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INFLUENCE OF OXYGEN ACTIVATION ON THE CATALYTIC CRACKING OF n-PENTANE ON ZEOLITES

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The catalytic cracking of n-pentane over sodium, cerium and aluminium exchanged Y zeolites and H-ZSM-5 zeolite has been studied. A promoting action of oxygen at 693–753 K on the catalytic activity has been found to follow the order: CeY > AlNaY > > NaY > H-ZSM-5. It is suggested that oxygen adsorbed on the CeY zeolite takes part in reactions with Ce^{3+} ions.

Изучены каталитические свойства цеолитов NaY, CeY, AlNaY, HZSM5 в реакции пиролиза н-пентана в интервале температур 693–823 К. Найдено, что влияние кислорода на каталитическую активность исследованных цеолитов уменьшается в ряду: CeY > AlNaY > NaY > H-ZSM5. Предложен вероятный механизм действия кислорода в реакции пиролиза н-путана.

INTRODUCTION

In an earlier work /1/ we reported on the catalytic cracking of n-pentane on the H-ZSM-5 zeolite. In this paper we describe the role of oxygen in the acceleration of n-pentane cracking over sodium, aluminum and cerium exchanged Y zeolite and H-ZSM-5 zeolite.

EXPERIMENTAL

Catalysts were prepared from NaY zeolite by repeated exchange with the aqueous solution of cerium nitrate (0.2 N) or aluminium nitrate (0.1 N) at room temperature; 67% and 21% of Na^+ ions being replaced by Ce^{3+} or Al^{3+}, respectively. H-ZSM-5 was prepared from Na–ZSM-5 by NH_4^+ exchange. The reaction was carcied out in an ordinary batch reactor. 500 mg of the catalyst (in powder-form) was packed into a quartz reactor closed with a septum and evacuated to about

1×10^{-5} Torr for 2 h at 823–850 K. Then the catalyst was cooled to the reaction temperature, and helium or an oxygen (3 vol. %)/helium mixture was introduced to the reactor until a pressure of 500 Torr was established. 50 μl of n-pentane was injected into the reactor. The products formed were analyzed by a gas chromatograph using flame ionization detection. The details of the analytical procedure are given elsewhere /2/.

RESULTS

Measurements were performed at 693–823 K and the results are shown in Figs 1 and 2, and Table 1. Blank experiments carried out in oxygen atmosphere showed an increase in the n-pentane conversion with increasing the reaction temperature. In principle, no influence of oxygen on the n-pentane conversion was observed at 823 K. R values (defined as the ratio of the conversion of n-pentane in presence of oxygen to that in absence of oxygen) at 823 K calculated for the zeolites studied

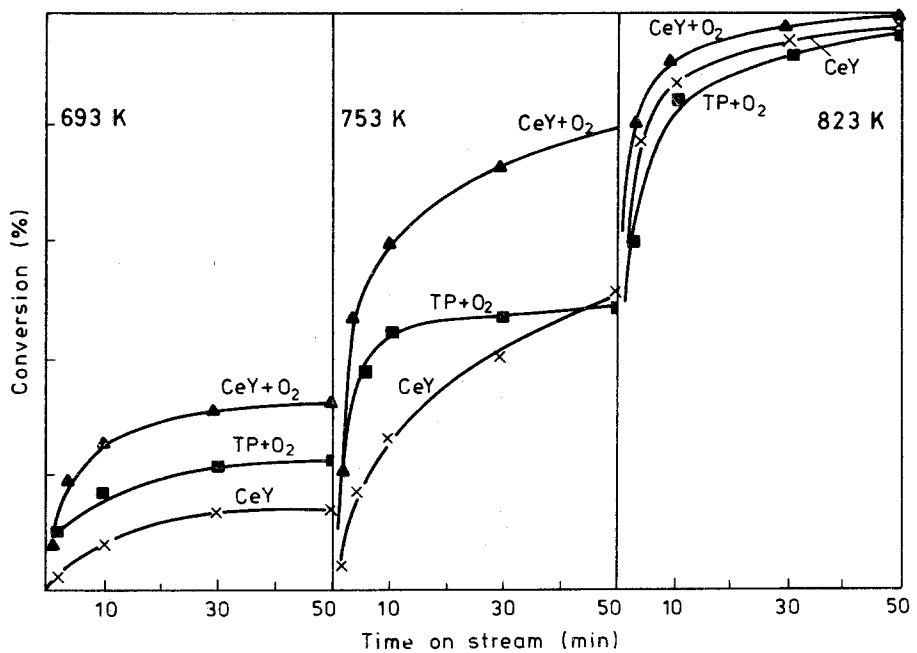

Fig. 1. The influence of oxygen on the conversion of n-pentane. Catalyst: CeY (67% exch.). TP + O_2 – thermal pyrolysis in the oxygen atmosphere.

