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Strongly Adsorbed Species to Form Linear Hydrocarbons over Partially Reduced CeO_2

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Partial reduction of CeO_2 led to strong adsorption of CO on the CeO_2. The amount of the strongly adsorbed CO was increased with an increase in the degree of the reduction. XPS measurements showed that the reduction of CeO_2 forms Ce^{3+}, the adsorption of CO on the partially reduced CeO_2 did not change the concentration of Ce^{3+}, and the amount of strongly adsorbed CO increased with an increase in the surface concentration of Ce^{3+}. The hydrogen treatment of the adsorbed species formed linear olefins, different from the catalytic CO hydrogenation over CeO_2. The forms of strongly adsorbed CO and the intermediate for the hydrocarbon formation were discussed.

INTRODUCTION

We have reported that the formation of branched carbon chain products is a characteristic of the CO hydrogenation over oxide catalysts (*1*). The CO–H_2 reaction over ZrO_2 at 623 K, CeO_2 at 523 K, and In_2O_3-CeO_2 at 523 K selectively forms isobutene (*2*), 2-methylpropanal (*3*), and isobutanol (*3*), respectively. C_5 hydrocarbons formed over CeO_2 and CeO_2–lanthanide oxide catalysts contain isoprene with selectivity of more than 70% (*4*). Furthermore, the formation of branched chain alkanes from CO and H_2 over "difficult-to-reduce" oxide catalysts is well known as isosynthesis (*5*). However, linear hydrocarbons such as linear butenes are also formed over oxide catalysts with different activation energies from that of isobutene formation (*6*).

On the other hand, the formation of linear carbon chain products from the CO–H_2 reaction over metal catalysts is naturally explained by the polymerization of C_1 species such as CH_2 which is formed by the hydrogenation of carbon species from the direct C–O bond cleavage of CO (*7*). However, differing from the metal surface, the direct cleavage of the C–O bond of CO without the aid of reducing agents must be very hard over oxide surfaces, since it should follow the oxidation of surface species. Therefore, the formation of linear carbon chain products from CO and H_2 over oxide catalysts as well as the branched chain product formation is interesting to understand the reaction over oxide catalysts. Here we describe the irreversible adsorption of CO on partially reduced CeO_2, its hydrogenation to form linear hydrocarbons, and the surface state by XPS analysis.

EXPERIMENTAL

CeO_2 was prepared by the precipitation of hydroxide from an aqueous solution of the nitrate with aqueous ammonia solution and the calcination at 773 K for 3 h after drying overnight at 393 K. Hydrogen and CO were purified by passing through a trap at liquid-nitrogen temperature. CeO_2 of 4.0 g was evacuated at 973 K for 3 h before hydrogen treatment at 67 kPa and at 673 or 773 K for a given time. The degree of reduction was estimated from an amount of H_2O produced. After evacuation of gas-phase

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hydrogen at the same temperature as the hydrogen pretreatment temperature, CO adsorption experiments were carried out in a quartz reactor of 80 ml equipped with a gas circulation pump and a vacuum system at 13 kPa of equilibrium pressure of CO at 273 K for 1 h. An amount of irreversibly adsorbed CO was estimated from the balance between the amount of adsorbed CO of the first run and that of the second run. The catalyst was evacuated at 273 K for 1 h between the first and the second runs. The hydrogenation of the adsorbed species was carried out at 473 or 673 K at 67 kPa. The surface areas were determined by BET methods by N_2 adsorption at liquid-N_2 temperature after the hydrogenation reaction.

The products were collected at liquid-nitrogen temperature except for methane and determined by gas chromatography. The amounts of remaining surface species after the hydrogen treatment at 673 K were determined from the amount of CO_2 formed by the O_2 treatment at 973 K. The determination of the products were carried out by GC equipped with a Porapak Q column for hydrocarbons and CO_2, VZ-7 and -10 columns for isomers of C_4 hydrocarbons, a PEG 6000 column for oxygenates, and a Molecular Sieve 5A for methane and CO.

