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Highly Active Aluminas for Isomerization of 1-Butene and Hydrogen Exchanges between Ethylene or Cyclopropane and Deuterium

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Synopsis. Among eleven kinds of aluminas, alumina V prepared from aluminium sulfate with urea exhibited a pronounced activity for the isomerization of 1-butene, while alumina III or II prepared from aluminium nitrate with ammonia or urea showed the highest activities for the exchange reactions between ethylene or cyclopropane and deuterium, respectively.

Alumina is one of the most interesting and useful oxide catalysts for hydrocarbon reactions. The exchange reaction of deuterium between CH_4 and D_2 is known to take place easily over alumina even at room temperature,[1,2] but not over the other oxides such as MgO, CaO, SrO, BaO, La_2O_3, CeO_2, Pr_2O_3, Tb_2O_3, TiO_2, ZnO, and WO_3 below 300 °C of reaction temperature,[3] indicating an anomalously high catalytic activity of alumina compared with the other oxides. However, the catalytic properties of various aluminas for the exchange reaction have been found to change remarkably depending on the preparation method.[4] In order to examine how the activity of alumina is affected by the preparation method and to know what kinds of aluminas are best for particular hydrocarbon reactions, eleven kinds alumina catalysts were prepared by different methods and subjected to the activity test.

Experimental

Various aluminas were prepared from various aluminium compounds by different methods as shown in Table 1. In the case of hydrolysis with ammonia or urea, the final pH was adjusted to 7—8. Precipitation with urea was carried out at ≈90 °C, precipitates of hydroxides being formed gradually in 4 h. Details of precipitation with urea were described previously.[5] The hydroxides of Al_2O_3 V and VI were washed with distilled water until sulfate ions were not detected with barium chloride in the washings. The hydroxide of Al_2O_3 XI was washed with 30 L of distilled water. The hydroxide of Al_2O_3 VII, VIII, and X were washed with 6 L of distilled water. In the latter case, halogen ions remained in the washings. The hydroxides were dried at 120 °C for 20 h and calcined in air at 550 °C. The aluminas which were evacuated at 600 °C for 3 h were used as catalysts. Surface area was determined by applying the BET method to the adsorption isotherm of nitrogen at −196 °C. The structure of aluminas was determined from the powder patterns obtained with a Rigaku Denki Giger flex X-ray diffractometer using filtered Cu K_α radiation.

The exchange reactions between ethylene or cyclopropane and deuterium were carried out at room temperature in a closed recirculation reactor that had a total volume of *ca.* 400 ml. A mixture of 5 Torr of each hydrocarbon and 40 Torr (1 Torr=133.322 Pa) of D_2 was used. The reaction products were analyzed by a mass spectrometer (Hitachi M-52 type), parent peaks of m/e=28—32 and m/e=42—48 being used for deuterated ethylene and cyclopropane, respectively. The catalytic activity was expressed by K_ϕ % per unit surface area of catalyst in thefollowing equation.[3]

$$d\phi/dt = K_\phi(\phi_\infty - \phi)/\phi_\infty WS,$$

where ϕ represents the average number of D atoms in 100 molecules of each hydrocarbon in time t, ϕ_∞ for $t=\infty$, W the weight of catalyst, and S specific surface area.

Isomerization of 1-butene was carried out at room temperature in the same reactor as above with 70 Torr of 1-butene. For analysis of the butenes, a 5-m column packed with VZ-7 and thermostated at 0 °C was used. Initial rates of the formation of 2-butenes were taken as the catalytic activity.

Results

Catalytic activities of various aluminas are shown in Table 2, where the activity for the exchange of methane with deuterium was cited from the literature.[4] Al_2O_3 VII which showed the highest activity for the exchange reaction of methane with deuterium did not show high activities for the exchange reaction between ethylene or cyclopropane and D_2 and was almost inactive for the

Table 1 Preparation methods, surface area and structures of aluminas evacuated at 600 °C

Al_2O_3	Preparation: Starting material	Preparation: Method	Surface area $m^2\ g^{-1}$	Structure
I	Isopropoxide	Hydrolysis	236	γ
II	$Al(NO_3)_3$	Precipitation with urea	110	γ
III	$Al(NO_3)_3$	Precipitation with ammonia	156	γ
IV	$Al(NO_3)_3$	Direct thermal decomposition	135	Amorphous
V	$Al_2(SO_4)_3$	Precipitation with urea	11	Complex, Broad
VI	$Al_2(SO_4)_3$	Precipitation with ammonia	216	γ
VII	$AlCl_3$	Precipitation with urea	147	γ
VIII	$AlCl_3$	Precipitation with ammonia	248	γ
IX	$AlCl_3$	Direct thermal decomposition	103	(χ), Broad
X	$AlBr_3$	Precipitation with urea	173	γ
XI	$NaAlO_2$	Precipitation with CO_2	194	γ

