Catalysis Letters, Vol. 117, Nos. 1–2, August 2007 (© 2007)
DOI: 10.1007/s10562-007-9109-6

Remarkable effect of addition of In and Pb on the reduction of N_2O by CO over SiO_2 supported Pd catalysts

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Received 24 March 2007; accepted 31 March 2007

The effect of addition of In and Pb on the reduction of N_2O by CO was studied over SiO_2 supported Pd catalysts, using a closed gas circulation system as well as in-situ infrared spectroscopy. Formation of intermetallic compounds such as $Pd_{0.48}In_{0.52}$, Pd_3Pb and Pd_3Pb_2 was observed which caused a drastic enhancement of the rate of N_2 formation. The infrared spectroscopic analyses revealed a weakening of the adsorption strength of CO on Pd metal by the formation of intermetallic compounds, which is likely the main reason for the enhancement of the reaction rate. From a kinetic investigation as well as in situ FT-IR observation during the N_2O-CO reaction, a redox mechanism was proposed involving the oxidation of the surface by N_2O followed by its reduction by CO. Over Pd/SiO_2, the former process seems to be the rate limiting step because of the inhibition of N_2O activation by strongly adsorbed CO. By adding In or Pb, the rate limiting step shifted to the latter process, which resulted in a large enhancement in the rate of N_2 formation.

KEY WORDS: methane; TPD; Mo; Pd–Ga; HZSM-5.

1. Introduction

The reduction of N_2O by CO over group 8–10 metal catalysts is an important reaction during the reduction of NO by CO in automobile catalytic converters [1,2]. During the cold start of three-way catalysts NO is mainly transformed to N_2O and its subsequent reduction by CO becomes the predominant reaction pathway for N_2 formation [3,4]. In three way Rh-Pt-Pd catalysts, Rh is recognized to be the active component for the selective reduction of NO to N_2 with low ammonia formation [5]. Several studies have been performed to determine the possibility of replacing Rh in automotive catalysts in view of its high cost and scarcity. The catalytic properties of Pd have received increasing attention because of its potential for the substitution of Rh in the conventional three-way Rh/Pt catalysts [6–9]. However, the Pd-only catalyst has a poor NO reduction efficiency compared to Rh, especially in an oxygen-rich environment [10,11]. 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. This was successfully achieved with Pd promoted by cobalt oxide [12], with Pd-Mn [13], Pd-Cr [14], or with Pd-VO_x/Al_2O_3 catalysts [15], which have shown lower light-off temperatures of conversion by 80 to 100 K compared with pure Pd.

In spite of its importance, efforts to improve the catalytic activity in the N_2O-CO reaction have been few. In fact, the N_2O-CO side-reaction during the reduction of NO by CO has been neglected for a long time probably because a few studies have shown that the rate of the isolated N_2O-CO reaction is substantially lower than that of the NO-CO reaction either on Pt or Rh based catalysts [16] In 1989, Cho *et al.* reported that a rate enhancement was observed for the intermediate N_2O-CO reaction (during the NO-CO reaction) in comparison with that of the isolated N_2O-CO reaction over a Rh/Al_2O_3 catalyst at 583 K [17]. This was explained as due to repulsive interactions between N atoms (from the dissociation of NO) and CO molecules in the adsorbed layers which favor the desorption of CO and the subsequent adsorption and decomposition of N_2O formed in the NO-CO reaction.

Recently we have investigated the effect of addition of In, Pb and Ce to silica- supported Pd in the reduction of NO by CO, and found that these additives produce a large acceleration effect on the rate [18]. Especially in the cases of Pd-In/SiO_2 and Pd-Pb/SiO_2, an intermetallic compound formed between Pd-In and Pd-Pb is extraordinarily active for the NO-CO reaction, and only N_2O and CO_2 are formed steadily even at room temperature. In the present study, we have investigated the effect of addition of In and Pb in the N_2O-CO reaction at lower temperatures over Pd/SiO_2 and found a similar enhancement effect for N_2 formation. We compare the intrinsic role of added In and Pb for both the NO-CO and N_2O-CO reactions and discuss the relationship these two reactions.

