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HIGHLY ACTIVE ALUMINA FOR ALDOL CONDENSATION OF ACETONE

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Eleven kinds of aluminas were prepared from various starting materials by different methods. An alumina prepared from sodium aluminate by precipitation with carbon dioxide was found to exhibit an extraordinarily high catalytic activity for aldol condensation of acetone at 0 °C.

Одинадцать типов алюминатов были получены из различных исходных материалов с помощью различных методов. Окись алюминия, получаемая из алюмината натрия высаждением двуокисью углерода, обладает необычно высокой каталитической активностью к альдольной конденсации ацетона при 0^oC.

INTRODUCTION

Aldol condensation of acetone to diacetone alcohol is an important reaction in industry. The reaction product, diacetone alcohol, is used as a solvent for nitrocellulose, cellulose acetate and many natural and synthetic resins and is an intermediate for the synthesis of methyl isobutyl ketone which is also an important solvent in industry. An alumina prepared at a mildly alkaline pH [1], an alumina used for chromatography [2], and a fused mixture of $Al(OH)_3$ gel and NaOH [3] have been reported as effective catalysts for aldol condensation. Since, however, no systematic study has been made of alumina catalysts, various kinds of aluminas have been prepared and tested for the condensation reaction.

EXPERIMENTAL

Various aluminas were prepared from various 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, the details having been described previously [4]. The hydroxides of Al_2O_3 IV and V were washed with distilled water until sulfate ions were not detected with barium chloride in the washings. The hydroxide of Al_2O_3 VIII was washed with 30 dm^3 of distilled water. The hydroxides of Al_2O_3 VI and VII were washed with 6 dm^3 of distilled water. The hydroxides were dried at 120 °C for 20 h and calcined in air at 500 °C for 2 h. Al_2O_3 IX and X are reference catalysts (JRC-ALO-2 and JRC-ALO-4) of Catalyst Society of Japan and Al_2O_3 XI is the JRC-ALO-4 on which 1 wt.% Na^+ was mounted by impregnation with $NaNO_3$ solution. These were calcined in air at 500°C for 2 h. All of the aluminas except Al_2O_3 X which were evacuated at 600 °C for 3 h were used as catalysts. In the case of Al_2O_3 X, evacuation temperature was 500 °C. Surface area was determined by the BET method. The structures of aluminas were determined from the powder patterns obtained with a Rigaku Denki Giger flex X-ray diffractometer using filtered CuK_α radiation.

The reaction of acetone was carried out at 0 °C for 1 h in a batch reactor with 50 mg of catalyst and 1 g of acetone. The reaction products were mainly diacetone alcohol and small amounts of mesityl oxide according to gas chromatography.

RESULTS AND DISCUSSION

Table 2 shows the results of aldol condensation reaction. Among eleven kinds of aluminas, Al_2O_3 VIII exhibited an outstanding activity and the highest selectivity (99.6%) for the formation of diacetone alcohol. The second best catalyst was Al_2O_3 XI, but the activity was only one third of Al_2O_3 VIII and the selectivity was also lower. The activities of the other

Table 1

Preparation methods, surface areas and structures of aluminas evacuated at 600 °C

Al_2O_3	Preparation		Surface area	Structure
	Starting material	Method	(m^2 g^{-1})	
I	$Al(OCH(CH_3)_2)$	Hydrolysis	236	γ
II	$Al(NO_3)_3$	Precipitation with urea	110	γ
III	$Al(NO_3)_3$	Precipitation with ammonia	156	γ
IV	$Al_2(SO_4)_3$	Precipitation with urea	11	Complex, Broad
V	$Al_2(SO_4)_3$	Precipitation with ammonia	216	γ
VI	$AlCl_3$	Precipitation with ammonia	248	γ
VII	$AlBr_3$	Precipitation with urea	173	γ
VIII	$NaAlO_2$	Precipitation with CO_2	194	γ
IX	JRC-ALO-2		285	η
X	JRC-ALO-4		177	γ
XI	JRC-ALO-4+1 wt.% Na^+		-	-

Table 2

Activities and selectivities of various aluminas for aldol condensation of acetone at 0 °C for 1 h

Al_2O_3	Conversion (%) to				Selectivity (%)
	Diacetone alcohol	Mesityl oxide	Unidentified substance	Total	
I	1.38	0.06	0	1.45	95.7
II	0.88	0.03	0	0.92	96.0
III	1.79	0.09	0.01	1.88	95.2
IV	0	0	0	0	--
v	1.04	0.05	0.01	1.09	94.9
VI	0.66	0.04	0.01	0.71	92.9
VII	1.31	0.06	0	1.37	95.4
VIII	12.9	0.05	0	12.9	99.6
IX	1.63	0.12	0.01	1.76	92.7
X	1.42	0.04	0	1.46	97.0
XI	3.53	0.10	0	3.63	97.3

nine aluminas were much lower, their selectivities being even worse. In particular, Al_2O_3 IV did not show any activity.

The amount of mesityl oxide formed was small over any catalysts. The largest amount was only 0.12 % over Al_2O_3 IX. Unidentified substance was formed over Al_2O_3 III, V, VI and IX, but the amount was negligible.

Aldol condensation is known to proceed at room temperature in the presence of basic catalysts such as NaOH, $Ba(OH)_2$, etc. [5]. Since, however, the basic property of Al_2O_3 VIII which showed the highest activity is reported to be almost the same as that of Al_2O_3 I, which showed much lower activity [6], it seems unlikely that the rate of aldol condensation of acetone is governed only by basic property of alumina surface. Another factor to control the reaction rate may be acidic property in the sense of acid-base bifunctional catalysis. However, there is not much difference in acidic property between Al_2O_3 VIII and I [6]. Therefore, the optimum structural arrangement of basic and acidic sites is considered to be vitally important for the reaction. The extraordinarily high activity of Al_2O_3 VIII is assumed to be due to such a structural arrangement created by the precipitation of $NaAlO_2$ with CO_2. Importance of preparation method of a highly active alumina for the aldol condensation reaction is emphasized in the present work.

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