A Low-pressure Guerbet Reaction over Magnesium Oxide Catalyst

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Propan-1-ol and 2-methylpropan-1-ol were synthesized selectively by the catalytic reaction of methanol and ethanol over magnesium oxide.

Numerous attempts have been made in the past to develop synthetic methods for higher alcohols, particularly from C_1 chemicals such as methanol and CO, and many processes have already been established. One of the important industrial processes is the so-called oxo reaction or hydroformylation of alkenes where CO is a key reactant.[1] Other reported methods include homologation of lower alcohols to higher ones using carbon monoxide and hydrogen in the presence of a metal complex catalyst, and metal- or metal oxide-catalysed direct synthesis of alcohols from syn gas.[1]

Another reaction for producing higher alcohols is the Guerbet synthesis, where a primary or secondary alcohol having a methylene group at the α-position is condensed with itself or with another alcohol, also having a methylene group, to produce a higher alcohol. This reaction has been much developed and various types of heterogeneous catalyst have been reported in patents.[2–4] Most of these catalysts comprise two catalytic elements; a solid-base catalyst for promoting condensation and a hydrogenation catalyst. The reactions are normally carried out at high pressure.

In an extension of our studies on catalysis by solid-base catalysts,[5,6] we found that the Guerbet reaction will readily proceed in the gas phase at atmospheric pressure and elevated temperatures over magnesium oxide without any added activator for hydrogenation. We herein report the reaction of methanol and ethanol to form propan-1-ol and 2-methylpropan-1-ol.

Table 1 summarizes the results of activity tests on various solid-base metal oxide and metal ion-containing magnesium oxide catalysts. The reactions were carried out at atmospheric pressure using a continuous flow reaction system with a quartz fixed-bed reactor. Details of catalyst preparation and the reaction conditions are given in Table 1. All catalysts deactivated gradually over the initial reaction period and then showed steady state activities over 20 h.

Magnesium oxide, a well known solid-base catalyst, showed the best catalytic performance in the reaction of methanol and ethanol, selectively yielding propan-1-ol and 2-methylpropan-1-ol (Table 1, runs 1–7). Total alcohol selectivity was about 80%. Minor products were C_2-, C_3- and C_4-unsaturated compounds. Very small amounts of methane, CO, and hydrogen were also formed and few methanol side reactions took place under these conditions; the excess methanol was recovered. ZnO is also a basic oxide but less active for the condensation, mainly catalysing the dehydrogenation of ethanol to ethanal (run 10). The catalytic activity of CaO was surprisingly poor (run 11), but the reason for this is not yet known. However, ZrO_2 is relatively more acidic than the above oxides and catalysed the dehydration of alcohols to ethers (run 12).

Table 1 Catalytic reaction of methanol and ethanol over various solid-base metal oxides[a]

Run	catalyst[b]	Surface area[c]/ $m^2 g^{-1}$	Reaction T/ K	Catalyst weight/g	Conversion of ethanol (%)	Selectivity/mol%				
						Propan-1-ol	2-Methyl-propan-1-ol	Butan-1-ol	Ethanal	2-Methyl-propanal
1	MgO[d]	137	613	1	7.9	64.2	7.7	0	23.7	0
2	MgO[d]	137	633	1	29.6	50.7	27.6	0.7	12.4	1.9
3	MgO[d]	137	643	1	42.1	41.6	36.2	0.6	9.4	3.2
4	MgO[d]	137	663	1	59.5	29.1	46.0	0.6	7.2	5.8
5	MgO[d]	137	633	0.5	16.0	57.8	16.9	0.7	19.0	0.9
6	MgO[d]	137	633	2	46.0	39.7	31.8	0.6	7.3	2.8
7	MgO[d]	137	633	4	58.2	32.0	39.8	0.7	6.0	4.3
8	MgO[e]	94	633	1	1.3	49.4	tr	0	50.6	0
9	MgO[f]	—	633	1	9.7	68.4	8.2	2.0	16.5	0
10	ZnO[g]	—	633	1	74.5	tr	tr	0	84.5	0.5
11	CaO	65	633	1	0.8	34.6	0	0	65.4	0
12	ZrO_2[h]	—	633	1	66.9	0	0	0	0	0
13	3 wt% Mn–MgO[i]	168	633	1	32.9	24.3	9.9	tr	31.9	3.7
14	3 wt% Cr–MgO[i]	105	633	1	35.1	16.0	7.3	tr	36.4	5.2
15	3 wt% Zn–MgO[i]	—	633	1	32.1	11.9	3.9	tr	47.4	2.9
16	3 wt% Al–MgO[i]	106	633	1	24.6	0	0	0	4.6	0
17	3 wt% Na–MgO[i]	—	633	1	0.8	33.3	0	0	66.7	0
18	3 wt% Cs–MgO[i]	—	633	1	3.9	54.3	7.0	tr	38.7	tr