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2. Experimental

Silica-supported Pd, Pd-In, and Pd-Pb (5 wt% Pd) catalysts were prepared by a conventional co-impregnation method using SiO_2 (Aerosil 300) and $(NH_4)_2PdCl_4$, $InCl_3 \cdot 4H_2O$ and $PbCl_4$ (Wako chemicals) as precursors. The molar ratio of Pd and the additive was 1:1 in the case of Pd-In and 1:0.75 and 1:1 in the case of Pd-Pb catalysts. The catalyst (0.2 g) was reduced by hydrogen at 733 K for 10 h to form intermetallic compounds. The N_2O-CO reaction was carried out in a closed gas circulation system (circulation rate = 80 cm^3/min) under a 1:1 ratio of N_2O and CO (4 kPa each). The composition of the gas phase during the reaction was followed by TCD gas chromatography (Shimazu GC-17A). To investigate the pressure dependence of CO (or N_2O) in the N_2O-CO reaction, only the partial pressure of CO (or N_2O) was changed from 2 to 8 kPa keeping the N_2O pressure (or CO) constant (4 kPa), and the initial rate of N_2 and CO_2 formation was measured. 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. After the same pretreatment mentioned above, the adsorbed species were measured with an IR spectrometer (JEOL, Diamond 20).

A transmission electron microscope (JEM2010, JEOL) with an acceleration voltage of 2000 kV and LaB_6 cathode was used to obtain the images of the supported catalysts. A X-ray photoelectron spectrometer (JPS-9010, JEOL) with Mg K_αX-ray source (10 kV, 10 mA) was used for the analysis of the electronic state of the supported catalysts. The samples were molded into thin disk shapes and introduced into an in situ cell of the preparation chamber. After reduction with H_2 at 573 K they were transferred to an analysis chamber without exposure to air. The catalysts were also characterized by XRD (Rigaku, RAD-γX) and H_2 and CO chemisorption (Beckman Coulter, Omnisorp 100CX).

3. Results and discussion

Figure 1 shows the time courses of the N_2O-CO reactions over Pd/SiO_2, Pd-In/SiO_2, Pd-Pb(1:0.75)/SiO_2 and Pd-Pb(1:1)/SiO_2 catalysts at various reaction temperatures. Table 1 summarizes turnover frequencies at initial conditions based on the dispersion of catalytically active sites estimated from the amount of adsorbed CO at room temperature. In the case of Pd/SiO_2, the reaction proceeded at around 450–550 K: both N_2 and CO_2 increased and N_2O and CO decreased with time as shown in figure 1(a). In all cases after about 1 h, the plots became linear, indicating that steady-state was reached. When In- or Pb-containing catalysts were used, the reaction temperature was lowered by more than 100 K as shown in figure 1(b)–(d). In the case of the N_2O-CO reaction at 330 K over freshly reduced Pd-In/SiO_2 catalysts, rapid N_2 and CO_2 formation were observed at initial stages, followed by a slower steady-state process (B-1). After 4 h, the gas phase was evacuated and the same amount of N_2O and CO gases was re-introduced. At this time N_2 and CO_2 were formed linearly from the beginning as shown in figure 1(B-2), suggesting that the steady-state reaction was proceeding over the slightly oxidized Pd-In intermetallic compound. On the contrary, such a rapid process was not observed in the case of Pd-Pb(1:0.75)/SiO_2 catalysts, and N_2 and

