Oxidation and Reduction of the Metal Surface in Supported Pt Using Dissociative N$_2$O Adsorption Coupled with H$_2$ and CO Titration

Moon Hyeon Kim[†], M. Albert Vannice*, Gi-Dae Kim and Joo-Heon Lee

Department of Environmental, Civil and Architectural Engineering, Daegu University,
15 Naeri, Jillryang, Gyeongsan 712-714, Korea
*Department of Chemical Engineering, The Pennsylvania State University, University Park, PA 16802-4400, USA
(*Received 8 October 2002 • accepted 19 November 2002*)

Abstract—Not only was the surface site density in a 0.78% Pt/SiO$_2$ catalyst determined by using selective chemisorption techniques, but the surface chemistry related to decompositive N$_2$O adsorption on the Pt surface was also described by *in situ* DRIFTS techniques. The "O" coverage established by N$_2$O decomposition at 363 K on a clean Pt surface was equal to that *via* hydrogen adsorption at 300 K; however, both the coverage of chemisorbed oxygen *via* O$_2$ chemisorption at 300 K and the CO$_{irr}$ coverage were somewhat lower than the "O" monolayer coverage. Surface titration of the "O"-covered Pt crystallites after N$_2$O decomposition at 363 K gave a consistent Pt$_s$ density with the hydrogen chemisorption. *In situ* DRIFTS spectra of CO adsorbed at 300 K on both clean and H-covered Pt surfaces exhibited a strong peak at 2,076 cm^{-1} for linearly adsorbed CO with a small extent of multi-coordinated CO near 1,803 cm^{-1}. The adsorption of CO at 300 K on an "O"-covered Pt surface *via* dissociative N$_2$O adsorption at 363 K appeared subsequently a band at 2,186 cm^{-1} due to a tiny amount of Pt$_s$O crystallites, which could be completely reduced to H-covered ones, when titrated with H$_2$ at 300 K. The adequate description for these CO adsorption behaviors on different surfaces is Pt$_s$O+2CO$_{(g)}$→Pt$_s$CO+CO$_{2(g)}$, although to very small extent, the addition onto Pt$_s$O occurs. Spectra of CO adsorbed on the oxidized Pt$_s$ *via* N$_2$O decomposition gave consistent surface chemistry with *in situ* gravimetric measurements. The surface reactions acquired by DRIFTS spectra potentially offer an approach to remove N$_2$O from emission sources by combining its catalytic dissociation with titration of the chemisorbed "O" atoms using either H$_2$ or CO, particularly H$_2$ because of complete recovery to a clean Pt$_s$.

Key words: N$_2$O, Titration, Chemisorption, DRIFTS, Dispersion

INTRODUCTION

Metals highly dispersed on rigid solid supports are widely used to catalyze industrial petroleum and chemical reactions. A fundamental concern in these metal-catalyzed reactions is to see if catalytic activity is closely related to the surface metal density (fraction exposed) in supported metal catalysts. Among the most sensitive and reliable methods for exploring the dispersion of metals as an answer to this principal question [Sinfelt, 1975], the first priority to be considered is the selective chemisorption of probe molecules, such as H$_2$, CO and O$_2$, in which these gases are strongly chemisorbed on the metal surface but not on the support being used, and the titration of an adsorbed species using another gas molecule, like the titration of chemisorbed oxygen by H$_2$ [Benson and Boudart, 1965; Vannice et al., 1970]. Hydrogen is well-known to be accommodated dissociatively on metals, such as Pt, Pd and Rh, and the adsorption stoichiometries on surface metal atoms around 300 K are widely accepted to be near unity [Benson and Boudart, 1965; Vannice et al., 1970; Wilson and Hall, 1970; Shin et al., 2000; Song et al., 2002]; however, some cases, such as on highly dispersed Pt metals, give surface stoichiometries near 2 [Mears and Hansford, 1967; Candy et al., 1980; Humblot et al., 1998]. In the case of CO

chemisorption on metal surfaces around 300 K, the stoichiometric ratios can be dependent upon the crystal planes exposed to oncoming CO, crystallite size, and mode of adsorption (on-top vs. multi-coordinated) [Vannice and Twu, 1983; Bare et al., 1984; Hayden et al., 1985; Haaland, 1987], while the stoichiometry for adsorbed oxygen *via* O$_2$ has been reported to be lower than that for hydrogen and O/Pt$_s$ values near 0.5 are shown on very small Pt crystallites [Mears and Hansford, 1967; Humblot et al., 1998].

