Deactivation of alkane oxidative dehydrogenation catalyst by deep reduction in periodic flow reactor

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The activity loss of β-$NiMoO_4$ catalyst has been studied in the oxidative dehydrogenation of propane with an operating periodic flow reactor. Under severe operating conditions (i.e., high temperature and long periods of the pulses), the lattice oxygen depletion is faster than the reoxidation one. After an induction period, carbon whiskers on the catalyst surface were detected together with noticeable amounts of cracking products in the gas phase as CH_4, C_2 hydrocarbons and H_2. Deep reduction dramatically changes the reaction path and irreversibly modifies the catalyst.

Keywords: propane oxidative dehydrogenation, catalyst deactivation, periodic flow reactor

1. Introduction

The development of alkanes selective oxidation (ODH) catalysts is still a challenging subject to be solved. It is commonly recognised that on metal oxide based catalysts this reaction occurs through a redox mechanism [1]: the hydrocarbon oxidation by surface oxygen reduces the active surface and the gas phase oxygen oxidises the reduced site. The $NiMoO_4$ catalyst has shown good performances among the catalytic systems suitable for alkane oxidative dehydrogenation in a continuous flow reactor, particularly in propane oxidation into propylene [2,3]. The activity and the selectivity have been linked to the polymorphic form of the catalyst [4]. Recently, the ODH has been studied using a periodic flow system [5] and the authors pointed out a good performance in terms of propylene selectivity. However, laboratory scale evaluation, in a periodic operating flow reactor, of alkane oxidative dehydrogenation catalysts is complicated due to their sensitivity and deactivation by coke deposition. Periodic test procedures, in spite of their complexity, allow separation of the oxidation and the reduction steps. In this way it is possible to simulate the performance of commercial units operating with separate continuous regeneration of the catalyst.

We hereafter report the results of the catalytic test performed with propane on $NiMoO_4$ using the periodic operating mode. This method allows a deep reduction of the catalysts by varying periods of pulses and temperature. Our aim is to investigate the catalyst behaviour getting more inside the lattice modification due to the oxygen consumption and the reaction rate.

2. Experimental

2.1. Catalyst preparation

The stoichiometric catalyst $NiMoO_4$ is prepared by coprecipitation from an equimolar molybdic acid (Aldrich) and nickel nitrate (Fluka) solution (0.25 M), at 85 °C with the pH adjusted at 5.25 by addition of ammonia. The precipitate obtained is hot filtered and dried at 120 °C for 15 h [6], and then heated 2 h at 550 °C. The catalyst particle size is 200–325 mesh.

2.2. Catalytic tests

The reaction apparatus [7] consisted of four quartz tubular flow reactors each containing 0.5 g of catalyst. The runs were performed by continuously repeating a cycle composed of four identically long periods in which different gases were admitted.

The catalyst was exposed firstly to a feed containing propane and, successively, to a helium washing flow; thirdly, an oxygen-containing gas mixture was admitted to reoxidise the catalyst surface; followed by a helium washing period after which the propane was newly fed. Each reactor was in time with one different phase.

A rotating automatic distribution valve with a variable rotation frequency has been especially designed to operate according to the described four-step sequence. Periods (P) were varied between 1 and 180 s. The outcoming flows from reactors are collected mixed and equalised.

2.3. Analysis

The reaction products (CO_x, C_2H_4, C_3H_6 and C_3H_4O) were analysed by gas chromatography: oxygen and carbon

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monoxide with a molecular sieve 5 Å column connected to a thermal conductivity detector (TCD), while ethylene, propene, propane and acrolein were separated and analysed using a Porapak QS column linked both to a flame ionisation detector (FID) and to a TCD one.

Thermal studies of the reduction of samples were performed on a Seiko TG-DTA instrument. Samples weighing about 20 mg were placed in alumina crucibles, then heated at 10 °C min^{-1}, while recording the DTA, TG and DTG curves. The tests have been conducted in both reductive (H_2) and inert (He) atmospheres (gas feed 6 Nl h^{-1}).

Scanning electron micrographs of catalysts were recorded using a Zeiss DSM 940 apparatus.