XPS spectra were recorded on a Shimadzu ESCA 750 equipped with a glovebox. The binding energies were corrected by $Au_{7/2}$ (83.8 eV). The samples for XPS measurement were evacuated, moved in vacuo from the reactor bed to a branched glass tube connected to top of the reactor and sealed. The sealed samples were placed in the glovebox, unsealed, and pasted on a sample holder under Ar.

RESULTS

(1) CO Adsorption

Table 1 shows the H_2 treatment conditions of CeO_2, the amounts of H_2O formed during the H_2 treatment, and the surface areas of CeO_2. The CeO_2 treated with H_2 at 773 K for 16 h is denoted as CeO_2(773K, 16h). The surface area decreases with an increase in the amount of H_2O formed, i.e., the extent of reduction. The composition of CeO_2(773K, 16h) was estimated as $CeO_{1.95}$ from the amount of H_2O formed. The adsorption of CO on the CeO_2(773K, 16h) at 273 K and at 26.3 kPa gave 86 μmol · g^{-1} of adsorbed CO. After evacuation at the same temperature for 1 h, the second run of CO adsorption was carried out. The amount of CO adsorbed in the second run was 22 μmol · g^{-1}, indicating that 64 μmol of CO g^{-1} remains after evacuation. Figure 1 shows the relation of the amount of strongly adsorbed CO to the extent of CeO_2 reduction. The increase in the extent of reduction results in the increase in the amount of the strongly adsorbed CO.

(2) Hydrogenation of the Strongly Adsorbed CO

The CO-adsorbed CeO_2 was evacuated at 273 K for 1 h and treated with H_2. The treatments at 273 and 373 K formed no

TABLE 1

The Relation of H_2O Formed and Surface Area to the H_2 Treatment Conditions of CeO_2

Catalyst	H_2 treatment		H_2O formed (μmol · g^{-1})	Surface area (m^2 · g^{-1})
	Temp. (K)	Time (h)		
CeO_2(673K, 1h)	673	1	35	31
CeO_2(673K, 16h)	673	16	120	26
CeO_2(773K, 8h)	773	8	360	21
CeO_2(773K, 16h)	773	16	630	19

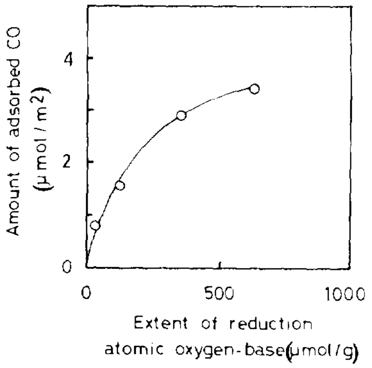

FIG. 1. Relation of amount of strongly adsorbed CO to the degree of CeO_2 reduction at 67 kPa under various temperature and reduction time.

products. The treatment at 473 K gave C_1–C_6 hydrocarbons, but no oxygenates were detected. CO gas was not detected in the gas phase. Table 2 shows the amount of strongly adsorbed CO, the initial formation rate of products, and the ratio of hydrocarbons formed from the hydrogen treatment of the adsorbed CO to the amount of CO adsorbed. The amount of strongly adsorbed CO is nearly parallel to the hydrocarbon formation rate, showing that the rate increases with an increase in the extent of reduction. The amounts of H_2O and CO_2, which formed during the hydrogen treatment, are much less than those of hydrocarbons.

CeO_2(673K, 16h) strongly adsorbs 42 μmol of CO g^{-1} at 273 K, as shown in Table 2. The hydrogen treatments of the adsorbed species at 473 K for 16 h and then at 673 K for 20 h gave both 15.9 and 15.6 μmol-C · g^{-1} of hydrocarbons, respectively. Thus, 75% of strongly adsorbed CO was recovered as hydrocarbons. The remaining 25% was recovered as CO_2 by oxygen treatment at 973 K. The hydrocarbon distributions obtained by hydrogen treatment at 473 K from the adsorbed species are shown in Table 3. No oxygenates could be detected. The deep reduction seems to prefer higher hydrocarbon formation. The hydrogen treatment at 673 K results only in the formation of more widely distributed hydrocarbons. The isomer distributions of C_4 hydrocarbons on CeO_2(673K, 16h) and CeO_2(773K, 16h) are shown in Table 4. Different from the distribution in the catalytic CO hydrogenation over CeO_2 (*2*), they consist mainly of linear olefins.

