PHYSICAL CHEMISTRY

ALKYLATION OF BENZENE BY ETHYLENE ON HYDROGEN AND RARE-EARTH CATIONIC FORMS OF Y ZEOLITE

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In [1-4], CaY zeolite was proposed as a catalyst of the alkylation of C_6H_6 by ethylene. The rare-earth (RE) cationic forms are usually more active catalysts, as was shown in the alkylation of C_6H_6 by propylene [5, 6]. In this work we studied the catalytic properties of type-Y zeolites in H-, RE-, and mixed polycation forms.

EXPERIMENTAL METHOD

Since individual salts of the rare-earth elements are expensive, it is advisible to use industrial concentrates of the rare-earths for the development of an economical process [6]. Therefore, for the preparation of the catalysts we used NaY* zeolite with a mole $SiO_2/Al_2O_3 = 3.6$, cerium concentrate containing 54.7% CeO_2, 24.5% La_2O_3, 14.8% Nd_2O_3, 4.4% Pr_2O_3, lanthanum concentrate containing 62.5% La_2O_3, 15% Nd_2O_3 and 2.5% CeO_2, and praseodymium concentrate containing 78% Pr_2O_3, 5% Nd_2O_3, and 2.5% CeO_2. The concentrates also contained CaO, Na_2O, and oxides of other rare-earth elements. Cation exchange was performed according to the well-known method [7]. Concentrates of the rare-earth elements were dissolved in 5% HCl, the pH was adjusted to 4 by the addition of NH₄OH, and they were used for ion exchange on the basis of 1 eq of Na⁺ for 3 eq of rare-earth elements. The degree of exchange of Na⁺ for cations of the Ce concentrate was 55%, for the lanthanum concentrate 58%, and for the praseodymium concentrate 61%.

Samples of HY were produced by treating NaY both with a 3% solution of HCl and with a 10% solution of NH₄Cl, followed by drying and calcination in a stream of air at 550°. The degree of exchange of Na⁺ for H⁺ is 80%. After exchange, all the samples were washed to a negative reaction for the chloride ion, dried, and calcined at 550°.

The secondary porosity was determined on a mercury porosimeter [8], acidity by titration with butylamine [9], mechanical strength according to the crushing of granules of the catalyst between parallel plates [10]. The testing of the zeolites for activity and selectivity was performed on a stand apparatus with an isothermal solution (inner diameter 20 mm) at 30 atm, mole ratio $C_6H_6:C_2H_4 = 3:1$, 110-350°, and a load in the reactor of 50 cm³ (36 g) of the catalyst. The duration of the experiments was 5-6 h. Samples of the catalyst were collected at 1-h intervals. The setup, experimental procedure, and analysis of the products were described in [1, 4].

DISCUSSION OF RESULTS

Just as we should have expected, NaY possesses a low index of acidity, 0.035 meq/g, and negligible activity: the yield of ethylbenzene (EB) at 350° was ~3% (Table 1). When Na⁺ was replaced by H⁺ (exchange of Na⁺ for NH₄⁺, followed by decomposition of NH₄Y), the zeo-lite was relatively inactive in the alkylation process, although the acidity of a fresh sample was substantial -1.05 meq/g (see Table 1). This value was lowered to 0.04 meq/g

*Granulated zeolite without binder.

