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Studies on the Mechanism and Kinetics of Propylene Oligomerization and Hydrooligomerization on Zeolites

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The propylene conversion process has been studied in the presence of synthetic zeolites of different types and metal ions. The NiX zeolite is selective for the oligomerization of propylene. On the zeolites of different other metal ions, the hydro-oligomerization process took place. It has been found that the obtained 3-methylpentenes are primary products of the propylene oligomerization. A scheme mechanism has been proposed assuming an intermediate of a cyclobutane derivative. The mechanism explains the formation of all the obtained products of propylene conversion on the synthetic zeolites.

Oligomerization of olefins is one of the most complicated reactions owing to its high exothermic effect. The heat liberated during the reaction accelerates different undesirable side reactions such as cracking, hydrogen transfer, double bond migration, and coke formation.[1-5] It is, therefore, difficult to study either the mechanism or the kinetics of this reaction, especially, on a solid catalyst.

To facilitate this study, two problems had to be solved. The first is the unstability of the temperature during the reaction, and the second is the competition of the side reactions, *i.e.* the selectivity of the used catalyst.

The first problem is solved[6] by making a reactor with a special construction which allows to withdraw the released heat out of the reaction zone and maintains the reaction proceed at constant temperature.

It is of interest to study the propylene oligomerization in the presence of synthetic faujasites of various metal ions for the purpose to obtain a selective catalyst. For this purpose the cations such as cobalt, nickel, manganese, and magnesium were used, the oxides of which possess a high selectivity in the propylene oligomerization.[7-10] Other cations were used for comparison.

Experimental

The various di- and trivalent cationic X and Y zeolites were prepared by exchanging the russian synthetic NaX ($Na_2O \cdot Al_2O_3 \cdot 2.4SiO_2 \cdot nH_2O$) and NaY ($Na_2O \cdot Al_2O_3 \cdot 48SiO_2 \cdot nH_2O$ zeolites).[3] The degree of exchange was maintained at ≈65% for the X Zeolites and ≈85% for the Y Zeolites. A catalyst with 80% of nickel-exchange was also prepared from the NaX zeolite. The ion-exchanged powders were compressed without binders into tablets, 4 mm in diameter and 5—6 mm in thickness.

Propylene conversion activity was measured under atmospheric pressure with 40 ml of catalyst in a fixed bed reactor of conventional design. The catalyst was calcined at 550 °C in a flow of dry air for 4 h and then in a flow of nitrogen for 1 h. After calcination the temperature was adjusted to the desired value. The feed in each run was 4 liters of 100% propylene.

Both gaseous and liquid products were collected separately. Each was analyzed by the gas and liquid chromatography. Liquid products were also analyzed by the infrared spectroscopy. The olefin products were determined quantitatively and separated by the thin layer chromatography using a fluorescene indicator[11]. The total catalytic activity of the catalyst was calculated by the percentage of converted propylene.

The initial temperature was 190 °C, but due to the exothermic behaviour of the studied reaction, it quickly increased by about 20—25 °C depending on the treated zeolite catalyst. For kinetic experiments a reactor of special design[6] was used which allowed to maintain the temperature constant.

The part of liquid products which cannot be obtained by suction after the run, was cracked by raising the temperature slowly to 550 °C. Gases and liquids of C_1—C_8 paraffins were formed and the colour of the catalyst became dark due to the formation of coke. The amount of the latter was determined.

Results and Discussion

Catalytic Activity of Zeolites. The catalytic activity of various ion-exchanged zeolites was tested at an initial temperature of 190 °C and space velocity of propylene 40 ml (ml catalyst)$^{-1}$ h^{-1} (Table 1). The overall order of activity is LaY$\simeq$LaX$\simeq$CeX$\simeq$MgY$>$NiY$>$CoY$>$AlY$>$MgX$>$MnY$>$NiX$>$CoX$>$CaX.

When cations are of the same group in the periodic table a certain relation may be obtained.[12] Attempts have failed to correlate the obtained catalytic activities with the ionic radii or ionization potential of the exchanged metal cations of different groups of the periodic table. Thus, each metal ion has its own ability to perform a certain change in the zeolite lattice depending on its own electronic configuration.

