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Influence of the metal oxide support on the surface and catalytic properties of sulfated vanadia catalysts for selective oxidation of methanol

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ABSTRACT

The selective oxidation of methanol to dimethoxymethane (DMM) was performed over a series of binary vanadia-based oxides (V_2O_5—TiO_2, V_2O_5—ZrO_2, V_2O_5—Al_2O_3 and V_2O_5—CeO_2) and the corresponding sulfated catalysts. The physicochemical properties of catalysts were characterized by BET, Raman, XPS, TPR–MS, ammonia adsorption calorimetry and sulfate TPD–MS techniques. The strength of the sulfate-support interaction depends on the nature of the oxide support and increases in the following order $CeO_2 > Al_2O_3 > ZrO_2 > TiO_2$. The catalytic reactivity was correlated with the nature of V—O-support bonds. Sample V_2O_5—TiO_2 exhibits the highest intrinsic activity of methanol oxidation. With the addition of sulfate, the selectivity to DMM was enhanced whereas the turnover frequency (TOF) value of vanadium sites decreased, with a rate depending on the strength of sulfate-support bonds. The best catalyst (V_2O_5—TiO_2—SO_4^{2-}) with higher DMM yield presented higher reducibility, proper acidity and moderate strength of sulfate species.

1. Introduction

Supported vanadia catalysts constitute a very important class of catalytic materials as they have started as model catalytic systems for fundamental studies of supported metal oxides and are extensively employed as commercial catalysts (selective catalytic reduction of NO_x with NH_3 to N_2 and H_2O, oxidative destruction of chlorinated hydrocarbons, oxidation of o-xylene to phthalic anhydride and selective oxidation and ammoxidation of C_1–C_4 hydrocarbons for olefins, oxygenates and nitriles) [1–6]. Supporting a metal oxide on the surface of another oxide was initially proposed to improve the catalytic activity of the active metal oxide phase due to a gain in surface area and mechanical strength. The support was first considered as an inert substance that provided a high surface to carry the active metal oxide component or to improve the mechanical strength of the catalyst material [7,8], but it can also behave as active phase if partly uncovered. Generally, supported vanadia catalysts may exhibit different catalytic properties since the metal oxide-support interaction affects both redox properties and dispersion of the active phase [9,10]. This is known as the metal oxide-support effect, although its exact origin and mechanism of operation is still unclear. The fundamental basis for the catalytic performances of supported vanadium oxides lies in the variability in geometric and electronic structure of surface vanadium oxides. Fundamental knowledge about the nature of supported vanadium oxides is of key importance in heterogeneous catalysis and spectroscopic tools are necessary to built up this knowledge.

Supported V_2O_5 catalysts are also widely studied in the reaction of methanol oxidation [11,12], which can be used as a probe reaction to characterize the activity of oxide catalysts [11,13] and further interpret it in terms of both structural and chemical (acidic and redox) properties. It appears from the literature that methanol can lead to different products by varying the nature of the catalyst and the reaction conditions (Scheme 1) [14–16]. Redox sites enable the production of partially oxidized species such as formaldehyde (HCHO, FA) or totally oxidized species (CO_2). Acidic sites enable condensation reactions, which can give dimethyl ether (CH_3OCH_3, DME), dimethoxymethane ($CH_3OCH_2OCH_3$, DMM) and methyl formate ($HCOOCH_3$, MF). Among the aforementioned products, DMM is especially interesting for industrial applications, since it is suitable as a fuel additive with a high stability. Further, it has been shown that the addition of SO_4^{2-} species to TiO_2 enhances the acidity and can lead to improving selectivity to DMM [17].

Therefore, in this work, as a sequel to studying the activity of methanol oxidation to DMM, sulfated vanadia-based oxides were evaluated by this reaction. The objective of the present investigation was to examine the influence of the host metal oxide on the acidic, redox and catalytic properties of vanadia and sulfated vanadia. Moreover, the effect of the host metal oxide on the nature of active VO_x phase and sulfate species was also investigated. The structural properties were characterized by Brunauer–Emmett–Teller (BET), inductively coupled plasma optical emission spectroscopy (ICP-OES), X-ray photoelectron spectroscopy (XPS) and

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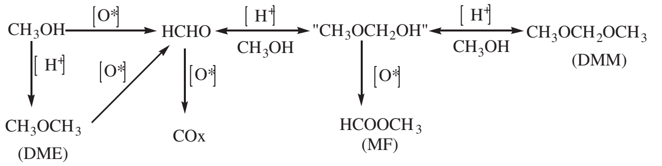

Scheme 1. Reaction pathways for the reaction of catalytic partial oxidation of methanol (adapted from Refs. [11,14]).

Raman spectroscopy and sulfate temperature-programmed desorption (TPD). The redox properties were examined by temperature-programmed reduction (TPR) coupled with mass spectrometer (MS) as a detector. In addition to this, the acidity of these catalysts was examined by using ammonia adsorption calorimetry.

