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Oxidative dehydrogenation of ethane on the α and β phases of $NiMoO_4$

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Abstract

The oxidative dehydrogenation of ethane on the α and β phases of $NiMoO_4$ was studied, and the results compared with those previously obtained on propane in the 500–600°C range. A reaction mechanism is proposed in accordance with the surface properties, preliminary kinetic studies and catalytic tests with ethanol as a probe molecule. © 1998 Elsevier Science B.V.

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1. Introduction

The oxidative dehydrogenation and selective oxidation of lower alkanes represent an attractive way for obtaining olefins and oxygenated products for the chemical industry, and many scientific papers have been published describing the behaviour of various catalytic systems tested on C_2, C_3 and C_4 hydrocarbons [1–3]. For light alkane activation, the first hydrogen abstraction by an active surface site to form a radical intermediate is considered to be the rate-limiting step of the overall reactivity [3]; the following reaction patterns leading to dehydrogenation, partial or deep oxidation products are not well understood and strongly depend on the nature of the hydrocarbon and of the catalytic system employed.

Starting from ethane, ethylene is generally the predominant product observed because of its high stability. Martin [2], working on Li/MgO, postulated a radical mechanism in which the ethyl radicals desorb from the surface and rapidly react with oxygen in the gas phase to produce ethylene with high selectivity. Gaseous radicals have also been detected in the oxidative dehydrogenation of propane employing a V–Mg–O catalyst [3], and the overall reaction pathway has been assumed to be heterogeneous, heterogeneous–homogeneous and, finally, homogeneous. Thorsteinson et al. [4], while studying the ODE with mixed Mo/V/Nb oxides, considers the formation of an ethoxide intermediate on Mo^{6+} centres, with successive β hydrogen abstraction and simultaneous release of ethylene and reduction to Mo^{4+} reoxidizing with added oxygen.

Very few works report the possibility of obtaining oxygenated products: at low temperatures, Merzouki et al. have observed high selectivity for acetic acid working on VPO [5], while acetaldehyde can be produced at high temperatures on BPO systems [6].

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Thorsteinson et al. have also observed acetic acid under pressure in the presence of water.

In this work, the ODE has been studied on the two different phases (α and β) of a stoichiometric $NiMoO_4$ catalyst, in an attempt to extend the results obtained, starting from propane with the same system [7]. In that case, the two phases have shown different activities and selectivities, the α phase being more active (stable from room temperature up to 650°C), and the high-temperature β phase being more selective (forming upon heating at a T>650°C and stable on cooling until 300°C) [8]. A preliminary kinetic study performed with propane showed that the reaction could proceed through an oxidation–reduction scheme, due to a strong dependence on the C_3 partial pressure (the reaction order is ca. one) while a zero order was found with respect to the oxygen partial pressure [9]. Tests have also been performed on both the nickel molybdate phases by adding ethanol to the feed mixture, with the aim of understanding the role of the intermediate ethoxy surface species.

2. Experimental

2.1. Catalyst preparation and physico-chemical characterisation

A Mettler RC1 reactor calorimeter is employed for the precipitation of the precursors under carefully controlled conditions according to the methodology described elsewhere [7]. As the catalytic activity strongly depends on the preparation conditions, several experiments have been carried out to characterise both, the evolution of the precursor and the final catalyst: TG-DTA coupled with mass spectroscopy, high-temperature XRD, I.R., XPS, B.E.T. and conductivity measurements. In previously published papers, the employed techniques are described in detail [7,8].

Table 1 resumes some physico-chemical characteristics of the $NiMoO_4$ catalytic system.

Table 1
Physico-chemical characteristics of $NiMoO_4$

Crystallisation temperature:	470°C
Evolved gas:	H_2O+NH_3
Surface area α phase:	36 m^2/g
Surface area β phase:	15 m^2/g
Ni/Mo atomic ratio bulk	1
Ni/Mo atomic ratio on surface	1
Oxygen vacancies on α phase	Ionised twice
Oxygen vacancies on β phase	Ionised once
Rate of reduction under H_2 (% w/min) at 350°C	
α phase	0.8
β phase	1.1

