Novel Catalysts Effective for Dehydrofluorination of CF_3CH_3 (HFC143a) into CF_2CH_2

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(Received February 29, 1996)

The catalytic dehydrofluorination of CF_3CH_3 into CF_2CH_2 was studied over various metal phosphates in a fixed-bed reactor. The $Mg_2P_2O_7$ catalyst exhibited moderate activity, higher selectivity and greater stability. The active sites for CF_2CH_2 formation are weak acid sites of the catalysts.

An increasing demand of HFC134a (CF_3CFH_2) as an alternative to CCl_2F_2 produces large amounts of CF_3CH_3 as a by-product. Therefore it has been expected to develop a new process of CF_3CH_3 conversion into CF_2CH_2 which is a useful raw material of polyfluroethane and CF_3CFH_2 synthesis. Practical catalysts for CFC reactions requires long catalyst life, because most of the CFC reactions involve HF which is extremely collusive.[1-5] Dehydrofluorination of CF_3CH_3 is just such a case. We searched for anti-fluorination materials by the thermodynamic examination and found that $Mg_3(PO_4)_2$ is a effective catalyst for dehydrofluorination of CF_3CH_3 with sufficient catalyst life. The Gibbs free energy changes of the formation of metal fluorides from corresponding metal oxides and HF are negative suggesting that metal oxides are not suitable for the CFC reactions. Those of metal phosphates are also negative but not as negative. For example;

$$HF+1/6Mg_3(PO_4)_2 \rightarrow 1/2MgF_2+1/3H_3PO_4 \quad \Delta G=-37.5 kJ/mol$$

$$HF+1/2MgO \rightarrow 1/2MgF_2+1/2H_2O \quad \Delta G=-95.7 kJ/mol$$

So that, metal phosphates were chosen for the catalyst.

Catalysts were prepared by the following procedure. A dilute ammoniacal solution was added dropwise into an aqueous solution of metal nitrate and H_3PO_4 until the solution became PH 7. The formed precipitate was thoroughly washed with water, filtered, and then dried at 120 °C overnight. The resulting solid was broken up and sieved into a 14-32 mesh. Finally it was calcined in a stream of air at 550 °C for 5 h. Mg and Ni salts were pyrophosphates and $AlPO_4$ was amorphous. Other catalysts were phosphates. The catalytic reaction was carried out using an ordinary flow-type system. A 10 mm I.D. stainless steel tubular reactor with a fixed catalyst bed inside was used. The gas effluent from the reactor was washed with distilled water to remove formed HF. One hour after the reactor reached the desired temperature, the composition of the feed and the effluent gases were analyzed by GC using a Porapak Q column for the separation of CFC's.

The results for the catalytic reaction over various phosphates are summarized in Table 1. The catalysts in Table 1 are in order from the highest conversion to the lowest. The $Zr_3(PO_4)_4$, BPO_4, $AlPO_4$ showed much higher catalytic activity and almost all the reactant disappeared at 550 °C. $CrPO_4$, $Ni_2P_2O_7$, $Mg_2P_2O_7$ showed moderate activity. The conversion of CF_3CH_3 was about 50% at 550 °C, and the other catalysts showed low activity. The products were CH_4, CO_2, C_2H_4, C_2H_6 and CF_2CH_2. Carbon and/or polymer deposition was suggested from the poor carbon recovery. Significant differences were observed in the product distribution. The selectivity of CF_2CH_2 was not significantly high over the $Zr_3(PO_4)_4$, BPO_4, and $FePO_4$ catalysts. The carbon recovery was not uniformed over these catalysts. Although the carbon recovery was very small over BPO_4, it was relatively high over $AlPO_4$. The C_2H_4 and C_2H_6 were produced over $AlPO_4$ catalyst suggesting that substitution of F in CF_2CH_2 by H and successive hydrogenation into C_2H_6 took place. High CF_2CH_2 selectivity, 80%-86%, was attained over $Mg_2P_2O_7$, followed by $CrPO_4$. Among $Ca_3(PO_4)_2$, $Fe_3(PO_4)_2$, and Li_3PO_4, Li_3PO_4 showed extremely high CF_2CH_2 selectivity. The addition of Li into active catalysts such as $AlPO_4$ may improve the CF_2CH_2 selectivity. It is concluded that the $Mg_2P_2O_7$ catalyst is the most suitable for the selective dehydrofluorination of CF_3CH_3.

