Catalysis Letters 63 (1999) 65–71

On the reactivity of K_2O-, CaO- and P_2O_5-doped nickel molybdate catalysts in a periodic-flow reactor

A. Kaddouri*, R. Del Rosso, C. Mazzocchia, P. Gronchi and P. Céntola

Industrial Chemistry and Chemical Engineering Department, Politecnico di Milano, P.zza L. da Vinci 32, I-20133 Milano, Italy

Received 24 May 1999; accepted 2 September 1999

The propane oxydehydrogenation with monolayer lattice oxygen of undoped and K_2O–, CaO– and P_2O_5–$NiMoO_4$ was investigated by using a periodic-flow reactor (PFR). The influence of the nature and the extent of the promoter has been emphasized relative to the doped catalysts with respect to pure $NiMoO_4$ phases. It was observed that calcium and potassium promoters satisfactorily enhance propylene selectivity, and phosphorus promoter specifically increases the total activity while maintaining the propylene selectivity. Evidence found by thermogravimetric (TG) analyses (oxygen depletion rate) has shown a dependence on lattice oxygen mobility due to the presence of promoters. This dependence has been correlated to the propane conversion while the propylene selectivity was attributed to the acid–base properties.

Keywords: propane ODH, periodic-flow reactor, $NiMoO_4$, promoters, acid–base, reducibility

1. Introduction

In the last few years in the area of paraffin oxidation, research aims have focused on functionalizing light alkanes to the corresponding alkenes in order to meet future world market chemical and polymer needs. One of the newer approaches has been selective oxydehydrogenation of lower alkanes. In this area, metal molybdates together with V-based systems [1] are particularly attractive showing high activity for alkanes at relatively low temperature. Particularly, stoichiometric $NiMoO_4$ is among the most active and selective catalysts for oxidative dehydrogenation of propane [2,3]. At atmospheric pressure stoichiometric nickel molybdate presents two polymorphic phases: the low-temperature α-phase, with molybdenum in a distorted octahedral environment, and the high-temperature β-phase, with molybdenum in a distorted tetrahedral site. The β-phase is formed after heating the α-phase up to 700 °C and undergoes reverse transition at low temperature on cooling at ca. 300 °C.

In the present study, the effect of the nature of the promoter as CaO, K_2O and P_2O_5 on $NiMoO_4$ catalyst activity and selectivity is conducted. Oxidative dehydrogenation (ODH) tests are carried out with propane in stationary conditions by using a periodic-flow reactor (PFR) [4]. Data were obtained for each promoter over a limited range of conversions by varying period of pulse and temperature in order to ascertain the reoxidation of the catalyst while using only monolayer lattice oxygen.

2. Experimental

2.1. Catalysts preparation

2.1.1. Precursor

The stoichiometric $NiMoO_4$ precursor (Mo/Ni = 1) is prepared by coprecipitation using a Mettler RC1 reaction calorimeter, which allows a careful control of the main experimental parameters (T, stirring speed, pH, etc.) which determine the structure and surface characteristics of the active catalysts. After drying, the precursor is heated for 2 h at 550 °C, leading to the stoichiometric α-$NiMoO_4$ catalyst [5,6].

2.1.2. Catalyst

An incipient wetness impregnation technique has been used to prepare $NiMoO_4$-supported K_2O, CaO and P_2O_5 catalysts. The impregnation was made starting from an α-$NiMoO_4$ calcined pure catalyst and KOH, $Ca(NO_3)_2$ and $(NH_4)_3PO_4$ salts. A further treatment at 550 °C for 2 h allows one to obtain the doped catalyst. The dopant percentages indicate the weight of the doping element with respect to the total weight of the catalyst. When using catalysts doped with Ca it was necessary to activate the compounds under a CO_2 atmosphere in order to avoid a decrease in selectivity and conversion with respect to the undoped ones. The activation is carried out by feeding CO_2 ($He/O_2/CO_2$: 70/10/20; flow rate 5 $l\,h^{-1}$) at 550 °C for 12 h. Carbonation of Ca seems to be important allowing an increase of the performance of the catalytic system in terms of propylene selectivity.