3. Results and discussion

In order to use only lattice oxygen and to avoid gas back mixing, periods larger than 10 s are required. The catalytic behaviour of $NiMoO_4$ at high conversion and high surface reduction was studied by increasing the temperature and the step time (period).

With low propane conversions only few percent of the oxygen of the monolayer is involved, and the redox periodic system operates under stationary conditions, with very high propene selectivity. Table 1 reports the overall conversion and products selectivity with a period of 40 s. The experimental data were taken for each temperature after 2 h in stationary periodic operating conditions.

The data reported in table 1 are consistent with an oxygen consumption less than 1% of the mobile oxygen content of the catalyst monolayer [3]. The calculated apparent activation energy of propane oxidative dehydrogenation reaction was found to be 10 kcal/mol.

On the other hand, by increasing temperature, the variation of lattice oxygen consuming rate was evidenced by TG analyses of catalyst reduction with H_2 in the same range of temperature. From these analyses the calculated apparent activation energy of the solid reduction was found to be 11 kcal/mol. In figure 1 is reported the % weight loss of the catalyst with temperature.

Referring now to very severe reaction conditions (i.e., high temperatures – 565 °C, long step time – 180 s or high propane partial pressure – 100%), a stationary periodic operating mode cannot be maintained and propane conversion rapidly becomes quite total. The available lattice oxygen is extensively consumed probably to a considerable depth as we observed that the reoxidation step was not successful in restoring the starting oxidation condition of the catalytic surface.

The data reported in table 2 refer to runs performed with intermediate reaction conditions between those of table 1 and the severe ones, and, therefore, it is possible to follow the catalytic behaviour with time. The data indicate the change with time of the conversion and the selectivity for the 90 s period operating modes, measured at 565 °C.

The data clearly indicate a change of the catalyst activity and of the reaction pathway during the occurrence of the solid reduction. The flexus on conversion vs. time dependence indicates the presence of an induction time. After the induction period, a great amount of cracking products as CH_4, C_2 hydrocarbons and H_2 formation was detected, together with a carbon [8] residue deposition (growing as whiskers on the catalyst) which is responsible of the CO_x species formation during the oxidation steps. Metallic Ni and carbonaceous products [9] can be indeed observed on the surface of the exhaust catalyst by X-ray diffraction and SEM techniques. It can be seen from figure 2 that filaments of coke were formed.

