OXIDATIVE DEHYDROGENATION OF ALKYLAROMATIC HYDROCARBONS ON THE Na FORMS OF CERTAIN ZEOLITES

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The zeolites which are active hydrocarbon oxidation catalysts all contain the transition metals in one form or another [1-11]. The deep oxidation of hexane and cyclohexane can, however, be catalyzed by cationic zeolite forms which do not contain transition metals [3-6]. The introduction of transition metals into such zeolites not only catalyzes the complete oxidation of cyclohexane, but, at the same time, promotes oxidative dehydrogenation of the latter with the formation of benzene [4-6]. The complete oxidation of the lower C_1-C_3 hydrocarbons to CO, CO_2, and H_2O is also promoted on these catalysts [7-11]. Only in the presence of water vapor is it possible to detect the formation of small amounts of acrolein from the partial oxidation of propylene on a Cu-containing, type Y zeolite [7]. The Na forms of type A, X, and Y zeolites show lower catalytic activity in such reactions. Considerable work has been devoted to the study of these relations.

This paper reports the results of a study of the possibility of carrying out the oxidative dehydrogenation of alkylaromatic hydrocarbons on cationic zeolite forms free of group VIII and transition metals.

EXPERIMENTAL

A study was made of the Na forms of A, X, and Y zeolites; mordenite (M); and the Na, K forms of chabazite- (Ch) and erionite- (E) type zeolites. The powdered catalyst was pressed into 3 × 3 mm binder-free pellets and loaded into the quartz reactor. The volume of the catalyst charge was 10 cm^3. The adsorption capacity of each zeolite was determined from measurement of low-temperature N_2 adsorption, following the procedure of [12].

Experiments were carried out in a flow system with automatically dosed liquid feed. Measurements were made on ethylbenzene (EB) and isopropylbenzene (IPB) containing 1.3% EB, each of these compounds being of cp grade. Air entered the reactor through a column filled with activated charcoal and NaA zeolite. Oxidative dehydrogenation of the various alkylaromatic hydrocarbons was carried out at temperatures ranging from 400 to 475°C, working at O_2-to-hydrocarbon ratios in the 0.4-1.0 interval with a 0.5 h^{-1} liquid space velocity. Gas – liquid chromatography was used to determine the product styrene (ST), α-methylstyrene, methylstyrenes, benzene, toluene, CO_2, and water. Acids, CO, acetaldehyde, acetone, benzaldehyde, benzoic acid, etc., were formed in insignificantly small amounts, and were not analyzed for in detail. The catalyzate was sampled at 30-min intervals, the catalyzate collected in the condenser representing at least 90% of the liquid entering the reactor.

The catalytic activity was expressed in terms of the rate r of oxidative dehydrogenation at low degree of hydrocarbon conversion as calculated from the equation [13]

$$r = v \cdot d \cdot X / M \cdot g \cdot 100, \text{ mole/g catalyst} \cdot \text{h}$$

TABLE 1. Certain Characteristics of the Catalysts

Zeolite	SiO_2/Al_2O_3	Adsorption capacity, ml/g
NaA	2,0	110
NaX	2,75	160
NaY	4,3	185
Na, KCh	5,1	100
Na, KE	6,2	75
NaM	10,0	80

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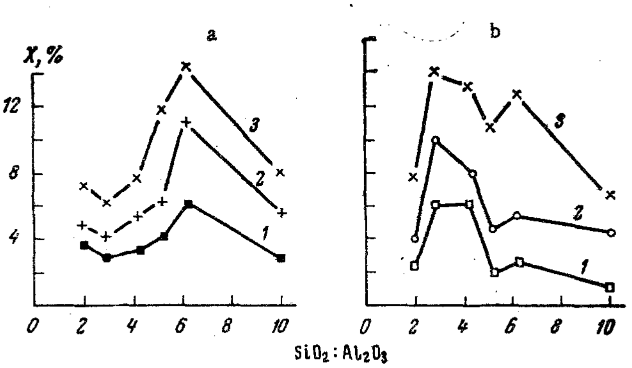

Fig. 1. Variation of the rate of oxidative dehydrogenation of ethylbenzene with the silicon oxide aluminum oxide ratio in the catalyst, at O_2 : EB ratios of 0.4 (a) and 1.0 (b): 1) 400°; 2) 425°; 3) 450°.

where v is the rate of liquid feed in ml/h; d is the hydrocarbon density in g/cm^3; X is the degree of conversion in %, M is the molecular weight of the hydrocarbon; g is the amount of catalyzate in g.

