Oxidative dehydrogenation of propane by continuous and periodic operating flow reactor with a nickel molybdate catalyst

R. Del Rosso [*], A. Kaddouri, R. Anouchinsky, C. Mazzocchia, P. Gronchi, P. Centola

Dipartimento di Chimica Industriale e Ingegneria Chimica Politecnico di Milano, P.za L. Da Vinci 32, 20133 Milan, Italy

Abstract

Oxidative dehydrogenation of propane with nickel molybdate catalysts (α NiMoO$_4$) has been investigated in flow reactors feeding the reactant gases continuously and periodically. The data obtained by the continuous operating system (COS) showed the determining role of lattice oxygen on the selectivity. Moreover, when only the lattice oxygen was consumed, very high propene selectivity was obtained. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Oxidative dehydrogenation of propane; Periodic operating flow reactor; Nickel molybdate

1. Introduction

Extensive research on light alkane oxidative dehydrogenation has been performed in the last years, with the aim of developing new catalysts to produce olefins more economically than by the classic dehydrogenation processes.

Among the different catalysts and processes that have been reported in the literature to be active and selective for the oxidative dehydrogenation of propane to propene, the NiMoO$_4$ catalytic system has proved to be one of the most effective [1] and the catalytic activity of this system was correlated with its polymorphic form [2,3].

Several reaction mechanisms have been proposed for this reaction but no detailed mechanistic studies are available [4]. Two hypotheses have been suggested: the first one involves free radicals [5,6] acting in both the heterogeneous and homogeneous system, while the second [7] suggests an oxido–reduction mechanism.

In the present work, catalytic tests have been carried out in the absence of oxygen and a preliminary kinetic study has been developed with the continuous flow reactor together with the investigation of the catalytic behaviour under a periodic operating mode. The aim was to explore the involvement of lattice oxygen during the oxidative dehydrogenation of propane.

[*] Corresponding author. Tel.: +39-2-23993200; fax: +39-2-70638173.

2. Experimental

2.1. Catalyst preparation

The stoichiometric catalyst $\alpha NiMoO_4$ is prepared by coprecipitation from an equimolar molybdic acid and nickel nitrate solution (0.25 M), at 85°C with the pH adjusted at 5.25 by the addition of ammonia. The precipitate obtained is hot-filtered and dried at 120°C for 15 h [8]. The active catalysts used for continuous and periodic operating flow reactors is obtained by oven heating of the dried precursor (2 h at 550°C). The BET surface area is 33 m^2/g, and the catalyst particle size is 200–325 mesh.

2.2. Continuous operating system (COS)

Catalytic experiments in a continuous flow reactor are achieved in a quartz tubular reactor (total volume = 30 cm^3, length of the catalytic zone $L = 10$ cm, diameter = 1 cm). A mass of 0.5 g of catalyst is mixed with about 10 g of silicon carbide powder of similar size in order to avoid severe temperature gradients within the catalytic bed. Preliminary tests have been run to verify the absence of diffusional limitations: several runs were performed by varying both the flow rate and the catalyst weight to maintain the same contact time. Other tests were carried out by using the same catalyst with different particle sizes. These tests have shown that the propane conversion and the product distribution was invariable.

Before the experiments, the reactor is heated at 550°C under a mixture of oxygen (18% volume) and helium for 1 h in order to stabilise the $NiMoO_4$ catalyst, then the reactor is cooled to the working temperature and propane is introduced after 30 min.

2.3. Transient operating system (TOS)

In the tests performed under continuous flow in the absence of oxygen, the mixture was composed of 3% propane and 97% helium, maintaining the same contact time as in the tests performed in the presence of oxygen. Sampling of the reaction products was performed using a Valco 16 positions valve along a period starting after 4 min and ending after 16 min from the moment the oxygen feed was turned off.

