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MINA K. MUNSHIEVA

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# Propylene Dimerization Over Nickel-Ion Exchanged Zeolites in the Liquid Phase

**Mina K. MUNSHIEVA**

*Institute of Inorganic and Physical Chemistry, Azerbaijan National Academy of Sciences, 370143, Baku, Azerbaijan Republic,  
29 H. Javid, Avenue-AZERBAIJAN*

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The possibility of the dimerization of propylene in the liquid phase over nickel-ion exchanged zeolites (Ni-zeolites) modified by treatment with  $\text{AlEt}_2\text{Cl}$  to provide enhanced activity is studied.

In order to determine the influence of the crystalline structure of zeolites on their catalytic activity and the selection of the most active catalyst the zeolites of faujasite ( $\text{NaX}$ ,  $\text{NaY}$ ), erylone and mordenite types with various structures and different cell sizes have been chosen. The samples of Ni-zeolites were prepared by ion exchange with nickel nitrate in a corresponding zeolite. The treatment of these zeolites with  $\text{AlEt}_2\text{Cl}$  leads to the formation of active dimerization of propylene catalytic systems. The activity of these systems reaches the maximum at an Al/Ni weight ratio approximately equal to 10.

It is assumed that the mechanism of propylene dimerization in the investigated catalysts is similar to the mechanism of olefin dimerization in Ziegler-Natta catalytic systems. The ESR results suggests Ni-ion participation in the formation of catalytically active species.

The distinctions in the catalytic behaviour of the studied zeolites are connected with their crystalline structure. It is probable that the dimerization process over Ni-zeolites of faujasite type goes on in the kinetic area, while in the case of Ni-erylone and Ni-mordenite, diffusional breaking, which decreases an activity of these catalysts, takes place.

The diffractographic investigation demonstrates a partial destruction of the crystalline structure of zeolite after the repeated treatment with  $\text{AlEt}_2\text{Cl}$ . The preservation of the crystalline structure from full decay presumably is the consequence of the exchanged reaction between the Ni-ion and proton - product of the interaction of Ni-zeolite with  $\text{AlEt}_2\text{Cl}$ .

## Introduction

The traditional catalysts of lower olefins' dimerization in the liquid phase are the complexes of transition metals, particularly nickel complexes in combination of organic compounds of aluminium<sup>1,2</sup>. The catalytic properties of nickel oxide supported on the various zeolites in gaseous phase olefins' dimerization are studied. However, these catalysts, which are active only at high temperatures, do not possess high selectivity<sup>3</sup>. Furthermore, the course of this reaction is generally complicated by the processes of cracking and coking. It is established that the activity of these systems can be increased by processing them by different modifiers. Thus, Japanese researchers have proposed<sup>4,5</sup> for the oligomerization of  $\text{C}_2$ - $\text{C}_6$  olefins a catalytic composition

consisting of metals (Cr, Fe, Co, Ni, Pt) or their oxides, supported on various solids possessing acidic properties, for instance  $\text{Al}_2\text{O}_3$  or zeolites, treated with organic compounds of aluminium under the atomic ratio  $\text{Al}/\text{metal}=0.05\text{-}10$ .

In the present study, the possibility of the dimerization of propylene in the liquid phase over nickel-ion exchanged zeolites (Ni-zeolites) which were modified by treatment with  $\text{AlEt}_2\text{Cl}$  to provide enhanced activity was investigated.

## Experimental

In order to study the influence of the crystalline structure of zeolites on their catalytic activity and selection of the most active catalyst the zeolites of faujasite (NaX, NaY), erylite and mordenite types with various structures and different cell sizes were chosen. The sample Ni-zeolites were prepared by ion exchange with nickel nitrate in a corresponding zeolite. The maximum exchange degree was 80% for faujasite-type zeolites and 65% in the case of erylite and mordenite.

The catalysts were prepared in a metallic reactor in a propylene environment by bringing one of the preliminarily pretreated at 623-673 K samples of Ni-zeolite into contact with  $\text{AlEt}_2\text{Cl}$  (2M) in toluene solution. By the end of the experiment the obtained product was washed of the catalysts, dried and analyzed by GLC.