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angara ana ang ang ang ang ang ang ang ang an						Produced by treat- ment of NaY with	a solution of HCI		Produced by treat-	a solution to the 4			Produced by treat- ment of HY (No. 2) with a solution of	REE		
	Selec tivity ac- cord- ing to EB, %				1	I			38 88	81 69 67		11	81 28	69	82 82 82	- 08 - 8
	Coke	composition	C			93	95 88	87 88	80 80	$91 \\ 92$	88	93	1		05	
			Ŧ			Ŀ•	n ĝ	13 12	11	သဆ	12	1	I	! !	1.a	1
		00 WL.				0,97	$^{1,56}_{2,3}$	0,5	6.0 0 0	1,3 8,1	$^{2,9}_{2,9}$	1,4	l		: 6, 8	1 1
	Physicochemical properties of the catalyst	strength	kg/ mm		2,8					0,86	1, 36	1,40	1 46	1.54		
			kg/_ mm²		1,2					0,30	0,59	0,63	0 50	0.72		
		sorption capacity,		xpt.	34,0					31,0	40,35	33,19	36. QI	37.2	,	
		porosity, Å		. i Before	112-500					After expt. 112-1000	Before expt. 65.6-314	After expt. 112-262	Before expt.	112-314 112-314	4 * *	
		acídity, meq			0,035					0,35	1,05	0,04	1 39	1.28		
	Concentration in catalyst	polyethyl benzenes			1		111	0.1	0.08	4 8,9 8,9 8,4		11	1,0	0.02 	5,5 7,5 7,5	4.0 1.0,
		ethyl- ben- zene			!	10,	040 040	5,2 5,2 7,8 7,8 7,8 7,8 7,9 7,9 7,9 7,9 7,9 7,9 7,9 7,9 7,9 7,9	4,9 6,0	13,6 13,6 13,6	11	100	, ⊂ 2 2 2 2 2 2 2	19 0,0 0,0 0,0	25.33	24,5
	Ethylbenzene	yield, from 1 % catalyst, g/h			1	0,001	0,000	0,002	0,10	0,25 0,41 0,35		0,001	0,170	0,500	0,650	0,560
						0,3	0 w 0 v 4 v	0,3 9,0	14,5 15,3	16,9 34,0 34,4		0,3	17,27 17,30	47,0 58,9	62,0 66,6	24.0 23.3
4	Catalyst				1	NaY		HY(II)	,		HY(I)			H-RFE-Y		
	Т., °С				150	300 300	330 350 110	$150 \\ 200$	250 275	350 350 350	150 200	300 300 100 100 100 100 100 100 100 100	410 110	200	275 300	350
	Sam- ple No.				1			57			က				4	

Influence of the Nature of the Cation on the Properties of Type-Y Zeolite [30 atm, $C_{e}H_{e}:C_{2}H_{4} = 3:1$ space velocity 3 h^{-1} , average values from five experiments] TABLE 1. (moles), s

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Fig. 1. Dependence of the yield of EB (a), output (b), and selectivity (c) of catalysts and coke formation (d) on the temperature at 30 atm, $C_6H_6:C_2H_4 = 3:1$ (moles), and space velocity 3 h⁻¹ (average values): 1) PrNaY; 2) LaNaY; 3) CeNaY.

for the spent catalyst. The sharp decrease in the acidity of HY(I) in comparison with a fresh sample is evidently due to dehydroxylation of the zeolite during the process of catalysis, while a decrease in the concentration of OH groups cause a decrease in the activity [11].

The low activity of HY(I) may be due to breakdown of the crystal structure of the zeolite in the case of preliminary heat treatment (500°) [12], but this evidently is not the only cause of deactivation. In the case of complete amorphization, there would be a sharp decrease in the sorption capacity of the catalyst after its unloading from the reactor. Actually, the sorption capacity (with respect to C_6H_6) would change only 1.3-fold - 33% instead of 40%. HY(II), produced by treatment of NaY with HCl, is characterized by an incomparably greater activity, especially at 330-350° (see Table 1). The possibility remains that in this case the activity is increased as a result of the elution of Al and an increase in the SiO₂/Al₂O₃ ratio in the zeolite.

Just like NaY, the catalyst HY promotes intensive coke formation. For example, the amount of coke formed on HY(II) at 200° is 2.9 g, as against 0.09 g for CaY.

The results cited show that zeolites with univalent cations are characterized by a negligible proton acidity and a low alkylating activity. Zeolites with di- and trivalent cations are active alkylation catalysts.

