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Experimental Evidence for the Role of Acidic Sites in the Side-Chain Alkylation of Alkylbenzenes with Methanol

In our recent paper (*1*), it has been shown by quantum chemical calculations that the following cooperative action of acidic and basic sites is important in the side-chain alkylation of toluene with methanol: the basic site determines the selectivity to the side-chain alkylation of toluene, whereas the acidic site adsorbs and stabilizes toluene. However, experimental results for side-chain alkylation have indicated the importance of only the basic nature of the catalyst (*2*). In the present note, we show that addition of an acidic cation to a basic zeolite accelerates side-chain alkylation.

The alkylation of *p*-xylene, as an example, was carried out with a flow reaction technique in essentially the same manner as described in the previous paper (*1*), except that the catalyst was precalcined at 773 K for only 1 h. The catalysts were LiX, RbX, RbLiX, and RbKX. LiX and RbX were prepared by a conventional ion-exchange procedure, while RbLiX and RbKX were prepared by the ion-exchange of NaX and KX with an aqueous solution of a mixture of RbCl and LiCl, and of RbCl, respectively.

The results are shown in Table 1. On the LiX catalyst, benzene-ring alkylation and disproportionation of *p*-xylene proceeded, that is, trimethylbenzenes and toluene were formed. But no side-chain aklylation occurred, as in the alkylation of toluene with methanol (*2*). This result indicates that Li ion exhibits an acidic nature. On the RbX catalyst, only side-chain alkylation proceeded. The aromatic products were only *p*-methylstyrene (MS) and *p*-ethyltoluene (ET). Addition of K to RbX, which would increase the basic nature of the catalyst, did not produce an increase in the yield of MS + ET. This result is interesting because, in the side-chain alkylation of toluene, emphasis has been placed on the basic nature of the catalyst (*2*). On the other hand, the

TABLE 1

ACTIVITY[a] AND ACID STRENGTH OF CATALYSTS

	Yield (%)[b]				MeOH conv. (%)	$H_{0_{max}}$[c]
	p-Methyl styrene	*p*-Ethyl toluene	Trimethyl benzenes	Toluene		
LiX(71)[d]	0	0	18.1	0.6	87.9	+3.3
RbLiX(46,8)[e]	5.3	2.7	0	0	67.7	+3.3
RbX(64)	3.4	0.5	0	0	65.9	+4.0
RbKX(68,13)	2.3	1.2	0	0	63.4	+4.0

[a] Alkylation of *p*-xylene with methanol; reaction conditions: temperature, 693 K; W/F, 40 g · h/mol; N_2 + He/F, 5.0 mol/mol; *p*-xylene/methanol, 6.0 mol/mol.

[b] Mol of product/mol of methanol fed × 100.

[c] Maximum acid strength.

[d] Degree of ion exchange (%) determined by atomic absorption spectrophotometry.

[e] Respective degrees of ion exchange of Rb and Li (%) determined by atomic absorption spectrophotometry.

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yield of MS + ET was doubled by the addition of Li, acidic cation, to the RbX catalyst. The acid strength of the catalyst was measured by the change in the color of the Hammett indicators and is shown in the last column of Table 1. All the catalysts had an acidic nature, though it was rather weak. The catalysts containing Li ion had a stronger acidic nature than the others. These results indicate that the addition of the acidic cation, Li, to the basic zeolite, RbX, increases the activity of the catalyst for the side-chain alkylation of *p*-xylene with methanol. Thus, the conclusion obtained by quantum chemical calculations in the previous paper (*1*) is proven experimentally.

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