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Oxidative dehydrogenation of ethane on Te-containing MoVNbO catalysts

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Abstract

Ethylene has selectively been obtained during the oxidative dehydrogenation of ethane on a Mo–V–Te–Nb–O mixed oxide catalyst. The catalyst was prepared hydrothermally and heat-treated at 600 °C for 2 h in a N_2-stream. For comparison, undoped and Te-doped Mo–V–Nb–O catalysts and Mo–V–Te–O and Mo–Te–Nb–O mixed oxides have also been prepared. The catalytic performance of the Mo–V–Nb–Te–O mixed oxide catalyst cannot be explained by the incorporation of Te on the surface of a Mo–V–Nb–O mixed oxide but by the presence of an orthorhombic $Te_2M_{20}O_{57}$ (M = Mo, V, Nb) crystalline phase. The role of tellurium in these catalysts is also discussed.

Keywords: Ethane oxidation to ethylene; Mo–V–Te–Nb mixed oxide catalysts

1. Introduction

V-containing catalysts exhibit interesting catalytic performances for the oxidative dehydrogenation (ODH) of ethane at temperatures below 600 °C [1-8]. From these, Mo–V–Nb mixed oxide catalysts seem to be one of the most active and selective in the ODH of ethane operating a relatively low reaction temperatures, i.e. 300–400 °C [2-5], although the incorporation of some promoters can enhance their catalytic performance [2,6]. Thus, yields of ethylene of about 50% have been reported for the ODH of ethane on Sb-promoted Mo–V–Nb mixed oxides catalysts [5].

Recently, it has been proposed that ethylene can selectively be obtained by the oxidative dehydrogenation of ethane using a multicomponent MoVTeNbO mixed oxide catalyst [7,8]. Yields of ethylene of about 75% were reported [7,8], which represents an interesting alternative to the current industrial processes used in the production of ethylene.

In this paper, we present a comparative study on the catalytic performance in the ODH of ethane over Te-containing Mo–V–Nb mixed oxide catalysts, in which Te was incorporated by different procedures. The results presented here suggest that the good catalytic performance of multicomponent MoVTeNbO catalysts is related to the presence of an orthorhombic $Te_2M_{20}O_{57}$ (M = Mo, V, Nb) bronze phase, which is mainly observed in the best catalyst.

2. Experimental

Mo–V–Nb–O, Mo–V–Te–O, Mo–Nb–Te–O and Mo–V–Nb–Te–O catalyst precursors have been prepared by hydrothermal synthesis at 175 °C for 60 h from an aqueous solution containing the corresponding salts [7–9]. The dried powders were finally heat-treated for 2 h in a N_2 stream at 425 (MVN-4 and MVNT-4) or 600 °C (MVN-6, MVT-6, MNT-6 and MVNT-6, respectively). For comparison, a MoVNbO catalyst precursor was also prepared by evaporation of an aqueous solution of the corresponding salts [6], dried at 100 °C overnight and heat-treated for 2 h in a N_2 stream at 425 or 600 °C (MVN-4L or MVN-6L, respectively).

Te-doped MoVNbO catalysts have been prepared by impregnation of heat-treated Mo–V–Nb–O samples (MVN-6 and MVN-6L) with an aqueous solution of telluric acid with a Mo/Te ratio of 1/0.025. The samples were dried at 100 °C overnight and heat-treated at 500 °C for 1 h in a N_2 stream.

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Table 1
Characteristics and catalytic behavior of Te-free and Te-containing MoVNbO catalysts