Selectivity of Zeolites. Depending on the zeolite form it is possible to obtain liquid products which contain only olefins, paraffins or mixtures of both. In the presence of all the tested zeolites no aromatics are detected by the infrared spectral analysis.

In the cases of CoX, MnX, and MgX, 18.9, 10.1, and 20.2% olefins are, respectively, separated from the liquid products by the thin layer column chromatography. The other products are C_4—C_9 paraffins. The IR spectra of the separated olefins indicate the presence of two bands at 910 and 965 cm^{-1} characteristic for double bonds of the vinyl and transvinyl types.[13] The 890 cm^{-1} band characteristic for the double bond of vinylidene type is absent.

In the presence of all tested zeolites except NiX only paraffinic hydrocarbons are formed, as indicated by both chromatographic and infrared spectral analyses. The composition of these paraffins are presented in

TABLE 1. PROPYLENE CONVERSION ON VARIOUS ZEOLITE CATALYSTS AT 190 °C AND 0.025 h

Catalyst	MgY	NiY	CoY	CaY	AlY	LaY	CaY	CeX	LaX
Propylene conversion, wt %	98.7	92.0	90.7	62.4	88.1	98.4	32.6	98.8	98.3
Liquid products, wt %	18.7	32.4	31.0	32.0	22.4	7.8	28.4	2.0	5.24
Propane, wt %	3.9	8.8	5.7	6.3	1.6	15.1	3.0	12.2	14.3
C_2, C_4, and C_5 paraffins, wt %	10.8	3.6	5.0	14.5	6.1	25.9	10.2	13.2	27.0
Unrecovered liquid converted into gas and liquid by heating,[a] wt %.	54.6	26.2	30.3	23.9	58.6	38.0	35.0	57.1	35.6
Unrecovered liquid converted into coke,[a] wt %.	9.8	28.9	27.6	21.7	10.9	13.2	22.5	15.1	17.8

a) These products were obtained by raising the temperature of the catalyst to 550 °C after the run.

TABLE 2. PRODUCTS OF PROPYLENE CONVERSION ON ZEOLITES AT 190 °C AND 0.025 h

Product	MgY	NiY	CoY	CaY	AlY	LaX	CaX	CeX	LaX
Isobutane	7.68	3.86	2.51	3.72	0.28	0.10	0.00	0.83	5.34
Butane	0.89	0.24	0.03	4.52	0.00	0.00	0.00	2.54	0.48
2-Methylbutane	28.05	21.40	17.83	11.22	8.59	5.02	2.77	18.11	23.11
Pentane	0.89	0.56	0.13	0.00	0.83	0.29	0.00	0.98	0.98
2,3-Dimethylbutane +2-Methylpentane	27.63	32.47	32.47	28.15	22.18	29.25	11.29	24.62	31.92
3-Methylpentane	9.90	18.43	11.65	8.74	7.70	12.92	4.62	13.11	14.81
Hexane	0.89	3.37	0.33	0.00	0.62	0.97	0.74	1.39	1.18
2,4-Dimethylpentane	4.43	3.21	6.17	8.00	6.47	4.47	5.74	3.61	3.50
2-Methylhexane	5.02	4.92	5.77	6.32	5.39	9.91	9.44	7.62	5.44
2,3-Dimethylpentane	6.21	3.47	8.56	10.40	8.68	6.21	13.14	4.92	3.05
3-Methylhexane	4.88	4.15	7.77	6.88	6.32	11.66	8.51	8.19	6.48
3-Ethylpentane	0.00	0.14	0.24	0.00	0.18	0.49	1.11	0.39	0.20
Heptane	0.00	0.17	0.30	0.00	0.28	0.47	0.00	0.08	0.00
2,2-Dimethylhexane	0.34	0.84	0.17	1.00	2.59	1.63	0.00	1.18	0.28
2,4- + 2,5-Dimethylhexane	2.17	1.39	0.41	4.28	5.54	3.47	12.76	2.52	0.38
2,3,4-Trimethylpentane	0.59	0.04	0.02	0.33	0.09	0.00	0.02	0.03	0.71
2,3,3-Trimethylpentane +2-Methylheptane	0.93	0.82	0.64	3.72	2.95	2.38	9.07	1.71	0.56
2,3-Methylethylpentane	1.25	0.64	0.30	0.40	1.80	1.28	0.00	0.10	0.02
2,3-Dimethylhexane	0.00	0.00	0.00	0.00	2.22	0.48	0.00	0.28	0.01
4-Methylheptane	0.35	0.29	0.21	0.46	0.92	1.04	2.04	0.72	0.02
3-Methylheptane + 3,4-Dimethylhexane	1.14	0.97	0.45	1.55	0.24	3.15	4.81	2.52	0.66
3-Ethylhexane	0.22	0.18	0.16	0.31	0.10	0.28	1.32	0.24	0.00
Total C_9	1.04	2.97	4.15	0.00	16.13	3.58	12.62	4.26	0.92
Calculated octane number	83.1	80	85	78	—	—	—	—	82

