STUDY OF THE CATALYTIC ACTIVITY OF DECATIONIZED L ZEOLITES IN TRANSFORMATIONS OF 0-XYLENE

UDC 542.97:547.534.2

D. A. Kondrat'ev, I. V. Mishin, T. Matkhé, A. A. Dergachev, A. M. Rubinshtein, and Kh. M. Minachev

Isomerization and disproportionation of o-xylene are frequently used as model catalytic reactions. Measurement of the total conversion of o-xylene on modified zeolites makes it possible to correlate the catalytic activity with the concentration of different cations and concentration of acidic centers [1]. The effect of the chemical composition of the zeolites on the selectivity of transformation of xylenes has been studied much less extensively.

In developing the systematic study of transformations of xylenes on high-silica zeolites with different structures and degrees of ion exchange [2], the sequence of the substitutions of K^+ ions for NH_4^+ ions in type L zeolites was studied, and the catalytic activity of a series of decationized zeolites was determined.

EXPERIMENTAL

A series of NH_4KL zeolites with degrees of exchange of K^+ for NH_4^+ ions of 17-82% were used. The K form of L zeolite, synthesized with a ratio of $SiO_2/Al_2O_3 = 5.2$, was used as the initial sample. Ion exchange was conducted by repeated treatment of the K form of the zeolite with 0.1 M of a solution of NH_4NO_3 at ~20°C. A sample with a 90% degree of exchange was prepared by the method in [3] by two-step treatment of the zeolite with a solution of NH_4NO_3 and intermediate heating at 450°C.

The catalytic activity was determined in both flow and micropulse systems. The experiments in the flow system were conducted at 0.1 MPa and 360°C in a He current; the catalysts were activated with air 3 at 425°C. The space velocity of the o-xylene was 180 h⁻¹, and the He:hydrocarbon molar ratio was 5.5. The products were analyzed by GLC in a capillary column packed with squalane (5%) at 70°C.

The reaction was conducted in the micropulse system at 320°C; the carrier gas, He, was fed in at the rate of 2.1 liters/h. The catalysts were heated for 2 h at 425°C in an He current before measurement of the activity. The products of the reaction were analyzed on a column (2 m) packed with Porolite containing 5% Bentone-34 and 5% phthalic acid dioctyl ester.

DISCUSSION OF RESULTS

Ion Exchange. The isotherm of exchange of K^+ ions for NH_4^+ ions in the zeolite, plotted from the results of the chemical analysis of the zeolites and equilibrium solutions, was almost totally below the diagonal line in the diagram (Fig. 1). This indicates the low selectivity of KL zeolite with respect to NH_4^+ ions.

The isotherm can be divided into two parts. The inflection point corresponds to removal of $\sim 30\%$ of the K⁺ cations. The cations near the walls of the large channels which are least stably bound with the skeleton (site D in Fig. 2) are probably exchanged first [4]. A further increase in the degree of exchange takes place, apparently due to removal of the cations located between the cancrinite cells (C sites) and partially in the cells themselves (B sites).

It was possible to replace 82% of the K^+ cations with the usual method of exchange at ~ 20°. The remaining cations [~1.5 in the unit cell (uc)] are most probably located inside the hexagonal prisms (position A). Actually, the 82% degree of exchange corresponds to total displacement of K^+ ions from sites B, C, and D (8.3 cations per uc).

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 11, pp. 2510-2515, November, 1982. Original article submitted February 22, 1982.



Fig. 1. Isotherm of exchange of K^+ cations for NH_4^+ ions in

zeolite L (1) and dependence of the separation factor $\gamma \frac{NH_4^+}{K^+}$

on the degree of exchange (2). X is the equivalent fraction of NH_4^+ in the solution, and Y is the equivalent fraction in the zeolite.

Fig. 2. Projection of the L zeolite skeleton on the plane perpendicular to axis C. The letters indicate the locations of the cations.



Fig. 3. Dependence of the catalytic activity of decationized L zeolites on the degree of ion exchange [1) flow reactor, 2) pulse reactor] and change in the number of centers (3) which adsorb NH_3 with heats > 115 kJ/mole according to the data in [6]; N is the number of centers with q = 115-125 kJ/mole.

