

Drastic Selectivity Change by SMSI Effect in the CO-H₂ Reaction over Pd/CeO₂

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Selectivity of CO-H₂ reaction over Pd/CeO₂ changed drastically from methanol to methane by higher temperature reduction (SMSI effect). Facile isotopic exchange reaction of ¹²C¹⁸O-¹³C¹⁶O indicated the dissociative adsorption of CO over reduced Pd/CeO₂, which corresponds to the acceleration of methane formation. Infrared spectroscopic investigation during the reaction suggested that methanol formation sites were formed by the transformation of methane formation sites.

It has been well recognized that the catalytic properties of Pd metal for CO hydrogenation are quite sensitive to the composition of the supports,^{1,2} as well as the particle sizes of Pd and the presence of promoters.³ High activity and selectivity for methanol synthesis are achieved when Pd is supported on rare earth oxides such as La₂O₃,⁴ whereas methane synthesis is preferred when Pd is supported on group 4 metal oxides such as TiO₂.⁵ The XPS analysis for Pd/La₂O₃ demonstrated the presence of negatively charged Pd metal, which suggests that thin LaO_x patches cover the surface of Pd crystallites to modify their morphology favorable for methanol formation.^{6,7} On the other hand, in the case of Pd/TiO₂, decoration of Pd surface by TiO_x moieties is considered to aid the dissociation of CO and raises the activity for methane formation.⁸

Cerium oxide is another important support for group 8-10 metal catalysts, because of their application in automotive pollution control and in syngas conversion. Fujimoto et al. have reported the promotive SMSI effect for hydrogenation of CO₂ to methanol over Pd/CeO₂ under high pressures.⁹ Recently, we have also found that Pd/CeO₂ exhibited remarkable catalytic behavior in the hydrogenation of CO under reduced pressures, whose selectivity changes drastically from methanol to methane by higher temperature reduction and is restored to the original selectivity by lower temperature reduction after oxidation (SMSI phenomena). In this letter we applied kinetic investigation as well as isotopic tracer method and infrared spectroscopy to elucidate the reaction mechanism of methane and methanol formation. We found, for the first time, that remarkably facile CO dissociation is the intrinsic feature for the acceleration of methane and that transformation of active sites during CO-H₂ reaction is the key step for the acceleration of methanol.

Ceria (20 m²/g) supported catalysts (0.5 and 4 wt%) were prepared by a conventional impregnation method, employing (NH₄)₂PdCl₄ as a precursor. After the reduction by hydrogen at 673 K, the catalysts were washed thoroughly by distilled water to remove a trace amount of chlorine. The reaction was carried out in a closed gas circulation system (CO:H₂ = 1:3, total = 120 Torr), and the products were analyzed by gas chromatography. Before each run the catalyst was reduced by hydrogen at 573 K (low temperature reduction: LTR) or 773 K (high temperature reduction: HTR). It was confirmed from XRD line width as well as the amount of sorbed hydrogen into Pd bulk, that these

treatments did not change Pd particle sizes. But the amount of adsorbed H(a) or CO(a) on the Pd surface decreased drastically by HTR treatment, indicating the modification of ceria onto the top layer of surface Pd atoms (SMSI effect). For infrared spectroscopic experiments, the catalyst was pressed into a 20 mm diameter disk) and put into an infrared cell.

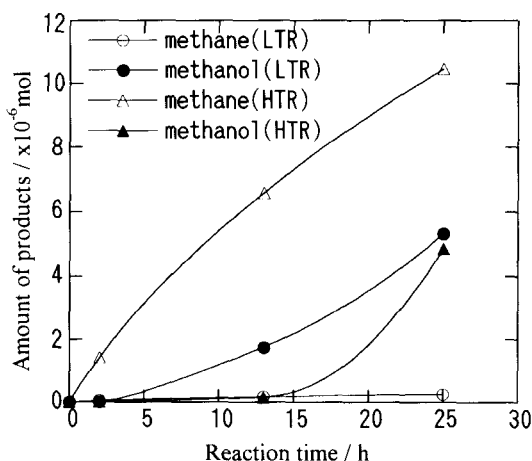


Figure 1. CO-H₂ Reaction over 4 wt% Pd/CeO₂ at 413 K.

Figure 1 shows the time courses of CO-H₂ reaction at 413 K over 4 wt% Pd/CeO₂ (dispersion D = 0.2). Under LTR, both methane and methanol were formed at the initial stage of the reaction. The rate of methanol formation exhibited an induction period of 2 h, and its formation rate increased drastically after the induction period, with a decrease in the rate of methane formation. After 25 h, more than 90% of the products was methanol. The situation was completely different and the selectivity changed drastically under HTR. The rate of methane formation was increased thirty times at the initial stage of the reaction, and the length of the induction period for methanol formation became much longer (13 h). Accordingly, the selectivity for methanol was only 30% even after 25 h. Similar time courses were obtained in the case of 0.5 wt% Pd/CeO₂ catalyst both for LTR and HTR. But the acceleration effect of SMSI was much larger for methane formation (eighty times), and the formation of methanol was not detected within 25 h under HTR, probably because of the extension of the induction period.