TABLE 2

Initial Formation Rate of Hydrocarbons Formed during Hydrogen Treatment of Strongly Adsorbed CO

Catalyst	Amount of strongly adsorbed CO [μmol · g^{-1} (μmol m^{-2})]	Formation rate[a] (μmol-C · h^{-1} · m^{-2})		Recovered hydrocarbons[c] (adsorbed CO)	
		Hydrocarbons[b]	$CO_2 + H_2O$	at 473 K	at 473 and 673 K
CeO_2(673K, 1h)	25 (0.8)	0.06 (0.07)	N.D.[d]	N.D.[d]	0.31[e]
CeO_2(673K, 16h)	42 (1.6)	2.2 (1.4)	0.5	0.38[f]	0.75[g]
CeO_2(773K, 8h)	61 (2.9)	7.9 (2.7)	N.D.[d]	N.D.[d]	0.68[e]
CeO_2(773K, 16h)	64 (3.4)	19 (5.6)	2.0	N.D.[d]	0.72[e]

[a] Average value of initial 3 h.

[b] Parentheses are the formation rate based on the amount of strongly adsorbed CO.

[c] μmol-C · g^{-1}.

[d] Not determined.

[e] The values were estimated from total amount of products formed by the hydrogen treatment at 473 K for 3 h followed by at 673 K for 10 h.

[f] The value was estimated from the products obtained by the hydrogen treatment at 473 K for 96 h.

[g] The value was estimated from total amount of products formed by the hydrogen treatment at 473 K for 96 h followed by at 673 K for 20 h.

TABLE 3

Hydrocarbon Distribution Obtained from Hydrogenation of Strongly Adsorbed CO on CeO_2 Which Are Treated with H_2 under Various Conditions

Catalyst	Hydrogenation temp. (K)	Selectivity (carbon base %)						Average C number of products
		C_1	C_2	C_3	C_4	C_5	C_{6+}	
CeO_2(673K, 1h)	473	28	32	18	8	9	5	2.5
CeO_2(673K, 16h)	473	24	9	10	15	27	15	3.6
CeO_2(773K, 8h)	473	1	20	14	32	30	4	3.6
CeO_2(773K, 16h)	473	1	15	13	34	27	10	4.0
CeO_2(773K, 16h)	673	17	13	13	18	19	20	3.7

(3) *XPS Measurements*

XPS spectra of the Ce 3*d* region of variously treated CeO_2 are shown in Fig. 2. The peaks A at 882.6 eV and A′ at 901.1 eV are due to $3d_{5/2}$ and $3d_{3/2}$ of Ce^{4+}, respectively. B, B′, C, and C′ are the shake-up and shake-down satellites (*8*). The peaks D at 885.9 eV and D′ at 904.4 eV are assigned to Ce^{3+} (*9*). CO adsorption on CeO_2(773K, 16h) at 273 K (Fig. 2d) does not seem to affect the peak intensity Ce^{3+} as shown in Fig. 2d. The peak intensities of Ce^{3+} increase with an increase in the degree of reduction, as shown in Fig. 3.

DISCUSSION

(*1*) *Surface Site of Strong CO Adsorption*

As shown in Table 2, the amount of adsorbed CO increases with an increase in the extent of reduction of CeO_2. Figure 2 shows that the XPS intensity of surface Ce^{3+} also increases with an increase in the extent of reduction. These results suggest that the adsorption site is a surface Ce^{3+}. To investigate this suggestion, the concentration of surface Ce^{3+}, $C(Ce^{3+})$, was estimated from the equation

$$C(Ce^{3+}) = Sr \times (2/Lc^2) \times (1/M) \times 10^6$$

where Sr is the ratio of surface Ce^{3+} to total surface cerium ion, Lc is a lattice constant of CeO_2 fluorite structure, 5.411×10^{-10} m (the unit cell contains 2 cerium atoms), and *M* is Avogadro's number. The Sr values of CeO_2(673K, 16h) and CeO_2(773K, 16h) estimated from Fig. 2 were 0.08 and 0.28, respectively. Therefore, their surface concentrations of Ce^{3+} are calculated from the above equation as 1 and 3 μmol m^{-2}, respectively. The values are very close to the amounts of strongly adsorbed CO presented in Table 2, although they are very approximate values. Thus, Ce^{3+} being the site of strong adsorption of CO is supported.