Table 2. Presence of hexane, methylpentanes, and dimethylbutane gives evidence that a hydrodimerization reaction takes place on these zeolites. The C_9 paraffins are formed by hydrotrimerization of propylene. In addition to that, C_2, C_4, C_5, C_7, and C_8 paraffins are formed. This suggests that hydrodimerization of propylene into trimers and tetramers is accompanied by a cracking and then by subsequent hydrogen transfer to the cracking products. The distribution of C_4—C_9 paraffins in the liquid products seems to depend on the exchanged cations (Table 2). The zeolites NiY and LaX give more dimers (47.9, 49.7%), while AlY and CaX give more trimers (16.1; 12.6%). Also the quantity of propylene converted into propane, and the part of the liquid which remained on the zeolite (Table 1) depend on the nature of the exchanged cation and the SiO_2: Al_2O_3 ratio.

The products which remain on the zeolites are probably propylene high oligomers, formed and captured within the pores of zeolites, which on heating crack into C_1—C_8 molecules and pass through the windows of the zeolite pores.

The most interesting zeolite catalyst is the NiX. The reaction products of this catalyst are pure oligomers and 95.49% of which are dimers (Table 3). The calculated octane number of these products is about 94. They contain more than 34% of hexenes which usually[14] do not exceed 10% if an acid catalyst is used. Within the other dimers 3-methylpentenes are present. The presence of these dimers were previously[15] attributed to secondary rearrangement.

In the presence of NiX with a higher degree of nickel ions (80%), C_5, C_7, and C_8 olefins are formed. Thus replacement of the more difficultly exchangeable sodium ions by nickel, enhances the cracking of the formed propylene oligimers.

Table. 3. Composition of propylene oligomers obtained on NiX at 190 °C and 0.025 h

Propylene oligomer	wt %
2-Methyl-2-pentene	27.40
trans-2-Hexene	23.50
trans-3-Methyl-2-pentene + *cis*-2-hexene	11.50
trans- and *cis*-3-hexene	10.24
cis-4-Methyl-2-pentene	1.57
trans-4-Methyl-2-pentene	8.35
2-Methyl-1-pentene + 1-hexene	8.53
cis-4-Meth–l-1-pentene	0.79
cis-3-Methyl-2-pentene	1.26
2,3-Dimethyl-2-butene	1.09
2,3-Dimethyl-1-butene	1.26
Trimers	4.51
Octone number	94

Kinetics of Oligomerization. It is of interest to determine the kinetic curves of the oligomerization to obtain information on the 3-methylpentenes, *i.e.* whether they are secondary products or not. Thus the oligomerization was carried out on the NiX zeolite at different temperatures (190, 205, 217, and 225 °C) and contact times (0.01—0.037 h). Figure 1 reveals a similar character of the decrease of the different dimer contents, as well as that of the 3-methylpentenes with the decrease of the contact time. The same results were obtained at the temperatures of 190, 205, and 217 °C. If 3-methylpentenes are secondary products, then their contents should decrease with a higher degree than the other dimers. With respect to the 3-methylpentane the same results were obtained[16] over the HNaY zeolite as an example of the zeolites over which hydrooligomerization takes place. These experimental facts indicate that the 3-methylpentenes and the 3-methylpentane are primary products of propylene dimerization and hydrodimerization, respectively. They cannot be produced under the used experimental conditions by secondary skeletal isomerization of either hexenes or 2-methylpentenes.