2.4. Periodic operating system (POS)

The flow reactor apparatus [9] consisted of four quartz tubular reactors containing 0.5 g catalyst each. Each reactor was first exposed to a feed containing propane for an assigned time period, followed by a period of the same duration of helium washing; during the third period, oxygen containing gas reoxidises the catalyst surface; a final helium washing period precedes the reintroduction of propane, and the complete cycle is continuously repeated.

For each period, the same gas volumes were introduced in the four reactors, and the same contact times were used to keep the pressure drop constant.

A rotating automatic distribution valve with a variable rotation frequency has been especially designed to operate according to the described four-step sequence: the system is designed in such a way that while two reactors are exposed to the helium washing, one is reacted with propane and the other reoxidised by oxygen. Periods were varied between 1 and 180 s.

2.5. Analysis

The reaction products (CO_x, C_2H_4, C_3H_6 and C_3H_4O) are analysed by gas chromatography: oxygen and carbon monoxide by a molecular sieve 5-Å column connected to a thermal conductivity detector (TCD), while ethylene, propene, propane and acrolein are separated and analysed by a Porapak QS column linked both to flame ionisation detector and TCD.

3. Results and discussion

The preliminary kinetic measurements on the α phase of $NiMoO_4$ were carried out in the COS mode at atmospheric pressure. The gas feed was varied between 15 and 22 Nl h^{-1} in order to limit the secondary reactions that lead to carbon oxides.

The propane pressure was kept constant at 15×10^3 Pa, and the oxygen pressure was varied between 1.5 and 18×10^3 Pa, with helium as the balance to study the influence of oxygen partial pressure on propene formation. The reaction was studied at three temperatures: 420, 435 and 450°C. The obtained results indicate that the global rate of propene formation is not affected by changing the oxygen pressure.

The same experiments were carried out at constant oxygen partial pressure (18×10^3 Pa) while varying that of propane between 2.5 and 20×10^3 Pa. In this case, the propene-formation rate depends on the propane partial pressure. From the experimental results, it follows that on the $\alpha NiMoO_4$ phase, the partial order with respect to propane m is equal to 1.2 ± 0.01 and with respect to oxygen n is equal to 0.04 ± 0.01. These values are based on average propene-formation rate, calculated from the results of several tests, with a maximum standard deviation of 10%. The effect of oxygen partial pressure on propene selectivity is reported in Table 1.

In the case of the more selective $\beta NiMoO_4$ phase, the kinetic study, performed with the
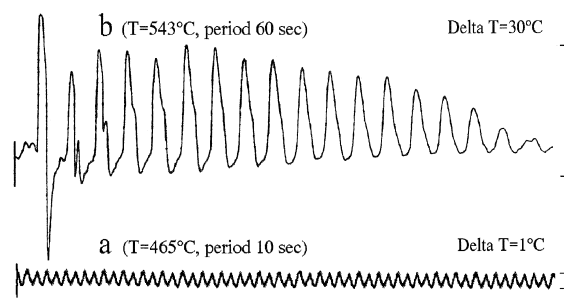

Fig. 1. Temperature difference between POS reactors in opposition of phase vs. time (arbitrary units). Gas feed: alternating sets of 30 cc/min C_3H_8, 30 cc/min O_2, 30 cc/min He. (a) Period = 10 s, $T = 465$°C, conversion 2.90%. (b) Period = 60 s, $T = 543$°C.

same experimental conditions [10], showed that the reaction orders with respect to propane and oxygen are 0.95 and 0.03, respectively. It can be concluded that with both phases, the change in the oxygen partial pressure does not affect propene production, which is instead dependent on the propane partial pressure.

From the data of the additional tests performed on the $\alpha NiMoO_4$ phase under continuous flow in the absence of oxygen, it is possible to withdraw that the lattice oxygen plays a crucial role in the formation of propene. At the beginning of the exposure of the catalyst to the propane feed, no cracking products (ethylene, methane) were indeed detected, and the only reaction products are propene and a few percent of CO and CO_2. Thus, it may be assumed that gaseous oxygen is not directly responsible for the selective oxidative dehydrogenation and a Mars and Van Krevelen type mechanism can be proposed.

