Vapor-Phase Synthesis of Symmetric Ketone from Alcohol over CeO_2-Fe_2O_3 Catalysts

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Formation of 3-pentanone via oxidative dimerization of l-propanol was investigated over CeO_2-based solid solution with various metal oxides. An addition of Fe_2O_3 into CeO_2 greatly enhanced the 3-pentanone formation, and both l-propanol conversion and 3-pentanone selectivity were maximized at Fe content of 20 mol%. It was found that the CeO_2-Fe_2O_3 effectively works as a catalyst for the formation of symmetric ketones such as 3-pentanone, 4-heptanone, 5-nonanone, etc.

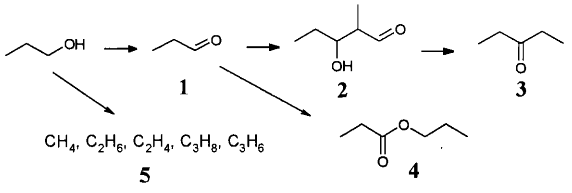
CeO_2 is an attractive catalyst for various reactions such as hydrogenation of CO[1] and alkylation of phenol.[2-4] In the alkylation of phenol using l-propanol, we found that 3-pentanone was observed as a by-product over CeO_2-MgO solid solution catalyst, and that the yield of 3-pentanone increased with increasing CeO_2 content in the CeO_2-MgO.[4] We have speculated that the total reaction proceeds as follows: l-propanol is dehydrogenated to propanal, followed by aldol addition to produce 3-hydroxy-2-methylpentanal, and finally it is decomposed to 3-pentanone.

In this work, we examine catalytic tests of l-propanol conversion over CeO_2-based solid solution with various metal oxides (MO_x), and discuss what in the catalyst essentially affects the 3-pentanone formation. Furthermore, we examine syntheses of symmetric ketones from the other alcohols.

All reagents were supplied by Wako Pure Chemical industries, Ltd. (Japan). CeO_2-based solid solution (CeO_2-MO_x) samples were prepared by using cerium (III) nitrate hexahydrate, another metal (M) nitrate, and citric acid monohydrate. The preparation procedure has been described elsewhere.[3] After the citrate precursor had been heated in air at 170 °C for 2 h, it was calcined in air at 550 °C for 2 h to provide a CeO_2-MO_x sample. The content of MO_x was defined as a mol percent of metal ion.

The reaction of 1-propanol was carried out in a usual fixed bed flow reactor under atmospheric pressure of N_2 at 450 °C. Prior to the reaction, a catalyst sample (0.15 g) was preheated in a glass tube reactor at 500 °C for 1 h. l-Propanol was fed into the reactor at 450 °C at the rate of 23 mmol h^{-1}, together with N_2 flow of 73 mmol h^{-1}. An effluent collected in an ice trap was extracted every an hour, and analyzed by FID-GC with a packed column of Silicon OV-17 (2 m) at temperatures controlled from 50 to 220 °C at a heating rate of 5 K min^{-1}. Gaseous hydrocarbons such as propane and propene were analyzed by FID-GC with a packed column of either PEG-HT (1 m) or VZ-7 (6 m) at a constant temperature of 40 °C. The catalytic activities are estimated by the average conversion of 1-propanol for 5 h. Most of catalysts tested showed stable activities and/or an inductive period for the initial 3h.

Table 1. Effects of various additives on the catalytic performance for 1-propanol conversion over CeO_2-MO_X at 450 ℃



Additive 10mol%	Conversion / %	Selectivity / mol%				
		1	**2**	**3**	**4**	**5**
Non	22.2	13.5	3.7	54.8	0.4	23.4
Mg	12.7	15.5	1.0	56.2	2.1	20.4
Ca	11.1	20.6	1.5	55.1	2.2	17.9
Sr	13.2	19.3	2.0	55.8	3.2	17.9
Ba	12.9	17.7	2.1	60.5	1.8	16.2
B	7.4	62.4	7.0	16.5	1.2	12.8
Al	12.7	12.5	1.3	51.3	0.8	33.3
Cr	17.2	23.6	6.3	55.3	0.6	10.9
Mn	34.5	13.3	11.2	64.5	0.7	4.7
Fe	47.2	14.5	11.7	61.6	1.2	5.4
Co	42.3	67.7	4.9	20.0	2.6	2.3
Ni	39.7	69.0	2.4	20.8	0.8	4.2
Cu	39.9	60.6	5.7	25.1	3.8	1.8
Zn	29.3	28.0	9.4	47.9	0.8	8.8