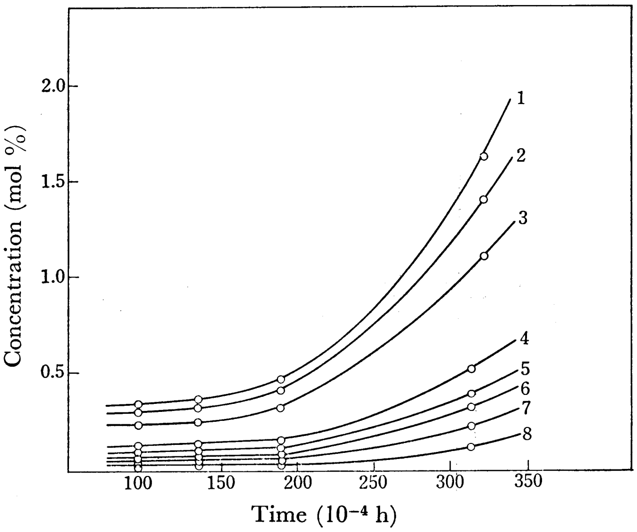
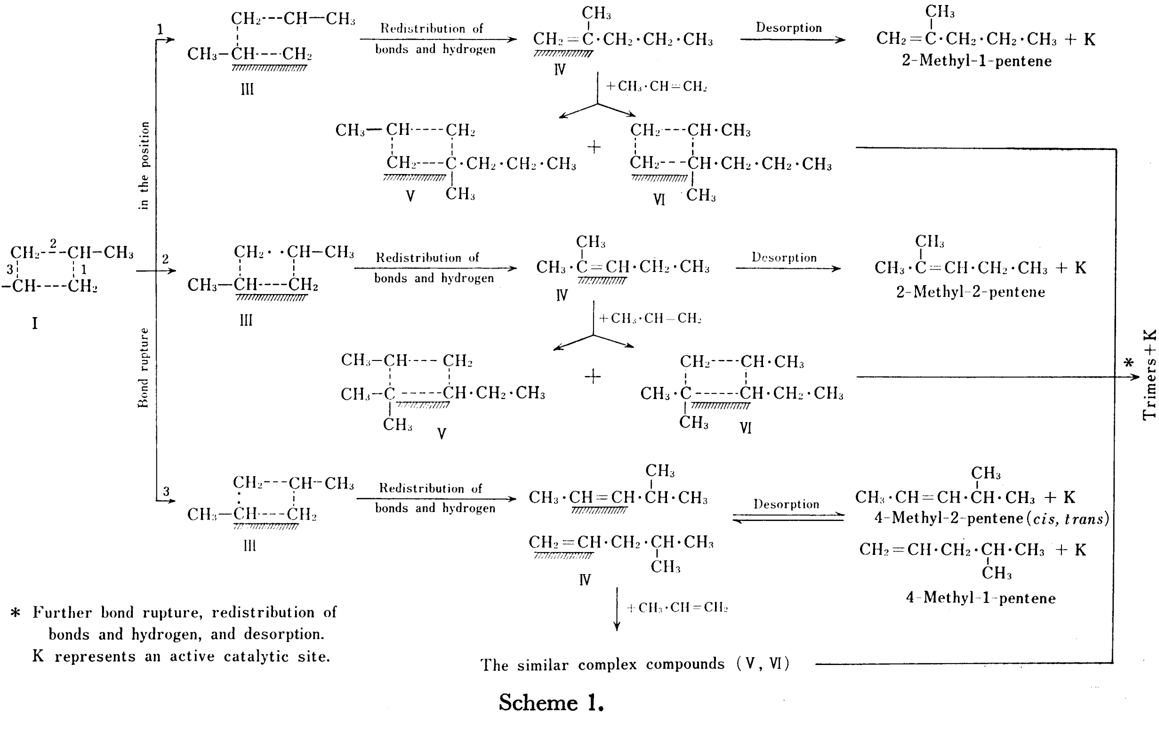


