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Ortho-Selective Alkylation of Phenol with 1-Propanol Catalyzed by CeO_2–MgO

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Vapor-phase alkylation of phenol with 1-propanol was investigated over CeO_2–MgO catalysts prepared utilizing a molten mixture of the corresponding nitrates and citric acid. The CeO_2–MgO had a stable catalytic activity at 475°C, and had an excellent selectivity to 2-propylphenol, higher than 82% based on phenol. Although a portion of the 2-propylphenol produced was decomposed into *o*-cresol and 2-ethylphenol, a sum of selectivities to the monoalkylated phenols exceeded 97%. During the alkylation, propanal and 3-pentanone was observed. In the results of 1-propanol conversion without phenol, it was found that 1-propanol was dehydrogenated to propanal and that the propanal produced was dimerized to 3-hydroxy-2-methylpentanal via aldol addition, followed by the deformylation into 3-pentanone. Namely, in the reaction of phenol and 1-propanol, the propylation of phenol and the dehydrogenation of 1-propanol occurred concurrently over the CeO_2–MgO. The pure CeO_2, having both the redox property with Ce^{4+}–Ce^{3+} and weak basic sites, catalyzed both the propylation of phenol and the 1-propanol transformation into 3-pentanone, while the pure MgO with strong basicity was less active for the 1-propanol transformation and had a low reaction rate in the alkylation. The reaction mechanism of the *ortho*-propylation over the CeO_2–MgO catalyst is speculated as follows. The *ortho* position of phenol adsorbed perpendicularly on weak basic sites of the catalyst is selectively alkylated by 1-propanol, which is possibly activated in the form of 1-hydroxypropyl radical on CeO_2 species rather than as a form of *n*-propyl cation. The redox property of CeO_2 is probably attributed to the homolitic activation of 1-propanol to produce 1-hydroxypropyl radical.

Key Words: **alkylation; phenol; 1-propanol; dehydrogenation; aldol addition; 3-pentanone; CeO_2–MgO; base; citric acid.**

INTRODUCTION

Alkylated phenols are important chemicals as intermediates in the agrochemical and polymer industries. In the vapor-phase alkylation of phenol with methanol, various oxides such as MgO (1–3), CeO_2 (3, 4), Mn_3O_4 (5), and Al_2O_3 (6–8), acidic zeolites such as H-ZSM5 (6, 7, 9, 10) and HY (6, 7, 10), and other mixed metal oxides such as MgO-based (1, 2, 4), Fe_2O_3-based (11–15), and V_2O5-based oxides (15–18) and Al-containing hydrotalcites (19–21) have been investigated. They are divided into three groups with respect to the reaction temperatures at which the catalyst acts efficiently. First, acidic catalysts such as Al_2O_3, H-ZSM5, and HY have methylation activities at temperatures lower than 300°C, whereas they are less selective because of their catalysis for both oxygen methylation and the ring methylation. Second, various mixed oxides (1, 2, 11–21) show catalytic activity at a temperature range between 300 and 450°C, and they are selective to the *ortho*-methylation of phenol. Third, simple oxides such as MgO, CeO_2, and Mn_3O_4 show catalytic activity at temperatures higher than 450°C, and most of them are highly selective to the *ortho*-position. Because the desorption process of acidic products as well as the activation of methanol is important in the catalytic reaction, acid–base properties of catalysts are suggested to be a major factor of determining the optimum reaction temperature.

In the previous report (4), CeO_2–MgO catalyst systems, which were prepared using a molten mixture of cerium (III) nitrate, magnesium nitrate, and citric acid, were found to have attractive catalytic performance without decay of activity and had excellent selectivities to the sum of *o*-cresol and 2,6-xylenol, higher than 98% at a temperature range between 450 and 550°C. The catalytic activity correlated well to the number of weak basic sites of CeO_2 dispersed in the MgO matrix: the turnover frequencies based on the weak basic sites are constant for the CeO_2–MgO system regardless of preparation methods. The reaction mechanism of the *ortho*-methylation over the CeO_2–MgO catalyst has been proposed: the *ortho*-position of phenol adsorbed perpendicularly on the weak basic site of CeO_2 species is selectively alkylated by methanol which is activated in the form of a formyl or hydroxymethyl group rather than as a methyl cation.

Other alcohols such as ethanol, propanol, and butanol were also used as alkylating reagents for the production of alkylphenols (22–25). In the alkylation of phenol with propanol, many alkylated products were observed over

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Al_2O_3 (23, 24) and Al-containing hydrotalcites (25). In this paper, we describe the characteristics of CeO_2–MgO catalysts for the alkylation of phenol with 1-propanol. During the alkylation, we found selective transformation of 1-propanol into 3-pentanone. Thus, we additionally report on the transformation of 1-propanol without phenol. As we have previously demonstrated the phenol adsorption on weak basic sites (4), here we discuss the activation of alcohol and the nature of active species.

EXPERIMENTAL

Catalyst Preparation

All reagents were supplied by Wako Chemical Ltd. (Japan). CeO_2–MgO samples with different CeO_2 contents were prepared by using cerium (III) nitrate hexahydrate, magnesium nitrate hexahydrate, and citric acid monohydrate. The preparation procedure is essentially the same as that for an amorphous citrate process (26), and the detail was described in the previous paper (4). 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 give a CeO_2–MgO sample. Pure CeO_2 and MgO were prepared from the molten salt of the individual nitrate and citric acid. A reference catalyst, DC-2282, a commercial alumina with a specific surface area of 195 $m^2\ g^{-1}$, was supplied by Dia Catalyst and Chemicals Ltd.