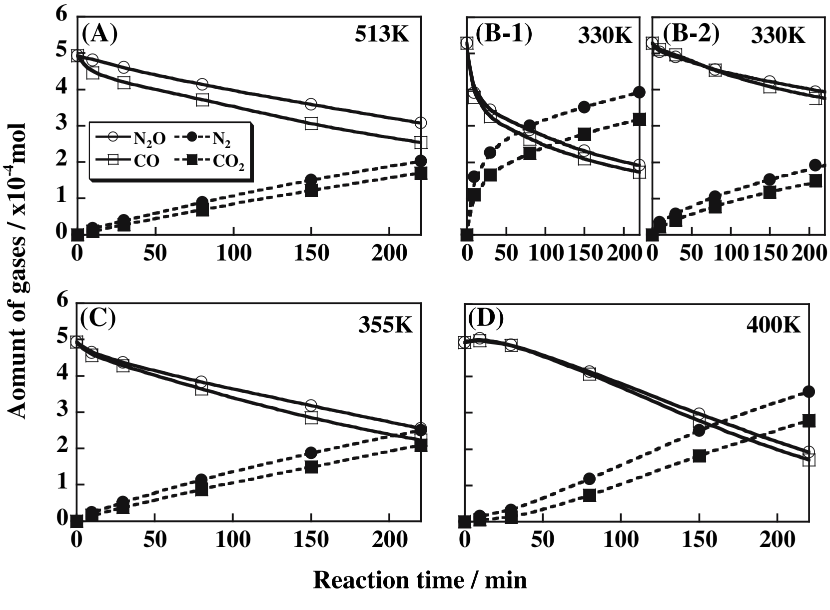

Figure 1. Time courses of the N_2O-CO reaction over various catalysts. (A) Pd/SiO_2 at 513 K, (B-1) Pd-In(1:1)/SiO_2 (over freshly reduced surface at 330 K), (B-2) Pd-In(1:1)/SiO_2 (reintroduction of reactants after (B-1)), (C) Pd-Pb(1:0.75)/SiO_2 at 355 K, (D) Pd-Pb(1:1)/SiO_2 at 400 K.

Table 1

TOF at 350 K, reaction orders and activation energies of N_2 formation in the N_2O-CO reaction over various silica supported Pd catalysts

Catalysts	Particle size (nm)	TOF N_2 ($\times 10^{-4} s^{-1}$)	Reaction orders		Ea (kJ/mol)
			P_{CO} m	P_{N2O} n	
Pd	8.4	0.012	−1.1	1.2	58.3
Pd-In(1:1)	2.6	5.5	−0.1	0.5	37.0
Pd-Pb(1:0.75)	4.1	2.5	−0.4	0.8	52.0
Pd-Pb(1:1)	5.4, 12.7	0.62	−0.5	1.5	54.6

CO_2 were formed linearly from the beginning over the freshly reduced surface (figure 1(C)). Moreover in the case of the Pd-Pb(1:1) catalyst, an induction period was observed at the beginning over the freshly reduced surface as shown in figure 1(D).

Figure 2 shows the temperature dependencies of the turnover frequencies of N_2 formation in N_2O-CO reactions over these catalysts. From the slopes of the Arrhenius plots, the activation energies were estimated as summarized in table 1. The most active catalyst for N_2O formation was Pd-In(1:1)/SiO_2 with the smallest activation energy. The pressure dependencies of the CO and N_2O partial pressures upon the initial rates of N_2 formation were also summarized as reaction orders (rate = k $P_{CO}{}^{m} P_{N2O}{}^{n}$) in table 1. In the case of Pd/SiO_2, a large negative reaction order for CO ($m = -1.1$) and a positive order for N_2O ($n = 1.2$) suggested inhibition of N_2O activation by strongly adsorbed CO. By adding In or Pb (1:0.75) the reaction orders decreased dramatically as shown in the table (Pd-In: $m = -0.1$, $n = 0.5$, and Pd-Pb: $m = -0.4$, $n = 0.8$). These changes suggest a shift in the rate-determining step from the oxidation of the surface by N_2O to the reduction of the oxidized surface by CO. The situation was rather different in the case of Pd-Pb(1:1)/SiO_2 catalysts: although a similar change was observed in the reaction order for P_{CO} ($m = -0.5$), the change was in the opposite direction in the reaction order for P_{N2O} ($n = 1.5$) probably because of the inhibition of N_2O adsorption by an excess amount of PbO_2 formed during the reaction.

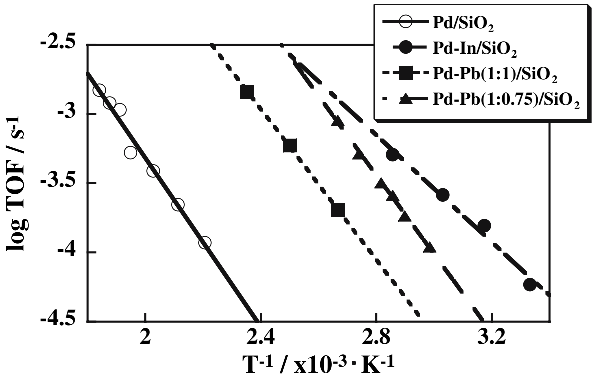

Figure 2. Arrhenius plots of the TOF of N_2 formation in the N_2O-CO reaction over various supported Pd catalysts.