2. Experimental

2.1. Catalyst preparation

The theoretical amount of vanadium pentoxide was fixed at 25 wt% whatever the host metal oxide used.

2.1.1. Prepared in two steps: co-precipitation of mixed oxides followed by ammonia sulfate impregnation

Binary vanadia-based oxides (denoted by VM(c1); M = Ti, Zr, Al and Ce) were prepared by modifying a previous reported co-precipitation method [18]. The vanadia, titania, zirconia, alumina and ceria precursors were $VOCl_3$, $TiCl_4$, $ZrOCl_2$, $Al(NO_3)_3$ and $Ce(NO_3)_3$, respectively. Briefly, $VOCl_3$ was dissolved into deionized water (1 mL $VOCl_3$ in 250 mL H_2O) mixed with 5–8 mL diluted HNO_3 (38 wt% HNO_3) with vigorous stirring to form a vanadium-containing solution (S1). The oxide-support precursor was dissolved into a limited deionized water to form the metal ion containing solution (S2), while $TiCl_4$ was dissolved in C_2H_5OH (1 mL $TiCl_4$ in 30 mL C_2H_5OH) in an ice bath. S2 was slowly dropped into S1 with continuous stirring to form a mixed solution (S3). Then, S3 solution was slowly dropped into diluted $NH_3 \cdot H_2O$ placed in an ice bath to form the precipitate. The precipitate was first aged for 1 h at room temperature, then filtered, washed several times with deionized water until free from chloride ions and the filtrate cake dried as reported in [18]. The samples were all calcined at 673 K in air for 5 h, except for sample VAl(c1) which calcination temperature was increased up to 773 K for a better decomposition of the precursor.

The corresponding sulfated catalysts (denoted by VMS(c1-i); M = Ti, Zr, Al and Ce) were prepared by incipient wetness impregnation of the above mentioned supported vanadia catalysts with an aqueous solution containing the theoretical percentage of $(NH_4)_2SO_4$ to achieve a theoretical amount of 5 wt% SO_4^{2-} (1.7 wt% S). The resulting solids were then dried at 373 K overnight and then calcined at 673 K in air for 5 h.

2.1.2. Prepared directly by co-precipitation from sulfated precursors

Sulfated binary vanadia-based oxides (denoted by VMS(c2); M = Ti, Zr, Al and Ce) were also prepared by co-precipitation. The precursors were $VOSO_4$, $TiOSO_4$, $Zr(SO_4)_2$, $Al_2(SO_4)_3$ and $Ce(SO_4)_2$, respectively. The details of such preparation method have been previously described in [18]. Specifically, $Ce(SO_4)_2$ was dissolved in deionized water and then the pH was adjusted to around zero by adding dilute HNO_3 (38 wt% HNO_3) in order to complete the dissolution. Then, the aqueous solution of $VOSO_4$ was added dropwise to $Ce(SO_4)_2$ solution with vigorous stirring to form the mixed aqueous solution for precipitation with ammonia. At last, the samples were all calcined at 673 K in air for 5 h, except sample VAlS(c2) which calcination temperature was increased up to 773 K.

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 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 × 300 μm. Charge neutralization was required for all samples. The peaks were referenced to the C—(C, H) components of the C 1s 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.

Raman spectroscopy measurements were taken using a LabRAM HR (Jobin Yvon) spectrometer under ambient conditions. 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-micrometer spot on the sample.

H_2–TPR measurements were taken using a TPD/R/O–1100 instrument (ThermoFisher). Prior to each 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 623 K 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 5 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: $K = S_0/(V^* C_o)$, where S_0 corresponds to current amount of reducible species (μmol), V^* relates to total flow rate of the reducing gas (cm^3(NTP)/s) and C_o is due to the current concentration of hydrogen at the reactor out (μmol/cm^3). A fixed K value between 60 and 140 s guarantees optimal conditions to obtain good TPR profiles [19,20]. The peak areas were calibrated with given H_2/Ar (4.98% v/v) mixture injections for TPR.

Gases evolving from the TPR reactor were analyzed by a mass spectrometer (Omnistar, Pfeiffer) with a heated capillary. The signals for $m/e = 34$ (H_2S) and 64 (SO_2) were recorded.

Temperature-programmed desorption (TPD) of sulfates was performed on a Setaram TG–DSC 111 device coupled with a mass spectrometer (Thermostar, Pfeiffer) as a detector. A capillary-coupling system was used. The TPD experiments were carried out in the range 298–923 K under helium flow as the carrier gas (35 mL min^{-1}). For each experiment, about 20 mg of sample with ammonia absorbed in previous microcalorimetric experiments was used. Initially, the samples were purged with helium at room temperature for 15 min and then heated with 5 K min^{-1} up to 373 K. The temperature was kept constant at 373 K for 30 min and then was linearly increased up to 923 K with same ramp of 5 K min^{-1}.

The microcalorimetric studies of ammonia adsorption were performed at 423 K in a heat flow calorimeter (C80 from Setaram)