Catalytic Reaction

The alkylation of phenol with 1-propanol was carried out in a usual fixed bed flow reactor under atmospheric pressure of helium at a temperature range between 425 and 500°C. Prior to the reaction, a catalyst sample (0.15 g) was preheated in a glass tube reactor at 500°C for 1 h. A mixture of phenol and 1-propanol with a molar ratio of 1 : 4 was fed into the reactor at a total flow rate of 17 mmol h^{-1}, together with helium flow of 50 mmol h^{-1}. An effluent collected in an ice trap was periodically extracted 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}. The reaction products were identified by GC-MS, HP5973, equipped by Hewlett Packard. The conversion of phenol is defined as a fraction of reacted phenol, and the selectivity to a product is as a fraction of the respective product to the reacted phenol. The catalytic activity was evaluated in terms of an average conversion of phenol for every hour. The reaction rate was calculated at 475°C from a slope of a W/F-conversion curve, where W and F were the catalyst weight (g) and the flow rate of phenol (3.4 mmol h^{-1}), respectively.

The transformation of 1-propanol was also performed in the fixed bed flow reactor at temperatures ranging from 400 to 525°C. Prior to the reaction, a catalyst sample (0.15 g) was preheated in a glass tube reactor at 500°C for 1 h. 1-Propanol (17.6 mmol h^{-1}) was fed into the reactor with helium carrier (50 mmol h^{-1}). Liquid products were analyzed by the same GC unit as the propylation mentioned above, and a gaseous product such as propylene was analyzed by FID-GC with a packed column of PEG-HT (1 m) at a constant temperature of 40°C. The conversion of 1-propanol is defined as a fraction of reacted 1-propanol.

Characterization of Catalyst

The temperature-programmed desorption (TPD) of adsorbed CO_2 was measured by neutralization titration using an electric conductivity cell immersed in an aqueous solution, as has been described previously (4). The total TPD profile was able to be deconvoluted into several Gausian peaks. The number of total basic sites was obtained by the amount of total desorbed CO_2, and the number of weak basic sites was calculated from peaks whose tops were at temperatures lower than 150°C in the deconvoluted TPD profile. The total surface area of the sample was calculated by BET method using nitrogen isotherm at −196°C.

RESULTS

Figure 1 shows changes in the phenol conversion of the CeO_2(11.2 mol%)–MgO with process time at 475°C, together with the results of pure CeO_2 and MgO, for the alkylation of phenol with 1-propanol. The catalytic activities decreased with process time in the initial period for 2 h and reached a stable conversion level. No decay in the catalytic activities of each catalyst was observed after the reaction started for 2 h. For the CeO_2(11.2 mol%)–MgO (curve b), the conversion level was higher than those of the pure MgO (curve a) and the pure CeO_2 (curve c).

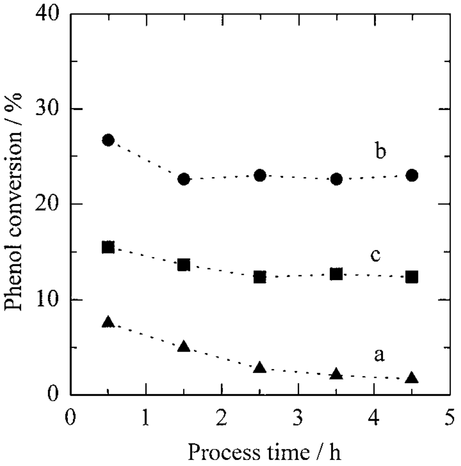


FIG. 1. Comparison of catalytic activities among CeO_2–MgO at a reaction temperature of 475°C. a, MgO; b, CeO_2(11.2 mol%)–MgO; c, CeO_2.

TABLE 1

Effect of Reaction Temperature[a]

Catalyst:	CeO_2(11.2 mol%)–MgO					Alumina[b]	
Reaction temperature (°C):	425	450	475	500	500[c]	300	300[c]
Conversion of phenol (%)	0.2	2.9	22.8	49.8	4.2	27.9	55.3
Selectivity (mol%)							
o-Cresol	2.2	8.7	12.5	13.3	28.8	18.5	0
2-Ethylphenol	1.2	0.9	1.8	2.5	66.8	0	1.3
2-*n*-Propylphenol	96.6	90.4	84.8	71.6	0	42.0	0
2-Isopropylphenol	0	0	0.1	0.6	4.4	7.4	82.0
n-Propyl phenyl ether	0	0	0.3	0.1	0	0.1	0
2,6-Di-*n*-propylphenol	0	0	0.5	2.8	0	19.5	0
4-*n*-Propylphenol	0	0	0	7.6	0	5.6	0
Others	0	0	0	1.5[d]	1.0	6.9[e]	16.7[f]

[a] Average conversion between 2 and 5 h, catalyst 0.15 g, phenol flow rate 3.4 mmol h^{-1}, 1-propanol/phenol = 4, carrier helium flow rate 50 mmol h^{-1}, selectivity was based on phenol.

[b] Commercial alumina.

[c] 2-Propanol was used as a alkylating reagent instead of 1-propanol, 2-propanol/phenol = 4.

[d] Contained 2-isopropyl-6-*n*-propylphenol (0.4%), 2,4,6-tri-*n*-propylphenol (0.3%), *n*-propyl 2-*n*-propylphenyl ether (0.5%), 2,6-xylenol (0.3%).

[e] Contained 2-isopropyl-6-*n*-propylphenol (4.5%), 2,4,6-tri-*n*-propylphenol (2.3%), *n*-propyl 2-*n*-propylphenyl ether (0.1%).

[f] Contained 4-isopropylphenol (3.8%), 2,6-diisopropylphenol (10.4%), 2,4-diisopropylphenol (2.6%).