To investigate the SMSI effect for the C-O bond dissociation process, isotopic exchange reactions between ¹²C¹⁸O and ¹⁶O of ceria, as well as between ¹²C¹⁸O and ¹³C¹⁶O were studied over 4 wt% Pd/CeO₂ catalysts. Table 1 summarizes the initial rates and activation energies of these exchange reactions over freshly reduced LTR and HTR state catalysts. The former exchange could be detected at the temperature range higher than room temperature, which was accelerated several times in the SMSI

Table 1. Isotopic exchange reactions over 4 wt% Pd/CeO₂

Type of exchange	Pretreat. condition	React. temp. (K)	Initial rate (x10 ⁻⁴ /s ⁻¹)	Activation energy (kJ/mol)
¹² C ¹⁸ O	LTR	413 K	3.6	-
-Ce ¹⁶ O ₂	HTR	413 K	14	-
¹² C ¹⁸ O	LTR	243 K	0.40	19
- ¹³ C ¹⁶ O	HTR	243 K	1.6	20
	CO-H ₂ ^a	273 K	0.0	-

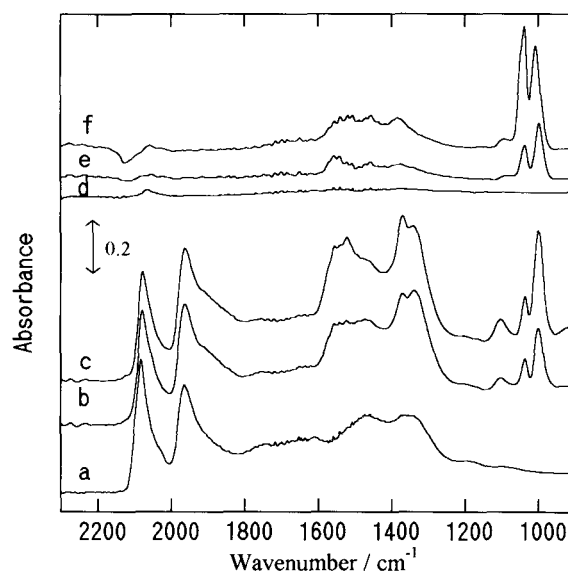
^a After induction period of methanol formation in CO-H₂ reaction.

state. On the other hand, the latter exchange proceeded much faster than the former and the formation of ¹³C¹⁸O and ¹²C¹⁶O could be detected even at around 200 K. SMSI also enhanced the exchange rate four times without changing the activation energies. Since isotopic exchange between ¹²C¹⁸O and CeO₂ was much slower than ¹²C¹⁸O-¹³C¹⁶O exchange, it is reasonable to suppose that dissociative adsorption of CO takes place on Pd/CeO₂ even at 200 K.

Herrmann et al. have measured the electron conductivity of Pd/CeO₂ during the reduction by H₂.¹⁰ They concluded the formation of oxygen vacancies in ceria upon reduction and the subsequent electron transfer from reduced ceria to Pd. It is also well known that ceria is reduced by hydrogen to form Ce₂O₃, which has been observed by Fujimoto et al. in the XRD and XPS measurements of Pd/CeO₂.¹¹ It is reasonable to suppose these low-valent ceria may accelerate the dissociation of C-O bond. The last column in Table 1 represents the result of ¹²C¹⁸O-¹³C¹⁶O reaction over the surface after CO-H₂ reaction for prolonged period. The exchange reaction of CO bond did not proceed at all on this methanol active surface, which indicates that CO bond dissociation directly correlates to methane formation and the active sites for CO dissociation may be transformed to methanol formation sites during the induction period.

Figure 2 shows the infrared spectra of adsorbed CO, as well as adsorbed species during CO-H₂ reaction over 4 wt% Pd/CeO₂ under LTR and HTR. When CO was introduced onto the freshly reduced (LTR) surface, strong peaks at 2076 and 1958 cm⁻¹ were observed at room temperature, which can be attributed to the linear CO(a) on small Pd crystallites and bridged CO(a) on Pd(100) plane, respectively (spectrum a).⁷ In addition, broad peaks emerged at around 1650-1350 cm⁻¹, which may be assigned to some carbonate species formed at the interface of Pd and ceria. In the case of HTR, the amount of adsorbed CO decreased drastically and only a weak band was observed at 2057 cm⁻¹ attributable to linearly adsorbed CO (spectrum d), which clearly shows the occurrence of the SMSI.

Spectra b, c and e, f were taken during CO-H₂ reaction at 413 K under both LTR and HTR, respectively (b and e: during induction period, c and f: after induction period of methanol formation). In the cases of spectra b and c, a new shoulder peak

**Figure 2.** IR spectra of adsorbed species over 4 wt% Pd/CeO₂
a:CO(LHR),b:CO-H₂(LTR,0.5 h),c:CO-H₂(LTR,2 h)
d:CO(HTR),e:CO-H₂(HTR,2 h),f:CO-H₂(HTR,15 h).

at around 1900 cm⁻¹ can be assigned to bridged CO(a) on Pd(111) plane,⁷ which seems to increase slightly as the reaction proceeded. Broad peaks at around 1600-1300 cm⁻¹ can be assigned to surface formate species together with carbonates, whose intensities were much stronger in the case of LTR. Three sharp peaks at around 1100-1000 cm⁻¹ can be assigned to different methoxide species adsorbed mainly on ceria.¹² By comparing spectrum b and c, and e and f, it is recognized that, after the induction period, the kinds of CO(a), formate and methoxide are altered to some extent, which may be explained by the change of the oxidation state of cerium oxides.¹³

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