin structures [3,11], or Lewis for Re-based catalysts [6]). Additionally, Wachs indicated that the surface Brönsted acid sites can facilitate oxidation reactions requiring the participation of dual

redox-acid sites [12]. Achieving an adequate balance between the two kinds of active sites is thus a crucial prerequisite for optimal DMM production.

Furthermore, the contributions of different VO_x species to the catalytic performance have been debated for some time in previous studies [13–24]. Many researchers claim that amorphous monomeric VO_x species with terminal V=O bonds are the most active species for reactant adsorption and C–H bond breaking compared to crystalline V_2O_5 [13–15]. Grzybowska-Swierkosz [16] pointed out the necessary participation of both monomeric and polymeric species. Tatibouët [17,18] proposed that a surface site constituted by a vanadyl V=O double bond standing up and a near "oxygen vacancy" constituted by the sixth coordination of a vanadium (vanadyl down) could be the most appropriate for DMM formation. In contrast, Gervasini et al. [19] found higher catalytic activity for polymeric rather than for monomeric VO_x species in partial oxidation of o-xylene to phthalic anhydride (PA), and Van Hengstum et al. [20] reported that vanadia multilayers and/or crystallites did not affect the selective oxidation of toluene. Weckhuysen et al. [21] stated that the V–O-support bond is important in methanol oxidation, a model reaction for V_2O_5/TiO_2 catalyst. Moreover, density functional theory (DFT) has demonstrated that the oxygen atom in the V–O–Ti bond is the most reactive toward atomic hydrogen adsorption, the limiting step of the oxidation reaction, because of the high stability of terminal V=O bonds [22]. Wachs

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and Weckhuysen [23], on the other hand, stressed the critical role of bridging oxygen in V–O–support as mentioned also by Bulushev et al. [24].

We have recently studied the reactivity of sulfated vanadia–titania catalysts prepared by various methods to selectively catalyze methanol oxidation to DMM [25]. These previous results [25,26] investigated how both the preparation method and the sulfate content impacted the DMM synthesis. In this work, the challenge lied in: (1) fixing the right amount of surface residual sulfate (with or without washing with deionized water) during the calcination step in order to tune the acidity of the coprecipitated $V_2O_5-TiO_2/SO_4^{2-}$ catalysts and (2) developing active surface structure most appropriate for DMM synthesis during the calcination process. The VTiS samples were characterized by X-ray diffraction (XRD), Brunauer–Emmett–Teller isotherms (BET), inductively coupled plasma optical emission spectroscopy (ICP–OES), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, ammonia adsorption calorimetry, and pyridine adsorption FTIR. This study reports, in detail, the effects of surface structure, nature, and strength of active acidic sites on the performance of the selective oxidation of methanol to DMM.

2. Experimental

2.1. Catalyst preparation

Five gram of $V_2O_5-TiO_2/SO_4^{2-}$ catalysts were prepared by a co-precipitation method [27] with 3.2 g of $VOSO_4 \times H_2O$ and 11.5 g of $TiOSO_4 \times H_2SO_4 \times H_2O$ as precursors, and 25 mL 28 wt.% $NH_3 \cdot H_2O$ solution as precipitant. Samples VTiS-573, VTiS-623, VTiS-673, VTiS-673, and VTiS-723 were prepared in this way, and then calcined in air for 5 h at 573, 623, 673, 723, and 773 K, respectively. Additionally, samples VTiSw50-673 and VTiSw300-673 were prepared by the same procedure of co-precipitation, washed with, respectively, 50 and 300 mL deionized water while filtering the precipitate and then calcined at given temperature of 673 K in air for 5 h.

2.2. Catalyst characterization

Elemental analysis was performed using ICP optical emission spectroscopy (ICP–OES) with an ACTIVA spectrometer from Horiba JOBIN YVON.

The surface areas and pore sizes were measured by nitrogen adsorption at 77 K on a Micromeritics 2010 apparatus after heat pretreatment under vacuum for 3 h at a temperature 100 K lower than the calcination temperature.

The X-ray diffraction (XRD) measurements were carried out on a Bruker D5005 powder diffractometer scanning from 3° to 80° (2θ) at a rate of 0.02 degree s^{-1} using a Cu Kα radiation (λ = 0.15418 nm) source. The applied voltage and current were 50 kV and 35 mA, respectively.