The undoped and doped β-$NiMoO_4$ phase is obtained *in situ* in the reactors by thermal treatment of the correspond-

---

[*] To whom correspondence should be addressed.

ing α-$NiMoO_4$ phase up to 720 °C for 10 min and then cooling to the reaction temperature.

Thermal studies of the catalysts were carried out on a Seiko TG-DTA instrument. Weighed samples (ca. 20 mg) were placed in alumina crucibles and reduction tests were carried out isothermally (ITR: *iso-thermal reduction*) under a hydrogen atmosphere (gas feed 6 $\mathrm{l\,h^{-1}}$) while recording the TG and DTG curves. The samples were preheated in air (10 °C/min) up to the reduction temperature (T_r) and were then washed with helium prior to reduction.

2.1.3. Acid–base measurements

Surface acid–base properties have been assessed by the catalytic decomposition of isopropanol in stationary conditions in the absence of oxygen. The reaction was carried out at 180 °C in a differential flow microreactor (0.2 g of catalyst) attached to an on-line gas chromatograph (FID and TCD). Isopropanol was introduced in a pressure of 4 kPa using He as carrier gas (total flow of 3.6 $\mathrm{l\,h^{-1}}$).

2.1.4. Catalytic tests

Catalytic runs were performed in the temperature interval 480–560 °C (measured with a thermowell placed at the centre of the catalyst bed) using a four quartz (volume 30 cm^3, 50 cm long with an internal diameter of 8 mm) tubular reactors system operating in a periodic-flow mode. The reaction apparatus [4] was developed in order to separate the reduction from the oxidation steps and was obtained by washing the system with a flux of inert gas between the two steps. The feed gas streams were metered with automated flowmeter controllers in order to have the same gas flow rate for each step. The gases were cyclically fed to the reactor in the following sequence: propane, helium (first washing), oxygen and then helium (second washing). The cycle frequency could be varied and the effect of the time on stream for each step (period) was investigated. With the aim to perform experiments in a wide range of periods and in order to avoid pneumatic disturbance due to the gas flow repeated “stop and go”, four identical reactors were simultaneously used.

The system works so that while two reactors were exposed to the helium washing phases, one was fed with propane (reduction phase) while the fourth was re-oxidised with oxygen (oxidation phase).

In order to built this apparatus a rotating automatic distribution valve was specifically designed to operate according to the described four steps sequence. The reactant gases from the four reactors were mixed and equalised in a chamber (volume = 120 cm^3, residence time ca. 1 min) prior to being analysed. The obtained values are thus representative of the overall conversions and selectivities, while comprehensive of substances produced in the regeneration steps.

The catalyst (ca. 0.5 g) was diluted with silicon carbide (ca. 10 g) in order to prevent severe temperature gradients within the catalyst bed. The contact time was 0.3 $\mathrm{g\,l^{-1}\,h}$ using helium as washing gas with a total feed of 3.6 $\mathrm{l\,h^{-1}}$.

3. Results

3.1. Acid–base properties

In table 1 is reported the effect of potassium, calcium and phosphorus addition on the surface acid–base properties of $NiMoO_4$. The data indicate that, following the potassium or calcium addition, the ratio $V_{\mathrm{acetone}}/V_{\mathrm{propene}}$ increases progressively showing that basic sites have become more important on the catalyst surface. In the case of calcium-doped catalysts a higher percent (ca. 10-fold increase) of the dopant was necessary to obtain the same basicity of K-doped catalysts. It should also be observed that a two-fold increase in K content has a more significant effect on the catalyst basicity than a two-fold increase in Ca.

The addition of a typical acidic element P_2O_5 induces an increase of the acidity and a decrease to a small extent of the basicity of the $NiMoO_4$ system.