The X-ray powder diffraction patterns of various catalysts are summarized in figure 3 after H_2 reduction at 733 K for 10 h, together with the reference data obtained from JCPDS cards. In the case of Pd/SiO_2, the diffraction pattern typical for a FCC metal was observed as shown in (a) ($2\theta = 40.0$, 46.5, 68.7 and 82.0). When In was added, four characteristic peaks were shifted as shown in (b) ($2\theta = 39.2$, 56.8, 70.9, 84.2), and the material can be assigned to a $Pd_{0.48}In_{0.52}$ intermetallic compound. When Pb was added to Pd/SiO_2 in a 1:0.75(Pd:Pb) ratio, some new XRD peaks emerged at $2\theta = 39.0$, 44.5, 67.5, 79.0 and 82.8 after higher temperature reduction as shown in Fig. 3(c), and the material can be assigned to a Pd_3Pb intermetallic compound. In the case of Pd-Pb(1:1)/SiO_2, a completely different diffraction pattern was observed as shown in Fig. 3(d) ($2\theta = 39.5$, 40.5, 52.7, 58.5, 71.2 and 79.5), which can be assigned to a Pd_3Pb_2 intermetallic compound. The particle sizes of Pd metal and the intermetallic compounds estimated from TEM images are also summarized in table 1. The Pd particles without additives were rather big (average 8.4 nm) after 733 K reduction, but became very small (2 to 3 nm) by the addition of In, forming $Pd_{0.48}In_{0.52}$ intermetallic compounds. These results are consistent with the change of dispersions estimated from CO adsorption at room temperature. In the case of Pd-Pb(1:1)/SiO_2, a binary distribution was observed with diameters around 5–6 nm and 10–15 nm and both particles contained Pd and Pb by EDS analysis.

Figure 4 represents the XPS spectra of Pd3d, In3d and Pb4f transitions in Pd/SiO_2, Pd-In(1:1)/SiO_2 and Pd-Pb(1:1)/SiO_2 catalysts after reduction at 573 K in the in situ cell. In the case of Pd/SiO_2, the binding energy of $Pd3d_{5/2}$ was close to the zero valent Pd metal value in the literature (335.0 eV), whereas the addition of In or Pb caused a 0.8 eV shift to higher binding energy (335.6 eV) even after the reduction at higher temperatures. On the other hand, the binding energy of $In3d_{5/2}$ in Pd-In/SiO_2 was 0.1 eV lower than the zero valent (443.7 eV) value, suggesting the formation of a Pd-In intermetallic compound. In the case of the Pd-Pb(1:1)/SiO_2 catalyst, two Pb $4f_{7/2}$ transitions were observed at 137.1 and 139.1 eV, which can be assigned to zero valent and positively charged Pb species assignable to PbO_2. As shown in Fig. 3(d), the Pd_3Pb_2 intermetallic compound