The effect of duration on the catalytic reaction was studied at 450 °C using the $Mg_2P_2O_7$ catalyst, and the results were shown in Figure 1. A small drop in the conversion of CF_3CH_3 was observed during the first 6 h and then it appears that CF_3CH_3

Table 1. Reaction of CF_3CH_3 over various metal phosphates

Metal	Temp	Conv.	Selectivity / %				
	°C	%	CH_4	CO_2	C_2H_4	C_2H_6	CF_2CH_2
Zr	400	48.1	0.6	7.3			36.4
	450	90.9	2.7	4.2			43.5
	500	94.6	9.0	2.0	1.1		37.7
	550	97.8	11.9	0.3	6.2		38.0
B	400	40.4		3.5			28.5
	450	81.5	1.2	2.6			22.1
	500	95.4	9.6	1.9	1.8		15.5
	550	95.2	23.1	1.2	7.5		27.2
Al	400	34.3		4.7		13.1	42.3
	450	64.3	0.5	2.3		10.0	59.6
	500	91.1	4.8	2.0	2.3	10.3	49.5
	550	96.5	7.9	0.2	10.3	32.6	47.0
Cr	400	28.9	1.7	5.2			50.5
	450	48.2	1.7	1.5			73.4
	500	49.5	4.0	0.6			62.0
	550	54.5	7.9				73.9
Ni	400	7.4					13.5
	450	12.1	2.5				31.4
	500	19.9	8.5				51.3
	550	34.9	13.5	1.1	2.3		53.9
Mg	400	12.1					59.7
	450	20.8	1.9				79.8
	500	44.6	1.1	2.0	3.4		86.8
	550	79.0	4.2	1.3	0.5	16.2	69.0
Ca	450	13.3					51.7
	500	19.6					49.7
	550	21.1	0.1	1.8			67.6
Fe	450	7.5	2.7				22.7
	500	18.2	7.7	1.1			29.8
	550	43.8	12.3	2.5			32.0
Li	450	8.3					90.3
	500	12.4					97.0
	550	16.1					91.0

Catalyst: 1.50 g, W/F=0.05 g·min·cm^{-3}, Feed gas composition: CF_3CH_3 5.0 mol%, H_2 15.0 mol%, balance N_2.

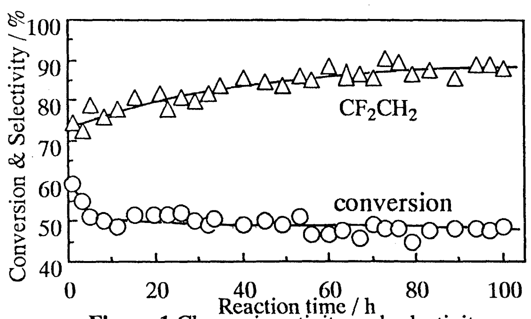

Figure 1. Change in activity and selectivity with time on stream over $Mg_2P_2O_7$ (450 °C)

Catalyst:2.0 g, W/F=0.067 g.min.cm^{-3},Feed gas composition: CF_3CH_3 2.0 mol%,$H_2$15 mol%, balance N_2;