3.2. Catalytic tests

Catalytic activity of doped $NiMoO_4$ catalysts for propane oxidative dehydrogenation has been studied in the absence of molecular oxygen under stationary conditions using a periodic-flow reactor [4]. Tables 2–4 show the effect of pure α- and β-phases and also promoters addition on the activity and selectivity of $NiMoO_4$ obtained by varying the period of pulses and temperature while keeping constant the contact time. In terms of propylene selectivity, it can be seen that noticeable differences are found and may be attributed to the role of the different promoters used. In fact it can be noticed that, following the promoters addition, the ratio propylene/CO_x increases, indicating that basic sites have become more important on the catalyst surface. The easier desorption of propylene from the more basic surface allows one to improve considerably its selectivity with respect to undoped catalysts, while CO and CO_2 production is drastically affected especially in the case of the α-$NiMoO_4$/0.12% K catalyst for 60 s periods. The effect of phosphorus promotion on α-$NiMoO_4$/0.12% K and α-$NiMoO_4$/1% Ca has led to enhancement of the propane conversion while maintaining a good propylene selectivity.

Previous catalytic results [3,6] obtained in a continuous-flow reactor (CFR) showed that the propylene formed is

Table 1
Isopropanol decomposition on undoped and K-, Ca- and P-doped $NiMoO_4$.[a]

Sample	Surface area ($\mathrm{m^2\,g^{-1}}$)	V_{propene} ($\mu\mathrm{mol\,h^{-1}\,m^{-2}}$)	$V_{\mathrm{acetone}}/V_{\mathrm{propene}}$
$NiMoO_4$	32.2	11.0	0.30
$NiMoO_4$/0.12% K	31.8	9.4	0.50
$NiMoO_4$/0.25% K	29.4	6.0	0.78
$NiMoO_4$/1.0% Ca	29.7	9.8	0.63
$NiMoO_4$/2.0% Ca	28.9	9.0	0.70
$NiMoO_4$/2.0% P[b]	30.2	45.4	0.12

[a] At 180 °C with a fixed feed composition (isopropanol pressure 4 kPa in He 60 $\mathrm{cm^3\,min^{-1}}$), catalyst weight 0.2 g.

[b] Negligible amounts of DIPE are detected in isopropanol transformation.

Table 2
Activity and selectivity of α- and β-$NiMoO_4$.[a]

Catalyst	Period (s)	C_3H_6 conversion (%)	Selectivity (%) C_3H_6	CO	CO_2	C_2H_4
α-$NiMoO_4$						
450 °C	40	1.93	75.54	9.88	14.56	0
	60	1.76	81.37	6.47	12.15	0
500 °C	40	3.74	74.62	10.89	14.48	0
	60	3.21	84.33	5.28	10.38	0
520 °C	40	4.48	74.59	9.77	14.97	0.65
	60	4.11	80	6.61	12.70	0.67
β-$NiMoO_4$						
470 °C	40	1.36	96.55	0	3.44	0
	60	0.84	96.33	0	3.66	0
500 °C	40	1.70	94.40	0	5.59	0
	60	1.52	94.64	0	4.35	0
520 °C	40	1.73	94.71	0	5.28	0
	60	1.70	95.22	0	4.77	0

[a] Contact time 0.3 $\mathrm{g\,l^{-1}\,h}$, helium washing gas feed 3.6 $\mathrm{l\,h^{-1}}$.

Table 3
Activity and selectivity of K- and Ca-doped α-$NiMoO_4$.[a]