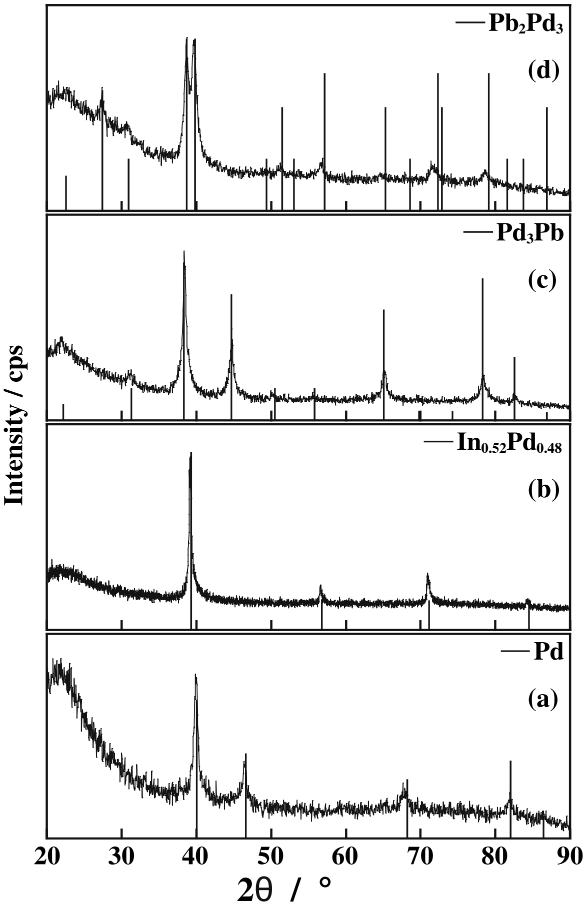

Figure 3. XRD patterns of various catalysts. (a) Pd/SiO$_2$, (b) Pd-In/SiO$_2$, (c) Pd-Pb(1:0.75)/ SiO$_2$, (d) Pd-Pb(1:1)/SiO$_2$.

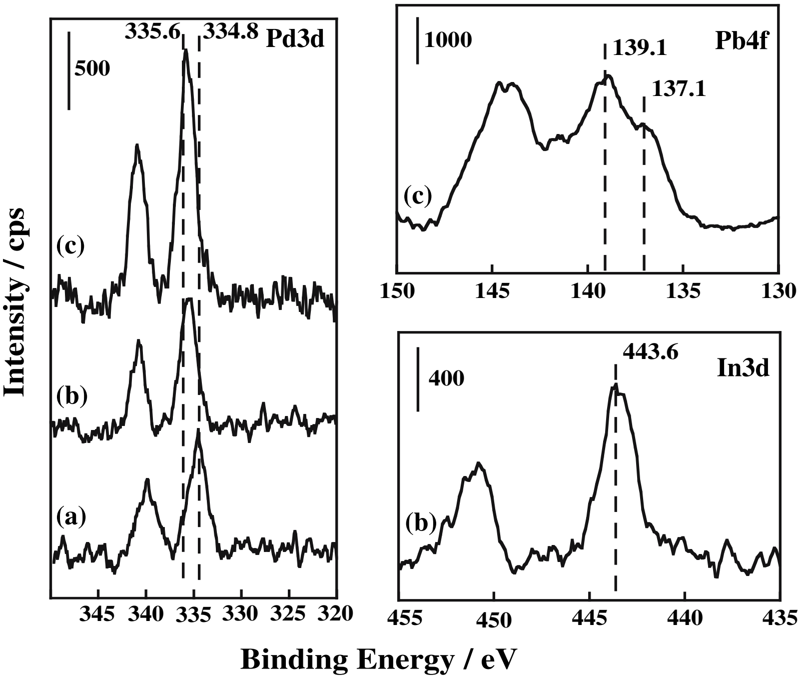

Figure 4. XPS spectra of Pd 3d, In3d and Pb4f transitions. (a) Pd/SiO$_2$, (b) Pd-In(1:1)/SiO$_2$, (c) Pd-Pb(1:1)/SiO$_2$.

is formed together with the oxidation of excess Pb to PbO_2. As will be discussed later, these surface PbO_2 species may inhibit the adsorption of CO and N_2O during the N_2O-CO reaction.

Figure 5(A) shows the FT-IR spectra of adsorbed CO over the Pd/SiO_2, Pd-In/SiO_2 and Pd-Pb/SiO_2 catalysts at room temperature. Spectrum (a) shows adsorbed CO on Pd/SiO_2, where two peaks can be assigned to linear (2083 cm^{-1}) and bridged (1976 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 (2073 cm^{-1}) was observed (spectrum (b)). This spectral change may be explained by an ensemble effect of In atoms on the surface of a Pd-In intermetallic compound. TPD experiments after adsorption revealed that over Pd-In/SiO_2 linearly adsorbed CO disappeared at around 373–423 K, while most of the bridged CO(a) still remained over Pd/SiO_2. From these results, we can conclude that one of the roles of added In would be the weakening of the adsorption strength of CO, which may enhance the reaction rate. As mentioned already, the decrease in the reaction order for P_{CO} from −1.1 to −0.1 by the addition of In agree with this interpretation. This situation also occurred in an even pronounced manner in the case of Pd-Pb/SiO_2, as shown in spectrum (c). No IR peak was observed probably because of the inhibition of CO adsorption by excess Pb oxide on the surface.