Catalyst	Composition Mo/V/Nb/Te[a]	S_{BET} ($m^2 g^{-1}$)	TPR results		W/F[c]	X_T (%)[d]	Selectivity (%)[d]		Catalytic activity[e]
			T_M (°C)[b]	H_2-uptake			C_2H_4	CO/CO_2	
MVN-4	1–0.10–0.19–0	nd	nd	nd	20	12.8	55.9	2.7	6.4
MVN-6	1–0.10–0.21–0	24.3	519	115	40	9.2	72.4	2.8	2.3
Te-MVN-6	1–0.10–0.21–0.01	21.2	nd	nd	40	13.6	72.2	2.3	3.4
MVN-4L	1–0.3–0.14–0	24.0	510; 570	131	20	21.4	60.3	3.2	10.7
MVN-6L	1–0.3–0.14–0	20.8	512	103	20	5.8	58.0	1.8	2.9
Te-MVN-6L	1–0.3–0.14–0.02	19.4	nd	nd	40	10.1	62.3	2.5	2.5
MNT	1–0–0.14–0.17	1.0	nd	nd	20	0.7	30.0	3.2	0.4
MVT	1–0.18–0–0.17	6.4	nd	nd	20	2.7	48.2	3.1	1.4
MVNT-4	1–0.14–0.17–0.19	nd	475	199	20	6.2	86.0	2.1	3.1
MVNT-6	1–0.14–0.17–0.19	9.1	500	175	20	27.3	94.9	1.5	13.7

[a] The atomic ratios of heat-treated samples were done by atomic absorption spectrometry.

[b] Temperature of the maximum hydrogen consumption (T_M) and H_2-uptake (in $cm^3 g^{-1}$) in TPR experiments at temperatures lower than 650 °C.

[c] Contact time, W/F, in $g_{cat}\,h\,mol_{C_2H_6}{}^{-1}$.

[d] Ethane conversion were achieved at 400 °C.

[e] Catalytic activity in $10^3\,mol_{C_2H_6}\,g^{-1}\,h^{-1}$.

They will be named as Te-MVN-6 and Te-MVN-6L, respectively.

The catalysts have been characterized by several physico-chemical techniques (S_{BET}, XRD, and TPR-H_2) [9].

The catalytic performance for ethane oxidation was measured at atmospheric pressure, in a fixed bed reactor, and at relatively low reaction temperature (340–400 °C), using a $C_2H_6/O_2/He$ molar ratio of 30/10/60 [7]. A blank run showed that under our reaction conditions the homogeneous reaction can be neglected.

3. Results

Table 1 shows the chemical composition and the surface areas of the catalysts. Relatively low specific surface areas have been obtained in samples heat-treated at 600 °C with respect to those observed in samples heat-treated at 425 °C.

Fig. 1 shows the XRD patterns of catalysts. XRD patterns of MVN-6 and MVN-6L catalysts confirm the presence of (V, Nb) substituted θ-Mo_5O_{14} phases, i.e. $(V_{0.07}Mo_{0.93})_5O_{14}$ and/or $(Nb_{0.09}Mo_{0.91})O_{2.80}$, and MoO_2