Catalyst	Period (s)	C_3H_8 conversion (%)	Selectivity (%) C_3H_6	CO	CO_2	C_2H_4
α-$NiMoO_4$/0.12% K						
480 °C	40	1.32	92.84	0	7.15	0
	60	1.02	93.36	0	6.63	0
500 °C	40	1.61	89.35	0	10.65	0
	60	1.24	91.78	0	8.21	0
520 °C	40	1.95	89.60	0	10.40	0
	60	1.65	90.92	0	9.07	0
540 °C	40	2.34	83.16	5.29	10.16	1.37
	60	2.23	90.12	0	9.87	0
560 °C	40	3.49	83.55	4.60	9.46	2.39
	60	2.77	85.83	4.80	9.36	0
α-$NiMoO_4$/0.25% K						
520 °C	40	1.07	82.84	0	17.15	0
	60	0.83	85.32	0	14.68	0
540 °C	40	1.33	83.81	0	12.80	3.38
	60	0.93	91.56	0	8.43	0
560 °C	40	1.58	82.62	1.3	10.56	5.52
	60	1.08	89.18	0	4.83	5.98
α-$NiMoO_4$/1% Ca						
480 °C	40	2.3	82.53	5.17	12.30	0
	60	1.65	90.89	0	9.11	0
500 °C	40	2.64	81.15	4.85	13.99	0
	60	2.22	89.46	0	10.53	0
520 °C	40	3.88	74.28	8.53	15.67	1.50
	60	3.37	81.49	3.79	13.26	1.44
α-$NiMoO_4$/2% Ca						
480 °C	40	2.03	82.75	4.97	12.28	0
	60	1.52	90.67	0	9.33	0
500 °C	40	2.60	81.82	5.86	12.31	0
	60	1.82	90.13	0	9.87	0
520 °C	40	3.23	80.63	5.56	13.80	0
	60	2.51	89.39	0	10.60	0

[a] Contact time 0.3 $\mathrm{g\,l^{-1}\,h}$, helium washing gas feed 3.6 $\mathrm{l\,h^{-1}}$.

reactive leading to a decrease of several points in propene selectivity, while when using a periodic-flow reactor (PFR) the observed decrease in propene selectivity was limited. This phenomenon can be explained by the contribution of the selective lattice oxygen of the catalyst which leads selectively to propylene formation. The level of propane con-

Table 4
Activity and selectivity of K–P- and Ca–P-doped α- and β-$NiMoO_4$.[a]

Catalyst	Period (s)	C_3H_8 conversion (%)	Selectivity (%) C_3H_6	CO	CO_2	C_2H_4
α-$NiMoO_4$/K–P						
440 °C	40	1.94	95.70	0	4.3	0
	60	1.62	96.39	0	3.6	0
480 °C	40	2.96	93.97	0	6.02	0
	60	2.26	95.54	0	4.45	0
500 °C	40	3.61	84.50	5.20	10.29	0
	60	2.40	91.88	1.43	6.68	0
520 °C	40	4.28	84.03	5.6	10.9	0
	60	3.85	90.94	1.8	7.75	0
β-$NiMoO_4$/K–P						
500 °C	40	2.78	94.01	0	5.90	0
	60	2.32	97.65	0	6.34	0
520 °C	40	3.12	92.42	0	7.57	0
	60	2.65	93.16	0	6.84	0
α-$NiMoO_4$/Ca–P						
440 °C	40	2.25	85.02	10.42	4.55	0
	60	1.56	91.26	0	8.74	0
460 °C	40	2.83	80.34	7.55	12.11	0
	60	1.87	89.47	1.17	9.35	0
480 °C	40	3.12	79.93	7.85	12.20	0
	60	2.46	85.26	4.84	9.90	0
500 °C	40	3.77	75.39	9.48	13.80	1.33
	60	3.03	86.37	4.85	8.77	0
520 °C	40	4.26	73.20	11.86	14.94	0
	60	3.65	84.40	5.50	10.10	0
β-$NiMoO_4$/Ca–P						
440 °C	40	1.71	95.01	0	4.98	0
	60	1.13	96.64	0	3.35	0
460 °C	40	1.95	94.48	0	5.51	0
	60	1.45	95.94	0	4.05	0
480 °C	40	2.36	90.28	3.05	6.66	0
	60	1.73	94.74	0	5.27	0
500 °C	40	2.85	87.86	5.23	6.9	0
	60	2.02	94.72	0	5.27	0
520 °C	40	3.26	84.53	6.24	9.23	0
	60	2.38	91.61	1.85	6.54	0

[a] Contact time 0.3 $g\,l^{-1}\,h$, helium washing gas feed 3.6 $l\,h^{-1}$.

version is limited by both lattice oxygen availability and mobility (as in the case of Riser reactor type) and also by monolayer depth. The conversions reported in tables 2–4 for the periodic-flow reactor are consistent with an oxygen consumption corresponding to a small percentage of the mobile oxygen content of the catalyst monolayer. In order to calculate total catalyst oxygen contained in the monolayer it is necessary to consider the monolayer depth and the exposed area of the $NiMoO_4$ cell. Monolayer calculations are reported in [7].

