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Condensation of alcohol over solid-base catalyst to form higher alcohols

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Condensations of various primary alcohols (C_2-C_5) with methanol were carried out at atmospheric pressure over various metal oxides having a solid-base property. The reactions gave one or two carbon higher alcohol than the reacted primary alcohol. MgO catalyst was most active for the reaction and yielded the alcohol products in high selectivity ($>80\%$). Based on the results of the exchange reaction between methyl hydrogen of methanol over MgO surface, it is concluded that a rapid hydride transfer between adsorbed alcohol and adsorbed carbonyl is responsible for the selective formation of alcohols.

Keywords: Methanol; alcohols; catalytic condensation; solid-base; isotope tracer

1. Introduction

Numerous attempts have been made in the past to develop synthetic methods for higher alcohols, particularly from C_1 chemicals such as CO and methanol, and many processes have already been established [1]. One of the important industrial processes is the so-called oxo reaction or hydroformylation of alkenes where CO is a key reactant. Other reported methods include homologation of lower alcohols to higher ones using carbon monoxide and hydrogen [2], and metal- or metal oxide-catalyzed direct synthesis of alcohols from syngas [3]. In addition, Guerbet reaction, where a primary or secondary alcohol reacts with itself or another alcohol to produce a higher alcohol, is also an important reaction as higher alcohol synthesis. This reaction has been much developed and various types of heterogeneous catalyst have been reported in patents [4–6].

In an extension of our studies on catalysis by solid-base catalysts [7–9], we recently developed a new catalytic reaction process for producing higher alcohols using methanol as a main building block [10]. In this reaction, methanol is condensed with other primary or secondary alcohol having a methyl or methylene group at the α-position over metal oxide catalyst having a solid-base property, and then higher alcohols are formed in high selectivities. In this report we will show some results on the catalytic condensations of various primary alcohols with methanol and also on the exchange reaction between methyl hydrogens of methanol over solid-base catalyst [11] in order to elucidate a reaction mechanism of the condensation.

2. Experimental

As reported in our previous paper [10], the reaction takes place only when MgO catalyst was used. Other solid-base metal oxides, such as CaO and ZnO, are inactive or non-selective. In this work, therefore, the MgO catalyst obtained by the following preparation and treatment was used. First, commercial MgO (Soekawa Rika, 99.92%, surface area 11 m^2/g) was suspended in boiling water with string and then solidified again by the evaporation of water and dried at 383 K overnight. By this procedure $Mg(OH)_2$ was obtained and was then heat-treated in a nitrogen stream at 873 K for 2 h, changing into MgO phase (137 m^2/g).

The reactions of primary alcohols ($C_nH_{2n+1}OH$, $n = 2$-5) with methanol were carried out at atmospheric pressure using a continuous flow reaction system with a quartz fixed-bad reactor. The following standard reaction conditions were used; feed gas composition, N_2: methanol: $C_nH_{2n+1}OH = 10:3:0.15$, total flow rate, 66 $ml.min^{-1}$, catalyst weight, 1 g, reaction temperature, 635 K. The same reaction system was used for the isotope exchange reactions of deuterated methanol over MgO. The reaction conditions are as follows; partial pressure, CD_3OD 8 kPa, CH_3OD 8 kPa, N_2 balance, total pressure atmospheric, total flow rate 62 $ml.min^{-1}$, reaction temperature 603 K. Under the conditions, no other reactions took place except the exchange reaction. Isotope distributions in methanol which was collected in a trap at dry-ice temperature for an hour reaction on stream was determined with a Hitachi M-80 mass spectrometer equipped with a field ionizer.

