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The oxidative dehydrogenation of ethane over molybdenum–vanadium–niobium oxide catalysts: the role of catalyst composition

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The oxidative dehydrogenation of ethane has been studied at atmospheric pressure using molybdenum–vanadium–niobium oxide catalysts in the temperature range of 350–450°C. The presence of all three oxides together is necessary in order to have active and selective catalysts. The best results have been obtained using a mixture having a Mo : V : Nb ratio of 19 : 5 : 1. Our studies of the variation of oxide composition suggest that the active phase is based on molybdenum and vanadium. Niobium enhances the intrinsic activity of the molybdenum–vanadium combination and improves the selectivity by inhibiting the total oxidation of ethane to carbon dioxide. The apparent activation energies for the conversion of ethane to ethylene, carbon monoxide and carbon dioxide were 18, 27 and 17 kcal/mol, respectively. The addition of water vapor to the gas stream does not affect the product distribution on this catalyst.

Keywords: Oxydehydrogenation of ethane; Mo–V–Nb oxide catalysts

1. Introduction

The oxidative dehydrogenation of hydrocarbons is of particular significance in processes to produce olefins. Because of the large resources of natural gas, the oxidative coupling of methane to higher hydrocarbons has been intensively investigated. Since ethane is the second major component of natural gas and also a main product in many methane coupling reactions, its transformation to ethylene at low temperatures is of considerable interest. When used as catalysts, oxides of transition metals, such as molybdenum [1] and vanadium [2,3], have shown moderate ethylene selectivity for this reaction. Alkali earth metal oxides, for example calcium and magnesium oxides, together with alkali metal oxides, such as sodium or lithium oxides, are also used as oxidehydrogenation catalysts [4]. Although temperatures as high as 600°C were needed, good selectivities at high conversions could be achieved. It has been reported [5,6] that molybdenum, vanadium and niobium oxides, when used together as catalysts, are highly selective for the oxidehydrogenation of ethane at 300–400°C. This temperature range is much lower than the operating temperature range of the catalysts listed above.

In this paper we present the study of oxidative dehydrogenation of ethane to ethylene catalysed by mixtures of molybdenum, vanadium, niobium oxides. We show that all three components are necessary to have a selective and active catalyst. By means of variation of the catalyst composition we show that niobium, when added to a molybdenum–vanadium oxide mixture, enhances the activity of the catalyst and improves the selectivity by reducing the total oxidation to carbon dioxide. The activation energies of formation of ethylene, carbon monoxide and dioxide over two different catalysts indicate that the products are formed via the same routes on the two catalysts. The lower reactivity of ethylene as compared to ethane suggests that most of the carbon oxides are coming directly from the alkane at low conversion. Although water is produced in situ during the oxidehydrogenation, we show that adding steam in the gas feed has no effect on the product distribution.

2. Methods

2.1. CATALYST PREPARATION

Catalysts comprising molybdenum–vanadium–niobium oxide in the desired ratios were prepared as follows. The calculated amount (for example 10 mmol) of niobium pentachloride ($NbCl_5$, Johnson Matthey 99%) was hydrolysed in water (50 ml) and the turbid suspension was neutralized with ammonium hydroxide (NH_4OH, Aldrich). The white precipitate was filtered, washed with water and dissolved in a hot solution of oxalic acid dihydrate (50 mmol) ($HO_2CCO_2H \cdot 2H_2O$, Aldrich 99%). This was added to an aqueous solution (50 ml) of ammonium metavanadate (NH_4VO_3, Johnson Matthey 99%) (50 mmol) at 90°C, followed by an aqueous solution of ammonium paramolybdate ($(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, Johnson Matthey 99%). The green slurry obtained was heated with stirring until the water was evaporated. The residue was dried for 16 h at 120°C, followed by the calcination in air at 400°C for 4 h. The fine powders obtained after that treatment were grey to dark blue. Similarly, catalysts comprising only two of the three metals were prepared using the same sequence and concentration as described above. The powders were pelletized, crushed and sieved to fractions of 0.25–0.42 mm (35–60 mesh) before testing their catalytic activity.

To describe the composition of the catalysts, the following convention is used: $Mo\alpha V\beta Nb\delta Ox$, were α, β and δ are the atomic proportions of the metals, based on the quantities of the precursors used in the preparation. For example, in Mo19N5Nb1Ox the Mo : V : Nb atomic ratio is 19 : 5 : 1.

2.2. CATALYST CHARACTERIZATION

The surface areas (BET) of the catalysts were measured with a flow apparatus equipped with a thermal conductivity detector. Except for the V5Nb1Ox which has a surface area of 22 m^2/g, the surface areas of the catalysts were in the range of 7.5–12 m^2/g.

The pore size distribution of the Mo19V5Nb1Ox and V5Nb1Ox catalysts were determined at liquid nitrogen temperature (−196°C) using a Micromeritic surface-area pore volume analyzer 2100D instrument. These measurements were performed at the University of Oulu in Finland. The pore size averages were 6.5 and 7.0 nm respectively.

The catalysts compositions at the surface region were determined by X-ray photoelectron spectroscopy (XPS) using a Perkin-Elmer Phi 5300 ESCA instrument. The catalysts were pressed into a gold foil before the XPS analysis. The samples were illuminated by 1253.6 eV X-ray photons from a magnesium anode. The error range for the surface composition determined by XPS was ±20%. The Mo : V : Nb ratios at the surfaces of Mo6V3Nb1Ox, Mo8V2Nb1Ox and Mo19V5Nb1Ox were, within the XPS error range, equivalent to the theoretical bulk compositions.

