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REACTION OF 3,3,3-TRIFLUOROPROPENE WITH BENZENE OVER Al_2O_3 TREATED WITH CF_3Cl

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The reaction between 3,3,3-trifluoropropene and benzene in a vapor phase was carried out over various Al_2O_3. Trifluoropropylbenzene was obtained selectively when CF_3Cl-treated Al_2O_3 was used as a catalyst.

Since trifluoromethyl group has a unique character, CF_3-containing aromatic compounds are expected to show a high dielectric constant and lipophilicity.1,2) As 3,3,3-trifluoropropene(TFP) has been industrially produced as a raw material in the production of fluorine-containing silicone, it is readily available and is relatively inexpensive. Hence, it is favorable to introduce CF_3 group to aromatic compound by using TFP as an alkylating agent. However, due to the extremely strong electron withdrawing effect of CF_3 group, TFP is not active so much as a reagent for the acid catalyzed alkylation. In fact, benzene was trifluoropropylated only in the presense of Nafion-H, BF_3, or HBF_4, which are known as strong acid catalysts, under a relatively high pressure in an autoclave.2) In the industrial production, it is preffered to carry out the alkylation over the solid catalysts, which can be easily regenerated and are easy to handle.

We reported that Al_2O_3 which was partially fluorinated with CF_3Cl showed a high activity for the acid catalyzed reactions, such as MTG3) and isomerization of paraffins.4) Therefore, we examined the catalytic activity of Al_2O_3 treated with CF_3Cl for the vapor phase reaction of TFP with benzene.

Aluminum oxide was prepared by a hydrolysis of aluminum isopropoxide, $Al(NO_3)_3$, or $Al_2(SO_4)_3$ (Wako Chemical Co.); these samples were washed, dried, and finally calcined at 600 °C for 3 h, and named Al_2O_3-A, Al_2O_3-N, Al_2O_3-S, respectively. A commercial product, Albes FF(Showa Tansan Co.) was also used. The HF-treated Al_2O_3 which was prepared by a wet impregnation method using aqueous HF solution, was used for comparison. For the partial fluorination of Al_2O_3, an Al_2O_3 sample (0.3 g) evacuated at 420 °C for 30 min was treated with CF_3Cl(60 Torr, 1 Torr= 133.3 Pa) at 420 °C for 30 min in a closed recirculation reactor(volume: 0.55 l). After the treatment and further evacuation at 420 °C for 30 min, a mixture of benzene and TFP was introduced into the reactor and reacted at 100 °C for 30 min.

The product distributions are shown in Table 1, in which bis-substituted compounds were omitted, because their amounts were negligibly small. The catalytic activities of untreated Al_2O_3 were low; furthermore the main product was not 3,3,3-trifluoropropylbenzene(TFPB) but $C_6H_5CH_2CH{=}CF_2$, except for Al_2O_3-S. The fact that Al_2O_3 containing SO_4^{2-}(Al_2O_3-S) showed higher selectivity for the formation of TFPB, was possibly due to the high acidity caused by SO_4^{2-} which remained in the catalyst

The catalytic activity of Al_2O_3 was somewhat increased by a usual fluorination with aqueous HF solution; it increased with an increase in a concentration of aqueous HF solution used for the treatment. The HF-treated Al_2O_3, however, did not remarkably promote the formation of TFPB; moreover, it still produced undesirable product, $C_6H_5CH_2CH{=}CF_2$.

Table 1. Catalytic activities of various Al_2O_3

Sample	Composition (mol%)		
	C_6H_6	$C_6H_5CH_2CH_2CF_3$	$C_6H_5CH_2CH{=}CF_2$
Al_2O_3-N	97.8	0.2	2.0
-A	97.7	0.2	2.1
-S	97.7	1.8	0.5
Albes FF	97.7	0.2	2.1
Al_2O_3-N-1.0 HF	94.1	3.7	2.2
-5.0 HF	92.6	6.5	0.9
$-CCl_4$	99.1	0.5	0.4
$-CFCl_3$	80.3	19.7	0
$-CF_2Cl_2$	78.7	21.3	0
$-CF_3Cl$	75.2	24.8	0
$-CF_4$	91.2	5.3	3.5
Al_2O_3-A-CF_3Cl	73.3	26.7	0
-S-CF_3Cl	83.0	17.0	0
Albes FF-CF_3Cl	76.7	23.3	0
AlF_3	99.2	0.5	0.3

The treatment with CF_3Cl enhanced the catalytic activities of various Al_2O_3 to a large extent; the selectivity for the formation of TFPB was also improved, and no $C_6H_5CH_2CH=CF_2$ was produced. Although untreated Al_2O_3-S showed a slightly higher activity than those of other Al_2O_3 samples, the CF_3Cl-treated Al_2O_3-S exhibited relatively low activity as compared with other CF_3Cl-treated Al_2O_3. It is suggested that SO_4^{2-} contained in Al_2O_3 might prevent the formation of active sites on the fluorinated Al_2O_3.