Table 1 summarizes catalytic activities of various CeO_2-MO_x catalysts containing MO_x of 10 mol%. In the catalytic tests at 450 °C, every catalyst we examined showed no decay in the catalytic activity with process time. Conversion levels of 1-propanol over CeO_2 modified with alkaline earth oxides (M= Mg, Ca, Sr, and Ba) and acidic oxides (M = B and Al) were lower than that of pure CeO_2, while the product distribution was similar to that of pure CeO_2. This indicates that the addition of the oxides into CeO_2 decreases the catalytic activity of pure CeO_2 because it dilutes the surface Ce concentration in the solid solution. Although the conversion levels over CeO_2 modified with transition metal oxides (M = Co, Ni, Cu, and Zn) were higher than that of pure CeO_2, selectivities to 3-pentanone were lower than that of pure CeO_2. Over the catalysts, propanal is not dimerized, whereas l-propanol is readily dehydrogenated to propanal. In contrast, not only 1-propanol conversions but also 3-pentanone selectivities of CeO_2-Fe_2O_3 and CeO_2-Mn_2O_3 catalysts were higher than those of pure CeO_2. The gaseous hydrocarbons such as methane, ethane, ethene, propane and propene were observed in the reaction effluent (Table l): ca. 50% of them was propane in case of CeO_2-Fe_2O_3. In addition, propyl propionate was detected as another by-product.

TPD experiments of adsorbed CO_2 and NH_3 have revealed that the CeO_2 has only weak basic sites without acidic sites.[3] In the present system, it was ascertained that the addition of Fe_2O_3 into CeO_2 did not change the basic strength (profiles not shown). Although it is known that aldol condensation is usually catalyzed by strong base,[5] the modification of CeO_2 with alkaline earth oxides with strong basic sites[3] has little effect on the product distribution (Table 1). Because strong basic sites are not always effective for aldol addition at a temperature as high as 450 °C, weak basic sites of CeO_2 efficient for the dimerization process of propanal. It is speculated that the surface property of CeO_2 is suitable for the redox processes such as the dehydrogenation of l-propanol to propanal and the decomposition of 3-hydroxy-2-metylpentanal to 3-pentanone.[4] Gaseous products like CO and CO_2 were also observed in the reaction: the major was CO_2 over the CeO_2-Fe_2O_3. Thus, the decomposition of 3-hydroxy-2-metylpentanal into 3-pentanone probably proceeds via oxidative-decarboxylation[6] rather than via deformylation.[4] It is reported that lanthanoide oxides, except for CeO_2, catalyze both the aldol addition of propanal and the following oxidative-decarboxylation into 3-pentanone under H_2 flow conditions,[6] whereas the present CeO_2 system is deactivated in H_2 flow. It is speculated that oxygen atom, which may be produced by decomposion of 1-propanol into propane, can be supplied for the oxidative-decarboxylation. In addition, neither propanoic acid as an oxidation product nor unsaturated aldehyde such as 2-metylpent-2-enal produced by dehydration of 3-hydorxy-2-methylpentanal was observed in the reaction.

In XRD patterns of CeO_2-Fe_2O_3 samples (profiles not shown), only peaks of fluorite-type structure of CeO_2 were observed up to the Fe content of 50 mol%, whereas the structure of pure Fe_2O_3 (100 mol%) was α-Fe_2O_3. This means that the CeO_2-Fe_2O_3 catalysts consist of solid solution. The dehydrogenation of 1-propanol to propanal was accelerated over the CeO_2 modified with transition metal oxides (Table 1). In particular, the addition of Fe and Mn enhanced the activity of pure CeO_2 for the dehydrogenation and the decomposition of 3-hydroxy-2-metylpentanal into 3-pentanone without losing the ability for aldol addition of CeO_2. However, it is not clear whether Fe and Mn themselves in the CeO_2-MO_x solid solution act as active sites for both the dehydrogenation of 1-propanol and the decomposition of 3-hydroxy-2-metylpentanal or not.

Table2. Catalytic properties of CeO_2-Fe_2O_3 at 450 ℃

Fe content / mol%	Conv.[a] / %	Selc.[b] / %	SA[c] / m^2g^{-1}	TOF[d] × 10^4 / mol $h^{-1}m^{-2}$
Non	22.2	54.8	41	4.6
5	33.1	60.2	24	13
10	47.2	61.6	25	18
20	52.7	67.9	31	18
30	51.0	66.6	46	11
40	36.5	64.3	28	13
50	26.7	61.3	19	13
100	6.2	2.6	8.0	0.3

[a] Conversion of 1-propanol. [b] Selectivity to 3-pentanone. [c] Specific surface area. [d] Space time yield of 3-pentanone per unit surface area.