2.2. Catalytic tests

A sample of 0.5 g of the catalyst is mixed with silicon carbide granules of the same size in order to avoid severe temperature gradients within the catalytic bed. The temperature inside the catalyst layer is measured by a type K thermocouple placed in a thin quartz tube (diameter 2.5 mm). The gas feed consisted in 18% O_2, 15% C_2H_6 and 67% helium, with a total flow rate of 15 l/h. Tests have been run with varying oxygen and ethane proportions and the evolution of the reaction in the absence of oxygen studied. Before each experiment, the catalyst was heated progressively from ambient until the desired temperature under a mixture of oxygen and helium (ratio of $O_2/He=0.7$). To perform the tests on the β phase, the reactor was heated at 700°C for 10 min under the same O_2/He mixture and then cooled to the reaction temperature. Ethane was introduced after 30 min. The reactor effluents (CO_x, CH_4, C_2H_4) were analysed by gas chromatography: O_2, and CO after separation by a 5-Å molecular sieve column connected to a thermal conductivity detector; ethane, ethylene, and other products after separation on a porapak Q column were analysed with both a flame ionisation and TCD detectors.

The tests with ethanol have been performed with, and without ethane in the feed mixture, using the same experimental conditions as for the reactivity runs.

3. Results and discussion

The ethane conversion at 600°C measured in the quartz reactor containing only silicon carbide was lower than 1%. A diffusional test was carried out in order to assess the absence of a physical control of the reaction: Several runs were performed by varying both the flow rate and the catalyst weight so to maintain the

Table 2
Ethane conversion and selectivities on the α phase of $NiMoO_4$ (feed composition: 18% O_2, 15% C_2H_6 and 67% He, 15 l/h)

	500°C			530°			560°C			600°C		
	CO	CO_2	C_2H_4	CO	CO_2	C_2H_4	CO	CO_2	C_2H_4	CO	CO_2	C_2H_4
Selectivity (%)	12.3	13.7	74.0	18.0	14.0	67.9	22.0	13.3	64.7	33.9	14.8	51.3
Production (mmol/h)	0.77	0.85	2.3	2.13	1.65	4.02	4.90	2.96	7.2	20.9	9.1	15.8
Conversion (%)		3.1			5.9			11.1			30.7	

Table 3
Ethane conversion and selectivities on the β phase of $NiMoO_4$ (feed composition: 18% O_2, 15% C_2H_6 and 67% He, 15 l/h

	500°C			530°			560°C			600°C		
	CO	CO_2	C_2H_4	CO	CO_2	C_2H_4	CO	CO_2	C_2H_4	CO	CO_2	C_2H_4
Selectivity (%)	28.1	0.0	71.9	29.9	8.2	61.8	31.0	8.7	60.3	32.1	9.9	57.9
Production (mmol/h)	0.88	0.0	1.12	1.74	0.48	1.80	3.90	1.10	3.8	9.9	3.0	8.9
Conversion (%)		1.15			2.9			6.3			15.4	

same contact time. Other tests were carried out by using the same catalyst with different particle size. These tests have shown that the ethane conversion and the product distribution do not vary.

In Tables 2 and 3 are reported the catalytic results obtained with the two phases of $NiMoO_4$. Ethylene is the predominant product and it can be observed that the CO selectivity increases more significantly with the temperature for the α phase: the ratio between the CO selectivity for β and α phases varies from 2.33 to 0.94 in the 500–600°C range. The opposite happens in the case of CO_2, with a β/α selectivity ratio varying from 0 to 0.66 in the same temperature range.

Figs. 1 nd 2 illustrate the dependence of the initial rate of product formation on oxygen and ethane partial pressures for the β phase of $NiMoO_4$.

The overall rate of C_2H_6 consumption can be described by

$$d(C_2H_6)/dt = k(C_2H_6)^{1.15}(O_2)^{0.21} \tag{1}$$

over the $5\% < C_2H_6 < 20\%$ and $2.5\% < O_2 < 18\%$ concentration ranges.

The kinetic order of the reaction products was determined from logarithmic plots of the various rates vs. reactant concentrations (Table 4).