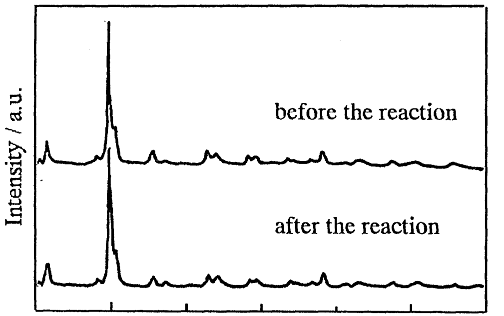

Figure 2. X-ray diffraction patterns of $Mg_2P_2O_7$

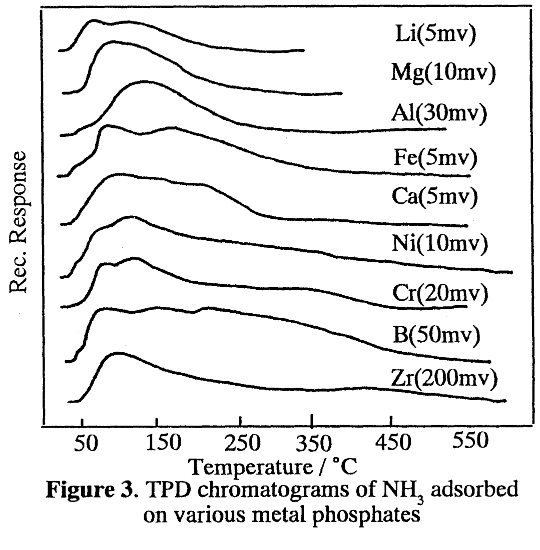

Figure 3. TPD chromatograms of NH_3 adsorbed on various metal phosphates

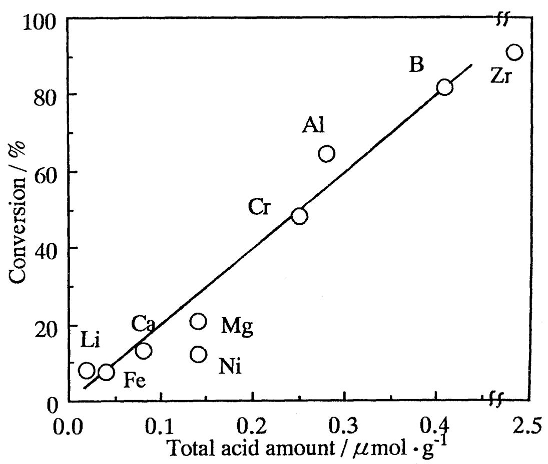

Figure 4. Relationship between total amount and catalytic activity (450 °C)

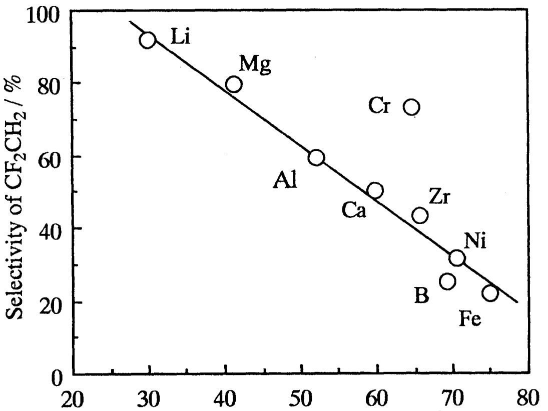

Figure 5. Relationship between acid strength and selectivity (450 °C)

conversion became a steady state. As for selectivity, initial selectivity of CF_2CH_2 was about 75%, which gradually increased to 90% at 100 h. From these results, one can see that the $Mg_2P_2O_7$ is a selective and stable catalyst. The crystalline phases of the catalysts before and after the 100 h reaction were analyzed by XRD (Figure 2).The XRD pattern of the catalyst before reaction is composed of the diffraction peaks attributable to $Mg_2P_2O_7$ and it was unchanged after the reaction. The acidic properties of the catalysts were determined by NH_3-TPD (Figure 3). Li, Mg, and Al phosphates gave a sole desorption peak at 50-250 °C. Fe and Ca phosphates gave two desorption peaks at 50-300 °C and the desorption continued up to 500-550 °C from Ni, Cr, B and Zr phosphates suggesting that these catalysts have the acidic sites of intermediate strength. The activities of various phosphates were plotted in Figure 4 against the total acid amounts. A linear relationship was found. This indicates that the active sites are acid sites. A linear relationship was observed between the portion of acid amount >150 °C and the CF_2CH_2 selectivity as shown in Figure 5. The larger the portion of relatively strong acid sites, the smaller the CF_2CH_2 selectivity. This result indicates that the active sites for CF_2CH_2 formation are weak acid sites. On the contrary, carbon deposition and polymerization take place on the strong acid sites. These reactions may be formed by the consecutive reaction of CF_2CH_2. $Mg_2P_2O_7$ which has no strong acid sites is preferred to dehydrofluorination of CF_3CH_3. Studies on the detailed reaction mechanism are now in progress.

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