Table 1 summarizes the effect of reaction temperature for the propylation of phenol over CeO_2(11.2 mol%)–MgO catalyst at a temperature range between 425 and 500°C. The data are average activities between 2 and 5 h. For the CeO_2–MgO catalyst, the average conversion of phenol increased with reaction temperature, and a main product was 2-*n*-propylphenol. The selectivity to 2-*n*-propylphenol decreased with increasing reaction temperature, and those to the decomposition products of 2-*n*-propylphenol such as *o*-cresol and 2-ethylphenol increased. At temperatures higher than 475°C, 2,6-di-*n*-propylphenol was produced, while a *para*-alkylated product like 4-*n*-propylphenol was produced at 500°C. In addition, we also examined the propylation of phenol over a commercial alumina at 300°C. Although the alumina catalyzed the reaction at the low temperature, many products were formed. Furthermore, we examined the alkylation of phenol with 2-propanol, instead of 1-propanol, over the alumina and the CeO_2–MgO. Over the alumina, the conversion of phenol with 2-propanol exceeded that with 1-propanol, and the main product was 2-isopropylphenol. However, a very small amount of 2-isopropylphenol was produced over the CeO_2–MgO with the main products of *o*-cresol and 2-ethylphenol, in addition to a low conversion of phenol.

Table 2 summarizes the catalytic results of several CeO_2–MgO catalysts with various CeO_2 content at 475°C. In the CeO_2–MgO catalysts, the average conversion of phenol was maximized at the CeO_2 content of 11.2 mol% (the second row of Table 2). For the CeO_2–MgO catalysts except for the pure MgO, the selectivity to 2-*n*-propylphenol was higher than 82%, and it decreased slightly with increasing CeO_2 content regardless of the phenol conversion level. The *ortho*-selectivity to the total of 2-*n*-propylphenol, *o*-cresol, and 2-ethylphenol exceeded 97% regardless of CeO_2 content while small amounts of 2,6-di-*n*-propylphenol and 2,6-xylenol were produced. For the pure MgO, however, the conversion of phenol was very low, and the selectivity to 2-propylphenol was low because of the production of 4-*n*-propylphenol. Because other products such as propene, propanal, and 3-pentanone were observed during the alkylation, both the conversion of 1-propanol and the product distribution based on 1-propanol were also calculated (Table 2). The 1-propanol conversion showed a maximum at a CeO_2 content of 72.1 mol%, in contrast to the phenol conversion showing a maximum at a CeO_2 content of 11.2 mol%. For the consumption of 1-propanol, the selectivity to the alkylation decreased with increasing CeO_2 content.

Because 1-propanol was converted into propanal and 3-pentanone during the alkylation, the transformation of 1-propanol without phenol was performed at temperatures ranging from 400 to 525°C. Table 3 summarizes the results of MgO, CeO_2, and CeO_2(40.2 mol%)–MgO catalysts. Several products, such as propanal, 3-hydroxy-2-methylpentanal, 3-pentanone, propene, and di-*n*-propyl ether, were observed.

TABLE 2

Catalytic Properties of CeO_2–MgO Catalysts with Different CeO_2 Content at 475°C[a]

CeO_2 content (mol%):	0	6.7	11.2	40.2	72.1	100
Conversion of phenol (%)	2.9	12.7	22.8	12.7	11.9	12.8
Selectivity based on phenol (mol%)						
o-Cresol	9.1	10.8	12.5	12.7	12.1	13.0
2-Ethylphenol	0	2.1	1.8	2.0	1.7	2.1
2-*n*-Propylphenol	46.5	85.0	84.8	83.2	84.4	82.6
2-Isopropylphenol	4.3	0.2	0.1	0.3	0.1	0.2
n-Propyl phenyl ether	4.3	0.5	0.3	0.9	0.9	1.3
2,6-Dipropylphenol	2.3	0.4	0.5	0	0	0
2,6-Xylenol	12.4	0	0	0.9	0.8	0.8
4-*n*-Propylphenol	21.1	1.0	0	0	0	0
Conversion of 1-propanol (%)	1.3	9.0	17.5	17.8	26.6	24.6
Selectivity based on 1-propanol (mol%)						
Total alkylation	56.0	35.4	31.4	8.0	11.2	13.0
Propanal	30.6	16.3	11.4	0.8	30.1	25.1
3-Pentanone	0	31.7	38.9	49.7	50.2	52.5
Propene	11.0	13.7	15.6	7.6	5.6	5.3
Others[b]	2.4	2.9	2.8	4.0	2.8	4.1

[a] Phenol flow rate 3.4 mmol h^{-1}, 1-propanol/phenol = 4, carrier helium flow rate 50 mmol h^{-1}, catalyst 0.15 g, average conversion between 2 and 5 h.

[b] Contained di-*n*-propyl ether, 3-hydroxy-2-methylpentanal, and propyl propionate, etc.

TABLE 3

1-Propanol Transformation over CeO_2–MgO[a]

Catalyst	Reaction temperature (°C)	Conversion of 1-propanol (%)	Selectivity[b] (mol%) (1)	(2)	(3)	(4)	(5)
MgO	400	0.9	99.0	0	0	1.0	0
MgO	425	1.5	13.4	85.3	0	1.3	0
MgO	450	2.6	36.2	56.7	4.6	1.6	0.9
MgO	475	8.0	47.8	36.0	5.6	1.6	0.3
MgO	500	23.1	65.2	16.9	4.4	1.5	0.6
MgO	525	50.9	83.4	7.1	2.4	2.1	0.4
CeO_2–MgO[c]	400	1.6	9.8	10.4	74.1	5.6	0
CeO_2–MgO[c]	425	4.3	6.5	5.5	84.7	3.3	0
CeO_2–MgO[c]	450	12.5	5.9	1.5	88.6	2.2	1.8
CeO_2–MgO[c]	475	37.3	2.7	0.6	76.3	1.0	1.4
CeO_2–MgO[c]	500	70.0	0.6	0	71.0	0.7	1.3
CeO_2–MgO[c]	525	87.9	0.3	0	56.1	0.7	9.4
CeO_2	400	2.1	10.9	18.2	66.9	4.0	0
CeO_2	425	4.5	6.5	6.0	83.6	3.9	0
CeO_2	450	20.8	5.4	2.0	89.1	2.0	0
CeO_2	475	30.4	3.4	0.4	82.9	2.0	1.3
CeO_2	500	44.4	2.1	0.1	75.1	2.1	0.8
CeO_2	525	80.1	3.7	0	64.8	2.1	0.2

[a] Average conversion between 1 and 2 h at the prescribed temperature.