The tests performed under continuous flow in the absence of oxygen (3% ethane and 97% helium, 5 l/h total feed) at 500, 550 and 600°C have led us to the conclusion that no ethylene is formed in the absence of oxygen. The only products detected after a few minutes of exposure were CO, CO_2 and CH_4 . The formation of the latter product normally implies the presence of metallic nickel on the surface of the partially reduced catalyst. The formation of metallic nickel is in agreement with previous experimental observations reported by some of the authors [10]. Under the cited conditions, it is safe to assume that no metallic molybdenum occurs since this requires a much more drastic reducing environment [11].

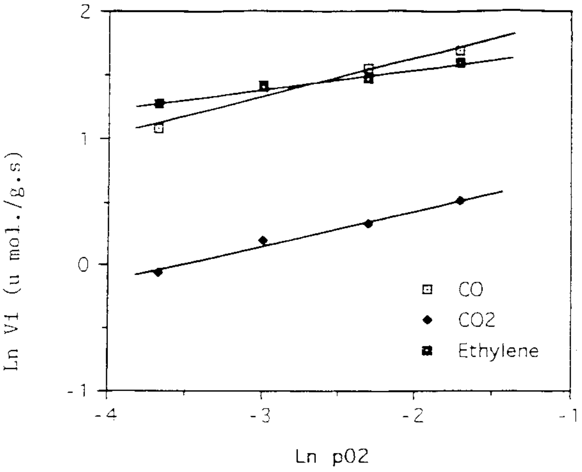

Fig. 1. Dependence of the initial rate of the product formation as a function of O_2 concentration at 580°C on the β phase of $NiMoO_4$.

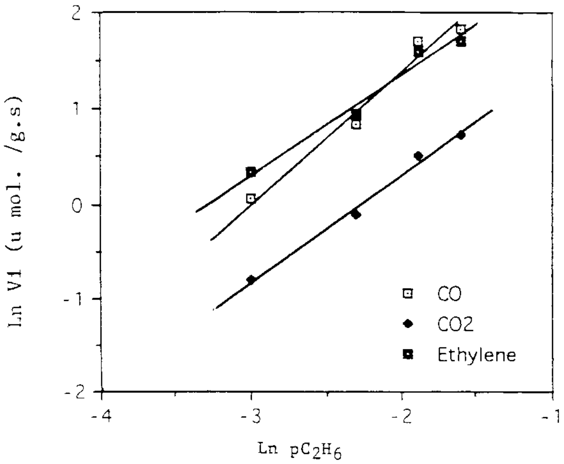

Fig. 2. Dependence of the initial rate of the product formation as a function of C_2H_6 concentration at 580°C on the β phase of $NiMoO_4$.

Table 4
Kinetic orders (at 580°C on the β $NiMoO_4$)

	With respect to oxygen	With respect to ethane
CO	0.25	1.35
CO_2	0.17	1.14
Ethylene	0.16	1.00

In this way, lattice oxygen does not seem to orientate the reaction towards dehydrogenation, in accordance with the order observed with respect to oxygen.

These results indicate that: (a) the α phase is not only more active but also more selective, behaving differently than in the case of propane oxidative dehydrogenation; and (b) the mechanism proposed in the case of propane [7]:

$$C_3H_8 + O_s^{2-} \rightarrow C_3H_6 + H_2O + V_O^{OO} + 2e^- \qquad (2)$$

does not apply to the case of oxidative dehydrogenation of ethane (ODE), so that the observed differences are not surprising.

Thorsteinson has advanced the hypothesis, for the ODE catalysed by mixed molybdenum oxides, of the intervention of lattice oxygen for ethylene production, but the runs performed in the absence of oxygen have led us to a different conclusion, and ethylene formation should be explained with a different mechanism. In addition, preliminary kinetic tests allowed us to calculate a reaction order of 0.16 for C_2H_4 formation with respect to oxygen. While investigating the propane oxidative dehydrogenation under fairly comparable conditions, a zero order was found which implies no oxygen dependence; and propene was found among the products (selectivity >95%) in absence of oxygen in the feed.

