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The selective oxidative dehydrogenation of ethane over hydrothermally synthesised MoVTeNb catalysts†

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Mo–V–Te–Nb metal oxide catalysts prepared by hydrothermal synthesis and heat-treated in N_2 at high temperatures (600–700 °C) show high activity and selectivity for the oxidative dehydrogenation of ethane to ethene. Yields of ethene of 75% have been obtained at 400 °C on the best catalysts.

The oxidative dehydrogenation (ODH) of short chain alkanes is an interesting alternative way for olefin production. In the ODH of ethane, the reaction conditions and the type of mechanism strongly depend on the catalytic systems:[1–4] (i) non-reducible catalysts (*i.e.* Li/MgO based) operating at reaction temperature higher than 600 °C;[2–4] and (ii) reducible metal oxides, working at reaction temperatures lower than 550 °C.[1–3] In the last case, Mo–V–Nb based catalysts appear to be one of the most promising materials at reaction temperature lower than 450 °C.[5,6] Thus, ethane conversions of 73% with selectivity to ethylene of 71% were reported using Sb-containing Mo–V–Nb mixed oxides.[6]

Recently, Ueda *et al.* proposed the hydrothermal synthesis of Mo–V–M–O (M = Al, Fe, Cr and Ti) catalysts.[7] These catalysts (heat-treated at 410 °C for 2 h in a nitrogen stream) presented relatively high selectivities to ethylene and acetic acid, but at a relatively low ethane conversion (yields to partial oxidation products of 10.5% were reported).

High-throughput synthesis and screening methods have been recently used to develop new catalytic systems for oxidation reations.[8] In this way, it has been reported that MoVTeNb mixed oxides are one of the most selective catalysts for the ODH of ethane.[9] We report here the catalytic performance of a Mo–V–Te–Nb oxide, prepared hydrothermally, and how the heat-treatment temperature of catalyst strongly influences its catalytic behaviour during the oxidation of ethane to ethylene.

MoVTeNbO catalysts were prepared by a hydrothermal method using vanadyl sulfate, niobium oxalate, ammonium hexamolybdotellurate and water with a Mo : V : Te : Nb atomic ratio of 1 : 0.36 : 0.17 : 0.12.[9] The gels were autoclaved in Teflon-lined stainless-steel autoclaves at 175 °C for 60 h. The resulting precursors were filtered, washed, dried at 80 °C for 16 h and heat-treated in the 500–750 °C temperature interval during 2 h in N_2-stream. X-Ray diffraction has been used to identify the crystalline phases of catalysts.[10,11]

The catalysts were tested in a fixed bed quartz tubular reactor, working at atmospheric pressure, at temperature ranging from 340 to 400 °C. The flow rate and the amount of catalyst were varied in order to achieve different ethane conversion levels. The feed consisted of a mixture of ethane–oxygen–helium with a molar ratio of 30 : 10 : 60 and 30 : 30 : 40. The catalytic tests refer to steady-state conditions; no deactivation was observed over about 120 h time-on-stream. A blank run showed that under our reaction conditions the homogeneous reaction could be neglected.

The catalytic results for the oxidative dehydrogenation of ethane on MoVTeNbO catalysts heat-treated at different temperatures are summarised in Table 1. Ethylene, CO and CO_2 were the main reaction products. However, oxygenated products other than CO_x were not observed. The catalytic results presented here show selectivities to ethylene higher than those obtained on the corresponding ternary (Mo–V–Nb–O or Mo–V–Te–O) catalysts. Moreover, the catalytic performance of these catalysts strongly depends on the temperature used in the heat-treatment. Thus, the yield of ethylene increases with the calcination temperature showing a maximum for the sample heat-treated at 650 °C. However, higher temperatures favours the achievement of less active catalysts. Since similar surface areas were observed for these catalysts (6–8 m² g⁻¹), the catalytic behaviour could partially be related to the nature of crystalline phases of catalysts.

