Alkylation of dichlorobenzene isomers by olefins on zeolites Y and pentasil

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Catalytic alkylation of dichlorobenzene isomers by ethylene and propylene on zeolite catalysts has been studied. It has been determined that using catalysts based on zeolite Y makes it possible to change the ratio of 1-alkyldichlorobenzenes formed within a wide range by varying the acidic properties of the catalysts.

Key words: alkylation, dichlorobenzenes, olefins, zeolites.

Practical methods for synthesizing alkyldichlorobenzenes (ADCB) are based on liquid-phase chlorination of alkylbenzenes in the presence of Lewis acids.[1] This usually results in a mixture of isomeric products. The selectivity of ADCB preparation can be improved by changing the order of introducing substituents into the benzene ring. This alternative and poorly studied method is alkylation of dichlorobenzene (DCB) isomers by olefins in the presence of zeolite catalysts.

Experimental

Dichlorobenzenes were alkylated by C_2—C_3 olefins under pressure in a laboratory catalytic installation with a flow-type isothermal reactor.[2] Zeolite Y (Si/Al = 2.2) in the lanthanum-calcium-decationized form and pentasil (Si/Al = 20) in the decationized form were used as catalysts. The degrees of sodium exchange were 99.0 and 99.5 %, respectively.

Physicochemical properties of catalysts were studied by X-ray diffractometry, thermal gravimetry, and atomic absorption spectroscopy. Acidic parameters of samples were determined by programmed thermal desorption of ammonia.[3]

Individual isomers of DCB (the content of the main substance was 98 %) and their mixture (16 % of 1,2-DCB, 54 % of 1,3-DCB, and 30 % 1,4-DCB) were used. The DCB : olefin ratio in the raw material for alkylation was 4.5 : 1 (mol mol^{-1}).

Initial compounds and reaction products were analyzed by GLC, GLC-MS, and ^{1}H and ^{13}C NMR. The structures of compounds were established by known procedures.[4,5]

Results and Discussion

The results of alkylation of individual DCB isomers with ethylene and propylene in the presence of LaCaHY are presented in Table 1. The selectivity of formation of monoalkyldichlorobenzenes in the alkylation of DCB isomers by propylene is somewhat higher than that for the alkylation by ethylene.

The GLC-MS analysis of alkylation products shows that the alkylation of DCB by ethylene results in the products with molecular weight up to 258, while the molecular weight of the products of propylene alkylation is not higher than 230 amu.

The activity (degree of conversion) of DCB isomers in alkylation is related to their basicity and reaches high values for 1,3-DCB (the degree of conversion is 25 %), and this value changes in the series

1,3-DCB > 1,4-DCB > 1,2-DCB.

Since chlorine is the *ortho—para*-orientant in the aromatic ring, it could be expected that alkylation of individual DCB isomers would result in the synthesis of certain alkyldichlorobenzenes.

In the case of 1,2-DCB, the inconsistent orientation of chlorine atoms in the aromatic ring could cause the synthesis of 1-alkyl-2,3-DCB and 1-alkyl-3,4-DCB. At the same time, the concerted orientation of both chlorine atoms for 1,3-DCB should result in the formation of 1-alkyl-2,4-DCB and 1-alkyl-2,6-DCB, respectively. However, the formation of the latter should be negatively affected by the steric factor, because position 2 in a DCB molecule is shielded by chlorine atoms.

The experimental data obtained partially confirmed these assumptions.

Table 1. Selectivity of the formation of alkyl-substituted DCB derivatives in DCB alkylation by ethylene and propylene on LaCaHY

Initial	Ethyl-substituted		Isopropyl-substituted	
DCB	mono	poly	mono	poly
1,2-DCB	98.5	1.5	99.5	0.5
1,3-DCB	97.0	3.0	98.7	1.3
1,4-DCB	99.8	0.2	99.9	0.1

Note. Experimental conditions: $T = 523$ K, $p = 3.0$ MPa, volume rate 1 h^{-1}, DCB : olefin = 4.5 : 1.