[b] (1) Propanal, (2) 3-hydroxy-2-methylpentanal, (3) 3-pentanone, (4) propene, (5) di-*n*-propyl ether.

[c] The CeO_2 content is 40.2 mol%.

The conversion of 1-propanol increased with increasing reaction temperature. For the pure MgO, the selectivity to propanal increased with increasing reaction temperature. Although the selectivity to 3-hydroxy-2-methylpentanal decreased with increasing reaction temperature, its yield, multiplied the selectivity by the 1-propnanol conversion, increased from 1 to 4%. The selectivity to 3-pentanone was very low regardless of the reaction temperature. For CeO_2–MgO and the pure CeO_2, however, the selectivity to 3-pentanone was maximized at 450°C, while the selectivities to propanal and 3-hydroxy-2-methylpentanal decreased with increasing reaction temperature. In addition, CO and CO_2 were observed in the transformation of 1-propanol. Regardless of the catalysts used and the reaction temperature, the selectivity to propene was constantly low, together with low selectivity to di-*n*-propyl ether. At 525°C, however, di-*n*-propyl ether selectivity increased for the CeO_2–MgO catalyst.

Figure 2 shows Arrhenius plots for the conversion data in Tables 1 and 3. 1-Propanol consumption based on unit surface area was logarithmically plotted against the inverse of reaction temperature. For the CeO_2–MgO catalyst (Figs. 2a and 2c), the 1-propanol consumption for the propylation was decreased about two and three orders of magnitude over that for 1-propanol transformation. The 1-propanol consumptions for 1-propanol transformation over CeO_2 and CeO_2–MgO were almost same (Figs. 2c and 2d), and it was higher than that over MgO by about one order of magnitude (Fig. 2b). An apparent activation energy can be calculated from a portion of straight line for the plots (solid line). The apparent activation energy for the phenol propylation over CeO_2–MgO was about 410 kJ mol^{-1} (Fig. 2a), while that for 1-propanol conversion was 180 kJ mol^{-1} (Fig. 2c). The activation energies for 1-propnaol conversion over MgO and CeO_2 were 190 and 160 kJ mol^{-1} (Figs. 2b and 2d), respectively.

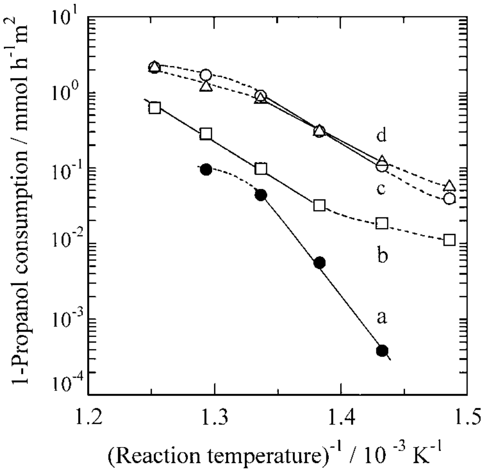


FIG. 2. Arrhenius plots for the data in Tables 1 and 3. a, 1-Propanol consumption for the alkylation, calculated from the phenol conversion in Table 1 of CeO_2–MgO; b, from the 1-propanol conversion in Table 3 of MgO; c, CeO_2–MgO; d, CeO_2.

Table 4 shows the catalytic results of alkylation of 2-*n*-propylphenol with 1-propanol, instead of the propylation of

TABLE 4

Propylation of 2-*n*-Propylphenol[a]

Catalyst:	CeO_2	Al_2O_3[b]
Reaction temperature (°C):	500	300
Conversion of 2-*n*-propylphenol (%)	31.3	27.9
Selectivity to (mol%)		
Phenol	4.8	0
o-Cresol	15.2	0.5
2,6-Xylenol	4.3	0
2-Ethylphenol	16.8	0.1
2-Isopropylphenol	15.9	0
4-*n*-Propylphenol	4.1	7.7
n-Propyl 2-*n*-propylphenyl ether	1.4	0.6
2,6-Dipropylphenol	1.5	70.6
2-Isopropyl-6-*n*-propylphenol	0	5.1
2,4,6-Tripropylphenol	0	8.8
2,3,4,6-Tetrapropylphenol	0	2.0
2,3,4,5,6-Pentapropylphenol	0	0.2

[a] Average conversion between 1 and 2 h, catalyst 0.15 g, 2-*n*-propylphenol flow rate 3.1 mmol h^{-1}, 1-propanol/2-*n*-propylphenol = 4, carrier helium flow rate 50 mmol h^{-1}.

[b] Commercial alumina.

TABLE 5

Physical Properties of Various CeO_2–MgO Catalysts

Catalyst	CeO_2 content (mol% (wt.%))	Number of total basic sites[a] (μmol g^{-1})	Number of weak basic sites[b] (μmol g^{-1})	Specific surface area (m^2 g^{-1})
MgO[c]	0	1075	177	96
CeO_2–MgO	6.7 (23.5)	1151	119	109
CeO_2–MgO[c]	11.2 (35.0)	1202	205	118
CeO_2–MgO[c]	22.3 (55.1)	1100	154	99
CeO_2–MgO[c]	40.2 (74.2)	471	75	48
CeO_2–MgO[c]	72.1 (91.2)	172	46	24
CeO_2[c]	100	115	115	44

[a] Total amount of CO_2 desorbed from the sample in the TPD profiles.