This reduction degree of monolayer is estimated to be minor of 3% which is necessary to ensure the *red–ox* cycle [7]. Therefore, using defined structures (stoichiometric $NiMoO_4$) it is not possible to obtain the same propane conversion levels per unit of catalyst that could be attained with mixed oxides [8]. Exceeding the monolayer catalytic surface by deep reduction was found to deactivate irreversibly the catalytic system by generating metallic nickel which leads to stable carbon filaments formation [9].

On the other hand, evidence found using thermogravimetric analyses (figures 1 and 2) by measuring at 440 °C the undoped and K-, Ca- and P-doped catalysts reduction rate (oxygen depletion) has shown a stronger dependence on lattice oxygen mobility. This stronger dependence has been correlated to propane conversion.

A low contact time and longer period have been found to improve propylene selectivity while lowering slightly propane conversion; this result can probably be due both to the progressive difficulty for lattice oxygen extraction when the depth becomes important and also to the decrease in the degradation of the products formed at the end of the cycle.

4. Discussion

Among the possible reaction steps during propane ODH are the adsorption of propane, the reaction with lattice oxy-

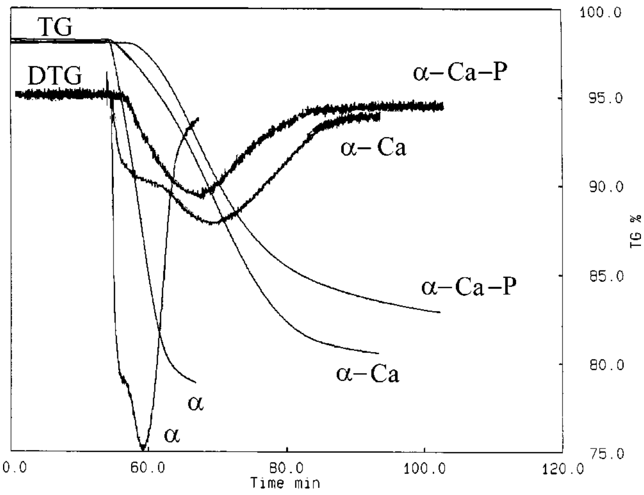

Figure 1. TG and DTG curves of undoped and Ca- and Ca–P-doped α-NiMoO$_4$.

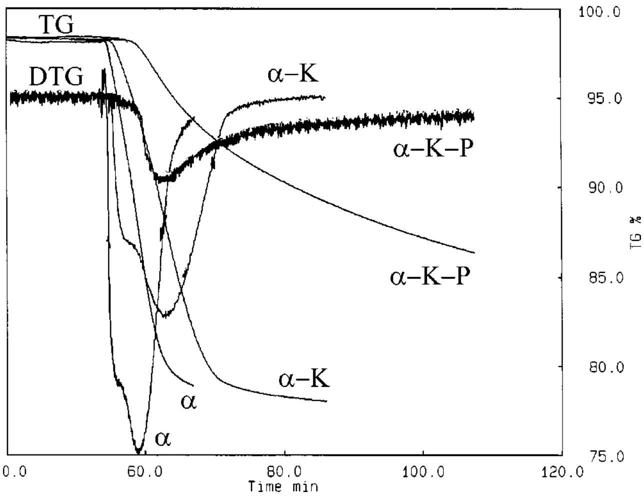

Figure 2. TG and DTG curves of undoped and K- and K–P-doped α-NiMoO$_4$.