(*2*) *Adsorbed Species on Partially Reduced CeO_2*

Figure 2 shows that Ce^{3+} concentrations are kept almost unchanged after CO ad-

TABLE 4

Isomer Distribution in C_4 Hydrocarbons Formed during H_2 Treatment at 473 K

Catalyst	Selectivity (%)					
	C_4H_{10}	1-C_4H_8	*cis*-2-C_4H_8	*trans*-2-C_4H_8	iso-C_4H_{10}	iso-C_4H_8
CeO_2(673K, 16h)	5	20	31	32	Trace	12
CeO_2(773K, 16h)	8	15	36	28	1	12

sorption. This indicates that the adsorption of CO brings about no oxidation of Ce^{3+}. Since the direct cleavage of CO without reducing agents such as hydrogen should cause the oxidation of low-valent metal (*10*), the fact that the adsorption of CO does not affect the surface Ce^{3+} concentration would deny the direct cleavage of C–O bond without any assistance of reducing agents such as adsorbed hydrogen. Therefore, if adsorbed species has already lost the C–O bond without oxidation of Ce^{3+} species, hydrogen taken up during the hydrogen treatment must participate in the C–O bond splitting. This indicates the formation of OH and/or H_2O species in addition to the C–Ce bond. However, the formation of OH and/or OH_2 species should result in the oxidation of the surface Ce^{3+} species to Ce^{4+} (*11*). Therefore, the cleavage of the C–O bond should again decrease the Ce^{3+} concentration even by the aid of adsorbed hydrogen, i.e., CO adsorbed on a partially reduced CeO_2 should keep the C–O bond.

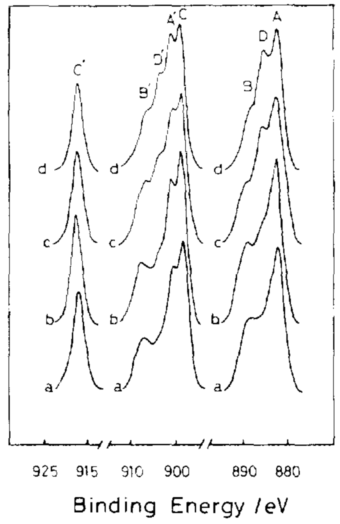

FIG. 2. XPS spectra of Ce 3*d* region of CeO_2 treated with H_2 at 67 kPa. H_2 treatment conditions: (a) 673 K and 1 h, (b) 673 K and 16 h, (c) 773 K and 16 h, and (d) after CO adsorption on CeO_2(773K, 16h).

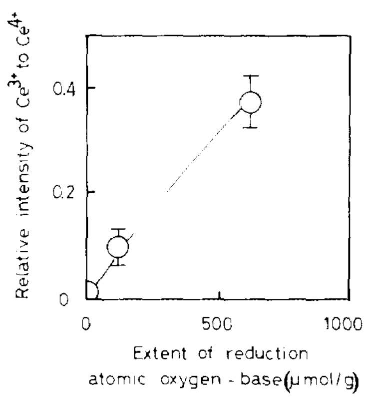

FIG. 3. Effect of extent of reduction on the relative intensity of Ce^{3+} to Ce^{4+}. The vertical lines over data points show the ranges of measurement inaccuracy of Ce^{3+}.