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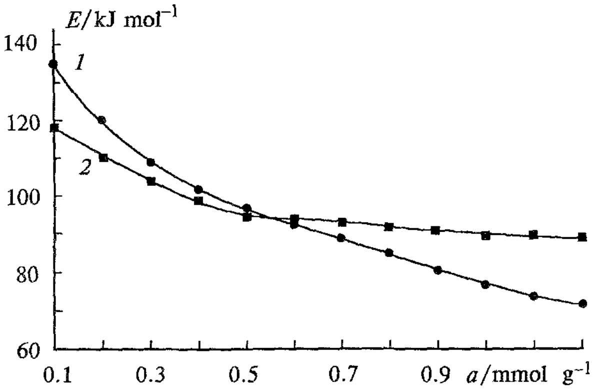

Fig. 1. Activation energy of ammonia desorption with catalyst samples that were thermally activated (*1*) and subjected to TVT (*2*).

Equal amounts of 1-alkyl-2,3- and 1-alkyl-3,4-DCB are obtained by the alkylation of 1,2-DCB with olefins, which is in accordance with the previously observed data.[6] The alkylation of 1,3-DCB with ethylene results in 1-ethyl-2,4- and 1-ethyl-2,6-DCB in the 1.5 : 1 ratio. In the case of alkylation of this DCB isomer with propylene, the ratio between 1-isopropyl-2,6- and 1-isopropyl-2,4-DCB is 4 : 1.

The alkylation of 1,4-DCB with olefins results only in the formation of 1-alkyl-2,5-DCB.

To increase time of the continuous work of the LaCaHY sample, which is metastable in DCB alkylation, the method of thermal vapor treatment (TVT) of the catalyst is used.

The experiments show that the TVT increases not only the catalytic stability of LaCaHY, but also considerably changes the selectivity of alkylation. For example, when 1,3-DCB is alkylated with ethylene, the amount of 1-ethyl-2,6-DCB formed is 1.5 times greater than that of 1-ethyl-2,4-DCB, which is probably related to a decrease in the effect of the steric factor. In the case of propylene, equal amounts of 1-isopropyl-2,4-DCB and 1-isopropyl-2,6-DCB are obtained. In addition, the ability of LaCaHY to selective alkylation increases after the TVT. As a result, the selectivity of alkylation of 1,3-DCB reaches 80—85 % when the mixture of DCB isomers is used as the raw material, while the selectivity does not exceed 50—55 % for the untreated catalyst sample.

The observed change in selectivity of LaCaHY after the TVT is probably caused by the change in acidic parameters of the catalyst (Fig. 1).

Starting from the results obtained and taking into account that zeolites Y have no molecular-sieve effect as compared to the pentasil-type zeolites, zeolite HZSM-5 is used in further experiments for DCB alkylation with ethylene.

The activity of HZSM-5 in alkylation of individual DCB isomers is nearly the same as that of LaCaHY. HZSM-5 just as easily catalyzes ethylene alkylation regardless of the initial DCB isomer, *i.e.*, no regularity of the activity of isomers similar to that in the case of LaCaHY is observed.

HZSM-5 exhibits the highly selective activity with respect to 1,3-DCB in alkylation of the mixture of DCB isomers with ethylene. The selectivity of alkylation of this isomer reaches 95 %. 1,4-DCB (of two other DCB isomers) is transformed insignificantly (the selectivity is not greater than 1.5—2 %) on the narrow-pored zeolite.

It should be also mentioned that, unlike LaCaHY, only 1-ethyl-2,4-DCB is formed (the selectivity is 98 %) and trace amounts of 1-ethyl-2,6-DCB are present in the catalysis of alkylation by HZSM-5 zeolites. The further modifications of pentasil do not result in noticeable changes in its activity and selectivity in alkylation.

Thus, the use of catalysts based on zeolite Y in alkylation of DCB with olefins allows one to vary the ratio of 1-alkyl-DCB formed within a rather wide range modifying acidic properties of catalysts. The pentasil-type zeolites possess a substantially narrower range of regulating regioselectivity of alkylchlorobenzene synthesis.

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