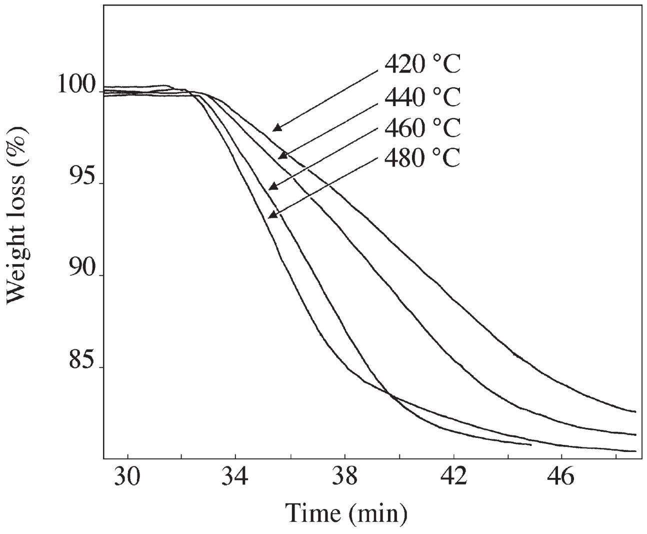


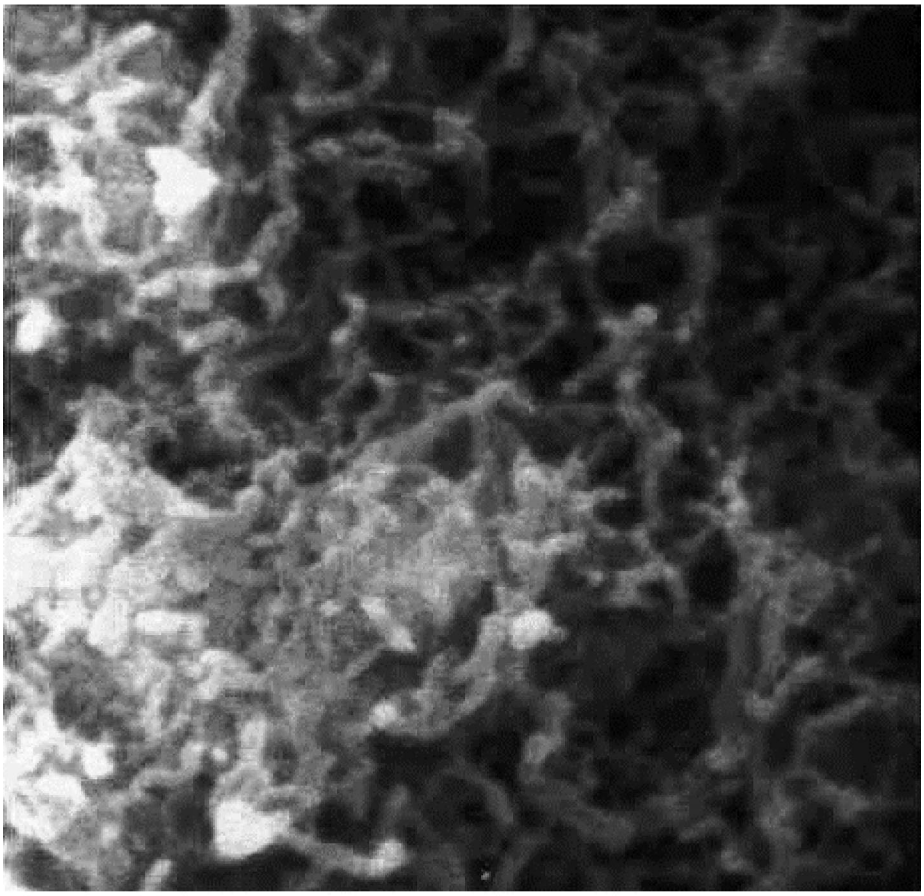
Figure 1. Weight loss on hydrogen stream with time at constant temperature T_{red} (from 25 °C to T_{red} in He).

Table 1
Propane conversion and products selectivities evolution with temperature for $P = 40$ s, $\tau = 1 \times 10^{-6}$ g s m^{-3}.

Temperature (°C)	Conversion (%)	Selectivity (%)			
		CO	CO_2	C_2H_4	C_3H_6
460	1.0	–	8.4	–	90.2
470	1.1	–	9.2	–	89.2
480	1.2	0.8	10.3	–	88.9
495	1.4	1.1	10.3	–	88.1
515	1.6	1.1	11.0	–	89.1

Table 2
Conversion and selectivity evolution with time at 565 °C and $P =$ 90 s, $\tau = 1 \times 10^{-6}$ g s m^{-3}.

Run time (h)	Conversion (%)	Selectivity (%)					
		CO	CO_2	C_2H_4	C_3H_6	CH_4	H_2
1	3.2	6.9	8.2	3.0	81.8	–	–
2	5.7	12.3	27.3	1.2	35.2	24.0	3.3
3	24.9	19.7	33.2	0.7	7.9	38.5	23.5
4	91.4	31.4	32.2	0.2	1.0	35.2	29.0
5	99.2	34.1	32.0	0.2	–	33.7	22.6



(x 30.000 1 cm = 200 nm)

Figure 2. SEM microphotograph of coke formed after catalytic test at 565 °C (see table 2).

4. Conclusions

The redox mechanism is responsible for the selective propene formation involving a limited catalyst reduction and restoring of surface oxygen. When the conditions adopted do not allow the completion of the redox cycle the catalyst progressively changes. It is possible to find in this incomplete regeneration of the intrinsic oxidative capacity of catalyst the reason of CO_x formation resulting from gaseous oxygen oxidation of hydrocarbon and carbonaceous species on the catalyst surface. The deep catalyst reduction and the metallic sites generation are responsible of the alkane cracking with ethylene, methane and H_2 formation.

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