To confirm the involvement of lattice oxygen, the catalytic behaviour of the $\alpha NiMoO_4$ catalyst was investigated using also the periodic operating system (POS) described in Section 2.

The ΔT existing between two of the four reactors operating in phase opposition (reduction vs. reoxidation and washing vs. washing), measured by the aid of two thermocouples placed within the catalytic bed, is continuously recorded. The constant amplitude of the cyclic

Table 1
Effect of oxygen partial pressure on conversion and selectivities[a]

(%)	P_{Oxygen} (kPa)		
	18	10	5
$Conv_{propane}$	11.02	8.71	7.72
Sel_{CO}	23.45	15.00	13.08
Sel_{CO2}	21.63	16.95	12.67
$Sel_{ethylene}$	0.57	0.74	0.00
$Sel_{propene}$	53.93	66.20	73.04

[a]Catalyst: $\alpha NiMoO_4$ 0.5 g/reactor diluted in 10 g of silicon carbide powder; $T_{Reaction} = 450$°C.

Table 2
Conversion and selectivities[a]

%	COS	Pseudo-COS	POS				
			Period (s)				
			10	30	60	90	180
$Conv_{propane}$	9.6	9.73	2.90	1.59	1.42	1.28	1.03
Sel_{CO}	23.0	6.07	3.68	–	–	–	–
Sel_{CO2}	21.4	39.98	14.10	9.04	8.32	8.25	8.20
$Sel_{ethylene}$	2.0	0.86	–	–	–	–	–
$Sel_{propene}$	53.6	53.10	82.22	90.96	91.68	91.75	91.80

[a]Catalyst: $\alpha NiMoO_4$ 0.5 g diluted in 10 g of silicon carbide powder.
POS system (gas feed): alternating sets of 30 cc/min C_3H_8, 30 cc/min O_2, 30 cc/min He; $T_{Reaction} = 465°C$.
COS system (gas feed): 37.5 cc/min C_3H_8, 44.5 cc/min O_2, 168 cc/min He; total feed 250 cc/min; $T_{Reaction} = 430°C$.

temperature oscillation indicates that the system is working under stationary conditions.

At low conversion, the amplitude is small (Fig. 1a, i.e., $T = 465°C$, conversion 2.90%, $\Delta T \cong 1°C$), while for higher conversion, the temperature difference becomes larger.

If the reaction conditions are such that the propene conversion determines an intensive consumption of the available lattice oxygen (i.e., high temperatures, low contact time or high propane partial pressure, etc.), the reoxidation step may not be capable of restoring the catalytic surface. In this case, the catalyst deactivation immediately begins, and a progressive reduction of the ΔT amplitude is monitored (Fig. 1b, i.e., $T = 543°C$, $\Delta T_{max} \cong 30°C$). Metallic Ni and carbonaceous products can be indeed observed on the surface of the exhaust catalyst.

Table 2 reports the conversion and propene selectivity as a function of the period for a set

of reaction conditions that allowed steady operation. The experimental data were taken for each different period after 2 h. The stationary operating conditions were maintained for several hours. The data obtained with the continuous flow reactor are included in the table for comparison purposes.

Data obtained with the null period (< 1 s, i.e., with a continuous revolution of the distribution valve) can be considered as obtained in a pseudo-continuous mode. Pseudo-continuous propene selectivity was found to be very similar to that obtained with the continuous-flow reactor operating at temperatures that allow isoconversion.

The passage from the null period to the cyclic operating mode causes an abrupt increase in the propene selectivity. As soon as the adopted period becomes long enough to assure a good separation between the gas containing the hydrocarbon and the one containing oxygen, the conversion decreases, and the propene selectivity improves. This indicates that the redox mechanism is the one leading to propene, while the reactions occurring in the presence of gaseous oxygen and propane, are responsible for the pronounced carbon oxide formation.

