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Reflux method as a novel route for the synthesis of $MoVTeNbO_x$ catalysts for selective oxidation of propane to acrylic acid

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ABSTRACT

This work reports the applicability of reflux to the synthesis of Mo–V–Te–Nb–O metal oxide catalysts for the first time. The well-formed and defined orthorhombic M1 phase, i.e. $Te_2M_{20}O_{57}$ (M = Mo, V, Nb), was found to be better developed when a longer time was used to reflux the mixed metal clusters. The catalysts efficient for propane selective oxidation to acrylic acid, reaching *ca.* 60% of selectivity to acrylic acid at propane conversion of *ca.* 50% and at a reaction temperature of 693 K. In addition, a parallel between catalytic activity and catalyst reducibility is also concluded.

1. Introduction

$MoVTeNbO_x$ mixed oxide is reportedly the most promising catalyst system for the selective oxidation of propane to acrylic acid. These catalysts were developed and patented by Mitsubishi Chemicals [1], who reports the highest acrylic acid yield (*ca.* 50%) up until today. Academic and industrial communities in the area of partial oxidation are enthusiastic about improving its catalyst performance. This is easily evidenced by a significant amount of work on these materials [1–24]. It is debatably suggested that their unique catalytic properties are due to the presence of two major structures, termed as orthorhombic M1 phase, $Te_2M_{20}O_{57}$ (M = Mo, V, Nb), and hexagonal M2 phase, $Te_{0.33}MO_{3.33}$ (M = Mo, V, Nb) [9]. Other phases such as $(Mo_{0.93}V_{0.07})_5O_{14}$, MoO_3, and $TeMo_5O_{16}$ can also be present depending on the preparation and activation [18,19]. The M1 phase alone can activate propane and selectively convert it to acrylic acid [18,20]. On the contrary, the M2 phase is inactive for propane oxidation, but selectively oxidizes free intermediately formed propylene to desired products [11,19]. Two additional topics have been stressed in the literature: the cooperation of phases [11–23] and the isolation of the active sites [11,15–18,20,21,23]. In the former, different authors have concluded that at least in the case of the (amm)oxidation of propane, the performance of the M1 phase could be improved by cooperation of the pseudohexagonal $Te_{0.33}MO_{3.33}$ phase (M = Mo, V, Nb) [11,16–18,20,21,23].

Despite the effort expended in synthesizing and characterizing mixed metal oxides, only a few methods have been used to synthesize these catalysts. Although Slurry [1,4,7,11,12] and hydrothermal [3,4,6,11,13,23,24] methods are the most common options, microwave-assisted hydrothermal synthesis has been also proposed [24]. Undoubtedly, these methods have produced the desired catalysts. This is especially true for the hydrothermal method, through which it is possible to obtain, in the appropriate conditions, the monophasic MoVTeNbO material with M1-like crystalline structures. The hydrothermal synthesis of these materials is usually performed at 448 K in a nitrogen atmosphere with a synthesis time of 48 h [11,23,24] and is mainly characterized by its high solvent effect and equilibrium conditions, which lead to the formation of the most favored crystalline phase. On the contrary, the slurry method uses a non-solution precursor, which implies a complexity in the formation of the active phase. For this reason, the slurry method contributes to the multiphase MoVTeNbO system in which the species is always present in different valence states due to its non-equilibrium state [1,4,7,11,12].

In the present work, a reflux method has been developed for the synthesis of $MoVTeNbO_x$ catalysts. The catalysts were prepared by refluxing the aqueous synthesis gel with a mixture of metals.

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This method has the advantage of allowing intimate mixing of corresponding species in a homogeneous state under atmospheric pressure and at the solvent's boiling point. This is the first reported work on the utilization of this method in synthesizing MoVTeNbO$_x$ catalysts for propane selective oxidation. The method has been found successful for the synthesis of $(VO)_2P_2O_7$ [25] based catalyst employed in the transformation of butane to maleic anhydride. The effect of the reflux period on the catalyst structural development was also studied. The activity of these catalysts in the propane conversion to acrylic acid was studied.

2. Experimental

2.1. Catalyst preparation

Commercial chemicals of ammonium heptamolybdate, AHM, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (Merck), vanadyl sulphate, $VOSO_4$ (Aldrich), telluric acid, $Te(OH)_6$ (Aldrich), and ammonium niobium oxalate, $(NH_4)_2Nb_2(C_2O_4)_5$ (CBMM), were used as the metal sources for Mo, V, Te and Nb respectively. The gel presented a Mo/V/Te/Nb atomic ratio of 1/0.3/0.17/0.12. The preparation process begins by dissolving AHM in deionized water, heated at 353 K and was followed by the addition of telluric acid to form the first solution. In another beaker, a second solution was prepared by dissolving $VOSO_4$ in deionized water heated at 353 K, and then added to the first solution, producing a dark green solution. A third solution was obtained by dissolving niobium oxalate in deionized water solution, which was added to the former mixture. The resulting dirty green mixture was left to stir for 10 min before being refluxed. The effect of reflux time was studied by conducting reflux for 1, 4, 7, and 14 days. Following the reflux, the solid phase was filtrated and a purplish-black solid was obtained which was then dried overnight in an oven at 373 K. The dried samples were heat-treated in flowing N_2 at 873 K for 2 h. The corresponding materials were denoted as A-1, A-4, A-7, and A-14 (Table 1).