[a] Reaction conditions: feed gas composition N_2 : methanol : ethanol = 10 : 3 : 0.15, total flow rate 66 ml min^{-1}. tr = trace. [b] Before the reaction, all catalysts were treated at 873 K for 2 h in a nitrogen stream (50 ml min^{-1}). [c] The surface area was measured by the BET method by N_2 adsorption at liq. N_2 temperature. [d] The catalyst was obtained after the following treatment: commercial MgO (Soekawa Rika, 99.92%) was suspended in boiling water and then solidified again by the evaporation of water and dried at 383 K. [e] Commercial magnesium carbonate was used directly. [f] The catalyst was prepared by precipitation from magnesium nitrate. [g] Other products were methyl formate, acrolein, and allyl alcohol. [h] Main products were dimethyl ether and methyl ethyl ether. [i] See ref. 5 for the method of catalyst preparation.

We also conducted the reaction using metal ion-containing magnesium oxide catalysts, some of which are effective as catalysts for the reaction methanol with saturated ketones, esters, and nitriles to produce the corresponding α,β-unsaturated compounds.[5,6] As shown in Table 1, most of the transition metal ion-containing magnesium oxide catalysts showed high activity (runs 13–15). However, the portion of unsaturated compounds in the product was relatively higher than obtained using the magnesium oxide catalyst. This suggests that these catalysts have stronger dehydrogenation activity than magnesium oxide and is consistent with the finding that they are highly active for the formation of α,β-unsaturated compounds. Al-MgO showed characteristic catalytic performance (run 16); the catalyst was active for the ethanol conversion but none of the higher alcohols were formed. Instead, the products were various ethers, including C_3 and C_4 ethers, dimethyl ether and methyl ethyl ether. Although Al–MgO is active for the formation of C_3 and C_4 alcohols, the alcohols formed may react subsequently with methanol to form ether *via* an acid-catalysed dehydration, due to the acid, as well as base, properties of the catalyst.[7] The addition of alkali metal ions mostly caused a decrease in the activity of magnesium oxide (runs 17, 18).

The catalytic activity of magnesium oxide was strongly influenced by its preparation conditions. The most active magnesium oxide was obtained by heat treatment (873 K) of $Mg(OH)_2$ which was prepared by suspending commercial magnesium oxide (surface area, 11 $m^2\ g^{-1}$) in boiling water. Magnesium oxide prepared from basic magnesium carbonate by heat treatment at 873 K showed extremely low activity and poor selectivity for higher alcohols (run 8). Magnesium oxide prepared by precipitation from magnesium nitrate also showed poor activity (run 9). The difference in the catalytic activities of these magnesium oxides cannot be explained only by the change in surface area; the surface states, which may affect solid-base properties or dehydrogenation activity, seem to be different.

When the ethanol conversion was increased by varying the reaction temperature (runs 1–4), the product distribution changed markedly; propan-1-ol was the main product at low conversion while 2-methylpropan-1-ol was produced highly selectively at high conversion. The total selectivity for higher alcohols was >70% for each ethanol conversion. The same selectivity change was observed when the contact time was varied (runs 2, 5–7). These results suggest that dehydrogenation, condensation, dehydration and hydrogenation proceed consecutively. It is interesting that such a multi-step reaction readily takes place on an oxide surface and that magnesium oxide in particular has a high ability to yield fully hydrogenated higher alcohols.

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