DISCUSSION OF RESULTS

Experiments on the NaY-type zeolite were carried out at low O_2 pressures, experience having shown that deep hydrocarbon oxidation results from operation of these catalysts at high O_2 concentrations [4-6]. Although the depth of oxidation could be reduced by reducing the O_2 concentration, the ratio of product yields was closely dependent on the nature of the zeolite, in both deep oxidation and oxidative dehydrogenation. It can be seen from Table 2 that reaction under the conditions in question here led largely to the oxidative dehydrogenation of EB to ST, with the formation of small quantities of CO_2, benzene, and toluene. It is interesting to note that the NaX and NaY faujasite zeolites differed from the other four zeolite catalysts, being more active in deep oxidation and showing a ~tenfold increase in the CO_2 yield under an increase of the O_2-to-EB ratio from 0.4 to 1.0. Below 450°C, an increase in the O_2 : EB ratio increased the ST yield on the faujasites, but reduced it on all of the other zeolites. Finally, the ST-yield-vs-time relation on the NaX and NaY zeolites was different from that observed on the other zeolites. A steady ST yield was established on the A-, Ch-, and E-type zeolites and mordenite after the first sampling, whereas 2-2.5 h were required for reaching steady ST yield on the faujasites.

It should be noted that the effect of variation of the O_2 : EB ratio on the oxidative dehydrogenation varied with the temperature. Thus an increase of this ratio had a negative effect on oxidative dehydrogenation on the NaM zeolite at 450°C, but increased the ST yield on this same catalyst at 475°C.

It can be seen from Fig. 1a that Na, KE showed the highest activity at O_2 : EB = 0.4.

The situation changed somewhat on raising the O_2 : EB ratio to 1.0, maximum activity then appearing in the NaX zeolite (Fig. 1b). As pointed out earlier, this shift is due to differences in zeolite sensitivity to

TABLE 2. Oxidation of Ethylbenzene on Various Catalysts

Catalyst	T., °C	O_2, EB	Conversion, %	Styrene, %	CO_2, %	Selectivity, %
NaA	425	0,4	6,4	6,0	0,4	94
	425	1,0	6,5	5,0	1,4	77
	450	0,4	9,9	9,2	0,6	93
	450	1,0	11,4	9,5	1,6	83
NaX	450	0,4	11,9	7,6	0,9	64
	450	1,0	27,9	16,8	7,6	60
NaY	450	0,4	14,3	7,2	0,7	50
	450	1,0	32,5	12,6	7,0	39
Na, KCH	450	0,4	17,3	14,8	1,4	85
	450	1,0	17,8	13,3	4,2	75
Na, KE	450	0,4	19,0	16,4	1,6	86
	450	0,8	19,2	15,3	3,2	80
	450	1,0	20,5	14,5	4,0	71
NaM	450	0,4	16,3	12,5	1,2	77
	450	1,0	15,0	10,0	2,0	67
	475	0,4	16,6	15,0	1,9	90
	475	1,0	22,1	18,8	2,8	85

TABLE 3. Activation Energies for the Oxidative Dehydrogenation of Ethylbenzene

Catalyst	E, kcal/mole	Catalyst	E, kcal/mole
NaA	16±2	Na,KCh	21±2
NaX	15±2	Na,KE	18±2
NaY	13±2	NaM	20±2

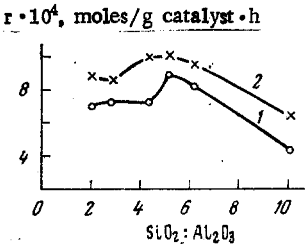

Fig. 2. Variation of the rate of oxidative dehydrogenation of isopropylbenzene with the $SiO_2 : Al_2O_3$ ratio in the zeolite, at O_2 : IPB = 0.4; 1) 425°; 2) 450°C.

alteration of the O_2 concentration in the reacting system. It can be seen from Table 1 that the fine-pored type A, Ch, and E zeolites and mordenite showed higher selectivity than the faujasites where deep oxidation and cracking come to the fore.

Apparent activation energies for oxidative dehydrogenation of EB on the various catalysts were determined from plots showing the logarithm of the reaction rate as a function of the reciprocal temperature. The data of Table 3 indicate that activation energies determined in this manner fell in the 13-15 kcal/mole range for the faujasites, and in the 18-21 kcal/mole range for the Ch-, E-, and M-type zeolites.