[b] Amount of CO_2 desorption peak at lower than 150°C.

[c] The data were referenced in Ref. 4.

phenol, over typical samples of CeO_2 and Al_2O_3. Although a dialkylated product, 2,6-di-*n*-propylphenol, was preferential to Al_2O_3 at 300°C, CeO_2 was inactive for the alkylation: the decomposition of 2-*n*-propylphenol into *o*-cresol and 2-ethylphenol and the isomerization to 2-isopropylphenol proceeded rather than the alkylation.

In the previous work (4), we elucidated the acid–base properties of CeO_2–MgO systems using TPD technique. The deconvolution results in the TPD experiment of adsorbed CO_2 indicate that the basic sites of the pure MgO and the CeO_2–MgO consist of at least four kinds of basic sites with different strengths and that CeO_2 has only weak basic sites of uniform strength (Fig. 7 in Ref. 4). Table 5 summarizes the number of weak basic sites calculated from a peak whose top was at temperatures lower than 150°C in the deconvoluted TPD profile, together with the number of total basic sites and the specific surface area.

We have demonstrated that the strong basic sites are irrelevant to the catalytic methylation of phenol with methanol at temperatures lower than 500°C and that only weak basic sites are effective for the methylation (4). Thus, we calculated two sets of turnover frequency (TOF) by dividing the reaction rate for the propylation at 475°C (the third column in Table 6) by the number of total basic sites (the third column in Table 5) as well as by that of the weak basic sites (the fourth column in Table 5). The TOF values are also summarized in Table 6. The reaction rate based on catalyst weight was maximized at the CeO_2 content of 11.2 mol% in a similar manner as the phenol conversion shown in the second row of Table 2. The reaction rate per unit surface area, however, had a maximum at the CeO_2 content of 72.1 mol%. Figure 3 exhibits the variations in the two series of TOF with CeO_2 content. The TOF values based on both the total basic sites (TOFt) and the weak basic sites (TOFw) of the pure MgO were much smaller than those of the pure CeO_2. The TOFt monotonously increased with increasing CeO_2 content (curve a). In contrast, the TOFw value greatly increased with addition of CeO_2 into MgO (curve b), and it showed a maximum at CeO_2 content of 72.1 mol%.

TABLE 6

Reaction Rates of Various CeO_2–MgO Catalysts

Catalyst	CeO_2 content (mol%)	Reaction rate[a] mmol h^{-1} g^{-1}	Reaction rate[a] mmol h^{-1} m^{-2}	TOFt[b] (h^{-1})	TOFw[c] (h^{-1})
MgO	0	0.3	0.003	0.3	1.7
CeO_2–MgO	6.7	3.4	0.031	3.0	29
CeO_2–MgO	11.2	5.7	0.048	4.7	28
CeO_2–MgO	22.3	4.1	0.041	3.7	27
CeO_2–MgO	40.2	2.5	0.052	5.3	33
CeO_2–MgO	72.1	2.3	0.096	13	50
CeO_2	100	2.7	0.061	23	23

[a] Reaction rate of the propylation at 475°C, 1-propanol/phenol = 4; the rate was calculated from a slope of a W/F-conversion curve, where W and F were the catalyst weight (g) and the flow rate of phenol (3.4 mmol h^{-1}), respectively, $W = 0.075$, 0.10, and 0.15 g.

[b] Turnover frequency per a basic site.

[c] Turnover frequency per a weak basic site.

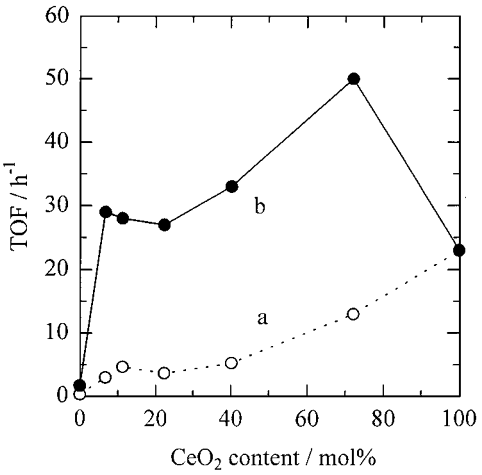


FIG. 3. Variation in the TOF value with CeO_2 content. a, TOF per a basic site (TOFt); b, TOF per a weak basic site (TOFw).