The X-ray photoelectron spectra were measured on a KRATOS AXIS Ultra DLD spectrometer equipped with a hemispherical electron analyzer and an Al anode (Al Kα = 1486.6 eV) powered at 150 W, a pass energy of 20 eV, and a hybrid lens mode. The detection area analyzed was 700 μm × 300 μm. Charge neutralization was required for all samples. The peaks were referenced to the C–(C, H) components of the C1s band at 284.6 eV. Shirley background subtraction and peak fitting to theoretical Gaussian–Lorentzian functions were performed using an XPS processing program (vision 2.2.6 KRATOS). The residual pressure in the spectrometer chamber was 5×10^{-9} mbar during data acquisition.

Scanning electron microscopy (SEM) was performed using a Philips 5800 SEM electron microscope. The samples were deposited onto scotch carbon and metallized by sputtering. A gold film ensures a good conductivity for the observation.

The recording of transmission electron micrographs was carried out using a JEOL 2010 equipment operating at 200 kV with a high resolution pole piece and an energy dispersive X-ray spectrometer (EDS) (Link Isis from Oxford Instruments). The samples were dispersed in ethanol using a sonicator and a drop of the suspension was dripped onto a carbon film supported on a copper grid and then ethanol was evaporated. EDS study was carried out using a probe size of 15 nm to analyze borders and centers of the particles and the small particles. Standard deviations were evaluated for atomic ratio from at least 10 analyzes.

Raman spectroscopy measurements were performed using a LabRAM HR (Jobin Yvon) spectrometer. The excitation was provided by the 514.5 nm line of an Ar$^+$ ion laser (Spectra physics) employing a laser power of 100 μW. The laser beam was focused through microscope objective lenses (100×) down to a 1-μm spot on the sample.

H_2-TPR measurements were performed using a TPD/R/O-1100 instrument (ThermoFisher). Prior to the TPR run, the fresh sample was treated in a stream of O_2/He (0.998% v/v, flowing at 20 mL min^{-1}), ramping the temperature at 10 K min^{-1} from RT to a temperature 100 K lower than the calcination temperature and maintaining it for 60 min, and then cooled to 313 K. The TPR measurement was carried out using H_2/Ar (4.98% v/v) as reducing gas mixture, flowing at 20 mL min^{-1}. The heating rate was 10 K min^{-1} from 313 K to 1073 K. The H_2 consumption was detected by a thermal conductivity detector (TCD). The sample size used was adjusted in order to have around 69 μmol of V_2O_5 independently of the vanadia loading of the sample. This allowed us to maintain a K value of 100 s. (The characteristic number, K, can be used to facilitate the selection of appropriate operating parameters; a fixed K value between 60 and 140 s guarantees optimal conditions to obtain good TPR profiles [28,29].) The TPR peak areas were calibrated with given H_2/Ar (4.98% v/v) mixture injections.

The skeletal FTIR and pyridine adsorption FTIR spectra were recorded at room temperature with a Bruker Vector 22 FTIR spectrophotometer (DTGS detector) operating in the 4000–400 cm^{-1} range, with a resolution of 2 cm^{-1} and 100 acquisition scans. In each skeletal FTIR experiment, 2 mg of sample was mixed with 198 mg of KBr. In each pyridine adsorption FTIR measurement, the self-supporting wafer (10–30 mg, 18 mm diameter) was first activated in situ at a temperature 100 K lower than the calcination temperature in oxygen flow for 14 h, then evacuated at the same temperature for 2 h and then exposed to pyridine (air liquid, 99.8%, vapor pressure 3.3 kPa) at room temperature for 5 min. The desorption was carried out by evacuation for 30 min each at room temperature, 373 K, 473 K, and 573 K, respectively. The spectra were recorded at room temperature after adsorption and desorption at each temperature.

The microcalorimetric studies of ammonia adsorption were performed at 423 K in a heat flow calorimeter (C80 from Setaram) linked to a conventional volumetric apparatus equipped with a Barocel capacitance manometer for pressure measurements. Ammonia used for measurements (air liquid, purity > 99.9%) was purified by successive freeze–pump–thaw cycles. About 100 mg of sample was pretreated in a quartz cell under evacuation overnight at a temperature 100 K lower than the calcination temperature. The differential heats of adsorption were measured as a function of coverage by repeatedly introducing small doses of ammonia gas onto the catalyst until an equilibrium pressure of about 66 Pa was reached. The sample was then outgassed for 30 min at the same temperature, and a second adsorption was performed at 423 K until an equilibrium pressure of about 27 Pa was