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CATALYTIC REARRANGEMENT OF TETRAHYDRODICYCLOPENTADIENE TO ADAMANTANE OVER Y-ZEOLITE

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Bifunctional rare-earth exchanged Y zeolite, has the high catalytic activity for the synthesis of adamantane from tetrahydrodicyclopentadiene in the presence of hydrogen and hydrogen chloride, in a fixed bed flow system. The catalyst deactivated by pore plugging with deposited hydrocarbons can be almost completely regenerated by hydrocracking.

Schleyer et al.1) first synthesized adamantane(AdH:tricyclo[3.3.1.1^{3,7}]-decane) from tetrahydrodicyclopentadiene(TCD:tricyclo[5.2.1.0^{2,6}]decane), a hydrogenated product of dicyclopentadiene. Thereafter, various catalysts based on aluminum halide,2-3) SiO_2-Al_2O_3 catalyst treated with sulfuric acid4) and Pt-chlorinated Al_2O_3 catalyst5) were also proposed, but their productivities(AdH/-catalyst weight ratio) were poor for industrial manufacturing processes. Meanwhile, the derivatives of adamantane have been actively developed.6) In the present letter, the authors report the RE-Y acts as a good catalyst for the industrial production of adamantane.

As the raw material, we used TCD obtained by completely hydrogenating dicyclopentadiene and subsequent distillation of the product. The purity of TCD was 95 wt% and the remaining impurities were C_{11} and C_{12} saturated hydrocarbons. The catalysts used were multi-valent cation exchanged zeolites derived from Na-Y, NH_4-Y, Na-Mordenite, and K-L. A rare earth exchanged zeolite, SK-500 of UCC, was also used. Bifunctional (Pt-Re loaded) catalysts were prepared according to the usual impregnation method on the exchanged zeolites by using chloroplatinic acid (H_2PtCl_4) and ammonium perrhenate (NH_4ReO_4) as metal sources. As the activation, the catalysts were calcined at 400 °C, followed by the reduction in a stream of hydrogen(50 ml/min) at 400 °C. The activity of the catalysts was evaluated by the batch and flow methods. In the batch method, the reaction was carried out in a 100 ml autoclave containing the mixture of 4 g of TCD and 2 g of an activated catalyst. In the flow method, a high pressure fixed bed reactor(25 mm in I.D. and 500 mm in length) was used. The raw material and products were analyzed by a gaschromatograph provided with a glass capillary column.

As a preliminary test, activities of typical solid acid such as SiO_2-Al_2O_3, HNaY, and LaNaY were compared in the presence of HCl and H_2 by the batch method. Since LaNaY was found most active, the relationship between the catalytic activity and the degree of RE^{3+}(La, Ce, Y, Nd, Yb) exchange was examined by the batch method. As shown in Fig. 1, the activity increases with the degree of exchange, especially over 50%, which corresponds to the degree of exchange at which RE-ions begin to be located at site II and III within the super cage.[7] The activity of LaY derived from NaY was higher than that from NH_4Y at constant degree of exchange.

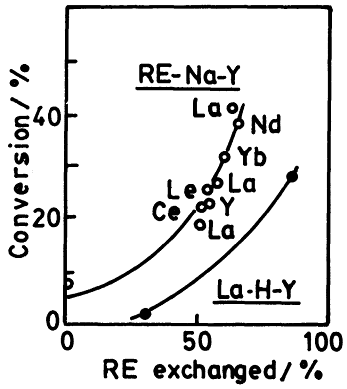

Fig. 1. Effect of exchanged RE^{3+} on TCD rearrangement.

Conditions : batch method, 250 °C, 5 h, P(HCl)= 1 atm, $P(H_2)$= 6 atm.

A long life is an important factor for industrial catalyst. The coke formation on solid acids like zeolites may occur simultaneously along with the desirable reactions. Thus, the effect of metal loading were evaluated by using bifunctional catalysts. The activities of bifunctional catalysts containing metals such as Co, Ni, and Pt-Re on RE-Y were higher than RE-Y(Table 1). In particular, Pt-Re-Co/REY had a high stability together with a high activity in a flow method(Fig. 2). The activities of bifunctional catalysts prepared by loading Pt, Re, and Co on various zeolites were determined(Table 2). While the H-type zeolite shows low activity, the Ca, La,and RE exchanged zeolites shows high activity, except for La-L. This is presumably because the acidity is preferably brought about by HCl in the multi-valent cation exchanged zeolites.

