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High surface area Mo–V–Te–Nb–O catalysts: Preparation, characterization and catalytic behaviour in ammoxidation of propane

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Abstract

Mo–V–Te–Nb mixed oxides with a molar ratio of 1:0.30:0.20:0.15 were prepared by citrate and dry-up method, both associated with hydrothermal treatments in the presence of a cationic surfactant (cetyl trimethylammonium bromide, CTAB), and tested in the ammoxidation of propane. The catalysts were characterized by adsorption–desorption isotherms of nitrogen at 77 K, particle size measurements, XRD, and XPS. By using the surfactant, the surface area increased significantly, and samples with surface area between 110 and 239 m^2/g were obtained. These catalysts exhibited a propane conversion near 48% with selectivity to acrylonitrile of about 32% for a space velocity 30 times higher than generally reported.

Keywords: Mo–V–Te–Nb mixed oxides; Citrate method; Dry-up method; Ammoxidation

1. Introduction

Catalytic selective oxidation is one of the primary tools of the current chemical industry. Among the reactions that exhibited a large interest, selective oxidation of alkanes still represents a hot topic. One of the target molecules is propane. Since its current price is about two times smaller than the cost of propylene, the direct transformation of propane to high value products for the chemical industry constitutes a difficult and stimulating scientific and technological challenge. In particular, the ammoxidation of propane to acrylonitrile is a very important application [1–3]. Therefore, the interest of industry and academia to improve the activity and selectivity of the catalysts for this reaction is justified. Mo–V–Te–Nb mixed oxides have been claimed as the most active and selective catalysts in the ammoxidation of propane to acrylonitrile (ACN) [4–6]. The activity of these catalysts was associated with two phases (called M1 and M2) consisting of orthorhombic $Mo_{7.8}V_{1.2}NbTe_{0.94}O_{28.9}$ (M1) and pseudo-hexagonal $Mo_{4.67}V_{1.33}Te_{1.82}O_{19.82}$ (M2) [6]. It has been reported that their concomitant presence is necessary to generate effective catalysts [7–11]. However, this catalytic system has not yet provided a competitive advantage in ACN productivity versus conventional propylene ammoxidation catalysts, which explains why the corresponding propane ammoxidation process has not yet been commercially scaled up. Currently, these mixed oxide catalysts are prepared by either commercial dry-up or lab-scale hydrothermal synthesis that usually leads to low surface area materials (<20 m^2/g) [3]. Although these catalysts exhibit a rather good selectivity for small space velocities, the improvement of the catalytic performances by increasing the productivity remains a challenge. A possible way to increase the productivity is to enhance the surface area of these catalysts.

The aim of this work was thus to investigate new routes for the preparation of Mo–V–Te–Nb mixed oxides with high surface area and to characterize these materials. The strategy was to add during the preparation step a cationic surfactant traditionally used as a structure-directing agent in the synthesis of mesoporous materials.

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2. Experimental

Samples with a molar ratio of Mo:V:Te:Nb = 1:0.30:0.20: 0.15 were prepared by two methods: (i) citrate method, and (ii) dry-up method [1], both associated with hydrothermal treatments in the presence of cationic surfactant (cetyl trimethylammonium bromide, CTAB). The dry-up method consists in mixing an aqueous solution containing all the metallic elements, after what the solution is evaporated to dryness at 423 K. The precursors used were ammonium heptamolybdate, ammonium metavanadate, ammonium niobium oxalate and telluric acid in desired amounts, namely 1.4×10^{-3} M, 3×10^{-3} M, 7×10^{-4} M and 2×10^{-3} M, respectively. The citrate method consists in starting from the same aqueous solution of precursors but adding equivalent amount of citric acid for complete complexation of the cataions. After a vigorous stirring, the resulting solution is evaporated until a gel-like liquid is obtained. The resulting gel is then dried under vacuum. For both synthesis routes, CTAB was added in two manners: (i) before the drying step, i.e. directly in the gel for the citrate method and directly in the precursor solution for the dry-up method, or (ii) after the drying step, i.e. suspending the crushed spongy "citrate" solid in CTAB for the citrate route and suspending the obtained dried powder for the dry-up method. In all the cases, the resulting suspension was hydrothermally treated into Teflon lined autoclave vessel, at 373 K for 4 days under autogenous pressure and static conditions. The product was then dried at 373 K and then calcined at 773 K for 5 h in air.