(*3*) *Intermediate to Form Linear Hydrocarbons*

The main products from the CO–H_2 reaction over CeO_2 at 523 K are oxygenates, which consist mainly of 2-methylpropanal and of diisopropylketone (*3*). Since the CO–H_2 reaction at 673 K forms mostly branched hydrocarbon as C_4 and higher products (*1*, *4*), CeO_2 produces branched carbon chain products as C_4 and higher products at from lower to higher reaction temperatures. On the other hand, the hydrogenation of adsorbed CO species on a partially reduced CeO_2 produces only linear hydrocarbons but no oxygenates, as shown in Table 2, 3, and 4. Since partially reduced CeO_2 is known to react with H_2O and CO_2 to form H_2 and CO and oxidized CeO_2 (*11*), no formation of oxygenates may be explained by the strong oxygen affinity of a partially reduced CeO_2, i.e., the strong oxygen abstraction ability from oxygen-containing intermediates could be the reason of hydrocarbon formation without oxygenates. The formation of hydrocarbons was observed above 473 K. Since the difference in reaction conditions between the catalytic reaction and the hydrogenation of adsorbed species is in the presence and the absence of CO in the gas phase, the difference in the product selectivity seems to suggest that the propagation process of the carbon chain is dependent on the gas phase, i.e., the catalytic reaction may be that of the strongly adsorbed species with the species formed from CO and H_2, while the hydrogenation of adsorbed species is just the reaction between the strongly adsorbed species. Thus, the investigation of adsorbed species is important, although the products between both reaction systems are different.

The adsorption of CO at room temperature on reduced CeO_2(673K, 2h) forms formate and formyl species (*12*). Since the formate species on partially reduced CeO_2 is stable for the evacuation at 473 K (*13*), it might be a candidate of the intermediate of linear hydrocarbon formation. On the other hand, IR measurement of the adsorbed species from CO adsorption and hydrogen treatment of the species over partially reduced CeO_2 showed that (1) the CO adsorption at room temperature forms formate species along with small amounts of formyl and methoxide species, (2) the absorbances of the formate species reaches the maximum at around 2-h reduction of CeO_2 even at the low reduction temperature of 673 K, and (3) the increase in the reduction time of CeO_2 results in the decrease after passing the maximum at the short reduction time in the absorbance of the formate species and the slight increase in that of dioxymethylene and methoxy species to compensate the decrease in the absorbance (*14*). However, an amount of strongly adsorbed CO increases with an increase in the extent of reduction of CeO_2, as shown in Table 2 and Fig. 1. These results indicate that the formate species cannot be fitting to the adsorbed species on the deeper reduced CeO_2. More deeply hydrogenated species with much weaker absorbance than the formate species could be an adsorbed intermediate. The formyl species is usually unstable, the amount on the surface is usually very little (*12*, *15*), and the stabilized form of the formyl species on oxide may be a formate species (*16*). Since the amount of strongly adsorbed CO increases with an increase in the degree of reduction, as shown in Fig. 1, and the deep reduction of CeO_2 at 673 and 773 K results in the take-up of hydrogen (*17*), the strongly adsorbed species could be a more deeply hydrogenated species than the formate or formyl species. A hydroxymethylene intermediate has been postulated as one of the intermediates of linear hydrocarbon formation (*18*). The fact that there are hydroxyl species but no hydride species on the CeO_2 surface treated with H_2 (*12*) might support the hydroxymethylene species as a surface species, because protonic hydrogen but not hydride may be needed as a hydrogen species to react with oxygen atom in the formyl species. However, the hydroxymethylene species is usually easy to decompose into a formyl and a proton (*19*).

On the other hand, it is reported that the heating of η,μ-formaldehydezirconium (IV) complex forms ethylene (*20*). This suggests that the heat treatment of η,μ-type adsorbed species of formaldehyde can form methylene species. The formation of the similar compounds on partially reduced CeO_2 catalysts could also form methylene species on the surface. This may explain the highly selective formation of ethylene from CO and H_2 over CeO_2 and CeO_2–In_2O_3 catalysts (*21*) and the formation of linear hydrocarbons, as shown in Table 4, since the formation of linear hydrocarbons over transition metal catalysts has been explained by the polymerization of methylene species (*7*). The deeper reduction of CeO_2 leads to the larger amounts of strongly adsorbed species, and therefore the preference of higher molecular weight compounds, as shown in Tables 2 and 3. This may support the methylene species intermediate to form linear hydrocarbon formation over oxide catalysts. However, since formaldehyde is an isomer of the hydroxymethylene species, hydroxymethylene might be a precursor of formaldehyde or vice versa. The formation of methylene species may explain the formation process of higher and linear hydrocarbons according to the methylene polymerization mechanism (*7*).

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