Fig. 1 shows the variation of the selectivity to ethylene with the ethane conversion obtained during the oxidative dehydroge-

Table 1 ODH of ethane at 360 °C on MoVTeNbO catalysts[a]

Heat-treatment temperature[b] (°C)	Ethane conversion (%)	Selectivity (%) C_2H_4	CO	CO_2
550	26.1	93.8	3.7	2.5
600	29.4	94.4	3.4	2.2
650	49.0	94.3	3.5	2.2
	88.5[c]	80.8	12.4	6.8
700	38.0	95.3	2.8	1.9
750	16.3	95.7	2.5	1.8

[a] Conventional flow reactor, integral reactor mode; $C_2H_6:O_2:He$ molar ratio of 30 : 10 : 60 (W/F = 70 g_{cat} h $mol_{C_2}^{-1}$). [b] Catalyst heat-treatment temperature. [c] $C_2H_6:O_2:He$ molar ratio of 30 : 30 : 40 (W/F = 70 g_{cat} h $mol_{C_2}^{-1}$) and a reaction temperature of 400 °C.

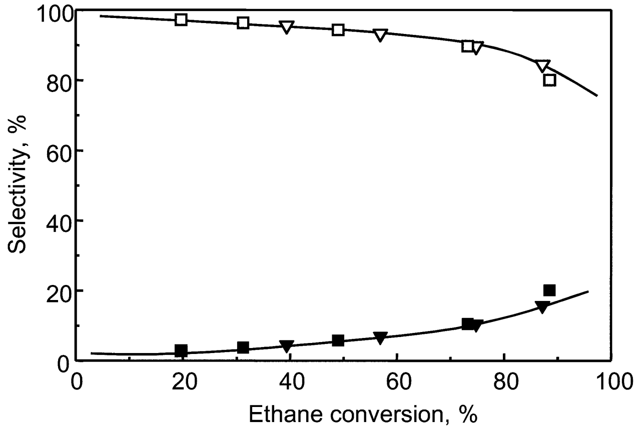

Fig. 1 Variation of the selectivity to the main reaction products, *i.e.* C_2H_4 (▽, □) and CO_x (▼, ■) with the ethane conversion obtained during the oxidation of ethane on a MoVTeNbO catalyst (heat-treated at 650 °C). Experimental conditions: 340–400 °C temperature interval; $C_2H_6:O_2:He$ molar ratio of 30 : 10 : 60 (▽, ▼) or 30 : 30 : 40 (□, ■).

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† Electronic supplementary information (ESI) available: Fig. S1: XRD pattern of sample heat-treated at 650 °C before (a) and after (b) the catalytic tests. See http://www.rsc.org/suppdata/cc/b2/b204037a/

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nation of ethane over the sample heat-treated at 650 °C. From these results, yields of *ca.* 75% with selectivities to ethylene of 85% have been achieved. These yields of ethylene are higher than those reported in the literature patent on Sb-containing MoVNb based catalysts.[6] On the other hand, space time yield (STY) of ethylene of 286 $g_{C_2H_4}$ kg_{cat}^{-1} h^{-1} can be obtained at 400 °C and a $C_2H_6:O_2:He$ molar ratios of 30 : 30 : 40.

Fig. 2 shows the XRD patterns of samples heat-treated in N_2 in the 500–750 °C temperature interval. The sample obtained at the lower temperature show a sharp diffraction peaks at 2θ *ca.* 22, in addition to a broad peak at 27.2 characteristics of Anderson-type heteropolyanion units (Fig. 2(a)).[7] The samples heat-treated at temperatures higher than 550 °C present new crystalline phases, as a consequence of the solid state reaction. Thus, the presence of $TeMo_5O_{16}$ and/or $TeMo_4O_{13}$, $(Mo_{0.93}V_{0.07})_5O_{14}$, $Nb_{0.09}Mo_{0.91}O_{2.80}$ and MoO_3 can be proposed (Fig. 2, spectra b–d).‡ In addition to these, the peaks observed at 2θ = 22.1, 28.2, 36.2, 45.2, 50.0° can be related to the presence of a new crystalline MoVTe and/or MoVTeNb phase.[11] The presence of a peak at 45.1°, in addition to a small peak at 28.2 in the sample heat-treated at 500 °C could indicate the incipient formation of this new crystalline phase at low temperature. In the sample heat-treated at high temperature there is a decrease of the intensities of some of the most important reflections with the appearance of new reflections related to the presence of $VOMoO_4$ (Fig. 2(f)). On the other hand, no changes in the spectra presented in Fig. 2 were observed for the catalysts after the catalytic tests.

