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On the nature of active sites in MoVTeO and MoVTeNbO catalysts: The influence of catalyst activation temperature

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ABSTRACT

MoVTeO and MoVTeNbO catalysts have been prepared, characterized (by XRD, Raman, IR, XPS, oxygen isotopic-exchange and IR of adsorbed methanol) and tested in the partial oxidation of propane to acrylic acid. The catalysts have been prepared hydrothermally and heat-treated at 500, 550 or 600 °C in a N_2 atmosphere. The heat-treatment has different influence on the formation and stability of M1, the surface characteristics of catalysts and the catalytic behavior of MoVTeO and MoVTeNbO catalysts. The more selective catalyst was the MoVTeNbO sample heat-treated at 600 °C, which present relatively high oxygen isotopic-exchange, the lower onset temperature of $^{18}O_2$-consumption and a very low number of acid sites. In addition, it is characterized by the presence of only a type of Mo^{6+} species and the absence of Te^{6+} species (only Te^{4+} is observed) on the catalyst surface. The characteristics of active and selective catalysts are also discussed.

1. Introduction

Multicomponent MoVTeNbO mixed metal oxides are an interesting catalytic system since they show high activity and selectivity in the (amm)oxidation of propane to acrylic acid and acrylonitrile [1–4] and in the oxidative dehydrogenation of ethane to ethylene [5,6]. After the publication of the first patents by Mitsubishi researchers [1,2], many groups have worked in the last ten years on the synthesis and characterization of these types of catalysts [3–33].

Although MoVTeO catalysts are active and relatively selective in partial oxidation of propane to acrylic acid [7–10], the Nb-containing materials show at present the best catalytic behavior [1–6,8,9,11–22]. In general two crystalline phases, the so-called M1 and M2 phases, have been proposed to be present in active and selective catalysts, although their proportions strongly depend on catalyst preparation, i.e. procedure, composition, etc. [3,4,8,9,11–29]. However, the catalytic behavior of these catalysts is strongly related to the presence of M1 phase [18,22,23], although the presence of M2, in some case, could have a synergic effect [17–19]. This is so, because M2 phase is active and selective in propylene oxidation to acrylic acid [8,28].

These crystalline phases can be directly obtained by hydrothermal synthesis [7–15], while a catalyst precursor is only achieved when using a slurry method [1–4,11]. Moreover, independently of the catalyst preparation procedure, the active and selective catalysts are obtained when the catalyst precursors are heat-treated at high temperature [1–27], generally about 600 °C in an inert atmosphere. However, there is not a clear explanation about the changes occurring in the catalyst during the heat-treatment. Ueda and co-workers [7] observed that both the catalytic behavior and the characteristics of the catalyst surface of MoVTeO materials change depending on the catalyst activation procedure. Schlögl et al. [24] observed an anisotropic growth of the needle-like M1 phase during the heat-treatment. Accordingly, changes in the catalyst surface could occur during the catalyst activation, especially in Nb-containing catalysts. Thus, it has been proposed that the incorporation of Nb^{5+} cations decreases the number of acid sites [16], stabilizes the crystalline structure [25], and could facilitate a less degradation of acrylic acid to carbon oxides [26].

Bulk oxidation state of different cationic element of MoVTeNbO catalysts has been studied by XANES [12,21,27] and Mössbauer spectroscopies [12]. In this way, tellurium has a role not only on catalyst structure but also as bulk component to storage oxygen in the hexagonal channels [28].

XPS results have suggested some differences between bulk and surface [8b,12,17,28], although the modifications in the oxidation state of elements could also be related to the catalyst activation procedure [7]. However, more important changes could occur on

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the surface of catalysts, which cannot be completely followed by XPS. Thus, it has been suggested that the zone of dynamics in these types of catalysts could be limited to a thickness of about 1 nm [29]. Accordingly, other characterization techniques should be used to determine changes in the surface of catalysts.

Methanol temperature programmed surface reaction (TPSR) spectroscopy has been also employed to determine the nature of active surface sites for MoVTeNbO catalysts [30], concluding that V^{5+} (redox) and Mo^{6+} (acid) cations are the more active surface sites while Nb^{5+} and Te^{4+} cations could be promoter ligands. On MoVO or MoVTeO catalysts, formaldehyde was only observed while both formaldehyde (on VO_x sites) and dimethyl ether (on MoOx sites) are observed over MoVTeNbO catalyst. This suggests modifications in both redox and acid sites depending on catalyst composition.

Guliants et al. studied the role of surface cations in propane oxidation in orthorhombic MoVMe (M = Te, Nb and Sb) catalysts using low-energy ion scattering (LEIS) [31], suggesting that the Nb cations were preferentially located at the topmost surface, while subsurface Te or Sb concentrations declined gradually into the bulk. More recently, this group has studied the methanol and allyl alcohol chemisorptions and surface reaction in combination with LEIS in order to investigate the surface compositions and chemical nature of active phase in these catalysts [32]. Methanol species were preferentially adsorbed at the surface of VO_x and MoO_x sites. In addition, they concluded that the topmost surface of catalyst shows a lower V- and Mo-content and an enriched Nb and Te with respect to both subsurface and the bulk composition, suggesting that the bulk of catalyst acts as a support.

