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Structural and reactive relevance of V + Nb coverage on alumina of V–Nb–O/Al_2O_3 catalytic systems

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Abstract

Vanadium and niobium species (together and separately) were loaded on gamma alumina, and the resulting catalysts were run in the methanol conversion. This reaction was studied by both GC analysis and FTIR study in the flow system. The catalytic properties are discussed based on the combined FTIR and ^{27}Al, ^{51}V and ^{1}H MAS NMR studies. The NMR studies revealed a different mechanism of interaction between Nb and Al_2O_3 than that between V and Al_2O_3. This predetermines the structure of vanadium sites in bimetallic VNb/Al samples. The effect of coverage was considered for various metal loadings ranging from below to above monolayer. One of our most interesting findings is that the surface Nb oxide species exhibited a redox character below monolayer but were acidic above monolayer. ^{27}Al MAS NMR revealed a strong alumina–Nb interaction that may account for its redox performance. Moreover, the role of sulfate from vanadium precursor is evidenced.

Keywords: Supported vanadia–niobia; Alumina; ^{27}Al MAS NMR; ^{1}H MAS NMR; FTIR; *In situ*; Methanol probe reaction

1. Introduction

Vanadium- and niobium-containing catalysts are used in oxidation processes. In their supported forms, the support plays a critical role. If the oxide support exhibits its own activity in the desired reaction, then the loading level plays a crucial role in the final activity and selectivity of the prepared catalysts. In this work, various loadings of V and Nb on gamma alumina were applied, and the prepared catalysts were tested in methanol conversion.

Methanol oxidation has been proposed for the characterization of the redox and acidic active species on the catalyst surface. The structural information at the molecular level on the catalytic sites can be deduced from the product distribution in this reaction, e.g. [1–4]. Selective formation of dimethoxymethane ($(CH_3O)_2CH_2$) can be assigned to a dual site that includes a redox dehydrogenating site and a Lewis acid center, whereas formaldehyde (CH_2O) formation requires only a redox dehydrogenating site. Methyl formate ($HCOOCH_3$) can be generated *via* an oxidation reaction (redox centers), followed by dehydration (on acidic sites). The surface basic sites are responsible for CO + CO_2 formation. The selective formation of dimethyl ether (CH_3OCH_3) is assigned to the presence of strong acid sites.

Busca et al. [5] and Tatibouët [3] have provided very useful and informative schemes showing the reaction steps leading to the various products. These schemes allow differentiation of the oxidative and acidic routes of methanol oxidation and also aid identification of the intermediate chemisorbed species. Keep in mind, however, that the nature and adsorption strength of such chemisorbed species determine further reactions. Therefore, the estimation of chemisorbed species under real reaction conditions is very important to optimize the catalyst content. Taking this into account, we used an *in situ* flow reactor cell

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that allowed us to measure IR spectra under dynamic conditions.

We used multinuclear ^{27}Al, ^{51}V, and ^{1}H solid-state NMR for structural characterization of alumina-supported vanadia, niobia, and vanadia–niobia catalysts. Today, ^{27}Al and ^{51}V solid-state NMR are indispensable to the study of many alumina- and vanadia-based catalysts and related materials. The coordination number of Al sites in AlOx can be readily determined from the value of the isotropic chemical shift [6,7]. ^{1}H NMR of hydroxyl groups is very informative regarding the extent of dispersion of supported metal [8].

In this paper, we report on the preparation and characterization of structural and reactive properties of alumina-supported vanadia and niobia, and the effect of total V + Nb coverage on alumina.

2. Experimental

2.1. Preparation of samples

The vanadium and niobium oxides supported on alumina were prepared using different V precursors. The VS series was prepared using a $VOSO_4$ precursor, and the VM series was prepared using an ammonium metavanadate precursor. Vanadia on alumina catalysts were prepared from an aqueous solution of $VOSO_4$ (Aldrich, 99.99%), which was maintained under stirring at 323 K for 50 min, after which γ-Al_2O_3 (SASOL, $S_{BET} = 193\ m^2/g$) was added. The suspension thus obtained was evaporated in a rotatory evaporator at 338 K. The resulting solid was dried at 388 K for 20 h and then calcined at 673 K for 4 h in air. The rate of heating was 5 K/min. The impregnation of alumina-supported V–Nb and Nb oxides was done using NH_4VO_3 (Sigma, 99.99%) and $NH_4NbO(C_2O_4)_2$ (Aldrich, 99.99%) solutions. Oxalic acid (Panreac, 99.5%) was added to an aqueous solution of ammonium metavanadate and of ammonium niobate (V) oxalate to facilitate dissolution of salts. The same niobium precursor was applied in the preparation Nb/γ-Al_2O_3 system. Oxalic acid also was used for the impregnation of niobium on alumina. As a reference value, the monolayer value (understood to be the dispersion limit loading of the supported oxides) was estimated as a total number of 8 atoms (V + Nb)/nm^2 of alumina support. The amounts of V, Nb, and V + Nb were calculated so that the total coverage of metals ranged from ca. 1/4 of a monolayer to above monolayer. The V/Nb atomic ratio was kept at 1. The general xVS/Al (or xVM/Al), xNb/Al and xVNb/Al nomenclature was applied, where x indicates the number of atoms per nm^2 of V and Nb, S represents vanadyl sulfate, and M represents ammonium metavanadate.