gen and the desorption of propylene. These steps are represented by three equations:

$$C_3H_8(g) + \sigma_1 \rightleftharpoons C_3H_8\text{–}\sigma_1, \quad (1)$$

$$\sigma_2 + C_3H_8\text{–}\sigma_1 \rightleftharpoons C_3H_6\text{–}\sigma_1 + H_2O\text{–}\sigma_2 + V_0^x \quad (2)$$

$$C_3H_6\text{–}\sigma_1 \rightleftharpoons C_3H_6 + \sigma_1 \quad (3)$$

A previous kinetic study performed with the NiMoO$_4$ system [10] shows that the limiting reaction step controlling the overall rate was the adsorption of propane on the catalyst surface or the reaction between adsorbed propane and the lattice oxygen of NiMoO$_4$. In our study we have first separate the reduction and reoxidation steps by using a periodic-flow reactor, then we tried to use acidic and basic dopants to promote the NiMoO$_4$ catalyst in order to act separately on the three steps (1), (2) and (3).

The reduction profile of NiMoO$_4$ catalysts is affected by promoters addition. In figures 1 and 2 it can be observed that the reduction rate is different for unpromoted and promoted NiMoO$_4$, showing also that the extent of reduction was significantly affected by the nature of dopants; CaO, K$_2$O and Ca–P and K–P combination. The results show that at constant reduction temperature (440 °C) the promoter leads to a significant increase of the reduction resistance of the nickel molybdate. Similar effects by Li, Na and K doping over molybdates catalysts were found by Driscoll et al. [11], and by Cs promoting of vanadium oxide catalysts by Owens and Kung [12]. Increased resistance to reduction by hydrocarbons due to alkali metal doping has also been reported by other authors [13]. According to Kung [14], there is a relationship between the reducibility of the catalysts and selectivity to dehydrogenation products if the lattice oxygen plays an important role in the reaction.

The difficulty to remove oxygen from the lattice of a solid is even related to the strength of the metal–oxygen bond. This feature can be evaluated by the reduction potential or by the re-oxidation heat. The weaker the strength, the easier the lattice oxygen mobility, and vice versa. However, in selective oxidation reactions, it is generally observed that the activity and selectivity of an oxide are related to its reducibility. High resistance to reducibility leads to a lower activity, while easier reducibility implies a higher activity but also a lower selectivity.

The decrease in propane conversion and the increase in propylene selectivity over K- and Ca-modified samples could be due to the increased difficulty of the catalyst to undergo the reduction step (see figures 1 and 2). It seems that catalytic activity for ODH of propane would be related to the reducibility of catalysts and selectivity to propylene would depend mainly on the acid–base character of the catalytic surface [15]. In addition, the selectivity depends also on the degree of catalyst reduction since propylene formation is improved with pulse period [16]. The decrease in propane conversion by K and Ca addition could not only be attributed to the decrease in the surface area (table 1) as the trend is the same if propane conversion is based on unity surface area.

Basicity increased by CaO and K$_2$O dopants was found to be fundamental to promote the selective ODH of propane, limiting propylene interaction with the catalytic surface, thus avoiding its oxidation. To compare the selectivity to propylene at iso-conversion, operating conditions have been adjusted for each catalyst but, as expected, an increase of reaction temperature was necessary when the K$_2$O and CaO content is increased, because the catalysts become progressively less active. Among all the studied catalysts the largest increase in reaction temperature was observed for the 0.25% K-doped NiMoO$_4$. In order to have a better comparison between the catalysts studied, the catalytic performances (see table 5) are reported in terms of propylene yield.