In order to verify the equivalence between the theoretical and the actual bulk compositions as well as the reliability of the catalyst preparation, the bulk composition of three different batches of Mo8V2Nb1Ox were determined by atomic absorption. The resulting Mo : V : Nb proportions were 7.3 : 1.3 : 1.0, 7.8 : 1.8 : 1.0 and 7.5 : 1.8 : 1.0.

2.3. CATALYST TESTING

The catalysts were tested under continuous flow conditions at atmospheric pressure. The tubular quartz reactor used had an inner diameter of 0.4 cm and a length of 20 cm. The reactor outlet was welded to quartz capillary tube (1 mm i.d.) so that the products could be rapidly removed from the heated zone. The catalysts were packed on a thin layer of quartz wool. The void volume was minimized by the introduction of a thermocouple covered with a 3 mm o.d. quartz tube in the center of the reactor. The temperature monitored at the top of the catalyst bed was controlled within ±1°C. The reagent gases (Matheson, CP grade) were mixed in the required amounts using mass flow controllers (Porter Instrument). When needed, water vapor was introduced at the top of the reactor through a heated (140°C) capillary tube connected to a syringe pump (Harvard Apparatus)

In the experiments, 0.50 g of catalysts were used with ethane : oxygen ratios of 10 : 1 to 2 : 1 and a flow rate of 50 ml/min, corresponding to a space velocity of 6820 h^{-1} at 20°C. The studies were performed under atmospheric pressure at temperatures varying from 350 to 450°C. When steam was involved in the feed, it was added when the set temperature was reached. Ethane : oxygen : steam ratios of

10 : 1 : 1.1 to 1 : 1 : 5 were used with total flow rates of 51–55 ml/min. For comparison, reactions were run in the absence of water, while replacing it by an equal flow of helium.

The products were analyzed by a gas chromatograph equipped with TCD detectors. Porapak Q (2 m, 25°C) was used to separate CO_2, C_2H_4 and C_2H_6. Molecular sieve 13X (2 m, 25°C) was used to separate O_2 and CO. Both columns were connected in series through a switching by-pass valve to isolate the MS-13X column while the CO_2 and the hydrocarbons eluted from the Porapak column. The carbon balance was 100 ± 5%.

3. Results

3.1. EFFECT OF THE CATALYST COMPOSITION

The conversion of ethane and the product selectivities, that have been determined at 390°C with a total flow rate of 50 ml/min of ethane and oxygen in a 10 : 1 ratio, are displayed in table 1 for the catalysts Mo19V5Nb1Ox, Mo19V5Nb0.1Ox, Mo8V2Nb1Ox and Mo6V3Nb1Ox. Among these mixtures, Mo19V5Nb1Ox shows the highest ethylene selectivity, reaching about 89% at 4.5% ethene conversion. Using Mo19V5Nb1Ox as a reference, an approximate ratio of 4 : 1 is kept between molybdenum and vanadium but the amount of niobium is increased from 0.04 to 0.09 in the Mo8V2Nb1Ox catalyst, with which 86% selectiv-

Table 1
Effect of the catalyst composition on conversion and selectivity (0.50 g of catalysts, 390°C, $C_2H_6 : O_2 = 10 : 1$, 50 ml/min)

Catalyst (surface area)	Time on stream (min)	Conversion (%)	Selectivity (%) for		
			C_2H_4	CO	CO_2
Mo19V5Nb1Ox	15	4.5	88	8	4
(8.4 m^2/g)	283	4.4	89	8	3
	1463	4.7	89	8	3
	4133	4.2	90	7	3
Mo8V2Nb1Ox	5	4.7	82	13	5
(12 m^2/g)	96	4.9	86	10	4
	1338	4.4	86	10	4
Mo6V3Nb1Ox	11	7.7	77	17	6
(10 m^2/g)	180	6.6	77	18	5
Mo19V5Nb0.1Ox	60	1.2	83	15	2
(8.3 m^2/g)	180	1.1	83	15	2

ity for ethylene are observed at 4.7% ethane conversion. However, if the amount of niobium is ten times smaller than it is in Mo19V5Nb1Ox catalyst, the activity of the resulting catalyst drops dramatically: only 1.2% of ethane are converted over the Mo19V5Nb0.1Ox composition catalyst. If the amount of niobium is kept at 0.1 but the ratio between molybdenum and vanadium is changed to 2 : 1, as it is in the Mo6V3Nb1Ox catalyst, 7% of ethane are converted with 77% ethylene selectivity.

The Mo6V3Nb1Ox catalyst prepared in our laboratory shows a slightly smaller ethylene selectivity and a higher activity than the selectivity of 81% at 3.0% conversion reported by Burch et al. [6] for that composition in the same experimental conditions. We have not been able to reproduce the 100% ethylene selectivity obtained by Thorsteinson et al. [5] with a Mo8V2Nb1Ox catalyst, although the experimental conditions are, in that case, very dissimilar as compared to the conditions used in our experiments.