In this case, similar conclusions cannot be proposed and rather than a Mars–Van Krevelen reaction pattern, the mechanism proposed by Lunsford for MoO_3 supported on silica [12] and by Solymosi for MoO_3 supported alkaline metal molybdates [13], which considers the intervention of O^- species in the determining step, better explains the observed results. In this mechanism, the activation of ethane involves the hydrogen abstraction by O^- to give ethyl radical:

$$C_2H_6 + O^- \rightarrow C_2H_5^{\bullet} + OH^- \qquad (3)$$

The C_2H_5 surface species may react further on the surface with O^- ions

$$C_2H_5 + O^- \rightarrow C_2H_5 - O^- \qquad (5)$$

The peculiarity of catalysts based on molybdenum oxides consists in the presence of Mo^{5+} sites important for the adsorption of active oxygen species [12,13]. Some authors have indeed pointed out the presence of such sites on $NiMoO_4$ [14] used for dehydrogenation reactions.

When dealing with oxides that activate oxygen, two aspects must be taken into account: (a) the quantity of adsorbed oxygen; and (b) the oxygen exchange rate. Data reported in the literature on $NiMoO_4$ indicate very low values both, for oxygen adsorption [15] and exchange rate [16]. These two characteristics, according to Haber [15], allow to explain the good selectivity obtained in the ODE reaction.

In order to understand the difference between the α and β phases, it must be taken into account that this last one has a reduced surface area (15 m^2/g), diminishing the quantity of oxygen that can be adsorbed, and that its initial reduction rate measured under hydrogen is lower (the weight loss is 0.8%/min for the β phase and 1.1%/min for the α phase). This could explain why the rate determining step of the reaction is slower ($C_2H_6 + O^-$) on the β phase. The α and β phases possess, respectively, an octahedral and tetrahedral co-ordination of the molybdenum ion, and according

Table 5
Catalytic activity of ethanol in the absence and presence of reactive feed on α-$NiMoO_4$

Catalysts	Feed composition (%)	Temperature	Formation	Rate (mmol/h)			Run
	$C_2H_6/O_2/He/C_2H_5OH$	(°C)	CO	CO_2	C_2H_4	CH_3CHO	
α-$NiMoO_4$							
	15/18/67/0	400	0.0	0.18	0.26	0.00	(1)
	0/18/61/11	400	13.2	23.5	2.40	10.30	(2)
	15/18/56/11	400	12.0	24.5	2.80	9.21	(3)
	15/18/67/0	500	0.77	0.85	2.30	0.00	(4)
	15/18/56/11	500	42.7	25.4	4.16	0.00	(5)

Table 6
Catalytic activity of ethanol in the absence, and presence of reactive feed on β-$NiMoO_4$

Catalysts	Feed composition (%)	Temperature	Formation	Rate (mmol/h)			Run
	$C_2H_6/O_2/He/C_2H_5OH$	(°C)	CO	CO_2	C_2H_4	CH_3CHO	
β-$NiMoO_4$							
	15/18/67/0	400	0.0	0.04	0.06	0.00	(6)
	0/18/61/11	400	9.86	13.4	2.49	12.32	(7)
	15/18/56/11	400	9.45	15.0	3.35	11.35	(8)
	15/18/67/0	500	0.88	0.00	1.12	0.00	(9)
	15/18/56/11	500	38.7	21.6	6.45	0.00	(10)

to Solymosi [13] this difference when acting on the evolution of the ethyl radical intermediate could play a role with respect to selectivity.

With the aim of identifying the importance of the ethoxy intermediate species for the oxidative dehydrogenation of ethane to ethylene, ethanol has been used as a probe performing several catalytic tests with, and without ethane in the 400–500°C range on both the α (Table 5) and β (Table 6) $NiMoO_4$ phases. Ethane conversion at 400°C in the absence of ethanol was limited.

The tests without ethane allowed to establish the alcohol reactivity; they showed that ethylene production was limited and that, mainly, acetaldehyde was formed. This last product was rapidly degrading into CO and, depending on the reaction temperature the CO/CO_2 ratio (<1 at 400°C), became much higher. At 500°C the aldehyde was totally decomposed (see Tables 5 and 6) [17]. The addition of ethanol to the reaction mixture (ethane plus oxygen) resulted in a modification of the product distribution, increasing both ethylene and carbon oxides production.

The formation of the surface ethoxy species directly from ethane can also explain why, when its conversion is low, the presence of a significant amount of CO can be observed while limiting the selectivity for ethylene. As both ethane and ethylene are stable in the operating condition adopted, the CO formed has to be derived from the degradation of a labile intermediate.