Figure 5(B) represents the adsorbed species during the N_2O-CO reactions at 373 K and 423 K over the various catalysts. We could observe only adsorbed CO species during the reaction, whose intensities and peak positions were strongly dependent on the type of catalyst as well as the reaction temperature. No N-containing adsorbed species were detected over any of the catalysts investigated. In the case of Pd/SiO_2, the peak position of the linearly adsorbed CO was almost the same as that observed when only CO was introduced although the bridge peak at 1976 cm^{-1} almost disappeared as shown in (a-1) and (a-2). These results suggest that the N_2O-CO reaction takes place over the reduced Pd surface, because the dissociation of the N = O bond in the N_2O molecule may be the rate-limiting step and the subsequent reduction of adsorbed O(a) species with CO(a) will be a rapid step. On the contrary, in the case of the N_2O-CO reaction over Pd-In/SiO_2 at 373 K, the peak position of linearly adsorbed CO was 17 cm^{-1} higher that that observed when only CO was introduced on the freshly reduced catalyst. This result suggests that over Pd-In/SiO_2 the reaction may take place over the oxidized surface, which is different from the case of Pd/SiO_2. No adsorbed species were observed during the N_2O-CO reaction over Pd-Pb(1:1)/SiO_2 catalysts at 373 K as shown in spectrum (c).

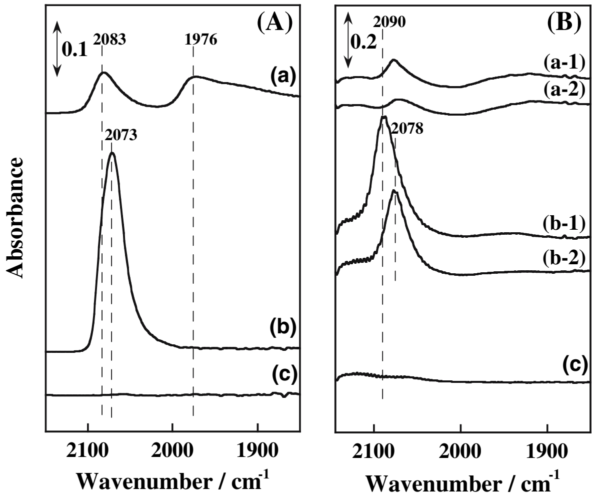

Figure 5. FT-IR spectra of adsorbed CO over reduced surfaces at room temperature (A), and during the N_2O-CO reaction over various catalysts (B). (A)-(a) Pd/SiO_2, (A)-(b) Pd-In(1:1)/SiO_2, (A)-(c) Pd-Pb(1:1)/SiO_2, (B)-(a-1) N_2O-CO reaction at 373 K over Pd/SiO_2, (a-2) at 423 K over Pd/SiO_2, (B)-(b-1) at 373 K over Pd-In(1:1)/SiO_2, (b-2) at 423 K over Pd-In(1:1)/SiO_2, (B)-(c) at 373 K over Pd-Pb(1:1)/SiO_2.

Figure 6(A) represents the FT-IR spectra of adsorbed species during CO-TPR over Pd/SiO_2 after the oxidation of the reduced surface by N_2O at room temperature(RT) and 553 K respectively. As shown in Fig.6(A)-(a), after the N_2O oxidation at RT for 2 h, the positions of adsorbed CO were at 2083 and 1976 cm^{-1} which are the same as those over the reduced catalyst (spectrum (f)). When the catalyst was oxidized by N_2O at 553 K for 2 h, the peak positions were shifted to 2105 and 1996 cm^{-1}, assignable to adsorbed CO over oxidized Pd surfaces. These results indicate that relatively higher temperatures are required for the dissociation of the N = O bond in the N_2O molecule over Pd/SiO_2 catalysts. After the evacuation of the gas phase at room temperature, the CO-TPR experiment was carried out from the room temperature, and the spectral changes are summarized in (b)–(e). The peak position of CO(a) began to shift to a lower wave number at 473 K (spectrum (d) to (e)), indicating that the reduction of O(a) by CO started at around this temperature.