3.2. EFFECT OF THE TEMPERATURE

Fig. 1 displays the temperature dependence of ethane conversion to ethylene, carbon dioxide and carbon monoxide between 350 and 450°C for the Mo8V2Nb1Ox catalyst with 50 ml/min of ethane/oxygen in a 10 : 1 ratio. The apparent activation energies are found to be 20 ,16 and 31 kcal/mol ±2 kcal/mol for the conversion of ethane to ethylene, carbon dioxide and carbon monoxide, respectively. Similarly, values of 18, 17 and 27 kcal/mol ±2 kcal/mol are measured over Mo19V5Nb1Ox for ethylene, carbon dioxide and carbon monoxide, respectively (fig. 1). Below 350°C, the rates are too low and have not been measurable reli-

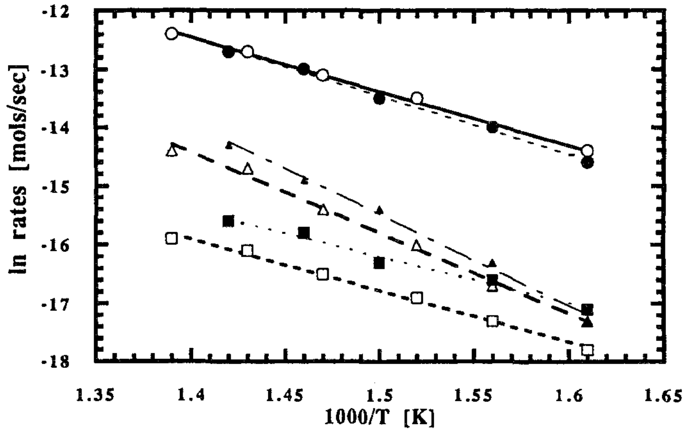

Fig. 1. Arrhenius plots for the transformation of ethane to ethylene, carbon monoxide and dioxide over the Mo19V5Nb1Ox and Mo8V2Nb1Ox (0.50 g of the catalysts, C_2H_6 : O_2 = 10 : 1, total flow rate: 50 ml/min): (○) C_2H_4 on Mo19V5Nb1Ox; (●) C_2H_4 on Mo8V2Nb1Ox; (△) CO on Mo19V5Nb1Ox; (▲) CO on Mo8V2Nb1Ox; (□) CO_2 on Mo19V5Nb1Ox; (■) CO_2 on Mo8V2Nb1Ox.

ably. At temperatures higher than 450°C, the sintering of the catalysts occurs with a significant reduction of the surface area. To determine what was the major source of carbon oxides, the reactivities of ethane and ethylene were compared at 390°C over the Mo19V5Nb1Ox catalyst (table 2). The rate of oxidation of ethylene was slightly lower than that of ethane.

3.3. EFFECT OF THE ETHANE TO OXYGEN RATIO

In these experiments, the Mo8V2Nb1Ox and the Mo19V5Nb1Ox composition catalysts are exposed at 390°C to 50 ml/min of ethane and oxygen in ratios of 10 : 1 and 2 : 1 (table 3). The conversion of ethane is increased from 4.9 to 7.6% over Mo8V2Nb1Ox and from 4.4 to 6.4% over Mo19V5Nb1Ox when a 2 : 1 gas mixture is used. The product distribution is only slightly affected by the change in the feed composition. The catalyst containing more niobium has its ethylene selectivity decreased from 86 to 81% while the carbon monoxide and carbon dioxide selectivities are increased from 10 to 12% and 4 to 7%, respectively. However, no significant changes are found in the selectivities with the Mo19V5Nb1Ox catalyst. About 90% of the ethane converted is transformed to ethylene, 8 and 2% to carbon monoxide and carbon dioxide, respectively.

3.4. EFFECT OF THE WATER

Although water is formed during the reaction, the effect of the addition of water vapor in the gas stream has been investigated. It has been reported that steam has an inhibiting effect on the total oxidation of ethane to carbon oxides over vanadium pentoxide [7]. A similar effect has been observed for methane coupling on calcium–nickel–potassium oxide catalysts [8]. In our experiments, a 50 ml/min flow of ethane : oxygen : steam in a 10 : 1 : 1.1 ratio is passed over the Mo19V5Nb1Ox at 390°C (table 4). The product distribution is compared to the results obtained when the water is replaced by helium. Whether or not the water is present, selectivities of about 91, 6 and 3% are obtained for the ethylene, carbon monoxide and carbon dioxide, respectively. In order to make more

Table 2
Comparison of the reactivity of ethane and ethylene at 390°C over Mo19V5Nb1Ox (0.5 g of catalysts, total flow rate: 50 ml/min)

Time on stream (min)	Conversion of C_2H_6 (%)	Conversion of C_2H_4 (%)	Selectivity (%) for		
			C_2H_4	CO	CO_2
15	–	3.6	–	82	18
317	–	3.0	–	82	18
10	4.5	–	88	8	4
205	4.4	–	89	8	3

Table 3
Effect of the ethane/oxygen ratio on conversion and selectivity (0.50 g of catalysts, 390°C, total flow rate: 50 ml/min)

Catalysts ($C_2H_6 : O_2$)	Time on stream (min)	Conversion (%)	Selectivitiy (%) for		
			C_2H_4	CO	CO_2
Mo8V2Nb1Ox	5	4.7	82	13	5
(10 : 1)	96	4.9	86	10	4
Mo8V2Nb1Ox	4	9.5	75	17	8
(2 : 1)	151	7.6	81	12	7
Mo19V5Nb1Ox	15	4.5	88	8	4
(10 : 1)	283	4.4	89	8	3
Mo19V5Nb1Ox	15	6.2	89	8	3
(2 : 1)	200	6.4	90	8	2

detectable the possible small effects, the same catalyst has been exposed to ethane : oxygen : steam helium feeds of 10 : 10 : 30 : 50 and 10 : 10 : 50 : 30 at 430°C (table 5). As described previously, an experiment is performed during which the water is replaced by helium. Again, no significant change occurs and the product distribution remains at 78–79% of ethylene, 14–17% of carbon monoxide and 7–4% of carbon dioxide.