Starting from α-$NiMoO_4$, and specifically at 400°C, the ethoxy route leading to ethylene (see run 2 Table 5) normally implies acetaldehyde formation while no aldehyde is observed (see run 1 Table 5) under normal reaction conditions. The same observations may be made for β-$NiMoO_4$ (see run 6 vs. 7), even at 400°C. It thus seems justified to hypothesise another minor route to ethylene which does not necessarily involve ethoxy intermediates. In this case, a gas-

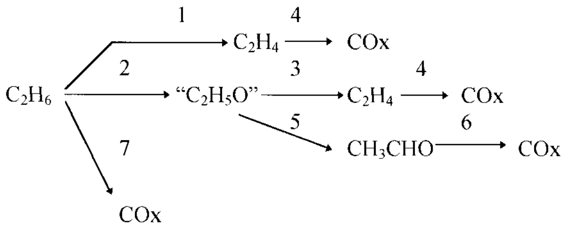

Fig. 3. Scheme of reaction pathways leading to total oxidation.

phase reaction mechanism [3] could explain the ethylene formation. The reaction pathways leading to total oxidation are illustrated in Fig. 3.

4. Conclusions

On the basis of the kinetic data observed and by performing reactivity tests involving lattice oxygen, the hypothesis that ODE could proceed through a reaction mechanism other than the redox one starting from propane was formulated.

As opposed to the oxidative dehydrogenation of propane, it has also be concluded that the α phase, possessing an octahedral molybdenum co-ordination and a higher surface area, is not only more active but also more selective.

The formation of carbon oxides is not only due to ethylene degradation but derives also from the transformation of the surface ethoxy intermediate into acetaldehyde, which easily transforms into CO and CO_2 in the temperature range adopted.

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References

[1] P. Michalakos, M. Kung, I. Jahan, H. Kung, J. Catal. 140 (1993) 226.

[2] G. Martin, S. Bernal, V. Perrichon, C. Mirodatos, Cat. Today 13 (1992) 487.

[3] K. Nguyen, H. Kung, J. Catal. 122 (1990) 415.

[4] E. Thorsteinson, T. Wilson, F. Young, P. Kasai, J. Catal. 52 (1978) 116.

[5] M. Merzouki, B. Taouk, L. Tessier, E. Bordes, P. Courtine, New frontiers in catalysis, vol. A, Proc. 10th Intern. Congr. Cat., Budapest, 1992, p. 753.

[6] Y. Uragami, K. Otsuka, H. Hatano, Catal. Today 13 (1992) 667.

[7] C. Mazzocchia, C. Aboumrad, C. Diagne, E. Tempesti, J.M. Hermann, G. Thomas, Cat. Lett. 10 (1991) 181.

[8] C. Mazzocchia, A. Kaddouri, R. Anouchinsky, M. Sautel, G. Thomas, Solid State Ionics 63–65 (1993) 731.

[9] C. Mazzocchia, A. Kaddouri, R. Anouchinsky, G. Hecquet, unpublished data presented at GECAT, 1992.

[10] J. Haber, in: P.C.H. Mitchell, A. Seamen (Eds.), Proceedings of 2nd Intern. Confer. on the Chemistry and Uses of Molybdenum, Climax, Oxford 1976, p. 119.

[11] C. Mazzocchia, F. Di Renzo, Calorimétrie et Analyse Thermique, Journées de Montpellier 20–22 May 1985, Volume XVI, p. 311.

[12] L. Mendelovici, J. Lunsford, J. Catal. 94 (1985) 37.

[13] A. Erdohelyi, F. Mate, F. Solymosi, J. Catal. 135 (1992) 563.

[14] N. Inoyatov, P. Nasirov, A. Khasanov, A. Kayumov, Kin. i Katal. 13 (1972) 1509.

[15] A. Bielanski, J. Haber, Cat. Rev. Sci. Eng. 19(1) (1979) 1.

[16] D. Klissurski, J. Catal. 59 (1979) 448.

[17] H.M. Swaan, A. Toebes, K. Seshan, J.G. Van Ommen, J.R.H. Ross, Catal. Today 13 (1992) 201.