Diffraction data of zeolites before and after their use in the process were registered by a DRON-2 with a Ni-filter and  $\text{CuK}_\alpha$ - radiation.

All the ESR measurements were carried out at 77 K with a JES-PE3x instrument. The ESR sample tube was connected to the gas circulating system so that the treatment conditions in both catalytic and ESR measurements were essentially identical.

## Results

It was established that the product of treatment of NiNaX and NiNaY with  $\text{AlEt}_2\text{Cl}$  exhibits high activity for propylene dimerization at 298-303 K. The conversion of propylene reaches 72 wt. %, while the samples untreated with  $\text{AlEt}_2\text{Cl}$  show no catalytic activity under the same operating conditions.

Other Ni-zeolites, such as Ni-mordenite and Ni-erylite, which have been so modified showed lower activity in propylene dimerization as compared to the aforementioned ones. These results are summarized in the Table. For convenience of comparison of catalytic activity, the Ni-zeolites with an  $\text{Ni}^{2+}$  exchange degree equal to 65% were used.

**Table 1.** Dimerization of propylene on the treated with  $\text{AlEt}_2\text{Cl}$  Ni-zeolites at 300 K;  $\text{Ni}^{2+}$  exchange degree -65%; Al/Ni weight ratio-10.

Catalyst: Ni-zeolite+ $\text{AlEt}_2\text{Cl}$	Propylene conversion, wt %	Dimers, wt%	Dimers distribution, wt%		
			methyl- pentenes	<i>n</i> -hexenes	dimethyl- butenes
NiNaX	70	90	58.5	7.8	33.7
NiNaY	72	90	55.9	3.8	40.3
Ni-erylite	40	85	39.2	3.4	51.4
Ni-mordenite	40	82	42.4	-	57.6

The dimerizing function of such systems is connected with the Ni-ion. Therefore their catalytic activity increases in an exchange degree of  $\text{Na}^+ \rightarrow \text{Ni}^{2+}$ . To show any catalytic activity of the investigated systems, it has been found the minimal must be no less than 39%.

It is assumed that the mechanism of propylene dimerization in Ni-zeolites treated with  $\text{AlEt}_2\text{Cl}$  is similar to the mechanism of olefin dimerization in the Ziegler-Natta catalytic system suggested by Wilke<sup>6</sup>.

The treatment with  $\text{AlEt}_2\text{Cl}$  imparts changes in the chemical compositions as well as catalytic properties of the investigated samples. From ESR experiments, the formation of  $\text{Ni}^+$  species with  $g_1=2.012$ ,  $g_2=2.086$  and  $g_3=2.2051$  at the reduction of  $\text{Ni}^{2+}$ -ions according to the scheme

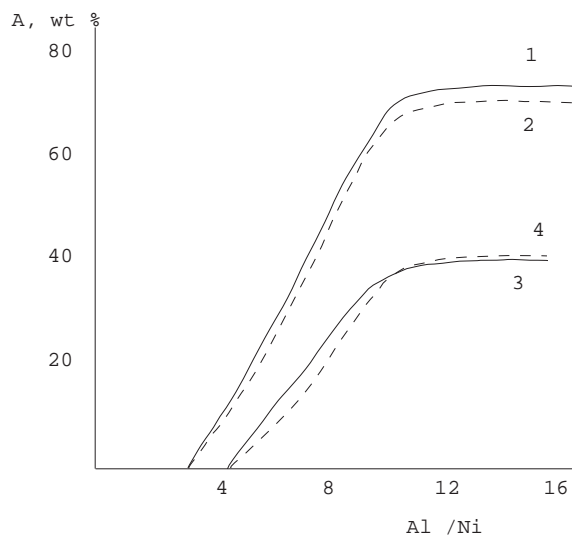


was concluded. There is no doubt that the appearance of  $\text{Ni}^+$  species results from the contacting of  $\text{AlEt}_2\text{Cl}$  with the accesible Ni-ions in zeolites. On the other hand, it is possible that the occurrence of the disproportionation reaction



also leads to the formation of  $\text{Ni}^+$ -ions. Therefore, we suppose that  $\text{Ni}^+$ -ions participate in the formation of catalytically active species<sup>7</sup>.