Fig. 4. Dependence of the selectivity of transformation of o-xylene (D/T) on conversion. Data obtained in flow (1) and micropulse (2) systems.

The degree of exchange was increased to 90% by two-step exchange with intermediate heating of the zeolite; this corresponds to the ion-exchange capacity of a dehydrated sample, equal to 3.6 meq/g. However, approximately half of the A sites remained unsubstituted in this sample.

The dependence of the separation factor (γ) on the degree of ion exchange calculated by the method in [5] shows that γ decreases continuously as the degree of ion exchange increases (see Fig. 1).

	Composition of products, %								
Zeolite	· ·	`````````````````````````````````	1	xylenes					
	benzene	toluene	<i>p</i> -	<i>m-</i>	0-	trimethylben- zenes			
NH4KL-56% NH4KL-82% NH4KL-90%	0,5	2,5 19,4 25,3	1,6 8,3 9.1	16,8 30,5 26,9	78,0 25,2 11,5	1,0 16,1 25,2			

TABLE 1. Composition of the Products of Transformation of o-Xylene on NH₄KL Zeolites in a Flow Reactor at 360°C

TABLE 2. Composition of the Products of Transformation of o-Xylene on NH_4KL Zeolites in a Micropulse Reactor at 320°C

	Composition of products, %								
	toluene	xylen	es	trimethylbenzenes					
Zeolite		p- and m-	0-	1, 2, 3-	1, 2, 4-	1, 3, 5-			
NH4KL-56% NH4KL-82% NH4KL-90%	6,45 14,9 15,3	16,9 34,9 34,9	70,2 37,5 34,8	0,6 0,7 1,9	4,2 8,4 9,6	1,7 3,5 3,4			

TABLE 3. Transformation of 1,2,4-TMB on NH₄KL-82% Zeolite

		Composition of products, %						
			xylenes	trimethylbenzenes				
Type of reactor	'T., ℃	toluene		1, 3, 5-	1, 2, 4-	1, 2, 3-	tetramethyl- benzenes	
Flow Pulse	360 320	0,9 1,6	16,1 12,5	12,7 22,1	41,3 49,2	4,2 5,8	24.9 8,7	

TABLE 4. Transformation of an Equimolar Mixture of 1,2,4-TMB and Toluene on NH₄KL-82% Zeolite

······································	T., °C	Composition of products, 7/0						
Type of re- actor		toluene	xylenes	trimethylbenzenes:				
				1,3,5-	1,2,4-	1, 2, 3-	tetramethyl- benzenes	
Flow Pulse	360 320	44,5 47,8	11,5 6,8	$6,2 \\ 3,8$	29.5 35,6	2,5 2,6	5,5 3,4	

The low selectivity of KL zeolite for NH_4^+ ions is apparently due to the fact that almost all of the cations in this type of zeolite are screened by the skeleton. The absence of nonlocalized cations in KL zeolite is demonstrated by x-ray diffraction data and is confirmed by measurements of the differential heats of adsorption of ammonia on the K form [6].

<u>Catalytic Activity</u>. Figure 3 gives an idea of the correlation between total conversion of o-xylene and the degree of ion exchange. Marked catalytic activity is exhibited by samples with a degree of decationization > 50%. In measuring the activity in the flow system, it was found that total conversion of o-xylene increases almost linearly from 22% for the NH₄KL-56% sample to 88.5% for NH₄KL-90% zeolite. The data obtained in the micropulse system show that the activity increased most significantly with an increase in the degree of exchange from 46 to 72%, while the activity increased weakly in the more deeply decationized samples. On the whole, the data from measurement of the catalytic activity by both methods are in good agreement and suggest the presence of a threshold concentration of K⁺ cations above which L zeolites do not exhibit any activity in transformation of o-xylene.

The presence of a threshold concentration of cations in the zeolites in carbonium-ion type reactions is well known for faujasites. The low catalytic activity of zeolites with small degrees of exchange are usually related to the absence or inaccessibility of strong acidic centers in these samples. Determination of the acidity of the NH_4KL zeolites used in this study by the method of adsorption calorimetry [7] showed that there are three types of acidic centers in these samples. In accordance with the findings of measurement of the heats of adsorption of NH_3 prior to removal of approximately half of the K⁺ cations, the acidic centers formed adsorb

 NH_3 with heats $\leq 115 \text{ kJ/mole}$. The appearance of stronger centers which adsorb NH_3 with heats > 115 kJ/mole is only observed in samples in which > 50% of the K cations have been removed. A comparison of the catalytic data reported in the present article with the results of measuring the heats of adsorption of NH_3 taken from [7] suggests that transformation of o-xylene primarily takes place in the strongest acidic centers (see Fig. 3).