3.5. STABILITY OF THE CATALYSTS

Fig. 2 reflects the time dependence of the activity of the Mo6V3Nb1Ox, Mo8V2Nb1Ox and Mo19V5Nb1Ox catalysts at 390°C with 50 ml/min of a 10 : 1 mixture of ethane and oxygen. The Mo6V3Nb1Ox oxide mixture loses part of its initial activity while the other two catalysts maintain their initial activity. The comparison of the surface areas between the fresh and used catalysts does not show any difference (table 6). In addition the XPS studies performed on the fresh and the used catalysts do not display any significant variation in the molybdenum–

Tabel 4
Effect of water at 390°C over the Mo19V5Nb1Ox catalyst (0.50 g)

Feed ratio of $C_2H_6 : O_2 : H_2O : He$ (55 ml/min)	Time on stream (min)	Selectivity (%) for		
		C_2H_4	CO	CO_2
10 : 1 : 1.1 : 0	11	89	8	3
	137	93	4	3
	376	92	6	2
10 : 1 : 0 : 1.1	5	87	9	4
	88	90	7	3
	361	91	6	3

Tabel 5
Effect of water at 430°C over the Mo19V5Nb1Ox catalyst (0.50 g)

Feed ratio of $C_2H_6 : O_2 : H_2O : He$ (55 ml/min)	Time on stream (min)	Selectivity (%) for		
		C_2H_4	CO	CO_2
10 : 10 : 30 : 50	20	77	16	7
	118	79	14	7
10 : 10 : 50 : 30	60	77	16	7
	120	78	15	7
10 : 10 : 0 : 80	24	79	16	5
	97	79	17	4

vanadium–niobium proportions at the surface region after the reaction (table 6). The Mo : V : Nb ratios are, within the XPS error range of ±20%, equivalent to the bulk composition. However, the amount of carbonaceous species present on the used catalysts are increased as compared to the fresh samples.

3.6. BINARY CATALYSTS

To determine to what extent the simultaneous presence of the three oxides of molybdenum, vanadium and niobium is required and how they interact with each other, we prepared a series of catalysts composed of two of the three transition metals (table 7). The atomic proportions between any two metals were held fixed relative to the proportions in Mo19V5Nb1Ox as a reference. Each binary mixture was tested at 390 and 450°C with 50 ml/min of ethane and oxygen in a 10 : 1 ratio.

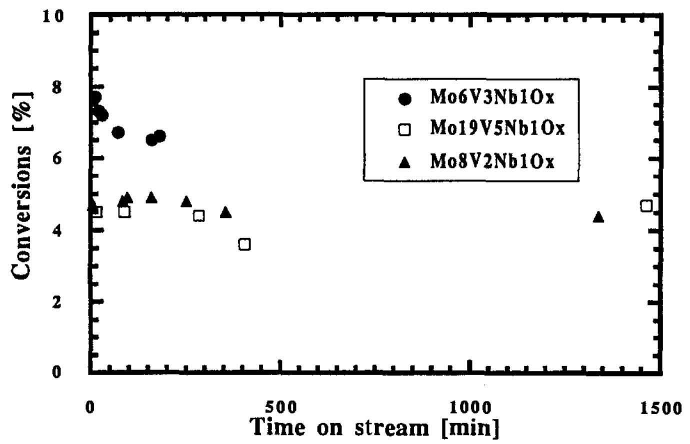

Fig. 2. Ethane conversions as a function of time over the Mo6V3Nb1Ox, Mo8V2Nb1Ox and Mo19V5Nb1Ox at 390°C (0.50 g of the catalysts, $C_2H_6 : O_2 = 10 : 1$, total flow rate: 50 ml/min).

Table 6
Surface composition of fresh and used[a] catalysts determined by XPS

Catalysts,	Surface area of the used[a] (unused) catalysts	Mo : V : Nb unused cat.	Mo : V : Nb used cat.	$C_{unused} : C_{used}$
Mo6V3Nb1Ox	10 m^2/g (10 m^2/g)	9 : 3 : 1	9 : 3 : 1	1 : 3
Mo8V2Nb1Ox	12 m^2/g (12 m^2/g)	11 : 3 : 1	11 : 2 : 1	–[b]
Mo19V5Nb1Ox	8.4 m^2/g (8.3 m^2/g)	14 : 3 : 1	14 : 3 : 1	1 : 2

[a] The Mo6V3Nb1Ox, Mo8V2Nb1Ox and the Mo19V5Nb1Ox catalysts (0.50 g) have been exposed at 390°C to 50 ml/min of $C_2H_6 : O_2 = 10 : 1$ for 180, 1338 and 4133 min, respectively.
[b] Not measured.