In this work, we present a comparative study on the catalytic behavior of MoVTe(Nb)O catalyst, heat-treated at 500, 550 and 600 °C. In addition, a comparative study of the surface characteristics of materials followed by XPS, FTIR studies of adsorption of methanol as well as exchange isotopic reaction of O^{18} will be provided. Strong differences in the catalytic behavior are observed, depending on the catalyst composition and the activation temperature, which can be explained by changes in the surface of the catalysts.

2. Experimental

2.1. Catalyst preparation

MoVTeO and MoVTeNbO catalysts have been prepared hydrothermally according to a procedure previously reported [15]. The gels, prepared from aqueous solutions of the corresponding salts, presented Mo/V/Te or Mo/V/Te/Nb molar ratios of 1/0.50/0.17 or 1/0.25/0.17/0.17, respectively [8]. Ammonium heptamolybdate, telluric acid or tellurium oxide, vanadium sulphate, niobium acid and oxalic acid were used, respectively, as Mo-, Te-, V-, Nb and oxalate sources. The gels were autoclaved in teflon-lined stainless steel autoclaves at 175 °C for 48 h. The resulting solids were filtered, washed, dried at 80 °C for 16 h. The Nb-free and Nb-containing catalyst precursors will be named as A-as and B-as, respectively.

The catalyst precursors have been heat-treated in the 500–600 °C interval during 2 h in N_2-stream. The Nb-free and Nb-containing catalyst were named as A-x and B-x, respectively, where x is the catalyst activation temperature (x = 500, 550 or 600 °C).

2.2. Catalytic tests

The catalytic experiments were carried out in a fixed bed quartz tubular reactor (i.d. 12 mm, length 400 mm), working at atmospheric pressure [15]. Catalyst samples (0.3–0.5 mm particle size) were introduced in the reactor and diluted with 2–4 g of silicon carbide (0.5–0.75 mm particle size) in order to keep a constant volume in the catalyst bed. The flow rate and the amount of catalyst were varied (from 50 to 100 $cm^3\,min^{-1}$ and from 1.0 to 2.0 g, respectively) in order to achieve different propane conversion levels. The feed consisted of mixture of propane/oxygen/water/helium (4/8/30/58).

Experiments were carried out in the 340–420 °C temperature range in order to achieve the highest selectivity to partial oxidation products. Reactants and reaction products were analyzed by online gas chromatography [15].

2.3. Catalyst characterization

The chemical composition was determined by atomic absorption spectroscopy. BET specific surface areas were measured on a Micromeritics ASAP 2000 instrument (adsorption of krypton) and on a Micromeritics Flowsorb (adsorption of N_2).

X-ray diffraction patterns (XRD) were collected using a Philips Xĭ Pert diffractometer equipped with a graphite monochromator, operating at 40 kV and 45 mA and employing nickel-filtered CuKa radiation (k = 0.1542 nm).

Scanning electron microscopy (SEM) and EDX microanalysis were performed on a JEOL JSM 6300 LINK ISIS instrument. The quantitative EDX analyses were performed using an Oxford LINK ISIS System with the SEMQUANT program, which introduces the ZAF correction.

Infrared spectra were recorded at room temperature in the 300–3900 cm^{-1} region with a Nicolet 205xB spectrophotometer, equipped with a Data Station, at a spectral resolution of 1 cm^{-1} and accumulations of 128 scans.

Raman spectra were recorded with an “in via” Renishaw spectrometer, equipped with a microscope (Olympus). The samples were excited by the 514.5 nm line of an Ar^+ laser (Spectra Physics Model 171) with a laser power of 2.5 mW. The following spectrometer characteristics were used: microscope objective, 50×; spectral resolution, 2.5 cm^{-1}; integration time 20 s per spectrum and number of scans 50, while the spatial resolution of each analysis is about 0.4 μm.

Photoelectron spectra (XPS) were recorded on a SPECS spectrometer using Al Kα radiation (Al Kα = 1486.6 eV) of a twin anode in the constant analyser energy mode, with pass energy of 50 eV. Samples were previously outgassed in the preparation chamber of the spectrometer and subsequently transferred to the analysis chamber. The pressure of the main chamber was maintained at ca. 5×10^{-10} mbar. The binding energy (BE) scale was regulated by setting the C_{1s} transition at 284.6 eV. The accuracy of the BE was ±0.1 eV. Spectra analysis has been performed using the CASA software.

IR spectra of adsorbed methanol were recorded at room temperature with a Nexus 8700 FTIR spectrometer using a DTGS detector and acquiring at 4 cm^{-1} resolution. For IR studies the samples were pressed into self-supported wafers and activated at 150 °C in vacuum (1×10^{-4} mbar) for 2 h prior to the adsorption experiments. Methanol has been adsorbed at room temperature at increasing pressure (1–6 mbar). The spectra shown are difference spectra between absorbances of the sample after and before adsorption of methanol.

Oxygen isotopic-exchange experiments have been performed using a quartz flow reactor equipped with mass flow controllers and an electrically heated oven. The reactor exit was connected by a heat inlet capillary system to a quadrupole mass analyser (Omnistar, Balzers) for on-line monitoring of the exit gas composition. The concentration profiles were obtained by acquiring the signals relative to the following mass-to-charge (m/z) values: 32 ($^{16}O_2$), 34 ($^{18}O^{16}O$), 36 ($^{18}O_2$). Before each experiment the sample (40 mg) was pre-treated at 250 °C in 20%O_2/argon for 2 h followed by argon flow 1 h at the same temperature and subsequent cool-