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Exchange Reaction between Methyl Hydrogens of Methanol over Solid-Base Catalysts

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An isotope exchange reaction of hydrogen in methyl group of methanol was found to occur over solid-base catalysts. A mixture of CD_3OD and CH_3OD (1:1), when passed over MgO at 330 °C, changed to a nearly isotopically equilibrated mixture of deuterated methanols.

In the course of our mechanistic studies on the methylenation with methanol over metal ion-containing magnesium oxide catalysts to form α,β-unsaturated compounds,[1)] we have found that the exchange reaction between methyl hydrogens of methanol occurred over such catalysts. The aim of this report is to show preliminary results on this novel exchange reaction.

When a mixture of CD_3OD and CH_3OD (1:1) is allowed to react over solid-base catalysts, four deuterated methanols (d_1-d_4) can be formed. The results obtained under the various conditions are summarized in Table 1. Isotope distributions in methanol, determined by mass spectrometry, were for the samples collected after an hour reaction on stream in a continuous flow reactor. Under the conditions no reactions were observed besides the exchange reaction. A nearly isotopically equilibrated mixture of deuterated methanols was yielded at a relatively longer contact time by the use of MgO catalyst (runs 1,2). The deuterium content in methyl group of methanol was practically unchanged after the reaction, so that it can be excluded that d_2- and d_3-methanol result from the uptake of hydrogens present originally on the surface by CD_3OD. It was also confirmed by the reaction of CH_3OD (run 5) that no exchange reaction between methyl hydrogen and hydroxyl hydrogen of methanol took place. In addition, when a small amount of CD_3CN was added in the reactant feed, the rate of the exchange reaction slightly decreased because of the strong adsorption of acetonitrile (runs 6-9) but no hydrogen atom was found in acetonitrile, although the exchange reaction of hydrogen between methyl group of acetonitrile and hydroxyl group of methanol readily occurs under the present reaction conditions.[2)] These results clearly prove that the exchange reaction takes place between methyl hydrogens of methanols. Among the catalysts tested here Mn-MgO catalyst showed the highest activity for the exchange reaction (runs 4,9). CaO, known as a typical solid-base, also showed the activity (run 8). The commercial MgO showed the low activity for the reaction (run 7) because of its low surface area (11 $m^2 \cdot g^{-1}$) compared to the others (above 130 $m^2 \cdot g^{-1}$).

The reaction mechanism is obscure at the present stage. The exchange reaction is, however, explicable rationally by the mechanism proposed for the transfer

Table 1. Isotopic Exchange Reaction of Hydrogen in Methyl Group of Methanol over Solid-Base Catalysts under the Various Conditions

Run	Catalyst a)		Reaction condition b)		Isotope distribution in methanol/% c)					Deuterium content in methyl group/%	%-age exchanged
		g			d_0	d_1	d_2	d_3	d_4		
1	MgO	2	A	BR	2	48	0	4	46	49.3	
				AR	0	14	36	35	15	50.3	94.5
2	MgO	1	A	BR	2	49	0	2	47	49.0	
				AR	0	18	32	33	17	49.7	86.7
3	MgO	0.2	A	BR	4	46	1	4	45	49.3	
				AR	1	29	18	21	31	51.3	50.0
4	Mn-MgO d) (3wt%)	0.2	A	BR	5	46	1	5	43	48.3	
				AR	1	22	27	27	23	50.3	70.2
5	MgO	0.2	- e)	BR	5	94	1	0	0	-	
				AR	3	93	2	2	0	-	-
6	MgO	0.2	B	BR	4	48	1	4	42	46.3	
				AR	1	39	15	12	33	46.3	38.9
7	MgO f)	2	B	BR	1	48	4	2	45	48.0	
				AR	2	47	5	5	41	46.7	4.3
8	CaO	0.2	B	BR	2	48	7	3	40	45.0	
				AR	1	37	17	12	33	47.0	29.9
9	Mn-MgO (3wt%)	0.2	B	BR	3	48	5	4	40	45.3	
				AR	0	30	22	20	28	48.7	52.0

a) Unless otherwise specified, the oxide catalysts used were obtained after the following treatment: Starting metal oxides were treated in water at an ambient temperature for 24 h and then in a boiling water until materials were solidified by the evaporation of water, followed by drying at 110 °C. Before the reaction catalysts were treated at 600 °C for 2 h in a nitrogen stream (50 $ml \cdot min^{-1}$). b) Two reaction conditions were employed. Condition A; reaction temperature, 330 °C; total flow rate, 63 $ml \cdot min^{-1}$; partial pressure, CD_3OD 8 kPa, CH_3OD 8 kPa, N_2 balance; total pressure, atmospheric. Condition B: CD_3CN (99.8 % D) was added in the reactant feed (partial pressure, 1.6 kPa). Others are the same as the condition A. c) Determined with a Hitachi M-80 mass spectrometer equipped with a field ionizer. BR; before reaction, AR; after reaction. d) Prepared by an impregnation method as described in our previous reports (Ref. 1) e) CH_3OD was allowed to react alone. f) Obtained from Soekawa Rika (99.9 %) and used after the heat treatment.

hydrogenation of ketones with alcohols.[3] Once a small amount of adsorbed formaldehyde is formed by the dehydrogenation of methanol, the hydrogen transfer, $CD_3O(a) + HCHO(a)$ $DCDO(a) + CD_2HO(a)$, may readily proceed and results in the formation of d_x-methanol. Since the adsorbed formaldehyde is always regenerated, formaldehyde can be regarded as a chain carrier in the mechanism.

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