Remarkable Addition Effect of In and Ga in the NO-CO Reaction over Pd/SiO_2

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Addition of In or Ga to Pd/SiO_2 accelerated the rate of NO-CO reaction dramatically, and N_2O and CO_2 were formed steadily even at room temperature. XRD measurements revealed that a Pd-In intermetallic compound plays an important role. The ensemble effect of In atoms weakened the adsorption of CO and NO, which may open a new reaction route for N_2O formation.

The reduction of NO by CO over supported transition metals has been investigated extensively due to its fundamental importance in automotive emission control.[1] Catalytic properties of Pd have received increasing attention because of its potentiality for the substitution of Rh in the conventional three-way Rh/Pt catalyst.[2-5] The main disadvantage of Pd lies in its relatively poor NO_x reduction efficiency compared to Rh. Attempts to improve the catalytic performance of Pd have been made by placing it in contact with various base metal oxides and rare earth oxides.[6,7]

In the present study we investigated the addition effect of In and Ga to silica supported Pd in the reduction of NO by CO, and found that these additives exhibit a large acceleration effect. Especially in the case of $Pd\text{-}In/SiO_2$, an intermetallic compound formed between Pd-In is extraordinary active for NO-CO reaction, and N_2O and CO_2 are formed steadily even at room temperature.

Metal supported (5wt% Pd) catalysts were prepared by a conventional impregnation method using silica (Aerosil 300) and $(NH_4)_2PdCl_4$, $InCl_3.4H_2O$ and $GaCl_3$ as precursors. The molar ratio of Pd and In (or Ga) was 1:1. The catalyst (0.2g) was reduced by hydrogen at 733K for 10 h. The reaction was carried out in a closed gas circulation system under 1:1 ratio of NO and CO (4 kPa each). The composition of the gas phase during the reaction was followed by TCD gas chromatography. For infrared spectroscopic experiments, the catalyst was pressed into a 20 mm diameter disk and put into an infrared cell, which was connected to a closed gas circulation system.

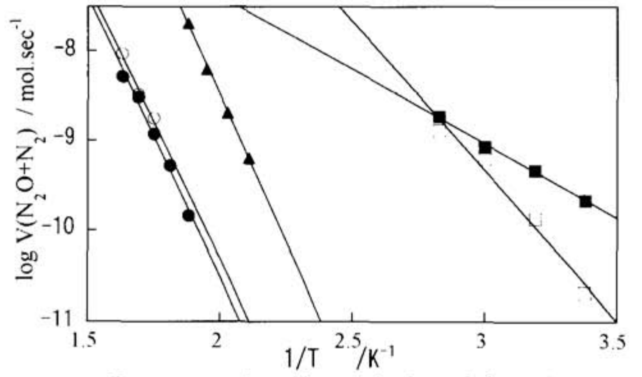

Figure 1. Temperature dependence of $NO+N_2O$ formation rates.
● Pd(NO-CO), ▲ Pd-Ga(NO-CO), □ Pd-In(N2O-CO),
○ Pd(N2O-CO), ■ Pd-In(NO-CO).

Figure 1 summarizes the temperature dependencies of NO-CO and N_2O-CO reactions over Pd/SiO_2, $Pd\text{-}In/SiO_2$ and $Pd\text{-}Ga/SiO_2$ catalysts. In the case of Pd/SiO_2, the reaction proceeded at around 500-600K, and the main product was N_2O with a smaller amount of N_2 at the initial stage, which increased considerably after gaseous NO was consumed. From the slope of the Arrthenius plot, the activation energy was estimated to be about 120 kJ/mol for (N_2O+N_2) formation rate. The rate of N_2 formation in N_2O-CO reaction was twice as fast as that of NO-CO reaction with a similar activation energy (116 kJ/mol).