In the case of the Mo4V1Ox mixtures, one batch was prepared in the presence of one equivalent of oxalic acid relatively to the vanadium. This was to simulate the possible reductive property of the organic counterpart of the niobium salt in the preparation step of the Mo19Nb1Ox catalyst. Although the three component catalyst shows a 4–5% ethane conversion at 390°C, few binary mixtures yield 2% conversion at this temperature. Only the V5Nb1Ox converts 3% of the ethane at 390°C. The Mo19Nb1Ox is the least active catalyst of the series with 0.5% of ethane conversion and 91% selectivity for ethylene at 390°C while, at 450°C, the conversion is 1.8% with 72% selectivity for ethylene. In the case of the Mo4V1Ox, the presence of five equivalents of oxalic acid during the catalyst preparation does not severely affect the product distribution. At 390°C, a conversion of 1.7% with 79% ethylene selectivity is obtained, while 1.1% of ethane is transformed with 78% ethylene selectivity over the catalyst prepared without the oxalic acid. Although

Table 7
Activity and selectivity of the binary catalysts (0.50 g of catalysts, $C_2H_6 : O_2 = 10 : 1$, total flow rate: 50 ml/min)

Catalysts (surface)	Temp. (°C)	Conversion (%)	Selectivity (%) for		
			C_2H_4	CO	CO_2
Mo4V1Ox	390	1.1	78	20	2
(10 m^2/g)	450	5.4	70	26	4
Mo4V1Ox (a)	390	1.7	79	16	5
(7.5 m^2/g)	450	3.0	74	22	4
V5Nb1Ox	390	3.0	43	52	5
(22 m^2/g)	450	6.5	39	57	4
Mo19Nb1Ox	390	0.5	91	9	–
(11 m^2/g)	450	1.8	72	22	6

[a] Catalysts prepared in the presence of 1 equivalent of oxalic acid relatively to the vanadium.

the most active mixture of the series, the V5Nb1Ox shows the worst selectivity. Only 43% of the ethane converted are transformed to ethylene at 390°C, while carbon monoxide is the major product with 52% selectivity.

3.7. EFFECTS OF FILM AND PORE DIFFUSION LIMITATIONS

To rule out the effect of gas film diffusion limitations on the conversions and selectivities presented above, the Wheeler [9] criterion is used. The first order rate constant for a completely diffusion limited reaction can be approximated using the equation

$$k_f = 10(V_L/Ma^3P)^{0.5}, \tag{1}$$

where V_L is the linear gas velocity, M the average molecular weight, a the pellet size and P the total pressure. According to Wheeler, film diffusion limitations do not affect the conversions results if the experimental first order rate constant is less than 10% of the k_f value.

Assuming that the reactions are following a first order kinetic on all the catalysts, the experimental rate constants were calculated and compared to the values for completely film diffusion limited reactions (table 8). The experimental rate constants were always much less than 10% of the k_f values by several orders of magni-

Table 8
Comparison of the experimental rate constant k_{exp} with the constant k_f for completely film diffusion limited reactions

Catalysts	Temp. (°C)	k_f [a] (s^{-1})	k_{exp} [a,c] (s^{-1})
Mo19V5Nb1Ox	350	1111	0.065
Mo19V5Nb1Ox	400	1162	0.309
Mo19V5Nb1Ox	450	1196	0.727
Mo19V5Nb1Ox	390	1140 [b]	0.279 [b]
Mo8V2Nb1Ox	350	1112	0.059
Mo8V2Nb1Ox	390	1150	0.193
Mo8V2Nb1Ox	450	1199	0.482
Mo8V2Nb1Ox	390	1140 [b]	0.339 [b]
Mo6V3Nb1Ox	390	1149	0.343
Mo19V5Nb0.1Ox	390	1149	0.052
Mo4V1Ox	390	1149	0.047
Mo4V1Ox	450	1199	0.259
V5Nb1Ox	390	1149	0.131
V5Nb1Ox	450	1199	0.314
Mo19Nb1Ox	390	1149	0.021
Mo19Nb1Ox	450	1199	0.085

[a] Ethane to oxygen ratio of 10 : 1, unless indicated otherwise.
[b] Ethane to oxygen ratio of 2 : 1
[c] $k_{exp} = -S \ln(1-X)$, where S is the space velocity (s^{-1}) and X the ethane conversion.

tude. Therefore it can be concluded that film diffusion limitations do not affect the results presented in this paper.

When the catalysts were introduced in the reactor as fine powders, pressure gradients were observed. To avoid this, the catalysts were pelletized, crushed and sieved to fractions of 35–60 mesh. Although the possible effects of pore diffusion limitations could not be tested experimentally, they were evaluated by calculations, in terms of effectiveness factor (eq. (2)) [10], for the Mo19V5Nb1Ox and V5Nb1Ox catalysts at temperatures from 350 to 340°C,

$$\eta = (3/\Phi_s)(1/\tanh \Phi_s - 1/\Phi_s). \tag{2}$$

The Thiele modulus Φ_s is defined as [10]

$$\Phi_s = r(k\rho/D_e)^{0.5}, \tag{3}$$

where r is the radius of the pellets, k the rate constant, ρ the catalyst density and D_e the effective diffusion coefficient. The pore diffusion limitation is considered to be negligible when the effectiveness factor η is greater than 0.95 and completely absent when η is unity.