Referring to apparent activation energy E_a of the ODH reaction, the values obtained for propane activation with CaO-, K$_2$O-, CaO–P$_2$O$_5$- and K$_2$O–P$_2$O$_5$-doped NiMoO$_4$ are reported in table 6. Regarding the CaO- and K$_2$O-doped samples the noticeable differences of E_a observed with respect to the undoped α- and β-phases of NiMoO$_4$ could

Table 5

C_3H_6 yield versus temperature and period of pulse for K-, Ca-, K–P- and Ca–P-doped α- and β-$NiMoO_4$.[a]

Catalyst	C_3H_6 yield							
	Period 40 s				Period 60 s			
	450 °C	480 °C	500 °C	520 °C	450 °C	480 °C	500 °C	520 °C
α-$NiMoO_4$	1.46	2.27	2.79	3.34	1.43	2.23	2.70	3.30
α-$NiMoO_4$/0.12% K	0.87	1.22	1.44	1.75	0.53	0.95	1.14	1.50
α-$NiMoO_4$/0.25% K	–	–	–	0.89	–	–	–	0.71
α-$NiMoO_4$/1% Ca	1.13	1.9	2.14	2.90	0.54	1.50	1.99	2.75
α-$NiMoO_4$/2% Ca	1.03	1.68	2.13	2.60	0.68	1.38	1.64	2.24
α-$NiMoO_4$/0.12% K–1% P	1.86[b]	2.8	3.05	3.60	1.60	2.46	2.90	3.50
α-$NiMoO_4$/1% Ca–1% P	2.09	2.5	2.84	3.12	1.54	2.31	2.74	3.08
β-$NiMoO_4$	1.14	1.31	1.60	1.64	0.17	0.81	1.43	1.62
β-$NiMoO_4$/0.12% K–1% P	1.61	2.37	2.61	2.88	1.45	1.98	2.26	2.47
β-$NiMoO_4$/1% Ca–1% P	1.73	2.13	2.50	2.76	1.24	1.64	1.91	2.18

[a] Contact time 0.3 $g\,l^{-1}\,h$, helium washing gas feed 3.6 $l\,h^{-1}$.

[b] $T = 440\,°C$.

Table 6

Apparent activation energy of propane ODH measured for different pulse periods.

Catalyst	Activation energy ($kcal\,mol^{-1}$)	
	Period 40 s	Period 60 s
α-$NiMoO_4$	13.8	15.1
α-$NiMoO_4$/0.12% K	14.4	16.1
α-$NiMoO_4$/1% Ca	15.5	21.2
α-$NiMoO_4$/0.12% K–1% P	11.3	13.9
α-$NiMoO_4$/1% Ca–1% P	9.0	12.4
β-$NiMoO_4$	11.9	13.6
β-$NiMoO_4$/0.12% K–1% P	7.0	8.1
β-$NiMoO_4$/1% Ca–1% P	9.4	10.6

probably be related with the resistance to reduction of the catalysts. This correlation and the observed relationship between the catalyst activity and reducibility (i.e., increasing the resistance to reduction by both doping and increasing the CaO and K_2O content decreases the propane conversion) confirm that this reaction occurs through a reduction–oxidation mechanism [17]. If compared to the corresponding pure $NiMoO_4$ phases the lowest E_a obtained with the CaO–P_2O_5- and K_2O–P_2O_5-doped catalysts could be explained in terms of compensation effect of both reducibility and surface acidity of the catalyst (i.e., increasing the resistance to reduction by CaO or K_2O decreases the propane conversion rate but the acidic P_2O_5 favours the adsorption of propane and consequently its conversion). Another role of the P_2O_5 promoter was evidenced by thermogravimetric analyses. TG and DTG curves of the undoped and doped catalysts are shown in figures 1 and 2. The pure α-phase and the Ca- and K-doped α-$NiMoO_4$ catalysts present two different peaks corresponding to two different types of metal oxide oxygen bonds. These two kinds of oxygen bonds could be attributed to Ni–O and Mo–O metal oxides present in the structure of $NiMoO_4$ since the oxygen coordination of the two metals is different. Nickel is surrounded by four oxygen atoms in a tetrahedral symmetry while molybdenum coordination is six in an octahedral symmetry.