2.2. NMR study

Solid-state NMR experiments were performed with Bruker AVANCE-400 (9.4 T) spectrometer at resonance frequencies 400.13, 104.26, and 105.20 MHz for ^{1}H, ^{27}Al, and ^{51}V, respectively. A Bruker 4.0 mm, 2.5 mm MAS probes and NMR Rotor Consult ApS (Denmark) 5 mm MAS probe were used for static and 15- to 35-kHz MAS spectra acquisition. The single pulse sequence with rf-pulse length of 1 µs (12° flip angle) and recycle delay of 1–5 s was used to acquire ^{27}Al and ^{51}V spectra. ^{1}H spectra were measured with pulse length of 10 µs (90°) and recycle delay of 1 s. The chemical shift values were referred to TMS for ^{1}H, 0.1 M $Al(NO_3)_3$ for ^{27}Al, and $VOCl_3$ for ^{51}V.

^{27}Al 3QMAS (Triple-quantum MAS) experiments were performed using a basic 3-pulse sequence with z-filter. The sequence starts with an excitation pulse p1 (3.5 µs, corresponding to 180°) that creates 3Q coherence, which is allowed to evolve during the evolution period, τ. A subsequent conversion pulse, p2 (1.0 µs, corresponding to 50°) flips magnetization back along the z-axis, which, after a short (20 µs) delay (to allow dephasing of undesired coherences), is read out with a weak CT-selective 90° pulse, p3 (6.5 µs).

The samples were dehydrated before the NMR experiments. The catalyst samples were placed into 7-mm glass ampules and dehydrated under vacuum ($<10^{-3}$ Torr) for 4 h at 623 K. Then they were calcined for 2 h at 723 K in dry O_2 and finally flame-sealed. Just before the measurements, the ampules were unsealed and the samples loaded into standard 5-mm rotors in a dry box under an argon flow. Hydration of the samples was achieved by exposing them to the humidity of the ambient air. ^{1}H MAS NMR measurements were performed with dehydrated samples; ^{27}Al NMR measurements, with hydrated ones. ^{51}V MAS NMR was performed with both hydrated and dehydrated samples.

2.3. IR study

The IR experiments were performed with Vector 22 (Bruker) FTIR spectrometer. IR spectra were recorded at a resolution of 2 cm^{-1} using 64 scans. The ∼20 mg catalyst samples were pressed into thin wafers and placed in the *in situ* flow cell equipped with KRS-5 windows (insensitive to humidity). The activation, adsorption, and oxidation of methanol were carried out in this *in situ* flow cell. Spectra were registered in a temperature range of 373–573 K. The spectra without any sample ("gas phase") were scanned before each catalyst spectrum. Before the measurement, the samples were activated at 623 K in a 50 cm^3/min flow of oxygen and helium, which had been passed through a molecular sieve trap to remove moisture traces. The O_2/He molar ratio was 20/80. The pretreated materials (2 h) were gradually cooled to 373 K. Adsorption of methanol was performed at 373 K in a ∼40 cm^3/min stream with a CH_3OH/He molar ratio 1.2/98.8. The methanol partial pressure was controlled by a methanol bubbler. IR spectra were recorded after 15 and 35 min of methanol adsorption. Methanol oxidation was carried out using gas mixture of CH_3OH/O_2/He (molar ratio 1.2/18.8/80) at a flow rate of ca. 40 cm^3/min. The temperature was gradually increased up to 573 K. IR spectra were obtained at given temperatures after 15 min of dwell time.

2.4. Methanol probe reaction

Methanol oxidation reaction was performed in a glass fixed-bed reactor equipped with a thermocouple. First, 0.03 g of cat-