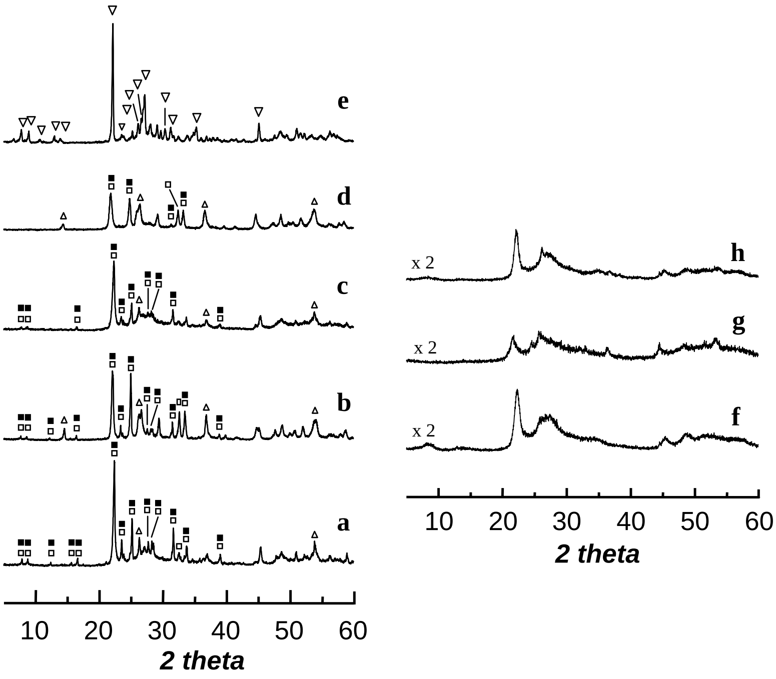

Fig. 1. XRD patterns of catalysts: (a) MVN-6; (b) MVN-6L; (c) Te-MVN-6; (d) Te-MVN-6L; (e) MVNT-6; (f) MVN-4; (g) MVN-4L; (h) MVNT-4. Symbols: $Te_2M_{20}O_{57}$ (▽); $(Mo_{0.93}V_{0.07})_5O_{14}$ (■); $Mo_{0.91}V_{0.09}O_{2.80}$ (□); MoO_2 (△).

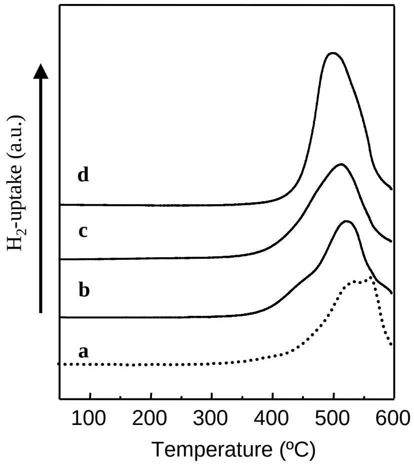

Fig. 2. TPR patterns of catalysts: (a) MVN-4L; (b) MVN-6; (c) MVN-6L; (d) MVNT-6.

(Fig. 1, patterns a and b) [3,4,10]. The intensity of these peaks changes from sample MVN-6 to sample MVN-6L, probably as a consequence of the different catalyst composition. On the other hand, the incorporation of Te on Mo–V–Nb catalysts does not modify the nature of crystalline phases (Fig. 1c and 1d).

A different XRD pattern is observed for the MVNT-6 catalyst, with peaks at $2\theta = 7.6$, 8.6, 12.2, 13.8, 16.4, 22.1, 23.5, 24.8, 26.3, 26.6, 26.9, 28.3, 30.5 31.4, 34.8 and 45.0 (Fig. 1e). This diffractogram was initially related to the presence of $(V_{0.07}Mo_{0.93})_5O_{14}$ and/or $(Nb_{0.09}Mo_{0.91})O_{2.80}$, $Te_{0.33}MO_{3.33}$ (M = Mo, V, Nb), and $TeMo_5O_{13}$ [9]. However, and according to recent SAED and HREM results [11], it should mainly be associated to a single orthorhombic $Te_2M_{20}O_{57}$ (M = Mo, V and Nb), whose structure has recently been described [12,13]. The presence of others minority phases cannot be ruled out.

Low crystalline Mo–V–Nb-containing phases are observed on samples obtained at 425 °C, which can correspond to V- and/or Nb-containing suboxides of MoO_3, which are transformed finally to (V, Nb) substituted θ-Mo_5O_{14} phases at temperatures higher than 600 °C, in good agreement to previous results reported on Mo–V–Nb–O catalysts [3,4,10]. A similar conclusion can be proposed in the case of MVNT catalysts, in which an amorphous phase is mainly observed in sample MVNT-4, which transforms into $Te_2M_{20}O_{57}$ (M = Mo, V, Nb) after the heat-treatment at 600 °C.

On the other hand, $Nb_{0.09}Mo_{0.91}O_{2.80}$ and $3MoO_2Nb_2O_5$ were only observed in MNT-6 sample, while $TeMo_5O_{16}$ (the most intense peaks) in addition to $(Mo_{0.93}V_{0.07})_5O_{14}$ and $Te_{0.33}Mo_{1-x}V_xO_{3.33}$ were observed in MVT-6 sample [9].