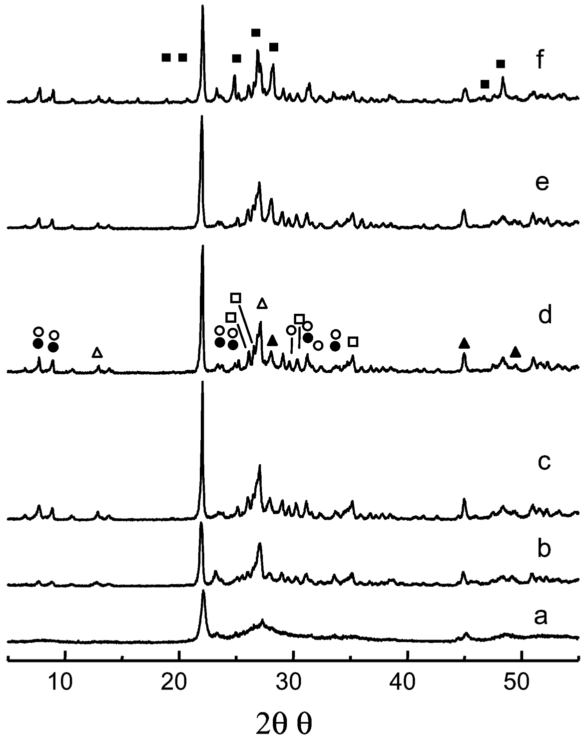

Fig. 2 XRD patterns of MoVTeNbO catalysts heat-treated at different temperatures: (a) 500; (b) 550; (c) 600; (d) 650; (e) 700 and (f) 750 °C. Symbols: MoO_3 (△), $TeMo_5O_{16}$ and/or $TeMo_4O_{13}$ (□), $(Mo_{0.93}V_{0.07})_5O_{14}$, (●), $Nb_{0.09}Mo_{0.91}O_{2.80}$ (○), $VOMoO_4$ (■) and the new crystalline phase (▲) (ref. 10).

Since the XRD patterns of these catalysts show changes depending on the heat-treatment temperature, it can be concluded that both the ethane conversion and the selectivity to ethene increase with the calcination temperature in a parallel way than the formation of the main of crystalline phases. The high efficiency of these catalysts could be related to the formation of a (V, Nb) substituted θ-Mo_5O_{14} phases[12] or a $Mo_{5-x}(V/Nb)_xO_{14}$,[13] which seem to be favoured in the 600–700 °C interval.[14] On the other hand, one of the roles of Te ions could be related to the elimination of non-selective Mo-containing crystalline phases (*i.e.* MoO_2 and related compounds, proposed in Te-free MoVNbO mixed oxide catalysts[5,12]) favouring the formation of inactive alkane oxidation phases, *i.e.* $TeMo_5O_{16}$ or the new MoVTe and MoVTeNb crystalline phases.[11] This hypothesis is speculative and confirmation will require detailed investigations, although it does explain the specificity of these catalysts in the ethylene formation.

In conclusion, MoVTeNb metal oxide catalysts, prepared by hydrothermal synthesis and heat-treated at high temperatures (500–750 °C) in N_2, present selectivities to ethylene higher than 80% at ethane conversions levels higher than 80%, operating at relatively low reaction temperatures (340–400 °C). Therefore, highly crystalline MoVTeNbO catalyst is an alternative for the ethylene synthesis using a low-cost feedstock such as ethane.

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Notes and references

‡ $TeMo_5O_{16}$ (JCPDS: 31-874); $TeMo_4O_{13}$ (JCPDS: 31-1372); $(Mo_{0.93}V_{0.07})_5O_{14}$ (JCPDS: 31-1437); $Nb_{0.09}Mo_{0.91}O_{2.80}$ (JCPDS: 27-1310); MoO_3 [JCPDS, 5-508]; $VOMoO_4$ [JCPDS: 18-1454].

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