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Unusual Activation of Irreversibly Adsorbed CO on CeO_2

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Irreversibly adsorbed CO at 273 K on partially reduced CeO_2 was hydrogenated to form C_1-C_{6+} hydrocarbons at 473 K. The amount of adsorbed CO and the rate of hydrocarbon formation increased with increasing the extent of reduction of CeO_2. Ce^{3+} and/or oxygen vacancy on the surface is an active center for the adsorbed CO hydrogenation.

The adsorption and hydrogenation of CO on metal oxides such as ZnO,[1)] and ZrO_2[2)] have been studied as an elementary step of the catalytic formation of methanol and hydrocarbons. However, there is only few mechanistic study of the activation of CO, dissociation of carbon oxygen bond and the hydrocarbon formation over the oxide catalysts.

The CO hydrogenation reaction proceeds over CeO_2-supported metal catalyst[3)] such as (Pt/CeO_2)[3)] and (Pd/SiO_2-CeO_2).[4)] We have recently reported[5)] that light alkenes, especially ethene were formed from CO - H_2 reaction at 673 K over CeO_2 and In_2O_3-CeO_2 catalysts.

We now report the irreversible adsorption of CO at 273 K and hydrocarbon formation from the adsorbed CO by H_2 treatment at 473 K over CeO_2. To our knowledge, this is the first example of the CO activation and the hydrocarbon formation over the oxide catalyst at low temperatures.

CeO_2 was prepared by the hydrolysis of Ce(III) nitrate solution with 5% of aqueous ammonia and calcined in air at 773 K for 3 h. The catalyst (4 g) was evacuated at 973 K for 3 h, treated by the H_2 reduction at 673 or 773 K, and evacuated for 1 h at the same temperature in a closed circulation system before the CO adsorption. The extent of the reduction was estimated from an amount of consumed H_2 and produced H_2O. Table 1 shows the reduction conditions, the extent of the reduction, and surface area of CeO_2. The average composition of CeO_2(D) is $CeO_{1.95}$. H_2 treatment of adsorbed CO was carried out under 67 kPa at 473 K for 3 h or 673 K for 10 h.

Table 1. The reduction conditions of CeO_2

Sample	Reduction conditions Temp/K	 Time/h	Extent of[a] reduction	Surface area /$m^2 \cdot g^{-1}$
A	673	1	35	31
B	673	16	120	26
C	773	8	360	21
D	773	16	630	19

a) Atomic oxygen base µmol/g.

Figure 1 shows the CO adsorption isotherm at 273 K over the reduced CeO_2(D). The adsorbed CO was not removed by evacuation at 273 K for 1 h, and about 70% of adsorbed CO remained even after the evacuation at 673 K for 10 h. An amount of irreversibly adsorbed CO at 273 K increases with an increase in the extent of reduction, as shown in Fig. 2. The values of CO adsorption are 3.4 $\mu mol/m^2$ (64 µmol/g) on the CeO_2(D).

Irreversibly adsorbed CO was hydrogenated to form C_1 - C_{6+} hydrocarbons above 423 K. The initial rate of hydrocarbon formation at 473 K increases with an increase in the extent of reduction of CeO_2, as shown in Table 2.

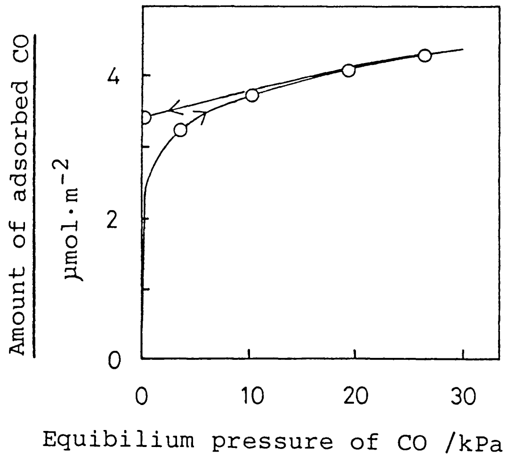


Fig.1. Isotherm of CO adsorption at 273 K on CeO_2 (D).