It was established (Table) that NiNaX and NiNaY treated with  $\text{AlEt}_2\text{Cl}$  exhibit higher activity in the dimerization of propylene than Ni-eryonite and Ni-mordenite under the same operating conditions. These distinctions in the catalytic behaviour of the studied zeolites are closely connected to their crystalline structure. It is probable that the dimerization process in Ni-zeolites of faujasite type goes on in the kinetic area, while in the case of Ni-eryonite and Ni-mordenite diffusional breaking, which decreases the activity of these catalysts, takes place. As can be seen in Figure 1, the catalytic activity of the studied system increases with increasing Al/Ni weight ratio reaching the maximum at the Al/Ni approximately equal to 10. It is necessary to have some excess of Lewis acid for the development of the catalytic systems<sup>8</sup>.

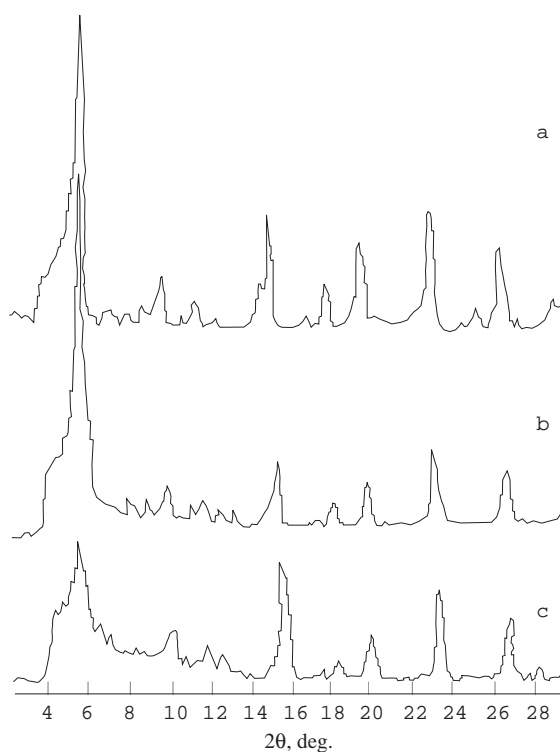


**Figure 1.** The influence of Al/Ni correlation on the conversion of propylene (A) on the catalytic system Ni-zeolite +  $\text{AlEt}_2\text{Cl}$  at 300 K ( $\text{Ni}^{2+}$  exchange degree-65%. 1) NiNaY; 2) NiNaX; 3) Ni-eryonite 4) Ni-mordenite.

To find out what changes take place in the crystalline structure of zeolites, diffractograms of the samples before and after their use in the catalytic process were taken off.

As seen in Figure 2, the process of ion - exchange does not lead to the destruction of the crystalline structure of zeolite, and after repeated processing of Ni-zeolite by  $\text{AlEt}_2\text{Cl}$  only partial destruction of the structure is observed (Fig. 2c). It should be noted that as a result of the exchange reaction, probably occurring between the Ni-ion in zeolite and the proton—the product of the interaction of Ni-ion with  $\text{AlEt}_2\text{Cl}$ , according to Wilke<sup>6</sup> – the crystalline lattice of zeolites is protected from full decay<sup>9</sup>.

In conclusion, the possibility of using zeolites in preference to the use of the faujasite type treated by organic compounds of aluminium as a catalyst for liquid-phase propylene dimerization certainly merits attention, since it enables the process to be carried out under uncomplicated operation conditions with a high product yield.



**Figure 2.** Diffractograms of samples

a) original NaY b) NiNaY c) NiNaY+ $\text{AlEt}_2\text{Cl}$

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