The situation was completely different in the case of Pd-In/SiO_2 catalysts as shown in Fig. 6(B). As shown in spectrum (a), after the exposure of the reduced surface by N_2O at room temperature, the peak position of CO(a) was at 2091 cm^{-1}, which can be assigned to the adsorbed CO over the oxidized Pd surface. These results indicate that the dissociation of the N = O bond in the N_2O molecule takes place even at room temperature over Pd-In/SiO_2 catalysts. Moreover, the peak position of CO(a) began to shift from 2091 to 2073 cm^{-1} at around 373 K (spectrum (c)), indicating that the reduction of the oxidized surface began to take place in this temperature range. From these experimental results we can conclude that a redox cycle (oxidation of the Pd-In surface by N_2O and its reduction by CO) proceeds at much lower temperatures over the Pd-In/SiO_2 catalysts than over Pd/SiO_2 catalysts. This is likely the main reason for the dramatic enhancement effect by adding In or Pb to Pd.

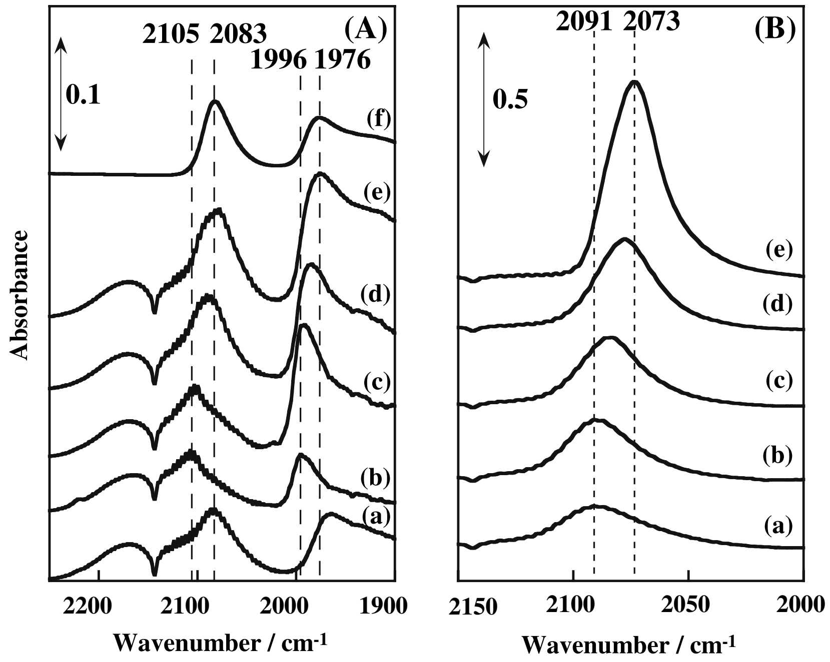

Figure 6. FT-IR spectra of adsorbed species during CO-TPR after the oxidation of the surface by N_2O at various temperatures: (A) Pd/SiO_2 and (B) Pd-In(1:1)/SiO_2. (A) over Pd/SiO_2. (a) R.T. after oxdn. at R.T., (b) R.T. after N_2O oxdn. at 553 K, (c) 373 K after oxdn. at 553 K, (d) 473 K after oxdn. at 553 K, (e) 573 K after oxdn. at 553 K, (f) CO(a) on the reduced surface at R.T. (B) over Pd-In/SiO_2. (a) R.T. after oxdn. at R.T., (b) 323 K after oxdn. at 323 K, (c) 373 K after oxdn. at 373 K, (d) 423 K after oxdn. at 423 K, (e) CO(a) on the reduced surface at R.T.

4. Conclusions

(1) Formation of intermetallic compounds was observed for both Pd-In/SiO_2 and Pd-Pb/SiO_2 catalysts, which caused the drastic enhancement of the reaction rate of N_2 formation in the N_2O-CO reaction.

(2) The infrared analyses revealed the weakening of adsorption strength of CO on Pd metal by the formation of intermetallic compounds, which is one of the main reasons for the enhancement of the reaction rate.

(3) Over the Pd/SiO_2 catalyst, the rate determining step of the N_2O-CO reaction may be the oxidation of the surface by N_2O because of the inhibition of N_2O activation by strongly adsorbed CO.

(4) Over Pd-In/SiO_2 or Pd-Pb/SiO_2 catalyst, the rate determining step may shift to the reduction of the oxidized surface, which causes a great enhancement of N_2 formation.

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