The characterization of these materials was carried out by XRD, XPS, BET, SEM and particle size measurement. BET surface area was measured using the single point method, using a Micromeritics Flow Sorb II 2300. Particle sizes were measured by laser scattering using Coulter LS130 equipment. XRD patterns were recorded using a Siemens D-5000 powder diffractometer equipped with a Ni-filtered Cu Kα radiation. For some special in situ experiments, a HTK100 furnace from Anton Parr was interfaced to the goniometer. SEM images were recorded with a LEO GEMINI 982 microscope. XPS spectra were collected with a SSX-100 Model 206 Surface Science Instrument spectrometer. The charge correction was made considering that the C 1s signal of contaminating carbon was centred at 284.8 eV. The C 1s, V $2p_{3/2}$, Nb $3d_{5/2}$, Te $3d_{5/2}$, Mo $3d_{3/2}$ and O 1s peaks were chosen for characterization, since they are the most intense and do not overlap.

Catalytic tests were performed in a fixed bed quartz microreactor at atmospheric pressure and in the temperature range 673–773 K, using 0.1 g of catalyst and working with W/F = 8 g h/mol of C_3H_8. The feed composition was 1.25:3:1 of C_3H_8:O_2:NH_3. Feed and products were analysed on-line using a gas chromatograph HP 5890 series II, equipped with FID and TCD detectors. The organic compounds were separated on a capillary column WCOT Fused Silica CP 8CB, and O_2, CO_2, CO, N_2 were analysed on two columns, MS 5A, 80–100 mesh, 2 m × 1/8″ and Haysep Q 100–120 mesh, 2 m 1/8″.

3. Results and discussions

3.1. Characterization of the fresh materials

Table 1 compiles the BET and particle size results as a function of the preparation method. The use of the structure-directing agent led to a significant increase in the surface area. For example, the sample RO4 prepared by dry-up method exhibits a surface area of 17 m^2/g, while the sample RO5 prepared by dry-up method associated with hydrothermal treatment in the presence of the surfactant CTAB exhibits a surface area of 239 m^2/g. Also, differences were observed as a function of the manner in which the surfactant was added: a higher surface area was systematically found when the surfactant was added before the drying step, namely, preliminary to the formation of the solid structure.

The particle size was also influenced by the preparation procedure. As a general feature, a higher surface area corresponded to a smaller particle size (Table 1). This indicates that a role of CTAB in these syntheses was to inhibit the tendency of the particles to agglomerate. Fig. 1 presents the SEM images of RO5 and RO7. The sample prepared by dry-up method associated with hydrothermal treatment in the presence of the surfactant CTAB (RO5) exhibits a fibrous morphology, while RO7 corresponds to plates. According to SEM measurements, the length of the RO5 fibbers was around 1 μm while the size of the RO7 plates was in the range 2–3 μm. The SEM micrographs give a more rigorous picture of the

Table 1
BET and particle size results, and catalytic properties of the Mo–V–Nb–Te–O catalysts

Catalyst	Preparation method	Surface area (m^2/g)	Particle size (μm)	Conversion (%)	Specific activity (% g/m^2)	Selectivities (%)			
						ACN	AcCN	Propylene	CO*x*
RO1	Citrate	98	73.9	46.8	0.47	29.7	15.4	13.2	32.7
RO2	Citrate + surfactant (gel)	110	63.0	48.2	0.43	31.8	9.5	12.2	36.8
RO3	Citrate + surfactant (powder)	53	153.4	18.5	0.34	32.2	8.5	10.0	42.4
RO4	Dry-up	17	98.7	29.8	1.75	17.8	12.6	19.3	46.6
RO5	Dry-up + surfactant (gel)	239	9.9	36.3	0.15	28.2	8.2	12.6	40.4
RO6	Dry-up + surfactant (powder)	66	165.8	23.4	0.35	24.8	13.4	16.6	39.8
RO7	Dry-up[a]	4	220.4	38.9	9.7	19.7	16.9	12.8	44.1

Reaction conditions: 723 K, 24 h, feedstock composition $C_3H_8/O_2/NH_3$ = 1.25/3/1, 0.1 g catalyst, GHSV = 16800 h^{-1}. ACN: acrylonitrile, AcCN: acetonitrile, CO*x*: carbon oxides.

[a] Calcined at 873 K in nitrogen flow for 2 h [1].