The nature of the dependence of the activity of NH_4KL zeolites on the degree of ion exchange can vary in reactions with other organic molecules. In studying the activity of NH_4KL zeolites in cracking of cumene, it was found that the degree of transformations of cumene into benzene and propylene increased in passing from KL zeolite to a 66% decationized sample [8]. It was shown in [9, 10] that NH_4KL zeolites are not distinguished by high thermostability, and destruction of the crystalline structure and dehydroxylation take place above 500°C. According to the data cited in [11], the cracking activity of NH_4KL zeolites heated at 550°C increases with small degrees of exchange, attains a maximum with α of 25–50%, and decreases sharply after removal of more than half of the K⁺ cations. The hypothesis that migration of protons into the cancrinite cells inaccessible to the reacting molecules takes place with large degrees of exchange was advanced to explain the results obtained in [11]. However, it is also very possible that the decrease in the activity of highly decationized samples is due to processes of dehydroxylation of NH_4KL zeolites during their activation.

The data on the composition of the products (Tables 1 and 2) show that transformation of o-xylene takes place in two directions: isomerization with formation of m- and p-isomers, and disproportionation into toluene and trimethylbenzenes (TMB).

Isomerization products are primarily formed on NH_4KL zeolites in a flow reactor with small degrees of transformation, and the contribution of disproportionation increases as conversion on the more active samples increases. An increase in the degree of exchange is accompanied by a decrease in the concentration of m- and p-isomers and an increase in the concentration of toluene and TMB.

The selectivity of transformation of o-xylenes, evaluated as the ratio of the yields of products of disproportionation and isomerization (D/I), increases with an increase in the degree of exchange from 0.2 for the $NH_4KL-56\%$ sample to 1.4 for the $NH_4KL-90\%$ sample. In experiments conducted in the micropulse reactor, the value of D/I varied insignificantly (0.78-0.86) and was almost independent of the degree of exchange.

Let us examine the dependence of the value of D/I on total conversion of o-xylene in flow and micropulse reactors. A change in total conversion was obtained not only due to an increase in the degree of exchange of K^+ for NH_4^+ , but also due to a variation in the temperature of activation of the zeolites and the temperature of the reaction. As Fig. 4 shows, the selectivity is almost constant in a wide range of conversions in the pulsed mode.

The differences found in the change in the selectivity of transformation of o-xylene are apparently related to the different conditions of conducting the reactions in the flow and micropulse reactors. In the pulse reactor, in contrast to the flow reactor, the catalytic process takes place in a nonstationary mode. This suggests that the small contact times characteristic of the micropulse reactor are less favorable for secondary transformations of the products of disproportionation.

Experiments were performed with 1,2,4-TMB on $NH_4KL-82\%$ zeolite in the pulse and flow reactors to assess the role of these secondary reactions. The conditions were selected so that the total conversions of 1,2,4-TMB were similar (Table 3). Transformation of 1,2,4-TMB takes place in two directions: isomerization and disproportionation, and the contribution of the products of disproportionation is higher in the flow reactor than that of the products of isomerization. In pulsed conditions, isomerization of 1,2,4-TMB predominates over disproportionation. The different distribution of the products of transformation of 0-xylene (Fig. 3) is probably due to the fact that the flow reactor conditions are more favorable for disproportionation of TMB than the pulsed conditions.

The high activity of L zeolites in transformation of TMB makes it possible to examine the participation of the products of disproportionation in isomerization of o-xylene. According to [11], isomerization of xylenes passes through a stage of formation of TMB isomers. In support of the intermolecular mechanism of isomerization, data are cited in [11] which indicate that xylenes are formed on type Y zeolite in the reaction of different isomers of TMB with toluene or benzene. As our findings indicate (Table 4), transformation of toluene takes place to a very small degree, and the toluene almost does not react with 1,2,4-TMB. Special experiments showed that toluene does not undergo pronounced transformation of 1,2,4-TMB. Based on the data obtained, it is possible to conclude that isomerization of xylenes on type L zeolites does not occur according to an intermolecular mechanism via transalkylation, but primarily by means of intramolecular transformations, for example, due to 1,2-shifts.