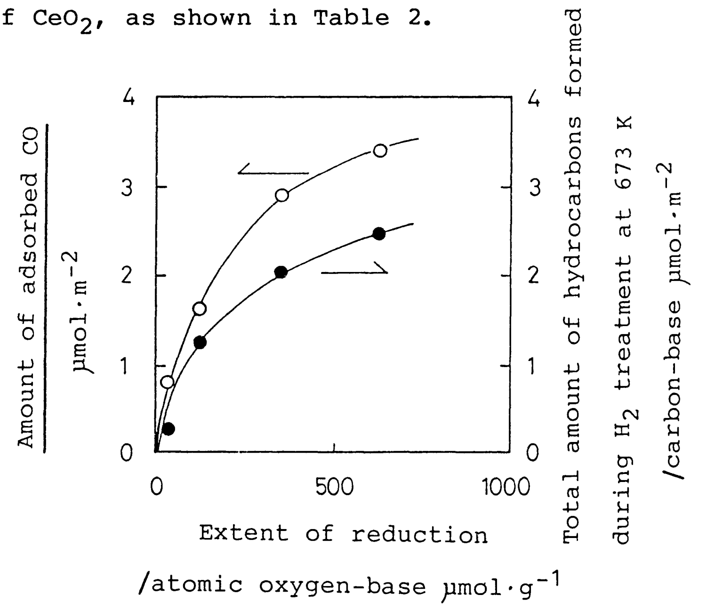


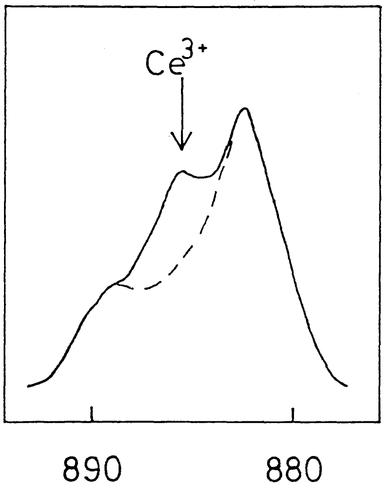
Fig.2. The effect of the extent of reduction to the CO adsorption and hydrocarbon formation.

Table 2. The activity and selectivity for the hydrocarbon formation on CeO_2 from irreversively adsorbed CO by H_2 treatment at 473 K

Sample	Initial rate of[a)] hydrocarbon formation	Selectivity (carbon-base %) C_1	C_2	C_3	C_4	C_5	C_{6+}
A	0.06	28	32	18	8	9	5
B	2.2	24	9	10	15	27	15
C	7.9	1	20	14	32	30	4
D	19	1	15	13	34	27	10

a) The values are average of initial 0 - 3 h.
Carbon-base 10^{-2} $\mu mol \cdot m^{-2} \cdot g^{-1} \cdot h^{-1}$.

It is noted that the amounts of H_2O and CO_2 formed are remarkably little comparing with those of hydrocarbons produced from adsorbed CO hydrogenation. This fact indicates that the oxygen atom of CO remains on the reduced CeO_2 surface during the hydrogenation reaction. The hydrocarbon distribution changes markedly from methane to higher hydrocarbons when the reduction and evacuation temperature are 773 K. For example, CeO_2(D) forms C_{4-6+} hydrocarbons with 71% of selectivity in total hydrocarbons, whereas it forms methane with only 1%. This suggests that the amount of hydrogen such as hydroxyl groupe remaining on the surface strongly affects the carbon-carbon bond formation. It is a unexpected result that such long chain hydrocarbons are formed under low temperature conditions on the oxide surface. The hydrocarbon formation is completed within about 10 h at 673 K and about 70% of adsorbed carbon was converted into hydrocarbons as shown in Fig. 2. No CO was detected in the gas phase during the H_2 treatment.



Binding energy / eV
Fig. 3. XPS spectra of Ce 3d region. CeO_2 (D) ——— ; CeO_2 none reduced – – –.

A peak of 885.9 eV which is assigned to Ce^{3+} 6) was observed by XPS on the reduced CeO_2, as shown in Fig. 3, and intensity of the peak increased with the extent of the reduction. Reduction of CeO_2 to metallic cerium by H_2 does not proceed under the mild conditions at 673 - 773 K.[7)] These results indicate that Ce^{3+} and/or oxygen vacancy on the reduced surface plays an important role for irreversible CO adsorption and hydrogenation. It is known that CeO_2 exhibits a characteristic behavior for some redox reactions. Otsuka et al.[8)] reported that reduced CeO_2 is able to reduce H_2O to form H_2 and White et al.[9)] reported that Ce^{3+} on the reduced Pt/CeO_2 surface plays the important role for CO_2 adsorption and reduction to form CO. Our results indicate that reduced CeO_2 is able to reduce adsorbed CO to form hydrocarbons in the presence of H_2 at 473 K. Further study on the hydrocarbon formation and spectroscopic study of the surface species on CeO_2 are now under investigation.

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