When In was added to the Pd/SiO_2, the activity of NO-CO reaction improved dramatically and only N_2O and CO_2 were formed steadily even at room temperature(300K), as shown in Figure 1. The activation energy for N_2O formation also decreased to the one fourth (32 kJ/mol) compared to the case of Pd/SiO_2. The selectivity for N_2 formation against N_2O depended greatly on the reaction temperatures, and at temperatures higher than 400K, the main initial product shifted from N_2O to N_2. The activation energy for N_2O-CO reaction was twice (64 kJ/mol) as large as that of N_2O formation in NO-CO reaction. In the case of $Pd\text{-}Ga/SiO_2$, the acceleration effect was not as large as the case of $Pd\text{-}In/SiO_2$ as shown in Figure 1. Since In/SiO_2 and Ga/SiO_2 exhibited lower activity for NO-CO reaction than Pd/SiO_2, a certain synergetic interaction may exist between Pd and In or Ga.

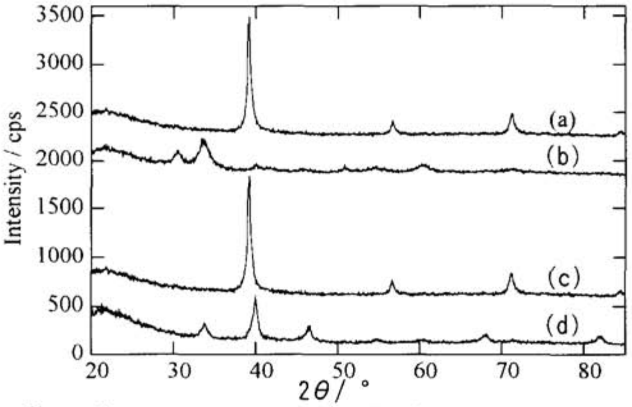

Figure 2. The XRD patterns of various catalysts.
(a)$Pd\text{-}In/SiO_2$ reduced at 733K,(b) Oxid. of sample(a) at 733K,
(c)Re-reduction of sample(b) at 733K,(d) Pd/SiO_2 reduced at 733K.

Figure 2 demonstrates the changes of X-ray powder diffraction patterns after various pretreatments of $Pd\text{-}In/SiO_2$, together with that of Pd/SiO_2 (pattern (d), Pd particle size = ca.200 Å). The pattern (a) was taken after the reduction of $Pd\text{-}In/SiO_2$ at 733K for 10 h, which shows four characteristic peaks (2θ= 39.2°, 56.8°, 70.9°, 84.2°) and can be assigned to $Pd_{0.48}In_{0.52}$ intermetallic compound (particle size = ca.3000 Å).[8] This sample exhibited quite high activity for NO-CO reaction as shown in Figure 1. The pattern (b) was taken after the oxidation of the sample (a) at 733K for 7 h, where the intermetallic compound is destroyed completely and several peaks can be assigned to PdO (2θ= 34.0°, 54.8°, 71.5°), In_2O_3 (2θ= 30.5°, 41.0°, 61.5°) and a small amount of Pd metal (2θ= 40.0°, 46.5°, 82.0°). The activity of this sample for NO-CO reaction was more than one order of magnitude lower than that of sample (a). The pattern (c) was taken after the re-reduction of the sample (b) at 733K for 10 h, and showed the recovery of the intermetallic compound, exhibiting the same high catalytic activity. These results strongly suggest that $Pd_{0.48}In_{0.52}$ is the key compound for the acceleration effect. In the case of Pd-Ga/SiO_2, new XRD peaks emerged at 2θ= 41.0° and 44.5° by higher temperature reduction, in addition to those of Pd metal. But the catalytic enhancement for NO-CO reaction did not correlate to the appearance of these new peaks, different from the case of Pd-In.