The catalytic activity of Al_2O_3 treated with $CFCl_3$ or CF_2Cl_2 was comparable to that of Al_2O_3 treated with CF_3Cl; on the other hand, Al_2O_3 treated with CF_4 showed less activity than those of Al_2O_3 treated with Cl-containing flon. As CF_4 was a stable compound, CF_4-treated Al_2O_3 was not considered to be sufficiently fluorinated. The catalytic activity of Al_2O_3 was not enhanced by the treatment with CCl_4. Therefore, it seems that the high catalytic activity was due to the F atom introduced by the fluorination with flon.

Table 2 shows the surface compositions of various Al_2O_3 samples measured by XPS. The fluorine content of the HF-treated Al_2O_3 increased with an increase in a concentration of aqueous HF solution used for the treatment. In the Al_2O_3 treated with 5.0 wt% of aqueous HF solution, however, a weak peak ascribed to crystalline $AlF_{1.96}OH_{1.04}$ was observed by XRD analysis.

The F content of CF_3Cl-treated Al_2O_3 was much higher than that of HF-treated Al_2O_3, nevertheless, the formations of crystalline AlF_3 and crystalline $AlF_{1.96}OH_{1.04}$ were scarecely detected by XRD analysis. The absence of crystalline AlF_3 was also confirmed by the result of XPS measurement; i.e. the peak position of Al_{2p} for the CF_3Cl-treated Al_2O_3 was very close to that for untreated Al_2O_3, and far from that for crystalline AlF_3.

Table 2. Surface compositions of various Al_2O_3

Sample	Composition (atomic%)				
	Al	O	S	F	Cl
Al_2O_3-A	35.6	64.4	0	0	0
-CF_3Cl	32.2	36.9	0	30.7	0.2
Al_2O_3-S	28.6	66.7	4.7	0	0
-CF_3Cl	28.6	34.9	3.9	32.2	0.4
Albes FF	37.0	63.0	0	0	0
-CF_3Cl	32.9	36.8	0	29.5	0.8
Al_2O_3-N-1.0 HF	34.6	57.0	0	8.4	0
-5.0 HF	36.6	49.3	0	14.1	0

Table 3. Specific surface area and surface acidity

Sample	Surface area$^{a)}$	NH_3 amount (at 400 °C)	
	(m^2/g)	(mmol/g)	(mol/m^2)
Al_2O_3-N	192.8	0.29	1.8
-1.0 HF	172.3	0.42	2.4
-5.0 HF	110.5	0.33	3.0
-CF_3Cl	159.3	0.58	3.7
Al_2O_3-S	137.3	-	-
-CF_3Cl	40.3	-	-
Al_2O_3-A	190.9	0.35	1.8
-CF_3Cl	139.1	0.59	4.2
Albes FF	223.2	0.41	1.8
-CF_3Cl	153.7	0.56	3.6

a) Determined by applying the BET method to the adsorption isotherm of N_2 at -196 °C.

As being shown in Table 3, the order of increasing amount of NH_3 adsorbed on the various samples at 400 °C is as follows;

$$Al_2O_3\text{-}CF_3Cl > Al_2O_3\text{-}5.0\ HF > Al_2O_3\text{-}1.0\ HF > Al_2O_3$$

This fact suggests that fairly strong acid sites were formed in abundance on the CF_3Cl-treated Al_2O_3; these strong acid sites may be responsible for the high catalytic activity of the CF_3Cl-treated Al_2O_3.

It was also observed that after the reaction, untreated Al_2O_3 contained ca. 6% of F atom by means of the XPS measurement. It seems that Al_2O_3 incorporated F atom from TFP to form AlF_3 which is thermodynamically more stable than Al_2O_3. As the result of elimination of F atom as HF from TFPB molecule, $C_6H_5CH_2CH{=}CF_2$ might be preferentially formed when the fresh, or untreated Al_2O_3 samples such as Al_2O_3-N and Al_2O_3-A were present as catalysts(as being shown in Table 1).

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