For the most active CeO_2-Fe_2O_3, variations in the conversion and selectivity were examined with different Fe content (Table 2). The l-propanol conversion together with the 3-pentanone selectivity was maximized at Fe content of 20 mol%. The higher the l-propanol conversion is, the higher selectivity to 3-pentanone formation is provided. Although the 1-propanol conversion steeply decreased with process time over pure Fe_2O_3, no degradation in the conversion was observed over the CeO_2-Fe_2O_3 (20 mol%) catalysts even after 48 h.

Table 2 also summarizes the specific surface area and turnover frequency (TOF) value defined as a space time yield of 3-pentanone based on unit surface area. Although the specific surface area varied with Fe content, the variation was not correlated to the 1-propanol conversion. The TOF value was maximized at Fe content around 10-20 mol%, while the specific surface area was maximized at Fe content of 30 mol%.

Table 3 summarizes the catalytic results of other alcohols over CeO_2-Fe_2O_3 (20 mol%) at 450 °C. As has been examined in 1-propanol, several primary alcohols with straight chain provided the corresponding symmetric ketones. However, in a branched alcohol such as 2-methylpropanol, the conversion of alcohol and the selectivity to symmetric ketone were lower than those in the straight-chain alcohols. 2-Phenylethanol also provides a symmetric ketone, 1,3-diphenylacetone, with poor yield, whereas no symmetric ketone was observed in phenylmethanol which has no α-hydrogen. This surely indicates that this reaction proceeds via aldol addition. The CeO_2-Fe_2O_3 (20 mol%) provides yields of symmetric ketones higher than those of pure CeO_2 and pure ZrO_2, which has been used for a commercial production of 2,4-dimetyl-3-pentanone from 2-methyl-1-propanol.[7] The reaction rate of 3-pentanone formation over the CeO_2-Fe_2O_3 is roughly 10 times as high as that of pure ZrO_2.

Table 3. Conversion of various alcohols and selectivity to the corresponding symmetric ketones over several catalysts

catalysts	CeO_2		CeO_2-Fe_2O_3[a]		ZrO_2[b]	
reactant	C.[c]	S.[d]	C.[c]	S.[d]	C.[c]	S.[d]
1-propanol	22	55	53	68	25	16
1-butanol	21	46	58	63	24	10
1-pentanol	23	60	48	65	19	13
1-hexanol	23	55	53	66	30	51
2-metylpropanol	8	12	17	5	20	17
2-phenylethanol	99	0.1	94	12	89	7
phenylmethanol	44	0	42	0	28	0

Liquid reactant of 1.62 cm^3h^{-1} was fed over the catalyst of 0.15 g at 450 ℃. [a] CeO_2-Fe_2O_3 (20mol%) catalyst. [b] Specific surface area of 44 m^2g^{-1}, prepared by precipitation using zirconylnitrate and NH_3 solution. [c] Conversion of alcohol (%). [d] Selectivity to symmetric ketone (mol%).

In conclusion, catalytic activity of CeO_2-Fe_2O_3 for the 3-pentanone formation from 1-propanol was found to be the highest among the other CeO_2-MO_x, and the highest space time yield of 3-pentanone was obtained at Fe content of 20 mol%. Both weak basic sites and redox property are needed to catalyze the stepwise reaction for the formation of symmetric ketone such as 3-pentanone.

References and Notes

1 C. Li, K. Domen, K. Maruya, and T. Onishi, *J. Catal.*, **141**, 540 (1993).
2 S. Sato, K. Koizumi, and F. Nozaki, *Appl. Catal. A*, **133**, L7 (1995).
3 S. Sato, K. Koizumi, and F. Nozaki, *J. Catal.*, **178**, 264 (1998).
4 S. Sato, R. Takahashi, T. Sodesawa, K. Matsumoto, and Y. Kamimura, *J. Catal.*, **184**, 180 (1999).
5 T. Matsuda, Y. Sasaki, H. Miura, and K. Sugiyama, *Bull. Chem. Soc. Jpn.*, **58**, 1041 (1985).
6 J. B. Claridge, M. L. H. Green, S. C. Tsang, and A. P. E. York, *J. Chem. Soc., Faraday Trans.*, **89**, 1089 (1993).
7 K. Tanabe, and T. Yamaguchi, *Catal. Today*, **20**, 185 (1994).