DISCUSSION

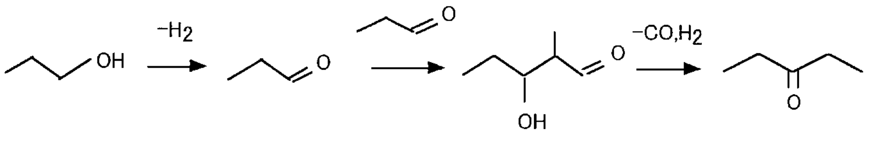
3-Pentanone Formation

We have reported on the methylation of phenol with methanol over the CeO_2–MgO systems (4). The active CeO_2 species have been proved to consist of the interstitial solid solution of fluorite-type $Mg_xCe_{1-x/2}O_2$ dispersed in the MgO matrix. In addition to the methylation of phenol, the CeO_2–MgO systems have a catalytic activity for the methanol decomposition to CO and methane. As shown in Table 2, propanal and 3-pentanone were produced during the propylation of phenol. The conversion of 1-propanol increased with increasing CeO_2 content, and the selectivity to the alkylation decreased with increasing CeO_2 content. From the facts, it is speculated that the CeO_2 component contributes to the activation of 1-propanol. In the transformation of 1-propanol without phenol (Table 3), for the pure MgO, the yields of both propanal and 3-hydroxy-2-methylpentanal increased with increasing 1-propanol conversion. Thus, 1-propanol is dehydrogenated into propanal at the first step of the reaction, and 3-hydroxy-2-methylpentanal is produced via aldol addition of propanal on the basic sites of MgO. However, 3-pentanone was not produced over the MgO. On the contrary, over the CeO_2-containing catalysts, the yield of 3-pentanone increased with increasing the 1-propanol conversion, while the selectivities to propanal and 3-hydroxy-2-methylpentanal decreased. Thus, the produced 3-hydroxy-2-methylpentanal is considered to be deformylized into 3-pentanone. Therefore, three reactions, dehydrogenation, aldol addition, and deformylation, successively proceed over the CeO_2-containing catalysts to produce propanal, 3-hydroxy-2-methylpentanal, and 3-pentanone, respectively. The reaction pathway can be proposed as Scheme 1. The scheme can be also supported by the following: a phenyl alkyl ketone such as 1-phenyl-2-propanone was produced by the decomposition of 3-hydroxy-3-phenyl-2-methylpropanal via aldol addition of benzaldehyde with propanal over thoria catalyst at 450°C (27).

Although 1-propanol is dehydrogenated into propanal both on the strong basic MgO and on the weak basic CeO_2 (Table 3), 3-pentanone is formed on CeO_2 not on MgO. In the decomposition of methanol over the CeO_2–MgO, methanol was decomposed into CO, CO_2, and methane without forming dimethyl ether, whereas MgO had no activity in the decomposition (4). In addition, CeO_2 itself is reported to have the ability of the hydrogenation of CO (28). The deformylation of 3-hydroxy-2-methylpentanal into 3-pentanone is possibly concerned with the redox property of CeO_2. Because aldol condensation is usually catalyzed by strong base (29, 30), strong basic MgO should catalyze the aldol addition of propanal. However, weak basic CeO_2 was more efficient for the formation of 3-pentanone (Table 3). In the dimerization process of aldol addition, redox property of CeO_2 is considered to be attributed to the activation of propanol in addition to the basic property. This will be discussed in connection with the nature of active species.

Phenol Propylation Related with Basic Strength

In our previous report on the basicity of the CeO_2–MgO catalysts (4), the basic sites of the pure MgO and the CeO_2–MgO consist of at least four kinds of basic sites with different strengths, whereas the pure CeO_2 has only weak basic sites of uniform strength. The other TPD results also indicated that acidic substrates such as phenol and *o*-cresol adsorbed strongly on the surface of the pure MgO, while they readily desorbed from the basic sites of CeO_2–MgO and CeO_2 at temperatures higher than 450°C. For the methylation of phenol with methanol, when we calculated the TOFt value by dividing the reaction rate by the number of total basic sites, the TOFt value monotonously increased with increasing CeO_2 content. This has indicated that total basic sites including strong basic sites are irrelevant to the methylation of phenol at temperatures lower than 500°C, because acidic phenol and products cannot be



SCHEME 1. Reaction pathway of 3-pentanone formation.

desorbed from the strong basic sites. In the present propylation, the TOFt monotonously increased with increasing CeO_2 content (Fig. 3a) in a similar manner as the methylation. Namely, the total basic sites are also indicated to be irrelevant to the propylation of phenol.

In the CeO_2–MgO system, the variation in the number of weak basic sites with CeO_2 content resembles the variation in the reaction rate for the methylation of phenol at 450°C (4), and the TOFw values for the methylation, calculated by dividing the reaction rate by the number of weak basic sites, are constant at CeO_2 content higher than 3.8 mol% (Fig. 8b in Ref. 4). This means that the methylation proceeds on the weak basic sites which act as adsorption sites of phenol. In contrast to the methylation, the TOFw value for the present propylation seems to be maximized at CeO_2 content of 72.1 mol%. Except for the CeO_2 content of 72.1 mol% and the pure MgO, the TOFw values can be regarded as roughly constant (Fig. 3b). This means that the propylation proceeds on the weak basic sites which provide adsorption sites of phenol. The reason why the TOFw is maximized at CeO_2 content of 72.1 mol% will be discussed in the last section.

One of the catalytic features of the CeO_2–MgO catalyst is the high selectivity of *ortho*-position of phenol. It is reported that the *ortho*-position of the phenol perpendicularly adsorbed on a basic site faces the surface of MgO on which the *ortho*-selective methylation proceeds (31). The CeO_2–MgO catalyst also provides effective adsorption sites for phenol: the *ortho*-position of the phenol perpendicularly adsorbed on the weak basic site faces the surface of the CeO_2–MgO catalyst. Although dimethylated phenol such as 2,6-xylenol was produced over the CeO_2–MgO system in the methylation of phenol (3, 4), the total selectivity to monoalkylated phenols was higher than 97% in the propylation (Table 2). In addition, 2-*n*-propylphenol was not alkylated with 1-propanol over the pure CeO_2, while the decomposition and the isomerization proceeded (Table 4). 2-*n*-Propylphenol is probably isomerized to 2-isopropylphenol followed by decomposition to *o*-cresol and 2-ethylphenol, since *o*-cresol and 2-ethylphenol are produced through the decomposition of 2-isopropylphenol in the alkylation of phenol with 2-propanol (the sixth column of Table 1). The *n*-propyl group of 2-*n*-propylphenol perpendicularly adsorbed on the catalyst is so large that the other *ortho*-position of phenol is probably blocked by itself from another 1-propanol molecule. Thus, 2,6-di-*n*-propylphenol is not formed on the CeO_2–MgO catalyst surface.