3. Results and discussion

CONDENSATION OF VARIOUS ALCOHOLS WITH METHANOL OVER MgO CATALYST

Table 1 summarizes the results of the condensation reaction of various alcohols with methanol over MgO catalyst at 653 K. Magnesium oxide, a well known solid-base catalyst, showed the best catalytic performance in the reactions, yielding higher alcohols in high selectivities in every reactant used. The catalyst deactivated gradually over the initial reaction period and then showed

Table 1

Condensation of alcohols with methanol over MgO catalyst at 653 K

Reactant($C_nH_{2n+1}OH$)		Conversion of $C_nH_{2n+1}OH$ /%	Selectivity(%) to *				
$n =$			$C_{n-1}H_{2n-1}$ CHO	$C_{n+1}H_{2n+3}$ OH	C_nH_{2n+1} CHO	$C_{n+2}H_{2n+5}$ OH	$C_{n+1}H_{2n+3}$ CHO
2	ethanol	50.3	8.0	35.7	2.6	40.3	3.9
3	1-propanol	48.3	6.7	82.5	7.3	–	–
4	1-butanol	60.2	6.1	78.5	8.2	–	–
5	1-pentanol	50.2	2.5	86.0	3.1	–	–

* Condensation products are 2-methyl form.

steady state activities over 20 h. When ethanol was allowed to react with methanol, ethanol was readily converted into propanol and 2-methylpropanol. Total selectivity of both products was about 80%. Minor products were C_2-, C_3- and C_4-saturated carbonyl compounds and thereby small amount of hydrogen was also formed. Very small amounts of methane and CO were also formed, indicating a few methanol side reactions took place under the conditions. However the extent of such reactions was low and thus the excess methanol was mostly recovered.

When the other primary alcohol was allowed to react with methanol (table 1), the reaction features were almost the same as described above for the ethanol conversion; that is, the reactions readily took place and formed the 2-methyl form of the higher alcohol mainly with small amount of aldehydes produced by the reactant and product alcohols. The only difference between the ethanol reaction and the other reaction is two alcohol products in the ethanol reaction but one higher alcohol product in the other. This is because the propanol produced in the ethanol conversion can subsequently react with methanol to form 2-methylpropanol.

Two points emerge from the table. First, the conversions obtained in each reaction under the standard conditions were essentially the same (50-60%). This strongly implies the rate independency of the reactant. Secondly, the product selectivity is little influenced by the reactant; the alcohol selectivity is around 80% in every case and the high molar ratio of alcohol to corresponding aldehyde is also similar in every reaction.

EXCHANGE REACTION BETWEEN METHYL HYDROGEN OF METHANOL

In order to obtain an insight on the highly selective formation of alcohol, we conducted exchange reactions between methyl hydrogen of adsorbed methanol over MgO catalyst at slightly lower reaction temperature than those for the condensation. The results are illustrated in fig. 1 and the additional data are shown in table 2. When a mixture of CD_3OD and CH_3OD (1 : 1) was allowed to react over the MgO catalyst at 603 K, two partially deuterated methanols, CH_2DOD and CHD_2OD, were readily formed and a nearly isotopically equilibrated mixture of deuterated methanols was yielded at a relatively longer contact time. The deuterium content in methyl group of methanol was found practically unchanged after the reaction, so that it can be concluded that the d_2- and d_3-methanol do not result from the uptake of hydrogens present originally on the MgO surface by D_3OD. The result clearly reveals that the exchange reaction takes place between methyl hydrogens of methanols. The result, however, does not give us any information about whether the exchange reaction proceeds through the surface or directly between adsorbed molecules.