The determination of the diffusion coefficient D_e needs, among other parameters, the average pore radius as well as the tortuosity factor and the porosity of the catalysts. For industrial catalysts, the tortuosity factor is in the range of 2–7, whereas the porosity value is between 0.2 and 0.7. As the tortuosity and the porosity of the Mo19V5Nb1Ox and V5Nb1Ox catalysts were not known, the calculations of the effectiveness factor η were performed using 2 and 7 for the tortuosity, respectively 0.2 and 0.7 for the porosity. The evaluated η values for these two catalysts were always greater than 0.98. Therefore it can be concluded that the pore diffusion limitations have a negligible effect on the conversion and selectivities results. It is assumed that it is also the case for the other catalysts tested in this paper.

4. Discussion

Let us first summarize our results that have significance in interpreting the activity and the selectivity of the molybdenum–vanadium–niobium oxide catalysts for the oxidehydrogenation of ethane. We found that the presence of the three transition metal oxides is necessary to have an active and selective catalyst. An oxide mixture having the atomic proportions of 19 : 5 : 1 for molybdenum, vanadium and niobium gives the best results. Although the Mo19V5Nb1Ox is more selective than Mo8V2Nb1Ox, niobium plays an important role. The very low carbon dioxide selectivity observed on the V5Nb1Ox indicates that niobium inhibits the total oxidation of ethane. The temperature dependence of the rates of formation of ethylene, carbon monoxide and carbon dioxide has been studied between 350 and 450°C. The resulting apparent activation energies are 20, 31, 16 kcal/mol ± 2 kcal/

mol, respectively, over the Mo8V2Nb1Ox catalyst and 18, 27, 17 kcal/mol ± 2 kcal/mol, respectively, over the Mo19V5Nb1Ox. The reactivity of the starting alkane and the main product ethylene has been compared under the same experimental conditions. It appears that the alkane is slightly more reactive than the alkene. By changing the ethane : oxygen ratio from 10 : 1 to 2 : 1 at 390°C over Mo8V2Nb1Ox and Mo19V5Nb1Ox, the ethane conversion increases. This leads to a slight deterioration of the ethylene selectivity over the Mo8V2Nb1Ox catalyst but not over Mo19V5Nb1Ox. The addition of water in the feed does not significantly affect the product distribution over Mo19V5Nb1Ox. Finally, we have found that Mo6V3Nb1Ox deactivates rapidly at the beginning of a run, whereas the Mo8V2Nb1Ox and the Mo19V5Nb1Ox catalysts are much more stable.

By comparing the catalytic activities and the ethylene selectivities of the binary catalysts and the three component catalysts Mo6V3Nb1Ox, Mo8V2Nb1Ox and Mo19V5Nb1Ox, it is obvious that the three component catalysts are much more active and selective than the binary catalysts. This is in agreement with the findings of Burch and Swarnakar [6] who observed a strong improvement in the efficiency from a Mo6V3Ox to a Mo6V3Nb1Ox catalyst. Similarly, Thorsteinson et al. [5] found that the Mo8V2Nb1Ox catalyzed ethane oxidation exclusively to ethylene at 215°C, whereas a temperature of 500°C was necessary for the catalyst without niobium. Moreover the activity and selectivity depend on the ratio of the three components. The Mo19V5Nb1Ox and the Mo8V2Nb1Ox have approximately the same Mo : V ratio of 4 : 1, but a niobium content of 0.04 and 0.09, respectively. When Mo19V5Nb1Ox is used instead of Mo8V2Nb1Ox, the product distribution is not severely altered and the ethylene selectivity is improved from 86 to 90% at 390°C. However, the Mo6V3Nb1Ox catalyst, which has approximately the same niobium content as Mo8V2Nb1Ox but a Mo : V ratio of 2 : 1, is the least selective and the most active of the three component catalysts with 77% ethylene selectivity and 7.7% ethane conversion at 390°C. Although the amount of niobium seems to be less critical as compared to the other metals, a minimum is required. The Mo19V5Nb0.1Ox has a comparable activity to the Mo4V1Ox catalysts. The superiority in terms of selectivity, of a 4 : 1 ratio between the molybdenum and the vanadium is not unique to our experiments. Many examples can be found in the results published by Thorsteinson et al. [5].

The tests performed on the series of catalysts composed of two of the three metals show several interesting features: (1) Mo19Nb1Ox is the poorest catalyst of the series; (2) the niobium in V5Nb1Ox inhibits the total oxidation of ethane to carbon dioxide as compared to the pure vanadium pentoxide [3]; (3) the Mo4V1Ox catalysts, with or without oxalic acid in their preparation, are still the most efficient in the series of the binary catalysts. These observations show that the combination of oxides of molybdenum and vanadium is already more active and selective than the vanadium–niobium or the molybdenum–niobium combinations. The intrinsic activity of the Mo4V1Ox is enhanced by the addition of niobium. Another major effect of this metal is emphasized by the results obtained with

V5Nb1Ox. In this catalyst, the presence of niobium inhibits the carbon dioxide formation to negligible quantities. The ethane oxidation over pure vanadium pentoxide has been reported to form considerable amounts of carbon dioxide and carbon monoxide [3]. This is also observed in the case of the Mo19V5Nb0.1Ox. Although the quantity of niobium is not enough to have a significant effect on the activity, the rate of formation of carbon oxides is reduced as compared to the Mo4V1Ox catalysts.