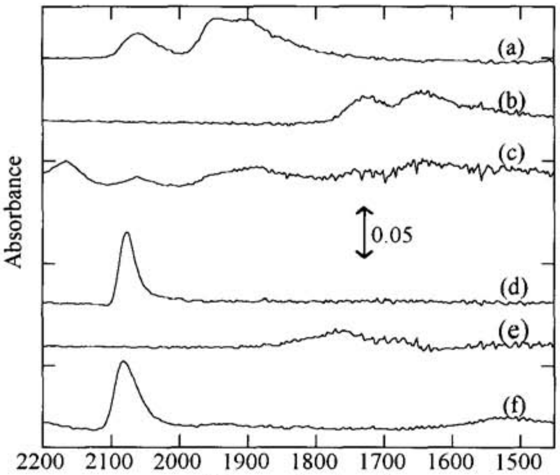

Figure 3. The FT-IR spectra of adsorbed species.
Pd/SiO_2:(a)CO ads.(b)NO ads.(c)during NO-CO reac.;
Pd-In/SiO_2:(d)CO ads.(e) NOads.(f)during NO-COreac..

Figure 3 demonstrates the FT-IR spectra of adsorbed species over Pd/SiO_2 and Pd-In/SiO_2 at room temperature. Spectrum (a) shows the adsorbed CO on Pd/SiO_2, where three peaks can be assigned to linear (2055 cm^{-1}) and bridged (1941,1901 cm^{-1}) CO(a) species. On the other hand, over Pd-In/SiO_2 the bridged CO(a) disappeared completely and only linearly adsorbed CO (2070 cm^{-1}) was observed (spectrum (d)). This spectral change may be explained by the ensemble effect of In atoms on the surface of a Pd-In intermetallic compound, indicating the weakening of CO adsorption by the addition of In. Actually, XPS analysis of Pd-In/SiO_2 indicated the enrichment of In atoms on the surface compared to Pd atoms. Spectra (b) and (e) demonstrate the adsorbed NO on Pd/SiO_2 and Pd-In/SiO_2, respectively. Two peaks at around 1725 and 1645 cm^{-1} can be assigned to linearly adsorbed NO(a) and bridged NO(a) species,[9] which shifted to 1761 and 1682 cm^{-1} by the addition of In. Desorption experiments after adsorption again indicated the weakening of NO adsorption by the addition of In. Spectra (c) and (f) represent the adsorbed species during NO-CO reaction. In the case of Pd/SiO_2, both CO(a) and NO(a) were observed during the reaction at 573K, but only CO(a) was observed in the case of Pd-In/SiO_2 at 373K.

Two reaction mechanisms have been proposed for the N_2O and N_2 formation in NO-CO reaction. The first one involves the dissociative adsorption of NO to form N(a) and O(a), followed by a rapid removal of O(a) by CO to form CO_2.[10] N_2O is formed by the reaction of N(a) and NO(a), whereas N_2 is formed by the recombination of two N(a). The second mechanism involves the direct bimolecular reaction between NO and CO to form N(a) and CO_2.[11] N_2O and N_2 may be formed by the same reaction scheme mentioned above. To distinguish these two mechanisms, only NO was introduced onto freshly reduced Pd/SiO_2 (618K) and Pd-In/SiO_2 (333K), and the (N_2O+N_2) formation rate was compared with that in NO-CO reaction. In the case of Pd/SiO_2, initial rates of both processes were almost the same, suggesting that NO-CO reaction involves NO dissociation process. It is well known that dissociative adsorption of NO on Pd is strongly structure sensitive[5] and requires higher temperatures as 500K,[12] which is consistent with the present study.

On the other hand, over Pd-In/SiO_2, the latter rate was much faster than the former one, suggesting that NO-CO reaction proceeds without NO dissociation. Accordingly our result may be explained by the bimolecular mechanism between NO and CO mentioned above, but reported activation energies for this process are larger (90-120 kJ/mol) than that obtained in this study (32 kJ/mol). Another characteristic point of Pd-In/SiO_2 is that N_2O formation from NO and CO is faster than N_2 formation from N_2O and CO with a smaller activation energy, which may suggest the involvement of a completely different reaction mechanism such as N_2O formation from NO dimer by the assistance of In. Further study is needed to clarify this point.

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