2.2. Catalyst characterization

BET specific surface area measurements were performed using a ThermoFinnigan Sorptomatic apparatus, with adsorption of N_2 at 77 K. Bulk composition of the catalyst was determined by inductive coupled plasma-atomic emission spectrometer (ICP-AES).

Powder XRD patterns were collected by employing a Philips X'Pert diffractometer equipped with a graphite monochromator, operating at 40 kV and 30 mA and using Ni filtered CuK$_\alpha$ radiation with wavelength, $\lambda = 0.1542$ nm. Samples were ground and put on a horizontal sample holder and XRD patterns were recorded in the 5–60° range.

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} with an accumulation of 128 scans. The pellets were prepared with 20 mg of sample mixed with 100 mg of dry KBr and pressed into disks.

Raman spectra were obtained with an "in via" Renishaw spectrometer, equipped with an Olympus microscope. The exciting wavelength was 785 nm from a Renishaw HPNIR laser with a power of *ca.* 15 mW on the sample.

Scanning electron microscopy (SEM) was performed using JEOL Model JSM 6400 to record the image at an accelerating voltage of 15 kV.

Temperature programmed reduction of hydrogen (H_2-TPR) was achieved by using a ThermoFinnigan TPDRO1110 apparatus, utilizing a thermal conductivity detector (TCD). Hydrogen (5% in Ar, 1 bar, 25 ml/min) flowed over the samples at temperatures ranging from room temperature to 1250 K following the evolution of water continuously on a mass spectrometer. The temperature was increased linearly at 10 K/min.

2.3. Catalytic test

Propane selective oxidation was carried out at atmospheric pressure in a fixed bed quartz tubular reactor (i.d. 12 mm, length 400 mm). The weight of the catalyst (with homogeneous particle size in the 0.3–0.5 mm range) was varied in order to achieve different contact times, Silicon carbide was added in order to keep a constant volume in the catalytic bed. The gas feed consisting of $C_3H_8:O_2:H_2O:He$ with a 4:8:30:58 (%) molar composition was supplied at flow rates of 30–100 ml/min. Experiments were carried out in the 613–693 K range. Reactants and products were analyzed by online gas chromatography using two packed columns: (i) molecular sieve 5 Å (3 m); and (ii) Porapak Q (3 m).

3. Results and discussion

Table 1 summarizes some of the main characteristics of MoVTeNbO$_x$ catalysts. No significant differences in the chemical composition can be seen in the activated samples, which are close to the atomic ratios used in the synthesis gel. On the other hand, heat-treated samples present BET surface areas ranging from 1.9 to 9.3 m^2 g^{-1} (Table 1), within the range of those previously described for similar materials [21,26,34]. A correlation between surface area and reflux time is observed, in that the longest reflux time is obtained by the highest surface area.

3.1. Characterization of as-synthesized samples

XRD patterns of the as-synthesized samples (before heat treatment) are displayed in Fig. 1A. The reflections set with a peak at $2\theta = 22°$, and two broad peaks at $2\theta < 10°$ (low intense) and at $2\theta = 27°$ are similar to those found in the precursor of the Mo/W orthorhombic and tetragonal phases [11,29,30]. The peak appeared at 2θ of *ca.* 22° is related to a kind of Mo-based oxides with layer-type structures closely related to the ReO_3-family [27,28]. Overlapping another set of reflections are observed only in the XRD patterns of as-synthesized samples prepared from 1 to 7 days, which indicate the presence of heteropoly-compounds (HPC) with Anderson-type structure $(NH_4)_6TeMo_6O_{24}\cdot 7H_2O$ [11], $(NH_4)_7TeMo_5VO_{24}\cdot 8H_2O$ [12], and/or $(NH_4)_8(V_{19}O_{41}(OH)_9)(H_2O)_{11}$ [ICSD 063213]. The narrow diffractions become broad bands during the reflux, which means that HPCs slowly turn into pseudo-crystallines with increasing time of up to 14 days' synthesis resulting in a homogeneous distribution of crystalline nano-domains without a trace of heteropoly-compound reflections (Fig. 1A, d).

Raman spectra of as-synthesized samples, before the heat-treatment, are shown in Fig. 2A. The A-1 sample presents a homogeneous composition with practically identical Raman spectra obtained at different discrete points of the sample, characterized by the presence of a band at *ca.* 950 cm^{-1}. This band is related to Mo–O$_t$ stretching vibration from Anderson-type HPC structures (more or less shifted depending on hydration), in agreement with XRD results [31,32]. On the other hand, the sample obtained at 4 days of reflux (A-4 sample) presents a heterogeneous composition with different Raman spectra at different selected areas of the sample (Fig. 2A, spectra b1–b3), similar to spectra of samples prepared in 1 day (indicating the presence of Anderson HPC). However, there is also a new Raman spectrum at 874 cm^{-1}, which can be associated with the presence of pentagonal $[M_6O_{21}]^{6-}$ (M = Mo, V, Nb) units [33]. In the case of the sample A-14 (Fig. 2A, spectrum c), only one type of Raman spectrum is observed with a wide band centered