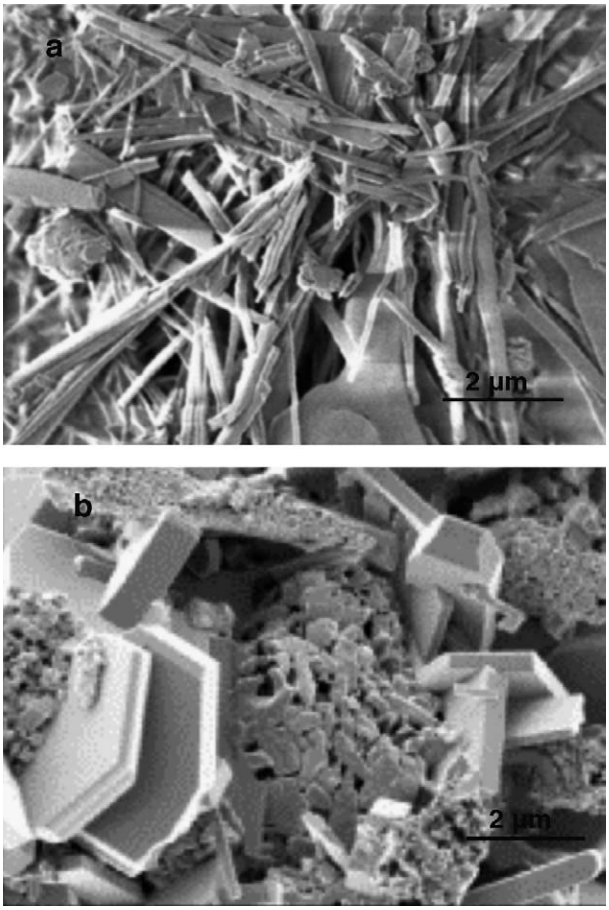

Fig. 1. SEM photographs of RO5 (a) and RO7 (b) samples.

dependency of the morphology and size of the catalyst particles to the preparation method and of the effect of the structure-directing agent. They fully support the tendency understood from the BET and particle size measurements.

Fig. 2 depicts the XRD patterns for the samples prepared by different methods. They contain reflection lines of different phases: TeM_3O_{10} (M = Mo, V, Nb) (I), $Te_2M_{20}O_{57}$ (M = Mo, V, Nb) (II), $Nb_{0.09}Mo_{0.91}O_{2.8}$ (III), and MoO_3 (IV). The relative intensities of several reflections changed only slightly relative to each other and these differences were not large enough to be considered. In situ XRD measurements of the dried samples indicated that the formation of phases (I) and (II) starts at 723 K, while those of phases (III) and (IV), start at 773 K. All these phases were previously observed and discussed in literature for such kind of catalysts [4,5]. The formation of MoO_3 could be explained by the fact that the catalysts were calcined in air.

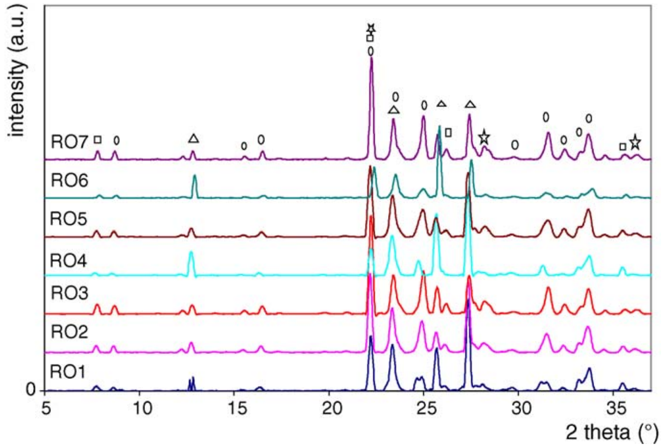

Fig. 2. X-ray diffraction patterns of fresh samples prepared by citrate (a) and dry-up method (b): ((○), $Nb_{0.09}Mo_{0.91}O_{2.80}$; (☆), TeM_3O_{10} (M = Mo, V, Nb); (□), $Te_2M_{20}O_{57}$ (M = Mo, V, Nb); (Δ), MoO_3).