CONCLUSIONS

1. L zeolite exhibits weak selectivity for NH_4^+ cations which decreases as the degree of ion exchange increases in substitution of potassium cations with ammonia ions.

2. Only L zeolites with a degree of decationization above 50% exhibit catalytic activity in transformation of o-xylene.

3. Isomerization of xylenes on L zeolites primarily takes place by means of intramolecular transformations.

LITERATURE CITED

- 1. J. Ward, in: Zeolite Chemistry and Catalysis, Am. Chemical (1976).
- Kh. M. Minachev, D. A. Kondrat'ev, A. A. Dergachev, I. V. Mishin, B. K. Nefedov, I. N. Oleshko, and T. V. Alekseeva, Izv. Akad. Nauk SSSR, Ser. Khim., 1076 (1982).
- 3. U. S. Patent No. 3794 600 (1974).
- 4. D. W. Breck, Zeolite Molecular Sieves: Structure, Chemistry, and Use, Wiley (1974).
- 5. F. Wolf, K. Georgi, and K. Pilchovski, Z. Phys. Chem., 259, No. 4, 717 (1978).
- 6. A. D. Rikhadze, Dissertation, Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow (1981).
- 7. T. R. Brueva, A. D. Rukhadze, A. A. Dergachev, and G. O. Glonti, Use of Zeolites in Catalysis: Collection [in Russian], Moscow (1981), p. 27.
- 8. G. Ono, M. Kaneko, K. Kogo, H. Takayanagi, and M. Keii, J. Chem. Soc. Faraday Trans. 1, 10, 2150 (1976).
- 9. C. F. Franco Parra, D. Ballivet, and D. Barthomeuf, J. Catal., 40, 51 (1975).
- 10. D. Ballivet and D. Barthomeuf, J. Chem. Soc. Faraday Trans. 1, 1581 (1977).
- 11. M. A. Lanevala and A. P. Bolton, J. Org. Chem., <u>34</u>, 3107 (1969).

REACTION OF ACETALS WITH ALIPHATIC

NITRO COMPOUNDS.

COMMUNICATION 4. REACTION OF ALIPHATIC AND ALICYCLIC KETALS

WITH NITROACETIC ACID ESTER AND SYNTHESIS

OF α,β -DEHYDRO- α -ACETYLAMINO ACID ESTERS

К.	Α.	Kochetkov,	К.	K. Babievskii,	UDC 542.91:547.284:
Ν.	s .	Tarbalinska	уа	, and F. M. Belikov	547.465.5'26:547.466

 α,β -Dehydro- α -amino acids (ΔAA) are necessary for the preparation of new antibiotics, phytotoxic peptides [1, 2], and other physiologically active compounds. ΔAA have also become increasingly important as substrates for asymmetric reduction to optically active α -amino acids (AA) [3].

The present article concerns the study of the alkoxyalkylation of nitroacetic acid ester (NAE) by openchain ketals (I) as a possible means of synthesis of difficult-to-obtain β , β -disubstituted ΔAA .

It was previously shown that open-chain [4, 5] and cyclic [6] benzaldehyde acetals and some ring-substituted derivatives easily alkylate NAE in the presence of Ac₂O with formation of α -nitrocinnamic acid esters; the latter were then used for synthesis of AA from the phenylalanine series. Cyclic ketals did not react with NAE in the conditions studied [6]. In the present article, it is shown that ketals (I) in the presence of Ac₂O react with NAE during heating in an inert solvent with formation of β , β -disubstituted β -alkoxy- α -nitrocarboxylic acids (II) with high yields (Table 1). The best results were obtained with a twofold excess of (I) and Ac₂O with respect to the ratio to NAE. The reaction of (I) with NAE is more difficult than in the case of aromatic acetals

A. N. Nesmeyanov Institute of Heteroorganic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 11, pp. 2515-2520, November, 1982. Original article submitted March 12, 1982.