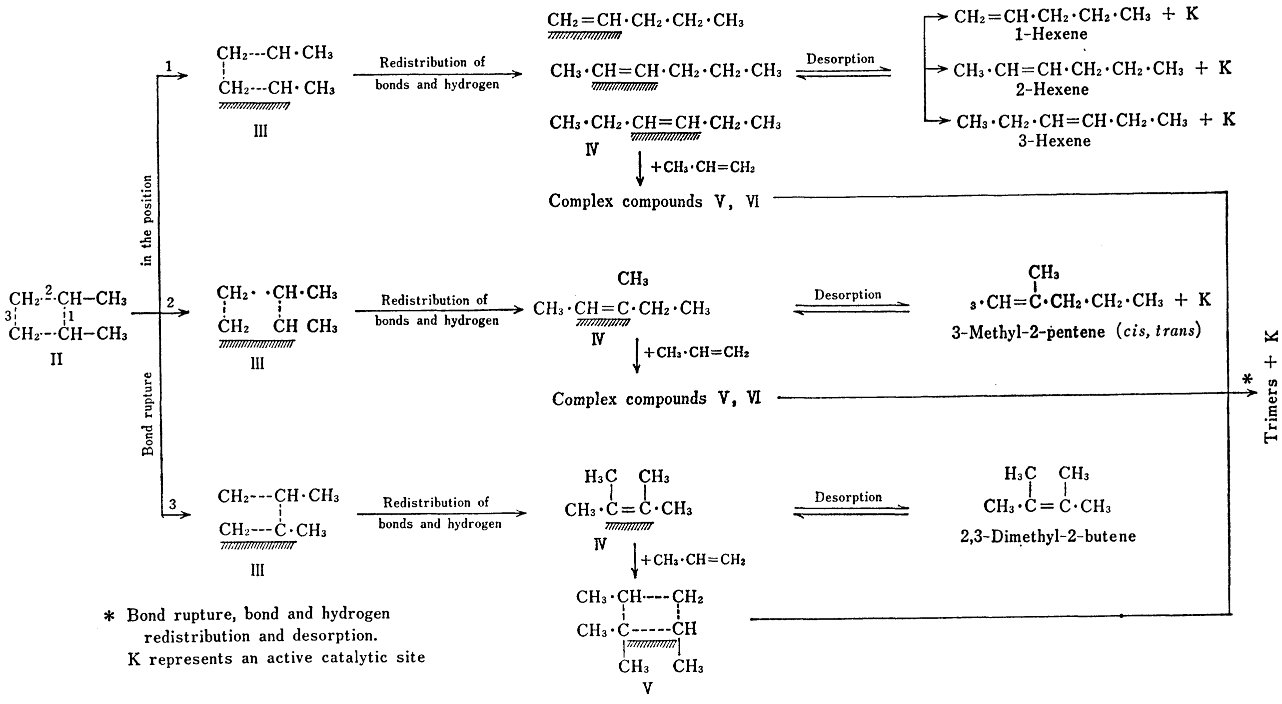
Fig. 1. Distribution of propylene dimers against contact time at a reaction temperature of 225 °C.
1: 2-Methyl-2-pentene, 2: *trans*-2-hexene, 3: *trans*-3-methyl-2-pentene+*cis*-2-hexene, 4: *trans*- and *cis*-3-hexene, 5: 2-methyl-1-pentene, 6: *trans*-4-methyl-2-pentene+1-hexene, 7: *cis*-3-methyl-2-pentene, 8: 2,3-dimethyl-2-butene.

Reaction Mechanism. The 3-methylpentenes cannot be explained as the primary products of propylene dimerization neither by a carbonium-ion mechanism nor by any other mechanism which assumes an open-chain hydrocarbon as the activated intermediate. A mechanism of dimerization has been proposed,[8] over the nickel oxide on silica-alumina catalyst, which



* Further bond rupture, redistribution of bonds and hydrogen, and desorption.
K represents an active catalytic site.

Scheme 1.

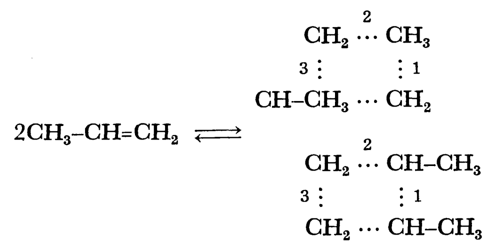


* Bond rupture, bond and hydrogen redistribution and desorption.
K represents an active catalytic site

Scheme 2.

assumes an intermediate of a cyclobutane derivative. Examination of the present results has shown that the same mechanism may hold for the conversion of propylene on the investigated zeolites.