Interesting results were obtained in a study of the activity of samples prepared from NaY and various concentrations of rare-earth elements. As can be seen from Fig. 1, in the range 250-350°, the average values of the yields of EB on the catalysts CeNaY, PrNaY, and LaNaY are approximately the same, 40-45%, with an average output of 0.45-0.50 g/h·cm³. At 150-200°, the activity of CeNaY is somewhat lower - 16%, as against 22-24% for PrNaY and LaNaY. However, the catalyst produced on the basis of the Ce concentrate is favorably distinguished by higher selectivity and low coke formation (see Fig. 1). Thus, the average value of the selectivity (ratio of the yields of EB and all the reaction products) for CeNaY at 200-350° was 70-75%, as against 55-60% for LaNaY and PrNaY zeolites. The minimum selectivity 50-55% was observed at 300°. At 350° the selectivity of the catalysts dropped during the experiment, evidently as a result of an increase in the concentration of di- and triethylbenzenes, the yields of which reached 30%. Coke formation on catalysts produced using Pr and La concentrates increased continuously with the temperature, reaching 12-13% of the weight of the catalyst at 350°. For a Ce sample, a characteristic minimum of coke formation was observed at 300°, equal to 1.6%. The composition of the coke varied depending on the temperature. At 110-200°, the composition was close to polyethylene, while at 300-350°



Fig. 2. Influence of the nature of the cation on the catalytic properties of type Y zeolite in the alkylation of benzene by ethylene (conditions the same as for Fig. 1): 1) CaY; 2) HY; 3) Ca-REE-Y; 4) H-REE-Y.

it was close to aromatic hydrocarbons. Nonetheless, samples containing only REE cations were characterized by a comparatively low activity, and most important, a low stability of work with time. For example, the yields of EB on CeNaY at 330° in 5 h dropped from 47 to 36%, and the selectivity dropped from 78 to 68%. It was found that the catalyst can be substantially improved by successively introducing Ca^{2+} , H⁺, and REE³⁺ cations into Y zeolite.

When HY(II) was treated with a solution of chlorides of the rare-earth elements (Ceconcentrate), its acidity and activity increased sharply: although the average values of the yields of EB at 200-300° for HY were 13-17%, for H-REE-Y with a degree of exchange of cations for REE³⁺ 48%, it was 47-66% (see Table 1), which corresponds to an output of 0.50-0.65 g/h·cm³ (Fig. 2). In comparison with HY zeolite, in REE-Na-Y the range of active work of H-REE-Y was expanded (110-350°, instead of 250-350°), and the catalyst can operate in an adiabatic reactor with a temperature drop of 150°. In comparison with REE-Na-Y (see Fig. 1), the yields of EB increased from 40-45 to 60-65%, while the output increased from 0.40-0.45 to 0.60-0.65 g/h·cm³. Catalysts produced by successive introduction of Ca²⁺ and REE³⁺ ions proved especially effective. In the range of 250-350°, the yield of EB on such catalysts was 62-72%, instead of 16-22% on CaY (see Fig. 2), while the output (0.67-0.78 g/h) was 50% higher than in samples that did not contain Ca²⁺ (see Fig. 1).

The catalyst REE-Ca-Y is characterized by good stability of operation and minimum coke formation. At 300°, only 0.6% coke was formed (on the catalyst H-REE-Y 27.7%). However, H-REE-Y possessed high selectivity with respect to the formation of EB - 77-80%, instead of 62-70% for REE-Ca-Y zeolite (see Fig. 2). Catalysts containing Ca²⁺, H⁺, and REE³⁺ ca-tions proved optimum.

CONCLUSIONS

1. The catalytic properties of type-Y zeolites with a mole ratio $SiO_2/Al_2O_3 = 3.6$ in hydrogen and rare-earth cationic forms were studied at $110-350^\circ$, 30 atm, 3 h^{-1} , mole ratio $C_6H_6:C_2H_4 = 3:1$, in the reaction of alkylation of benzene by ethylene.

2. Samples produced from NaY zeolite and lanthanum, praseodymium, and cerium concentrates of the rare earths (degree of exchange 55-61%) are characterized by approximately the same activity and different selectivity.

3. The highest and most stable activity is possessed by zeolites simultaneously containing Ca²⁺, H⁺, and REE³⁺ cations.

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