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REACTIVE FORM OF 12-MOLYBDOSILICATE CATALYST ON FRIEDEL-CRAFTS-TYPE REACTION 1)

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Stepwise replacement of protons in $H_4[SiMo_{12}O_{40}]$ by tetrabutylammonium cation and catalysis by the replaced compounds for alkylation of toluene with benzyl chloride have been investigated. Only three-protonated compound showed comparable activity with that of parent one.

Heteropolyacids are characterized by their strong acidity and oxidizability. 2) Recently we have found the catalytic reactions relating to the former character, where the Keggin-structure acid H_4[A] **1**, ($A=SiMo_{12}O_{40}{}^{4-}$) shows remarkable activities for polycondensation of benzyl alcohol leading to polybenzyl 3) and for Friedel-Crafts-type reactions such as alkylation, acylation and sulfonylation. 4) They proceed via carbonium-ion generation mechanism. In these reactions, the four-protonated form of A shows the effective activity, whereas the substituted form of all protons by four tetrabutylammonium cations Y, Y_4[A] **2**, shows no activity, indicating the protons play an important role in the catalysis.

In order to clarify the role of the protons, stepwise replacement of four protons in H_4[A] by Y and reactivities of the replaced compounds for the alkylation of toluene with benzyl chloride and polymerization of benzyl alcohol have been examined.

The compounds **1** and **2** were prepared by the usual method. 3) The work-ups of the alkylation and polymerization, and the analyses of products were performed according to the previously reported manner. 3,5)

New catalysts were prepared by mixing of appropriate molar ratio of **1** and **2**, and offered to the alkylation of toluene 92 g (1 mol) with benzyl chloride 6.3 g (0.05 mol). 4) The catalyst was refluxed in toluene for ca. 2 hours before addition of the halide. Products were 2- and 4-tolylphenylmethane. The reaction conditions and results were presented in Table 1. The data indicate that the intercation exchange, i.e. the exchange between proton and Y, could take place during the reflux and lead to the equivalent distribution of all cations existing in the system. Consequently the catalyst in run 1 will be converted to the type of Y_2H_2[A] **3**, in run 3 to that of YH_3[A] **4**, and in run 2 to the mixture of **3** and **4**, and in run 4 to the mixture of **4** and **1**, indicating that the replacement of more than two protons in **1** leads to the dropping of activity. This was also assured by using the new catalyst prepared from **1** and YBr in the molar ratios of 1:1 and 1:2 in toluene (runs 5 and 6). In this case, although once a mixture of some compounds of $Y_{4-n}H_n$[A]-type may be produced, during the reflux of that in organic substrate, the cation-exchange leading to the same ratio rearrangement will be fulfilled, resulting that the catalyst in run 5 will be converted to **4**, and that in run 6 to **3**.

The manners by runs 5 and 6 rather than by runs 1 and 3 are favorable to the isolation of analytical pure samples **3** and **4**. As a matter of fact, the compounds **3** and **4** could be isolated by cation-exchange reaction of **1** and YBr in CH_3CN. Analytical results of them are shown in Table 2, together with the data of compound **2**. The isolated compound **3** showed no activity, whereas the compound **4** did the comparable activity with **1**, both for the alkylation of toluene and the polycondensation of benzyl alcohol.

Above-mentioned cation-rearrangement is observed only in organic solvent system. In aqueous solution, for instance, the reaction of **1** with YBr gives a heterogeneous mixture of different protonated species.

Table 1. Examples of some catalyst systems for the alkylation of toluene

Run	Catalyst system (10^{-5} mol)		Molar ratio	Reflux time h	Yields %
	$H_4[A]$				
	(9.90)			8	74
	$Y_4[A]$				
	(9.90)			18	no reaction
	$H_4[A]$	+ $Y_4[A]$			
1	(9.90)	(9.90)	1 : 1	18	no reaction
2	(9.90)	(4.95)	1 : 1/2	17.5	20
3	(9.90)	(3.30)	1 : 1/3	17.5	56
4	(9.90)	(2.48)	1 : 1/4	18	60
	$H_4[A]$	+ YBr			
5	(9.90)	(9.90)	1 : 1	18	77
6	(9.90)	(19.8)	1 : 2	18	no reaction

Table 2. Analytical data of $Y_{4-n}H_n[A]$

	Formula		Found (%) C	H	N	Calcd (%) C	H	N
n=0	$[(C_4H_9)_4N]_4[SiMo_{12}O_{40}]\ CH_3CN$	**2**	27.27	5.47	2.16	28.00	5.20	2.47
n=2	$[(C_4H_9)_4N]_2H_2[SiMo_{12}O_{40}]$	**3**	16.65	3.31	1.33	16.66	3.21	1.21
n=3	$[(C_4H_9)_4N]H_3[SiMo_{12}O_{40}]$	**4**	9.21	2.17	0.93	9.30	1.89	0.68

References and Notes

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