TPR patterns of heat-treated samples are comparatively shown in Fig. 2, while the temperatures of the maximum hydrogen consumption (T_M) obtained in the TPR experiments are shown in Table 1. We must indicate that a second broad peak is also observed at temperatures of 800 °C, but this second peak has not been considered for the general discussion. Two maximum hydrogen-uptake peaks at 525 and 570 °C are observed for sample MVN-4L (Fig. 2a), while the maximum hydrogen consumption for MVN-6 and MVN-6L samples is observed at 519 and 512 °C (with hydrogen consumptions of 115 and 103 $cm^3 g^{-1}$, respectively) (Fig. 2, patterns b and c). The peak observed at 570 °C in the TPR of sample MVN-4L could be related to Mo^{6+} species, which disappear, in samples MVN-6 and MVN-6L, as a consequence of the partial reduction of the sample during the heat-treatment at 600 °C in N_2.

In the case of MVNT-6 sample, the maximum hydrogen consumption shifted to 500 °C with a hydrogen consumption of about 175 $cm^3 g^{-1}$. No important differences in the T_M are observed when comparing the last results with those obtained with the corresponding samples heat-treated at 425 °C, i.e. MVN-4L and MVNT-4, although the highest hydrogen consumption corresponds to samples heat-treated at 425 °C. On the other hand, the hydrogen consumption observed in these samples could suggest the following trend in the oxidation state of these samples: MVNT-4 > MVNT-6 > MVN-4L > MVN-6 ≈ MVN-6L. In addition, a higher reducibility of V and Mo ions in multicomponent MoVTeNbO catalysts (MVNT-4 and MVNT-6 samples) with respect to those obtained in the Te-free catalysts can also be concluded.

The catalytic results obtained during the oxidative dehydrogenation of ethane on Te-free and Te-containing catalysts are summarized in Table 1. In all cases, ethylene and carbon oxides were mainly observed. Te-free Mo–V–Nb–O (MVN-6 and MVN-6L) catalysts are active in the ODH of ethane, although they present lower catalytic activities for ethane oxidation than the corresponding samples heat-treated at 425 °C. However, relatively low selectivities to ethylene have been achieved on these catalysts. The presence of $(V_{0.07}Mo_{0.93})_5O_{14}$ and $(Nb_{0.09}Mo_{0.91})O_{2.80}$, or a $Mo_{5-x}(V/Nb)_xO_{14}$ crystalline phase [5,6,12] could be responsible for the oxidative activation of ethane on MoVNbO catalysts obtained by heat-treatment at 600 °C. However, the presence of MoO_2 could favor the achievement of relatively low selectivities to ethylene [3].

The incorporation of a small amount of tellurium on the surface of these catalysts does not modify their catalytic performances, and selectivities to ethylene similar to those obtained in the corresponding Te-free MoVNbO catalysts have been obtained.

Higher activities and selectivities in the ODH of ethane to ethylene have been obtained on samples MVNT-4 and MVNT-6 (Table 1). In this way, a yield of ethylene of 65% has been achieved over MVNT-6 sample at a reaction temperature of 400 °C and a contact time, *W*/*F*, of 175 $g_{cat}\,h\,mol_{C_2}{}^{-1}$. This corresponds with a formation rate of ethylene over 155 $g_{C_2H_4}\,kg_{cat}{}^{-1}\,h^{-1}$, keeping selectivities close to 85% (Fig. 3), which represents a yield of ethylene higher than those reported previously on Te-free Mo–V–Nb–O based catalysts [2–6].

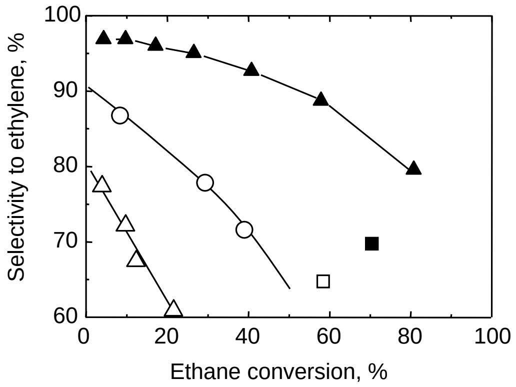

Fig. 3. Variation of the selectivity to ethylene with the ethane conversion obtained during the oxidation of ethane over MoVNbO and MoVNbTeO catalysts: MVN-4 (△); MVNT-4 (○); MVNT-6 (▲). For comparison, results reported in Refs. [2] (□) and [6] (■) have also been incorporated.