For periods longer than 30 s, the CO disappears and only CO_2 is formed. It follows that CO_2 production, due to the deep oxidation of the hydrocarbon species remaining at the end of the reduction step on the surface, is responsible for the loss of propene selectivity.

By increasing the period, CO_2 production decreases because the amount of hydrocarbon residue, which is quite constant at the end of

Table 3
Cell parameters of $NiMoO_4$ catalyst[a]

Catalyst	Cell dimensions (Å)			Angle β (deg)	Cell volume (Å³)	Cell surface area (Å²)		
	a	b	c			S_{ab}	S_{bc}	S_{ac}
$\alpha NiMoO_4$	9.555	8.745	7.693	113.62	588.7	83.55	63.80	67.35
$\beta NiMoO_4$	10.13	9.280	7.020	107.20	630.0	94.00	62.23	67.93

[a]Number of molecules/cell $Z = 8$.

each reduction step, is less frequently washed and reoxidized.

The conversions reported in the table for the POS are consistent with an oxygen consumption corresponding to a small percentage of the mobile oxygen content of the catalyst monolayer.

To calculate the total catalyst oxygen contained in the monolayer, it is necessary to consider the monolayer depth and the exposed area of the $NiMoO_4$ cell. Crystallographic data reported in the literature [11] and the theoretical surface area of the $NiMoO_4$ cell are summarized in Table 3 according to the different planes considered as exposed.

The amount of exposed elementary cells is evaluated according to the surface area of the catalyst ($33 \ m^2/g$) and to the mean exposed area of the $\alpha NiMoO_4$ cell ($\cong 75 \ Å^2$). It is therefore possible to estimate the values of 44×10^{18} elementary cells/g of the catalyst and of 3.5×10^{20} for the mobile oxygen atom/g. If it is assumed that 5 cell layers may represent the

Table 4
Effect of propane dilution on conversion and selectivities[a]

%	Pseudo-COS $P_{propane}$ (kPa)		POS $P_{propane}$ (kPa)	
	101	66	101	66
$Conv_{propane}$	9.73	4.21	1.42	1.43
Sel_{CO}	6.07	–	–	–
Sel_{CO2}	39.98	30.47	8.32	11.30
$Sel_{ethylene}$	0.86	–	–	–
$Sel_{propene}$	53.10	69.53	91.68	88.70

[a]Catalyst: $\alpha NiMoO_4$ 0.5 g/reactor diluted in 10 g of silicon carbide powder; $T_{Reaction} = 465°C$.
Gas feed: alternating sets of 30 cc/min C_3H_8 (or C_3H_8/He 2/1), 30 cc/min O_2, 30 cc/min He.
Period: POS system 60 s, Pseudo-COS <1 s.

so-called monolayer region, the total mobile oxygen atoms are 17.5×10^{20}, which means 2.9×10^{-3} oxygen g-atom/g catalyst.

Similar calculations applied to the $\beta NiMoO_4$ (surface area $13 \ m^2/g$) give 1.1×10^{-3} oxygen g-atom/g catalyst.

Considering as an example the data reported in Table 2 for the period of 60 s, during the oxidation step 30 N ml of propane are introduced in the reactor and 19 μmol are converted. The corresponding theoretical oxygen consumption is 19 μatoms, which means 1.3% of the oxygen contained in the $\alpha NiMoO_4$ catalyst monolayer region are calculated as above.

Fig. 2 represents conversion vs. temperature for the pseudo-continuous and the 60-s period operating modes. It can be seen from the values of the apparent activation energy relative to propane consumption that the COS mode is chemically controlled while the POS one is limited by the diffusion of lattice oxygen. This confirms that it is the redox mechanism that is responsible for the selective propene formation.

Table 4 shows the conversion and selectivity for the pseudo-continuous and the 60-s period operating modes, measured with two different propane partial pressures.