The Ca–P- and K–P-doped $NiMoO_4$ did not show two reduction peaks as with pure $NiMoO_4$ and with K- and Ca-doped catalysts. The presence of phosphorus oxide led to an inhibition of the formation of the first peak, which probably means that a rearrangement of the oxygen network occurs giving a situation where only one oxygen type is available for reduction. Otherwise the presence of P_2O_5 did not increase the overall reduction rate of the catalysts (Ca–P- and K–P-doped $NiMoO_4$) although the observed propane conversion is enhanced with respect to Ca- and K-doped catalysts. Further experiments to clarify these observations are underway.

As for secondary reactions, during washing and re-oxidation steps, the gaseous oxygen tends to replace the consumed lattice oxygen re-oxidising the solid also reacting with the surface adsorbed carbon species which were formed at the end of the reduction step thus leading to the formation of carbon oxides. Combustion products decreased with promoters addition.

5. Conclusion

Under stationary conditions, monolayer oxygen of potassium and calcium supported $NiMoO_4$ have proved to be effective in oxidative dehydrogenation of propane into propylene carried out in a periodic-flow reactor.

Specifically with phosphorus promotion the propane conversion is enhanced while the propylene selectivity is maintained.

The catalytic activity of the $NiMoO_4$ doped system is related to the reducibility of the catalysts *and* propylene selectivity to both the degree of the catalyst reduction and the acid–base character of their catalytic surface.

A long period (good degree of catalyst reduction) and a short contact time allow one to limit the formation of coke (evaluated by CO_2 formed during regeneration steps) and at the same time improves the selectivity of propylene.

References

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

[2] C. Mazzocchia, E. Tempesti and Ch. Aboumrad, Eur. Patent 90-400137 (1990); US Patent 5086032 (1992).
[3] C. Mazzocchia, Ch. Aboumrad, C. Diagne, E. Tempesti, J. Herrmann and G. Thomas, Catal. Lett. 10 (1991) 181.
[4] R. Del Rosso, C. Mazzocchia, P. Gronchi and P. Centola, in: *Proc. X Natl. Congr. on Catal.*, L'Aquila, Italy, 8–11 September 1996, p. 143.
[5] C. Mazzocchia, R. Anouchinsky, A. Kaddouri, M. Sautel and G. Thomas, J. Therm. Anal. 40 (1993) 1253.
[6] C. Mazzocchia, A. Kaddouri, R. Anouchinsky, M. Sautel and G. Thomas, J. Solid State Ionics 63–65 (1993) 731.
[7] R. Del Rosso, A. Kaddouri, R. Anouchinsky, C. Mazzocchia, P. Gronchi and P. Centola, J. Mol. Catal. 135 (1998) 181.
[8] G.E. Vrieland and C.B. Murchinson, Appl. Catal. A 134 (1996) 101.
[9] R. Del Rosso, A. Kaddouri, D. Fumagalli, C. Mazzocchia, P. Gronchi and P. Centola, Catal. Lett. 55 (1998) 93.
[10] M. Sautel, G. Thomas, A. Kaddouri, C. Mazzocchia and R. Anouchinsky, Appl. Catal. A 155 (1997) 217.
[11] S.A. Driscoll, D.K. Gardner and U.S. Ozkan, J. Catal. 147 (1994) 379.
[12] L. Owens and H.H. Kung, J. Catal. 148 (1994) 587.
[13] C. Martin, V. Rive and A. Gonzalez-Elyse, J. Catal. 114 (1988) 473.
[14] H.H. Kung, in: *Adv. in Catal*., Vol. 40, eds. D.D. Eley, H. Pines and W.O. Haeg (Academic Press, New York, 1994) p. 1.
[15] T. Blasco, J.M. López Nieto, A. Dejoz and M.I. Vazquez, J. Catal. 157 (1995) 271.
[16] D. Creaser, B. Adersson, R.R. Hudgins and P.L. Silveston, J. Catal. 182 (1999) 264.
[17] P. Mars and D.W. Van Krevelen, Chem. Eng. Sci. (spec. suppl.) 3 (1954) 41.