Table 1

R values vs. time on stream for the various catalysts.
Reaction temperature: 823, 753 and 693 K

Time [min.]	$R = \frac{\text{conversion } (+O_2)}{\text{conversion}}$			
	HZSM-5	NaY	AlNaY	CeY
	823 K			
1	1.25	1.07	1.40	1.80
2	1.05	1.16	1.20	1.42
4	1.01	1.11	1.11	1.20
10	1.00	1.04	1.00	1.05
30	1.01	1.01	1.01	1.01
50	1.02	1.00	1.01	1.00
70	1.00	1.00	1.00	1.00
	753 K			
1	2.90	2.01	3.85	5.50
2	2.25	2.00	2.85	5.40
4	1.60	1.65	3.00	4.90
10	1.15	1.33	1.94	3.14
30	1.00	1.21	1.65	2.35
50	1.02	1.12	1.50	1.55
70	1.00	1.14	1.45	1.37
	693 K			
1	4.00	3.85	3.80	6.20
2	3.50	3.80	3.30	6.00
4	2.44	3.50	3.00	5.30
10	1.61	2.60	3.33	4.60
30	1.06	1.75	3.65	4.20
50	1.00	1.82	3.20	2.10
70	1.00	1.91	3.20	1.75

(Table 1) are equal about to 1. However, the conversion of n-pentane increased very distinctly at 693–753 K when oxygen had been added before starting the reaction. The promoting effect of oxygen on the catalytic activity of zeolites has been particularly observed for the CeY zeolite. The conversion of n-pentane and the yield of paraffins increased 2–4-fold, but the olefin yield reached a maximum and then decreased with the time on-stream. This can be explained by consecutive reactions of olefins /3–4/ and the coking of the catalyst.

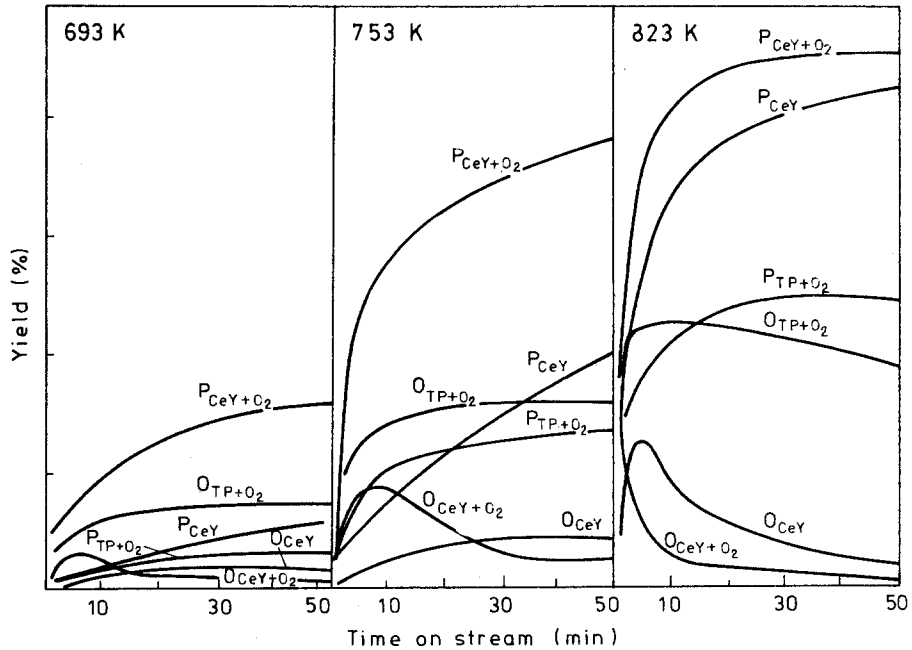

Fig. 2. The influence of oxygen on the yield of paraffins and olefins. Catalyst: CeY (67% exch.). O – olefins, P – paraffins

DISCUSSION

It is well known /5–8/ that small amounts of oxygen (1 vol. %) accelerate the catalytic cracking of hydrocarbons. Oxygen initiates the process better than thermal treatment. $RH + O_2 \rightarrow R^{\bullet} + HO_2^{\bullet}$. The $HO_2^{\bullet}$ takes part in the propagation reaction as follows:

$$RH + HO_2^{\bullet} \rightarrow R^{\bullet} + H_2O_2$$

$$H_2O_2 \rightarrow 2HO^{\bullet}$$

$$RH + HO^{\bullet} \rightarrow R^{\bullet} + H_2O$$

From our results we can summarize the following conclusions. The promotion action of oxygen in the catalytic cracking of n-pentane over zeolites can be explained by two parallel reactions occurring 1) in the gas phase and 2) on the catalyst surface. At higher temperatures, a free radical mechanism of the reaction in the gas phase

is preferred and oxygen does not influence strongly the rate of the reaction. The influence of the catalyst on the course of the reaction at high temperature (823 K) has not been observed, either. However, at lower temperatures the oxygen adsorbed on the catalyst surface can be transformed to the following oxygen species:

$$O_{2g} \rightarrow O_{2ads} \qquad O_{2g} \rightarrow 2O_{ads}$$

$$O_{2ads} + e^- \rightarrow O^-_{2ads} \qquad 2O_{ads} + e^- \rightarrow O^-_{ads}$$

$$O^-_2 + e^- \rightarrow 2O^-$$

which can enhance the catalytic activity /9/. Previously it was shown /10–11/ that oxygen adsorbed on NaCeY takes part in a reaction with Ce^{3+} ions:

$$2Ce^{3+} + O_2 \rightarrow 2Ce^{4+} + O^{2-}_2$$

$$Ce^{3+} + O_2 \rightarrow Ce^{4+} + O^-_2$$

It is suggested that O^{2-}_2 and O^-_2 species can react with hydrocarbon molecules and carbonium-ions are formed. These will take part in the catalytic cracking of n-pentane increasing thereby the conversion observed at lower temperatures.

In NaY, AlNaY and H-ZSM-5 zeolites investigated, Na^+, Al^{3+} and H^+ do not react with oxygen in the same way like Ce^{3+}. The rate of catalytic cracking of n-pentane on the above zeolites is about 2-fold lower than that found over the CeY zeolite (Table 1). In conclusion, the promoting action of oxygen on the catalytic activity of the zeolites studied in the catalytic cracking of n-pentane the following sequence can be given: CeY > AlNaY > NaY > H-ZSM-5.

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