In pseudo-COS, the overall conversion changes with the propane partial pressure.

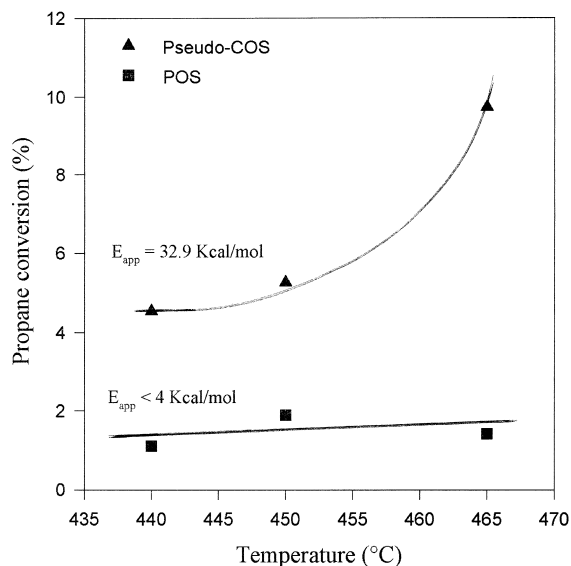Any difference in conversion was not noticeable when operating in the POS mode. In this

Fig. 2. Propane conversion vs. temperature for the pseudo-continuous and the 60-s-period operating modes. Gas feed: alternating sets of 30 cc/min C_3H_8, 30 cc/min O_2, 30 cc/min He.

case, the propane disappearance reaction is first order with respect to the propane partial pressure as the propene formation reaction, meaning that the selective propene formation mainly occurs.

4. Conclusions

The oxidative dehydrogenation of propane with nickel molybdate catalysts has been kinetically studied, and the lattice oxygen appears to play a determinant role in propene selectivity. With the aim of confirming this catalytic behaviour, a periodic-flow apparatus has been specifically designed for the reaction of propane with the lattice oxygen.

With a conversion less than 2% only 1% of the oxygen of the monolayer is consumed, and the reaction is controlled by monolayer oxygen diffusion within the catalyst.

The periodic system operates under stationary conditions, with high propene selectivity.

The catalyst deactivation takes place when metallic Ni is irreversibly formed on the catalyst surface.

References

[1] C. Mazzocchia, E. Tempesti, C. Aboumrad, Eur. Patent, 90-400137, 1990.
[2] C. Mazzocchia, F. Di Renzo, C. Aboumrad, G. Thomas, Solid State Ionics 32–33 (1989) 228.
[3] C. Mazzocchia, C. Aboumrad, C. Diagne, E. Tempesti, J.M. Hermann, G. Thomas, Catal. Lett. 10 (1991) 181.
[4] G. Centi, F. Trifiro, Symp. on Hydroc. Oxidation, Am. Chem. Soc., New Orleans Meeting, August 30, September 4, 1987, p. 754.
[5] M.A. Chaar, D. Patel, H.H. Kung, J. Catal. 109 (1988) 463.
[6] K.T. Nguyen, H.H. Kung, J. Catal. 122 (1990) 415.
[7] D. Siew, H. Sam, V. Soenen, J.C. Volta, J. Catal. 123 (1990) 417.
[8] C. Mazzocchia, R. Anouchinsky, A. Kaddouri, M. Sautel, G. Thomas, Therm. Anal. 40 (1993) 1253.
[9] R. Del Rosso, C. Mazzocchia, P. Gronchi, P. Centola, Proc. X Natl. Congr. on Catal., L'Aquila, Italy, September 8–11, 1996, p. 143.
[10] M. Sautel, G. Thomas, A. Kaddouri, C. Mazzocchia, R. Anouchinsky, Appl. Catal. 155 (1997) 217.
[11] A.W. Sleight, B.L. Chamberland, J.F. Weiher, Inorg. Chem. 7 (1968) 1672.