Conversely, both MNT-6 and MVT-6 samples exhibit very low catalytic activities, in good agreement to previous results obtained during the selective oxidation of propane on these catalysts [9].

4. Discussion

The catalytic performance of Mo–V–Nb mixed oxide catalysts (heat-treated at 600 °C) can be related to the presence of (V/Nb)-containing θ-Mo_5O_{14} crystalline phases [3,4,10], although the presence of MoO_2 in these catalysts could favor a large deep oxidation of ethane and/or ethylene. No important modifications in the crystalline phases and in the catalytic behavior have been observed after the incorporation of small amounts of Te on the surface of the catalysts. So, the catalytic behavior of the multicomponent MoVNbTeO catalysts (specially that obtained on the sample heat-treated at 600 °C, i.e. MVTN-6), cannot be explained by a promoter effect of Te ions. However, the good catalytic performance of this catalyst could be explained by the presence of an active and selective crystalline phase [7], which is also very active and selective in the oxidation of propane to acrylic acid [9].

The catalytic behavior in propane amm(oxidation) of MoVTeNbO catalysts was initially related to the presence of at least two different crystalline phases [9,12,14,18]: $Te_{0.33}MO_{3.33}$ and $Te_2M_{20}O_{57}$ ($M = Mo, V, Nb$). So, one could expect that these crystalline phases could be involved in the ethane oxidation.

$Te_{0.33}MO_{3.33}$ ($M = Mo, V, Nb$) bronzes, derived from the HTB-type structure [15], are minority in our catalysts. In addition, it is known that they are inactive in the propane activation but selective in the oxidation of propylene to acrolein/acrylic acid [15,16]. For this reason, this crystalline phases should be not involved in the ethane oxidation.

Orthorhombic $Te_2M_{20}O_{57}$ ($M = Mo, V, Nb$) phase, however, is mainly observed in our catalysts. It is characterized by the presence of MO_7 pentagonal bipyramids, with all of their five equatorial edges in common with MO_6 octahedra, as in $Mo_{5-x}(V/Nb)_xO_{14}$. Since $Mo_{5-x}(V/Nb)_xO_{14}$ is active and relatively selective in the ODH of ethane to ethylene [4,10], $Te_2M_{20}O_{57}$ can be considered as the active and selective crystalline phase in the oxidative activation of ethane on multicomponent Mo–V–Nb–Te–O catalysts. In addition, $Te_2M_{20}O_{57}$ can also be proposed as the active and selective crystalline phase during the oxidation and ammoxidation of propane on MoVNbTeO catalysts prepared by hydrothermal synthesis [9,11,13,17].

The role of Te in the most active and selective catalyst should be not directly involved in the ethane activation but in the formation of an active and selective crystalline phase for the oxidative activation of both ethane and propane, i.e. $Te_2M_{20}O_{57}$, and for the elimination of non-selective Mo-containing crystalline phases, i.e. MoO_2 and/or other Mo–V–Nb–O related compounds, generally proposed in Te-free MoVNbO mixed oxide catalysts [2–6,10].

In conclusion, Mo–V–Nb–Te–O mixed oxide catalyst, prepared by hydrothermal synthesis and heat-treated at 600 °C in N_2 stream, presents selectivities to ethylene higher than 80% at ethane conversions higher than 80%, operating at relatively low reaction temperatures (340–400 °C). This catalytic behavior can be explained by the presence of relatively high amounts of tellurium cations, which favors the formation of a highly selective crystalline phase, i.e. $Te_2M_{20}O_{57}$ ($M = Mo, V, Nb$) and the elimination of other Mo–V–Nb–O non selective crystalline phases, specially MoO_2.

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