According to these findings, it appears that the active phase of these catalysts is based on molybdenum and vanadium. The introduction of niobium considerably enhances the activity and improves the selectivity by inhibiting the total oxidation reaction. Taken together with earlier published results, our studies show that a 4 : 1 ratio between molybdenum and vanadium is optimum.

The temperature dependence of product formation rates has been studied between 350 and 450°C on the Mo8V2Nb1Ox and the Mo19V5Nb1Ox catalysts. The loss of surface area by sintering prevents operation at temperature higher than 450°C. The apparent activation energies obtained using the two catalysts are similar within the error range and follow the same trends. In both cases the rates of formation of ethylene and carbon dioxide vary slowly with the temperature and yield activation energies of E_a = 18–20 kcal/mol for ethylene and E_a =16–17 kcal/mol for carbon dioxide. Although the error range does not allow the differentiation between these two activation energies, the formation of carbon dioxide on both catalysts is less sensitive to temperature variation than the ethylene formation. On the other hand, the carbon monoxide formation, with E_a = 27–31 kcal/mol, is strongly temperature dependent. These results suggest that the products are formed via the same routes on these two catalysts.

The reactivity of ethylene proves to be lower than that of ethane over the Mo19V5Nb1Ox catalyst. Thus, during the oxidehydrogenation of ethane, it appears that the carbon oxides are being formed mainly by the direct oxidation of ethane and to a lesser extent by the secondary oxidation of ethylene. This is in agreement with the findings of Burch et al. [6] who observed that most of the carbon monoxide and the carbon dioxide was produced directly from ethane over their Mo6V3Nb1Ox catalyst. It has to be pointed out that over a totally different catalyst, a lithium-promoted magnesium oxide, Lunsford et al. [11] also observed that the oxidation of ethane yielded most of the carbon oxides formed during the reaction. However, in the unselective oxidation of ethane over vanadium oxide [7], it was reported that 25% of the COx were formed from ethane, 41% from ethylene and 34% from ethane. This apparent conflict is not surprising. Indeed, one of the generally admitted mechanistic routes for the oxidehydrogenation of ethane, is the generation of a surface ethoxide [6,7]. This surface ethoxide reacts further to form ethylene or to form acetaldehyde [7].

The reaction order with respect to the ethane and oxygen partial pressures has not been determined over the Mo8V2Nb1Ox and the Mo19V5Nb1Ox catalysts. However, Burch et al. [6] reported a first order rate with respect to ethane partial pressure over Mo6V3Nb1Ox. The reaction order with respect to oxygen showed a more complex pattern. The reaction was almost independent of the oxygen partial pressure at low temperatures, whereas the reaction was half order at high temperatures for oxygen partial pressures below 7 kPa. In a pressure range of 7.5–15 kPa, the reaction was again almost independent of the oxygen at high temperatures. The first order dependence with respect to the ethane partial pressure was described as consistent with a mechanism in which breaking of a C–H bond is rate determining. The dependence of the oxygen reaction order on the temperature was explained in terms of lability of the lattice oxygen and speed of reoxidation of the catalyst. Therefore at low ethane conversions, i.e. at low temperatures, the reoxidation of the catalyst is so fast that it is not a rate limiting process. However, at high conversions, i.e. at high temperatures, the reoxidation is rate limiting if the oxygen partial pressure is low. In other words, the reaction rate is dependent on the oxygen partial pressure. The lability of the lattice oxygen had been demonstrated by Thorsteinson et al. [5] using thermogravimetry analysis. They also reported that the presence of vanadium increased the oxidation rate of the molybdenum dioxide [5]. Using pulse experiments, it has been found [6] that molecular oxygen may be responsible for the total oxidation of ethane whereas lattice oxygen is involved only in ethylene formation.

It can be reasonably assumed that the breaking of a C–H bond is also rate limiting over Mo8V2Nb1Ox and Mo19V5Nb1Ox and, as a consequence, that the reactions are first order with respect to ethane partial pressure over these catalysts. Therefore, the results obtained by varying the ethane : oxygen ratio should reflect an eventual effect of the niobium atomic content on the catalyst reoxidation rates. It appears that the ethane conversion increases on both catalysts, when the ethane : oxygen ratio is decreased from 10 : 1 to 2 : 1 in the feed. Moreover the rates of formation of the carbon oxides increased with oxygen partial pressure over Mo8V2Nb1Ox, while they remain unchanged over Mo19V5Nb1Ox. The small difference between the increases of ethane conversion over Mo8V2Nb1Ox and Mo19V5Nb1Ox with the amount of oxygen is not significant enough to elucidate the effect of niobium on the catalysts reoxidation rates. Without any doubts, a complete determination of the effect of the oxygen partial pressure on the reaction rates would give the missing information. That is to say, making experiments at different oxygen partial pressures while keeping the ethane pressure constant, and varying the niobium content of the catalysts while keeping a Mo : V ratio of 4 : 1. Along with pulse experiments, this should give a good insight in the role played by the niobium on the lattice oxygen mobility and on the reoxidation rates of the catalysts.

Oyama at al. [7] reported that the rate laws for ethane oxidation over supported vanadium pentoxide were of negative order with respect to water partial pressure. Moreover, such a rate order dependence was more pronounced for the formation of carbon oxides than for ethylene formation. A similar inhibiting effect was found for the methane coupling reaction over calcium–nickel–potassium oxide catalysts

[8]. This is not the case with Mo19V5Nb1Ox. Moreover, no changes in the carbon monoxide and carbon dioxide distribution occur. It is likely that these catalysts are not efficient for the water–gas shift reaction under our experimental conditions.