Improvement of the activity by adding HCl to RE exchanged Y-zeolite was reported to be caused by Bronsted acid freshly produced in the vicinity of cation (RE^{3+}) by dissociative adsorption.[8] The effects of the partial pressure of HCl were examined using Pt-Re/RE-Y. As shown in Table 3, both the yield and the selectivity of adamantane were improved in bifunctional catalyst (Pt-Re/RE-Y) with the HCl molar fraction of up to 0.4, but in the range of molar fraction 0.5 to 1.0 , the activity was gradually decreased.

Table 1. Activity of RE-Y zeolite

Catalyst	Conversion %	AdH Yield %	Selectivity %
RE-Y	43.6	18.0	41.2
Co/REY	54.7	26.0	47.5
Ni/REY	50.0	23.0	46.4
Pt-Re/REY	93.5	23.0	24.6
Pt-Re-Co/REY	91.5	31.0	33.8
Pt-Re-Ni/REY	68.7	30.0	43.1

Conditions : batch method, 250 °C, 2 h,
P(HCl)= 1 atm, $P(H_2)$= 15 atm.

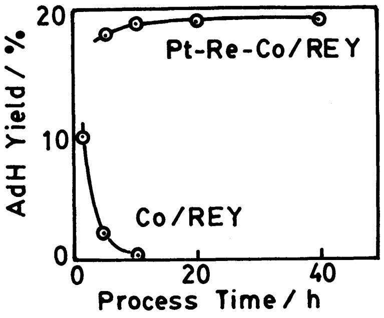

Fig. 2. Activity of bifunctional catalysts.

Conditions : flow method,
W/F = 2 h, H_2+HCl(2%),
200 °C, 20 atm.

Table 2. Activity of bifunctional catalysts

Zeolite	Conversion %	AdH Yield %	AdH Selectivity %
H(82)-Y	25	7	28
H(98)-Mordenite	22	3	14
Ca(62)-Y	72	18	25
La(18)-Y	31	5	16
La(50)-Y	55	18	33
La(72)-Y	56	20	36
RE(57)-Y	75	24	32
La(45)-X	98	13	13
La(24)-L	5	2	40

Conditions : 250 °C, 2 h, P(HCl)=1 atm, $P(H_2)$=15 atm.
Catalysts : Pt-Re-Co/Zeolites. ( ) : Ion Exchange %.

Table 3. Effect of hydrogen chloride and hydrogen on TCD rearangement

Molar fraction			Conversion	AdH Yield	AdH Selectivity
HCl	H_2	He	%	%	%
0	1	0	80.0	8.0	10.0
0.06	0.94	0	93.0	22.0	24.0
0.39	0.61	0	85.0	30.0	35.0
0.69	0.31	0	30.0	14.0	47.0
1	0	0	5.0	1.7	33.0
0	0	1	12.0	5.1	43.0

Catalyst : Pt(0.75%)-Re(0.25%)/REY.
Conditions : batch method, 250° C, 2 h, Total Pressure = 16 atm.

The bifunctional catalysts were deactivated to some extent. For example, the activity(AdH yield) of Pt-Re-Co/REY catalyst was gradually decreased around 200 hours of process time under following conditions : the time factor(W/F), 2 h ; partial presure of hydrogen, 20 atm ;and reaction temperature, 200-210 °C.

The physical properties of the fresh and used catalysts were compared to determine the factors of deactivation. The deactivated catalysts (treated for 400 h) contained carbon (7.9 wt%) and had a smaller specific surface area than the fresh catalyst. There were little differences in the CO chemisorption, indicating that the surface area of platinum metal was not affected by the reaction. Thus, it is concluded the deactivation is caused by plugging of the pores in zeolites with higher hydrocarbons incapable of diffusing out. Therefore, these catalysts could be regenerated by hydrocracking of the hydrocarbons in the pores. The physical properties of the catalyst, carbon content, specific surface area and activity were found to be fully recovered by reactivation by keeping the used catalyst in a hydrogen stream of 40 atm for 20 h at 300 °C. Thus, hydrocracking of higher hydrocarbons is effective for the reactivation of the catalysts.

Table 4. Physical properties and activity of catalysts

	Carbon wt %	S.A.(BET) $m^2\ g^{-1}$	CO Chemisorption relative values	P.V.[a] $ml\ g^{-1}$	AdH Yield[c] %
Fresh	0.0	429	1.0	0.38	21
Deactivated	7.9	52	0.9	0.34	1
Regenerated[b]	0.1	348	0.9	0.40	19

a) Pore volume was measured with Hg porosimetry.
b) $P(H_2)$=40 atm, 300 °C, 20 h (flow system).
c) Flow method : W/F=1.6 h, 225 °C, $P(H_2)$=20 atm, Process time=15 h.

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