Nature of Active Species

Acidic alumina is reported to be active for the alkylation of phenol with propanol (23, 24), while more than 15 alkylphenols are produced at high phenol conversions of nearly 100%. Over a commercial alumina, 2-isopropylphenol is produced at 300°C even if 1-propanol is used as an alkylating reagent (Table 1). This indicates that *n*-propyl cation produced on the acidic alumina can readily transform to isopropyl cations, because secondary cation is more stable. As has been suggested by Klemm *et al.* (23) and Velu *et al.* (25), propyl cations are said to be alkylating species of phenol on the acidic catalyst.

On the other hand, no acidic site is concluded to be on the CeO_2–MgO catalysts because neither dimethyl ether formation in the methylation nor ammonia adsorption in the TPD experiment is observed (4). Although propene and di-*n*-propyl ether are produced over the CeO_2–MgO catalyst during both the propylation and the transformation of 1-propanol, the dehydrogenation into propanal is dominant (Tables 2 and 3). The facts do not mean that *n*-propyl cation can be produced on the nonacidic CeO_2–MgO at temperatures lower than 500°C. In addition, neither 2-*n*-propylphenol nor 2-isopropylphenol is produced over the CeO_2–MgO catalyst in the alkylation of phenol with 2-propanol (the sixth column of Table 1). The fact also suggests that isopropyl cation cannot be produced on the CeO_2–MgO at temperatures lower than 500°C. This is a significant difference from the behavior of acidic alumina.

Both the conversion of phenol (Table 2) and the reaction rate (Table 6) are maximized at CeO_2 content of 11.2 mol%. However, only a third of the consumed 1-propanol is used for the alkylation at the CeO_2 content. On the other hand, the 1-propanol conversion in the propylation is highest at CeO_2 content of 72.1 mol% (Table 2), while a fraction of the 1-propanol consumed for the propylation is at most 11%. Thus, the propylation of phenol and the formation of 3-pentanone can be said to be catalyzed by different functions.

In the transformation of 1-propanol without phenol (Table 3), propanal is initially produced by the dehydrogenation of 1-propanol. In addition to the 1-propanol consumption over MgO being obviously lower than those on the CeO_2 containing catalysts (Figs. 2b, 2c, and 2d), the apparent activation energies for 1-propanol conversion were slightly decreased with increasing CeO_2 content. Over CeO_2, aldol addition and the following deformylation are assumed to be faster than the dehydrogenation of 1-propanol. In, contrast, the deformylation was not catalyzed by MgO even at higher temperatures, although an aldol product, 3-hydroxy-2-methylpentanal, was formed at higher temperatures (Table 3). It can be said that the calculated activation energies of 160–190 kJ mol^{-1} for 1-propanol conversion are for the dehydrogenation of 1-propanol to propanal. Although the activation energy for the propylation is as high as 410 kJ mol^{-1} (Fig. 2a), we cannot discuss about it any further at the present time.

The weak basic CeO_2 is more effective for the dehydrogenation than the strong basic MgO (Figs. 2b and 2d). Because the density of weak basic sites of the pure MgO is similar to those measured in the CeO_2–MgO samples (4), basic sites of the catalysts are not assumed to be related to the dehydrogenation of alcohol. It has been reported that only CeO_2 is effective for the methylation of phenol among various rare earth oxides (3). Although Pr and Tb also have the oxidation state of 4+, PrO_2 and TbO_2 are unstable to produce partially reduced oxides as Pr_6O_{11} and Tb_4O_7, respectively (32). They are inactive for the methylation of phenol (3). Only Ce in the rare earth metals provide stable oxide as CeO_2 with the highest oxidation state of 4+ (32). The dehydrogenation is probably attributed to the hydrogenation of CO (28). Thus, CeO_2 with the redox property is said to be effective for the activation of 1-propanol in the present CeO_2–MgO system.

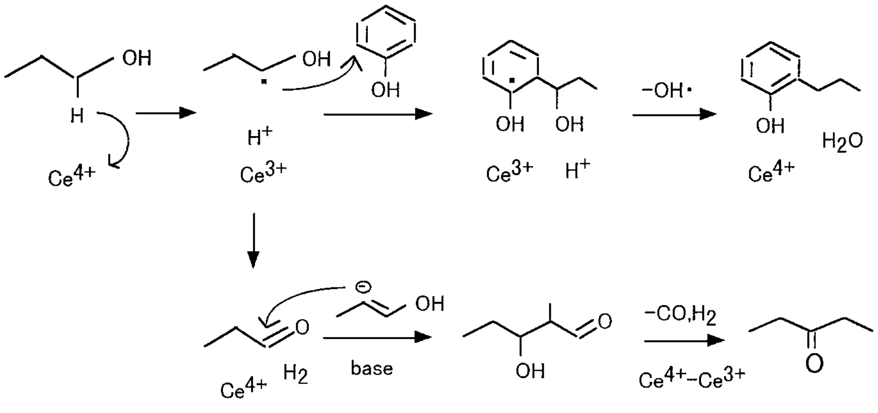
The reaction mechanism can be speculated as Scheme 2. A hydrogen radical is probably eliminated from 1-propanol to produce radical species such as 1-hydroxypropyl radical rather than propoxy radical. The hydrogen radical can reduce Ce^{4+} into Ce^{3+} to convert proton. In other words, Ce^{4+} cation oxdatively eliminates proton from 1-propanol. The 1-hydroxypropyl radical possibly attacks the electron-rich *ortho*-positions of phenol perpendicularly adsorbed on the weak basic sites in the CeO_2–MgO system because the *alpha*-position of 1-hydroxypropyl radical is slightly positive. A hydroxy radical is readily eliminated from the alkylated intermediate to produce 2-*n*-propylphenol and water, together with the oxidation of Ce^{3+} to Ce^{4+}.