It is possible that these intermediate compounds can be formed when a propylene molecule reacts with an adsorbed one on the zeolite surface as follows:



$$2CH_3\text{-}CH{=}CH_2 \rightleftarrows \begin{array}{l} \begin{array}{ccc} & 2 & \\ CH_2 & \cdots & CH_3 \\ 3\vdots & & \vdots 1 \\ CH\text{-}CH_3 & \cdots & CH_2 \end{array} \quad (I) \\ \begin{array}{ccc} & 2 & \\ CH_2 & \cdots & CH\text{-}CH_3 \\ 3\vdots & & \vdots 1 \\ CH_2 & \cdots & CH\text{-}CH_3 \end{array} \quad (II) \end{array}$$

The formed dimethylcyclobutanes, I and II, are unstable complexes, and therefore they either converted to the initial molecules or undergo a bond rupture. The latter may take place in the bond 1, 2, or 3. The bond rupture of complex I (Scheme 1) or complex II (Scheme 2) leads to the formation of extremely unstable complexes III, which undergo rearrangement and hydrogen redistribution. As a result, the propylene dimers, II, are formed on the zeolite surface.

Depending on the catalyst selectivity and the experimental conditions the redistribution of hydrogen can lead to the formation of propylene dimers as in the case of NiX zeolite (Table 3) and hydrodimers (paraffins) as in the case of other zeolites (Table 2).

The hydrodimerization leads to the formation of hydrodimers and compounds of poor hydrogen content. Dimers (Table 3) and hydrodimers (Table 2) of different structures are formed due to the rupture of different bonds of I and II. Thus if the rupture occurs at positions 1, 2, or 3, then 4- or 2-methylpentenes are formed in the case of complex I (Scheme 1), and hexenes, 3-methylpentenes or 2,3-dimethylbutenes in the case of complex II (Scheme 2). The formation of 2-methyl-2-pentene and *trans*-2-hexene in large quantities (Table 3, Fig. 1) indicates that the rupture at position 2 (complex I) and position 1 (complex II) occurs much easier than at other positions.

If the rate of desorption is relatively slow, the formed dimers, IV, on the zeolite surface can adsorb another propylene molecule forming the complex V or VI which are unstable as well as complexes I and II. They are converted either to the initial state or undergo bond rupture, bond and hydrogen redistribution and desorption to give propylene trimers or hydrotrimers.

The presence of C_2, C_4, C_5, C_7, and C_8 paraffinic hydrocarbons (Table 2) indicates that bond ruptures may take place for two bonds of complexes V and VI.

Similarly if trimers are not relatively rapidly desorbed they can adsorb another propylene molecules forming, in the same manner, tetramers and so on.

The above mechanism explains the formation of obtained products during the propylene conversion over the zeolites studied. However, the difference in the selectivity of the various cation-exchanged zeolites is not clear. This difference can be explained in view of some recent works[17-20)] which reported the existence of two types of active sites with different acidic strengths on faujasite. Barthomeuf and Beaumont[21)] reported that weak active sites are related to the cationic sites which are easily exchangeable. Thus, it can be concluded that hydrooligomerization and the accompanied cracking reaction require the stronger active sites compared to the oligomerization. This conclusion is supported by the fact that exchange of the more difficultly exchangable sodium ions by nickel cations, leads to cracking of some of the formed propylene oligomers. On the other hand, it is evident[17,22] that the ratio of strong acidic sites to all the sites on faujasite increases with the increase of the SiO_2: Al_2O_3 ratio. This may explain the reason why the hydrooligomerization takes place on NiY (SiO_2: Al_2O_3=4.8) and oligomerization takes place on NiX (SiO_2: Al_2O_3=2.4). As the conclusion, the difference in selectivity of the various cation-exchanged zeolites in propylene conversion, probably, relates to the change in the acidic strength distribution of the active sites on the zeolite surface, which is due to the SiO_2: Al_2O_3 ratio and the different effect of each cation. However, this conclusion requires further studies on the quantitative basis.

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