Concerning the XPS characterization for all the fresh catalysts, the binding energies of the investigated bands were not affected by the preparation method. They corresponded to the highest oxidation state of these elements. The binding energy of V $2p_{3/2}$ (517.3 eV) agrees well with the V $2p_{3/2}$ binding energy in V_2O_5 and NH_4VO_3 (517.3 eV) [12]. The oxidation state of niobium also corresponded to 5+ (Nb $3d_{5/2}$ binding energy of 207.1 eV, as in the case of the Nb_2O_5 [13]). The Te $3d_{5/2}$ (576.5 eV) peak position was due to Te^{6+} [14], and of Mo $3d_{5/2}$ (232.8–233.0 eV) to Mo^{6+} [15]. For all the samples, the molar ratio V/Mo, as determined from XPS analyses, was lower than the theoretical one. This shows that the surface vanadium content was smaller than the bulk one [7].

3.2. Characterization of the catalysts after reaction and catalytic performances

XRD patterns of tested catalysts are slightly different from those of the fresh catalysts. Reflection lines typical of MoO_3 completely disappeared, while new reflection lines assigned to $TeMo_5O_{16}$ (for 2θ = 21.7, 24.7, 26.2, 26.7, 30.5) were detected for the samples prepared by dry-up method. Concerning the XPS characterization, a slight decrease in the oxidation state of all the elements could have been expected for the tested catalysts. However, the facts that the recorded shifts were smaller than 0.5 eV, and that the peaks remain symmetrical, may be an indication that, if it happens, such reduction only corresponds to a slight tendency. The only exception is for Mo whose Mo 3d peak presented two components, one corresponding to Mo^{6+} and the second one being assigned to Mo^{5+} or Mo^{4+} (230.2 eV) [16]. No change in the molar ratios was denoted by comparison with the fresh catalysts.

3.3. Catalytic performances

Table 1 also presents the catalytic results obtained in propane ammoxidation. The data were collected after 24 h of time-on-stream. A comparison of the two preparation procedures indicates that, in terms of productivity, the conversions obtained on catalysts prepared using the citrate route are higher than those of the catalysts prepared using the dry-up procedure. Higher levels of propane conversion were obtained for the samples where the surfactant was added during the synthesis. RO2 catalyst is a good example in this sense. The conversion of propane reached 48% on this catalyst, while for RO3, the conversion was only around 18%. However, it is important to note that the specific activity, namely, the conversion divided by surface area measured before the catalytic tests, remains almost the same for all the catalysts prepared using the citrate route. Even for the sample in which the surfactant was introduced after that the catalyst was dried, the specific activity (0.34% g/m^2) was very close to that of catalysts prepared either without surfactant (0.47% g/m^2), or with surfactant during the synthesis (0.43% g/m^2). The role of the surfactant was different for the samples prepared using the dry-up. The catalyst RO5 exhibited the highest conversion, in accordance with its high surface area. But in terms of specific activity, this catalyst was the poorest one (Table 1). However, no difference of specific activity was noticeable for RO3 and RO6, i.e. samples for which the surfactant was introduced after that the catalysts were dried. The specific activity of the catalysts prepared by dry-up procedure without surfactant, and especially following the conventional route, was superior to the others. This means that the increase of the surface area induced by CTAB enhances the number of accessible sites, but the density (number of sites per area unit) is smaller than those in catalysts prepared by dry-up. Differences were also obtained for selectivities. The selectivity to acrylonitrile for the samples prepared following the citrate route was higher than that obtained for the samples prepared by dry-up. As discussed for the specific activity, almost no differences were denoted between RO1 and RO3. As a general tendency, the amount of propylene diminished with the increase of the selectivity to acrylonitrile, suggesting that propylene is a reaction intermediate. A higher amount of acetonitrile was observed for the samples prepared in the absence of surfactant, namely, those presenting the lowest surface area. The low selectivity of the sample prepared by dry-up could be explained by the fact that $TeMo_5O_{16}$, detected by XRD for these catalysts after reaction, is active in propane total oxidation [17,18]. Therefore the higher selectivities of the catalysts prepared by citrate method should be related to the presence of other crystalline phases, i.e. TeM_3O_{10} (M = Mo, V, Nb) (I), $Te_2M_{20}O_{57}$ (M = Mo, V, Nb) (II), $Nb_{0.09}Mo_{0.91}O_{2.80}$ (III). The role of the MoO_3 over the catalytic activity is likely not crucial since this phase disappeared during the catalytic test.

It is remarkable that these results were obtained for a space velocity 30 times higher than generally reported in the literature. In conclusion, these results prove the benefit to incorporate structure-directing agent, such as CTAB, to prepare complex mixed oxide catalysts with larger surface area. In the particular case of the ammoxidation of propane, the fact that the catalysts were active and exhibited several of the phases of the conventional catalysts shows that CTAB is a promising route to further improve this system.

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