In the reaction of CH_3OD, the extent of the exchange between methyl hydrogens and hydroxyl hydrogens was low (table 2). The fact supports a

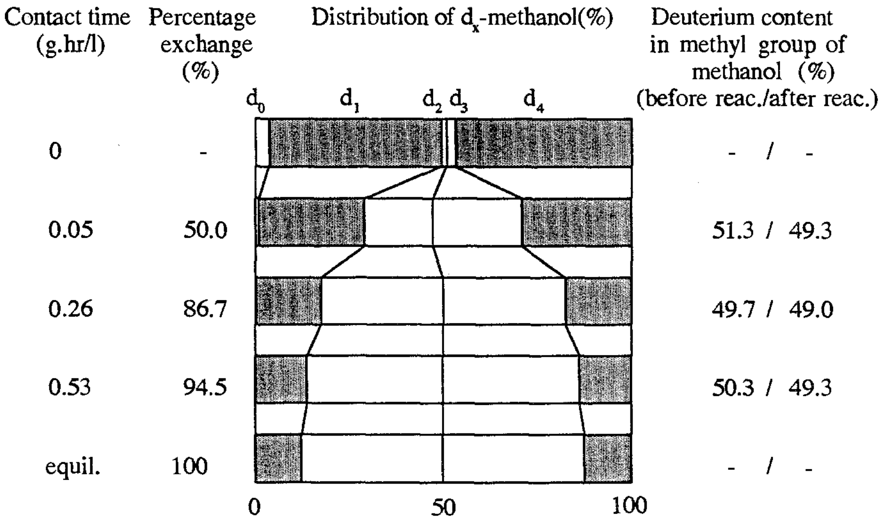


Fig. 1. Isotopic exchange reaction of hydrogen in methyl group of methanol over MgO catalyst.

possibility of the involvement of the surface reaction but its rate is not rapid enough for the observed exchange reaction. When a small amount of CD_3CN(99.8% D, 1.6 kPa) was added in the reactant feed, the rate of the exchange reaction was slightly decreased because of the strong adsorption of acetonitrile, and no hydrogen atom was found in acetonitrile, in spite of that it is known that the exchange reaction of the protonic hydrogen between methyl group of acetonitrile and the hydroxyl hydrogen of methanol occurs quickly under the same conditions. The result suggests two pathways for the exchange, a direct hydride transfer and a hydride transfer via the surface without scrambling with surface proton. We further conducted the reaction of a mixture of CD_3OD, H_2 and D_2 over MgO catalyst (table 2). We observed a reasonable rate of the H_2-D_2 exchange reaction and an appreciable amount of CD_3OH. The result clearly indicates that there are both proton and hydride species on the MgO surface but only proton was incorporated into methanol, that is, a direct hydride transfer is the major route for the exchange reaction of the methyl hydrogen of methanol.

The exchange reaction is, now, explained rationally on the basis of the mechanism proposed for the transfer hydrogenation of ketones with alcohols [12–15]. Once a small amount of adsorbed formaldehyde is formed by the dehydrogenation of methanol, the hydrogen transfer

$$CD_3O(a) + HCHO \longrightarrow DCDO(a) + CDH_2O(a)$$

may readily proceed directly through adsorbed species and results in the formation of d$_x$-methanol. Since the adsorbed formaldehyde is always regenerated, formaldehyde can be regarded as a chain carrier. From this mechanism, it

Table 2

Isotopic exchange reaction of hydrogen in methyl group of methanol over MgO catalyst under the various conditions

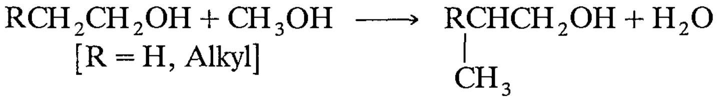
Reactant feed composition (ml/min)		Isotope distribution (%)											
		Methanol					Acetonitrile				Hydrogen		
		d_0	d_1	d_2	d_3	d_4	d_0	d_1	d_2	d_3	H_2	HD	D_2
$N_2+CH_3OD+CD_3OD$ (52:5:5)	BR	4	46	1	4	45	–	–	–	–	–	–	–
	AR	1	29	18	21	31	–	–	–	–	–	–	–
N_2+CH_3OD (52:10)	BR	5	94	1	0	0	–	–	–	–	–	–	–
	AR	3	93	2	2	0	–	–	–	–	–	–	–
$N_2+CH_3OD+CD_3OD$ $+CD_3CN$ (52:5:5:1)	BR	5	48	1	4	42	0	0	0	100	–	–	–
	AR	1	39	15	12	33	0	0	0	100	–	–	–
$H_2+D_2+CD_3OD$ (47:5:10)	BR	0	0	0	2	98	–	–	–	–	90	0	10
	AR	0	0	0	15	85	–	–	–	–	87	5	8