Table 2. Catalytic activities of various aluminas for hydrocarbon reactions at room temperature

Al_2O_3	Exchange reactions[a]			Isomerization of 1-butene	
	CH_4-D_2[b]	C_2H_4-D_2	Cyclo-C_3H_6-D_2	Rate[c]	*cis*/*trans*[d]
I	4.2	7.9	29.0	5.0	4.3
II	2.7	9.1	65.6	2.1	5.4
III	4.1	13.3	49.4	2.7	4.2
IV	0.0	1.7	14.6	10.2	7.4
V	0.0	0.0	0.0[e]	140.6	0.8
VI	1.8	2.4	18.9	5.9	7.4
VII	18.7	3.6	6.0	1.4	3.2
VIII	4.4	3.8	7.0	0.3	3.2
IX	1.0	0.4	2.0	2.9	9.4
X	2.3	10.1	45.7	2.7	4.4
XI	0.0	1.1	9.6	20.0	5.8

a) $10^4 k_\phi$ m^{-2} s^{-1}. b) Cited from Ref. 4. c) 10^2 mmol m^{-2} s^{-1}. d) *cis*-2-Butene/*trans*-2-butene. e) Isomerization to propylene occurs.

isomerization of 1-butene. The aluminas which showed the highest activities for the exchange of D_2 with ethylene or cyclopropane and the isomerization of 1-butene were Al_2O_3 III, Al_2O_3 II, and Al_2O_3 V, respectively. Al_2O_3 V exhibited a pronounced activity for the isomerization, but was completely inactive for the exchange reactions. In the case of Al_2O_3 V, the ratio of *cis*-2-butene to *trans*-2-butene is very low (0.8) compared with that of other aluminas. This suggests that the acid sites play an important role for the isomerization of 1-butene.[6] For the exchange reaction of methane with deuterium, the proton abstraction from methane by basic sites is reported to be important.[3,7] However, the activity per unit basic sites of alkaline earth oxides whose basic strength is higher than that of alumina is much lower than that of alumina.[3] The *cis*/*trans* ratio which is sometimes used as an indication of basic property of catalyst[8,9] does not correlate with the exchange activity. Thus, besides basic sites, acidic sites are considered to be important as active sites for exchange reaction to stabilize carbanion intermediates formed by proton abstraction. In the present work, we demonstrate highly active aluminas for the exchange and isomerization reactions and emphasize that the activity of alumina is remarkably controlled by the preparation method.

In order to characterize the activities of various aluminas, the activities for four hydrocarbon reactions were plotted against the eleven kinds of alumina which are arranged in the order of activity for the exchange between methane and deuterium in Fig. 1. The higher the activity for the exchange of methane with deuterium, the lower the activity for the isomerization of 1-butene. On the other hand, the aluminas which are less active for the above two reactions showed the maximum activities for the exchange reaction between ethylene or cyclopropane and deuterium.

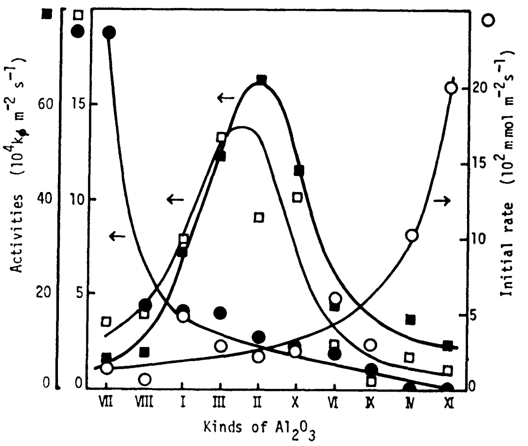

Fig. 1. Activities of various kinds of Al_2O_3 for hydrocarbon reactions. ●; CH_4–D_2, □; C_2H_4–D_2, ■; C_3H_6–D_2, ○; isomerization of 1-butene (Kinds of Al_2O_3 were arranged in decreasing order of the activity for the exchange reaction of CH_4 with D_2).

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