The reaction mechanism of 3-pentanone formation also can be speculated (Scheme 2). When phenol is not adsorbed on the neighboring sites of the activated 1-hydroxypropyl radical, it is dehydrogenated into propanal to release hydrogen. If the produced propanal is activated by basic sites to produce enolate anion, the enolate anion attacks another propanal or 1-hydroxypropyl radical to produce 3-hydroxy-2-methylpentanal as an aldol product. The enolate anion possibly attacks the *alpha*-position of another 1-hydroxypropyl radical, since MgO without redox property is not efficient for aldol addition. 3-Hydroxy-2-methylpentanal can be probably decomposed into 3-pentanone to release CO through a catalysis of CeO_2 with Ce^{4+}–Ce^{3+} redox character because of no activity of MgO.

We assume that the alkylation mechanism over the CeO_2-containing catalysts is different from that of acidic catalysts in a viewpoint of the activation of alcohol. It can be said that bifunctional catalysis, such as adsorption of phenol on weak basic sites and homolytic activation of 1-propanol by the redox property, efficiently work in the propylation over the CeO_2–MgO systems. In the methylation of phenol, we have speculated that methanol is activated on the CeO_2 species as a form of formyl or hydroxymethyl group rather than methyl cation on acidic sites (4). From the present discussion, a hydroxymethyl radical rather than formyl group can be also proposed as an active methylating species in the methylation of phenol.

Different Catalytic Activities in the System

The TOFw value for the propylation is exceptionally high at a CeO_2 content of 72.1 mol%, as mentioned above, and the TOFw value of the pure CeO_2 is somewhat less than that for the other CeO_2–MgO catalysts (Table 6 and Fig. 3b). The structure of the CeO_2–MgO has been clarified by XRD measurement: the CeO_2–MgO catalyst is a mixture of MgO and an interstitial solid solution of $Mg_xCe_{1-x/2}O_2$, and the CeO_2(72.1 mol%)–MgO consists of only the solid solution of $Mg_{0.4}Ce_{0.8}O_2$ without MgO phase (4). For the CeO_2(72.1 mol%)–MgO, the dehydrogenation is more preferential than the alkylation (Table 2). This indicates that the solid solution of $Mg_{0.4}Ce_{0.8}O_2$ has both high dehydrogenating power of 1-propanol and high alkylation potential of the 1-hydroxypropyl radical. We can provide another explanation: the basic strength of optimum adsorption sites must be dependent on the reaction temperature. Although the TOFw values for the methylation at 450°C are constant at CeO_2 content higher than 3.8 mol%, basic sites with medium strengths of the solidsolution of $Mg_{0.4}Ce_{0.8}O_2$, stronger than the weak basic sites of the pure CeO_2, may act



SCHEME 2. Probable reaction mechanism of phenol propylation and 3-pentanone formation over the CeO_2–MgO system.

as adsorption sites of phenol at temperatures higher than 475°C.

Variations in the catalytic behavior with process time over the CeO_2–MgO system are different between the methylation (Fig. 1 in Ref. 4) and the present propylation (Fig. 1). The catalytic activity for the methylation shows a gradual increase in the initial reaction period for 2 h, in contrast to the propylation in which the catalytic activities decrease with process time in the initial period for 2 h. They reach a stable conversion level after the reactions have been running for 2 h: the activation of methanol probably has an induction period. On the other hand, because a part of the basic sites are used for aldol addition in the propylation, adsorption sites for phenol are reduced. Actually, an induction period of 2 h was observed in the 1-propanol conversion over the pure CeO_2 (data not shown), although the conversion was retarded over the pure MgO in the initial period. The effective sites for the propanal formation and the methanol activation are suggested to be attributed to an optimum redox state of CeO_2, which is possibly produced by reduction with 1-propanol and methanol in the initial reaction period. It is our next interest to clarify the optimum redox state of CeO_2 catalysts.

CONCLUSION

Vapor-phase alkylation of phenol with 1-propanol was investigated over CeO_2–MgO catalysts prepared utilizing a molten mixture of the corresponding nitrates and citric acid. The CeO_2–MgO had a stable catalytic activity at 475°C and had an excellent selectivity to 2-*n*-propylphenol higher than 82% based on phenol. Although a portion of 2-propylphenol was decomposed, a sum of selectivities to monoalkylated phenols such as 2-propylphenol, *o*-cresol, and 2-ethylphenol exceeded 97%. The highest catalytic activities for the propylation, high reaction rate, and high selectivity to 2-*n*-propylphenol were obtained at CeO_2 content of 11.2 mol%.

During the propylation, 1-propanol was converted into propanal and 3-pentanone. The dehydrogenation was maximized at CeO_2 content of 72.1 mol%. In the results of the transformation of 1-propanol, it was found that 1-propanol was dehydrogenated into propanal, and that the produced propanal was converted to 3-hydroxy-2-methylpentanal via aldol addition, followed by the production of 3-pentanone through the deformylation of 3-hydroxy-2-methylpentanal. The pure CeO_2, which had only weak basic sites together with the redox property, selectively catalyzed the 1-propanol transformation to 3-pentanone, while the pure MgO with strong basicity showed a very low reaction rate in the alkylation and inefficient formation of 3-pentanone in the transformation.

The redox property of Ce^{4+}–Ce^{3+} is probably attributed with the activation of 1-propanol to produce 1-hydroxypropyl radical. We speculate the reaction mechanism of the *ortho*-propylation over the CeO_2–MgO catalyst: the *ortho*-position of phenol adsorbed perpendicularly on weak basic sites on the catalyst is selectively alkylated by 1-propanol, which is possibly activated in the form of 1-hydroxypropyl radical rather than propyl cation, as illustrated in Scheme 2.

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