The stabilities with time of the Mo6V3Nb1Ox, Mo8V2Nb1Ox and Mo19V5Nb1Ox catalysts have been examined at 390°C. It has been observed that the Mo6V3Nb1Ox deactivates at the beginning of the run. The equivalence of the surface areas measured before and after the reactions excludes sintering as the cause of the activity deterioration. The surface compositions of the fresh and the used catalysts determined by XPS do not show any significant variation in the molybdenum–vanadium–niobium proportions, which correspond, within the XPS error range, to the bulk compositions. However, the XPS data show that the amount of the carbonaceous species doubles, even triples, on the surfaces of the used Mo19V5Nb1Ox and Mo6V3Nb1Ox, respectively. Although both used catalysts are accumulating carbonaceous species, only one is deactivating. This surprising phenomenon is difficult to rationalize, unless one admits a difference in sensitivity towards carbon deposition, which could depend on the catalyst composition.

5. Conclusion

Our results suggest that the active phase of these MoαVβNbδOx catalysts, studied for the oxidehydrogenation of ethane, is based on molybdenum and vanadium. The introduction of niobium enhances considerably the intrinsic activity of the molybdenum–vanadium combination. Moreover, the niobium improves the selectivity for ethylene by inhibiting the total oxidation reaction. In the presence of niobium, a 4 : 1 atomic ratio between molybdenum and vanadium seems to be the optimum in terms of selectivity. The activation energies determined for the transformation of ethane to ethylene, carbon monoxide and carbon dioxide on Mo8V2Nb1Ox and Mo19V5Nb1Ox are equivalent, within the error range (± 2 kcal/mol), and follow similar trends. Carbon monoxide formation is the most sensitive to temperature variation, which corresponds to $E_a = 31$ kcal/mol over Mo8V2Nb1Ox and $E_a = 27$ kcal/mol over Mo19V5Nb1Ox. Carbon dioxide is the least sensitive with $E_a = 16$ kcal/mol and $E_a = 17$ kcal/mol, respectively. Ethylene formation has an intermediate position between CO and CO_2 with $E_a = 20$ kcal/mol and $E_a = 18$ kcal/mol, respectively. This indicates that the products are formed via the same mechanistic routes on these two catalysts. The reactivity of ethylene is lower than that of ethane over the Mo19V5Nb1Ox catalyst. It shows that the carbon oxides are being formed mainly by the direct oxidation of ethane and, to a lesser extent, by the secondary reaction of ethylene. The Mo8V2Nb1Ox and the Mo19V5Nb1Ox catalysts were also compared as a function of different ethane : oxygen ratios. The ethane conversion increases on both of the catalysts when the ethane to oxygen ratio is shifted from 10 : 1 to 2 : 1. The ethylene selectivity decreases slightly over Mo8V2Nb1Ox but not over Mo19V5Nb1Ox. Due to the similar responses of the two catalysts to the variation in the ethane : oxygen ratio, it is not possible to correlate the atomic concentration of niobium with the rate of lattice oxygen replacement. The lattice oxygen is believed to participate in the oxidehydrogenation of ethane to ethylene. Although water is produced during the reaction, the addition of steam in the feed does not affect the product distribution over Mo19V5Nb1Ox. The stabilities with the time on stream of Mo6V3Nb1Ox, Mo8V2Nb1Ox and Mo19V5Nb1Ox were compared. The Mo6V3Nb1Ox deactivates rapidly at the beginning of a run. An increase of the amount of the carbon species on the surface may be the cause of the loss of activity.

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References

[1] L. Mendelovici and J.H. Lunsford, J. Catal. 94 (1985) 37.
[2] A. Erdöhelyi and F. Solymosi, J. Catal. 123 (1990) 31.
[3] S.T. Oyama and G.A. Somorjai, J. Phys. Chem. 94 (1990) 5022.
[4] E. Morales and J.H. Lunsford, J. Catal. 118 (1989) 255;
C.H. Lin, J.X. Wang and J.H. Lunsford, J. Catal. 111 (1988) 302.
[5] E.M. Thorsteinson, T.P. Wilson, F.G. Young and P.H. Kasai, J. Catal. 52 (1978) 116.
[6] R. Burch and R. Swarnakar, Appl. Catal. 70 (1991) 129.
[7] S.T. Oyama, A.M. Middlebrook and G.A. Somorjai, J. Phys. Chem. 94 (1990) 5029.
[8] J. Raskó, P. Pereira, G.A. Somorjai and H. Heinemann, Catal. Lett. 9 (1991) 395.
[9] A. Wheeler, *Reaction Rates and Selectivities in Catalysts Pores*, Catalysis, Vol. 2 (Reinhold, New York, 1955) p. 105.
[10] C.N. Satterfield, *Mass Transfer in Heterogeneous Catalysis* (MIT Press, Massachusetts, 1970) p. 267;
C.N. Satterfield, *Heterogeneous Catalysis in Practice* (McGraw-Hill, New York, 1980) p. 416;
R.C. Reid and R.K. Scherwood, *The Properties of Gases and Liquids* (McGraw-Hill, New York, 1958).
[11] E. Morales and J.H. Lunsford, J. Catal. 118 (1989) 255.