A study of isopropylbenzene conversion in air showed (Table 4) that the highest yield of alkylaromatic hydrocarbons was attained with the Ch- and E-type zeolites, and the highest selectivity with the NaA zeolite. A 25°C increase in the temperature had little effect on the α-methylstyrene yield, clearly because of the low activation energy for the IPB reaction. The rate of α-methylstyrene formation varied with the $SiO_2 : Al_2O_3$ ratio in the zeolite (Fig. 2), reaching a maximum in the Ch-type zeolites. Comparison of the oxidative dehydrogenation of EB and IPB on a single catalyst showed the ST selectivity to be almost invariably higher than the selectivity for α-methylstryrene formation. This could reflect the fact that the IPB reaction is more involved than the corresponding EB reaction.

The Ch- and E-type zeolites were subjected to spectral analysis with a view to elucidating the role played by contaminating metals in these catalysts. The chabazite contained 0.004% Fe and the erionite 0.1%. The total content of other metals was 10^{-3}% or less. Despite the fact that the Fe content of the erionite was 25 times greater than that of the chabazite, the activities of the two zeolites in the EB dehydrogenation differed by no more than a factor of 1.3-1.8 (cf. Fig. 1a, b). The activity of the chabazite was even higher than that of the erionite in the case of the IPB reaction (cf. Fig. 2). Although these figures do not give definite information concerning the nature of the catalytically active centers, they do suggest that the catalyst activity is largely determined by the zeolite itself rather than the contaminating metals. This question can be finally resolved by special experiments using zeolites which have been synthesized so as to preclude the possibility of introducing contaminants into the system.

TABLE 4. Conversion of Isopropylbenzene on the Various Zeolites, at O_2 : IPB = 0.4

Catalyst	T., °C	Conversion, %	α-Methyl styrene, %	Styrene + methylstyrenes, %	CO_2, %	α-Methylstyrene selectivity, %
NaA	425	12,5	10,0	0,4	1,0	87
	450	16,8	12,4	1,9	1,4	74
NaX	425	15,8	10,0	0,8	1,2	63
	450	22,8	12,3	1,5	1,8	54
NaY	425	11,0	8,0	0,4	0,8	73
	450	22,8	11,0	1,0	1,0	50
Na, KCh	425	19,9	13,1	2,1	1,0	66
	450	20,4	14,5	3,0	1,3	71
Na, KE	425	18,3	11,0	4,5	0,6	60
	450	25,1	12,7	6,2	1,0	51
NaM	425	11,5	8,6	1,4	1,1	75
	450	18,9	12,2	1,3	1,3	64

CONCLUSIONS

1. In the presence of air, ethylbenzene and isopropylbenzene undergo oxidative dehydrogenation on NaA-, NaX-, NaY-, Na-, KCh-, Na-, KE-, and NaM-type zeolites.

2. Zeolites of the chabazite and erionite types show high activity and selectivity in oxidative dehydrogenation, while the faujasites are more active in deep oxidation.

3. Increasing the oxygen-to-hydrocarbon ratio increases the rate of oxidative dehydrogenation of ethylbenzene on faujasites, and reduces the rate of oxidative dehydrogenation on chabazite and erionite.

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KINETICS OF OXIDATIVE DEHYDROGENATION OF ETHYLBENZENE ON A Pd/NaY ZEOLITE

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There has, as yet, been no in-depth study of the catalytic activity of the zeolites in oxidation reactions [1]. The C_1-C_3 hydrocarbons undergo deep oxidation to CO_2 and H_2O on type X and Y zeolites incorporating the transition elements [2-5]. It is true that small amounts of acrolein can be obtained from water — propylene mixtures on Cu zeolites, but the catalytic selectivity is very low in such systems [2]. Cyclohexane undergoes deep oxidation on NaY-type zeolites, oxidative dehydrogenation with the formation of benzene being attained only after the catalyst has been impregnated with some transition metal and then subjected to complete combustion [6-9]. Since gentle selective hydrocarbon oxidation is of considerable practical interest, study of catalysts for such processes would appear to be timely.

In the presence of atmospheric oxygen, ethylbenzene (EB) and isopropylbenzene largely undergo oxidative dehydrogenation on NaY and Pd/NaY zeolite catalysts [10]. The kinetics of the oxidative dehydrogenation of EB on Pd-containing type NaY zeolites have been studied in the present work.

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