BR: before reaction, AR: after reaction.

can be imagined that MgO surface is covered with many protons and adsorbed methanols, and hydride transfers quickly through the adsorbed methanol.

MECHANISTIC ASPECT FOR CATALYTIC CONDENSATION OF ALCOHOLS

The catalytic condensation of higher alcohols with methanol is characterized by the following two features; carbon-carbon bond formation always takes place at α-position of reactant and the final products are always in the 2-methyl form. The reaction, therefore, can be regarded as an aldol type reaction and the general reaction equation is written as follows;



$$\underset{[R = H,\ \mathrm{Alkyl}]}{RCH_2CH_2OH + CH_3OH} \longrightarrow \underset{\substack{|\\ CH_3}}{RCHCH_2OH} + H_2O$$

The reaction of dehydrogenation, condensation, dehydration and hydrogenation need to proceed consecutively. According to the reaction type, therefore, one may expect the formation of α,β-unsaturated compound and allyl alcohols as intermediates. However, in the results as already described, no such products were detected in every reaction as far as MgO catalyst was used. Since the rapid hydrogen transfer between adsorbed species was proven by the isotope exchange reaction, it is most likely that a hydrogen transfer from methanol takes place to hydrogenate C=C and C=O bonds of adsorbed unsaturated species before desorption and thus facilitates the formation of saturated alcohols. It is interesting that such a multi-step reaction readily takes place on an oxide surface and that MgO in particular has a high ability to yield fully hydrogenated higher alcohols.

References

[1] R.A. Sheldon, *Chemicals from Synthesis Gas* (Reidel, Dordrecht, 1983).
[2] M. Ichikawa, J. Catal. 56 (1979) 127.
[3] T. Mizorogi and M. Nakayama, Bull Chem. Soc. Jpn. 39 (1964) 236.
[4] M.W. Farrar (Monsanto Chemcal Co.), US Pat. 2 971 033 (1961).
[5] G. Pregalia, G. Gregorio and F. Conti (Montecatini Edison S.p.A), French Pat. 1 531 2612 (1968).
[6] R.T. Clark (Celanese Corporation), US Pat. 3 972 952 (1976).
[7] W. Ueda, T. Yokoyama, H. Kurokawa, Y. Moro-oka and T. Ikawa, J. Jpn. Petrol. Inst. 29 (1986) 72.
[8] H. Kurokawa, T. Kato, W. Ueda, Y. Morikawa, Y. Moro-oka and T. Ikawa, J. Catal. 126 (1990) 199.
[9] H. Kurokawa, T. Kato, T. Kuwabara, W. Ueda, Y. Morikawa, Y. Moro-oka and T. Ikawa, J. Catal. 126 (1990) 208.
[10] W. Ueda, T. Kuwabara, T. Ohshida and Y. Morikawa, J. Chem. Soc., Chem. Commun. (1990) 1558.
[11] W. Ueda, T. Kuwabara, H. Kurokawa and Y. Morikawa, Chem. Lett. (1990) 265.

[12] Y. Okamoto, T. Imanaka and S. Teranishi, Bull. Chem. Soc. Jpn. 45 (1972) 3207.
[13] H. Niiyama and E. Echigoya, Bull. Chem. Soc. Jpn. 45 (1972) 938.
[14] C.L. Kiby and W.K. Hall, J. Catal. 31 (1973) 65.
[15] A. Miyamoto and Y. Ogino, J. Catal. 43 (1976) 143.