Not only can incomplete monolayer coverage of oxygen be formed when introducing O$_2$ onto metal surfaces, but any bulk oxidation, as with Cu, also occurs; therefore, these lead to difficulty in determining surface stoichiometries. Such an improbability additionally exists if O$_2$ can react with or adsorb on the support being used, as in the representative case of carbonaceous materials. An alternative approach to avoid and/or alleviate such problems may be the chemisorption of "O" atoms *via* the adsorptive decomposition of N$_2$O under specified conditions, as first employed by Dell et al. [1953] to characterize metallic Cu surfaces according to the following reaction,

$$2Cu_s + N_2O_{(g)} \rightarrow Cu_s\text{-O-}Cu_s + N_{2(g)}, \tag{1}$$

where the subscript s represents a surface metal atom. Subsequent evidence for the formation of only a single Cu$_2$O (designated the Cu$_s$-O-Cu$_s$ surface) layer during N$_2$O decomposition at temperatures near 373 K on unsupported and supported copper metals was provided early by Scholten and Konvalink [1969], and that surface reaction was additionally verified from a UPS study [Narita et al.,

1982]. However, adsorption stoichiometries different from that in Eq. (1) have been indicated with Ag and Ru surfaces [Seyedmonir et al., 1984; Berndt and Muller, 1999]. Under UHV conditions at low temperatures, very weak interaction of N_2O with Cu, Ni and Pt has been deduced from UHV studies for its adsorption on single crystals of Cu, Ni, Pt, Rh, Ru, and W [Fuggle and Menzel, 1979; Daniel et al., 1981; Umbach and Menzel, 1981; Kim et al., 1982; Hoffman and Hudson, 1987]. At higher temperatures, dissociative N_2O adsorption occurred on Re, Rh and CaO [Gasser and Marsay, 1970; Barker and Gasser, 1973; Shun et al., 2001] but not on Pt (111) [Avery, 1983].

Recently, we first investigated decompositive N_2O adsorption on metallic Pt surfaces at much higher temperature and pressure, *i.e.*, 363 K and 76 Torr, compared to typical UHV conditions. The monolayer coverage of chemisorbed oxygen on Pt *via* the N_2O dissociation was slightly greater than that established by O_2 chemisorption at either 300 or 363 K but the same as that obtained by H_2 chemisorption, and this oxygen was completely titratable using H_2 at 300 K. Such a surface stoichiometry of these reactions could be described successfully to be [Kim et al., 2001, 2002]:

$$Pt_s + N_2O_{(g)} \rightarrow Pt_sO + N_{2(g)}, \tag{2}$$

$$Pt_sO + 3/2H_{2(g)} \rightarrow Pt_sH + H_2O_{(ad)}. \tag{3}$$

This paper primarily focuses on O coverages established *via* the titration of the oxygen atoms, produced through Eq. (2), by either CO or H_2 and to compare them with those obtained by H_2 and CO chemisorption, thereby assuring the earlier novel method for determining a Pt dispersion value and verifying surface chemistry of the titration technique. With that information, this study inquires about subsequently potential processes for catalytic N_2O reduction by consecutive use of dissociative N_2O adsorption at low temperatures on supported Pt following the titration of the chemisorbed oxygen.

EXPERIMENTAL

SiO_2 having a surface area of 220 m^2/g (Davison 57) was ground to a 60/80 mesh size and used for preparing a supported Pt catalyst. Prior to the Pt being loaded onto the SiO_2, it was calcined at 773 K for 4 h in flowing O_2 (Korea Speciality Gases, 99.999%, and MG Ind., 99.999%) at 1.5 L/min. A 0.78% Pt/SiO_2 catalyst was obtained by an ion exchange method. The calcined SiO_2 was first brought into an NH_4OH solution with a pH value of 9.8, and then an aqueous solution of $Pt(NH_3)_4Cl_2$ (Aldrich, 99.995%) was slowly added dropwise to that mixture. The pH value of the solution-solid mixture was maintained by periodically adding dropwise the NH_4OH solution to it. Details of such procedures regarding the ion exchange technique have been described elsewhere [Benesi et al., 1968; Kim et al., 2001].

The adsorption of probe gases, such as N_2O (BOC, Medical Grade, 99.9%, and Korea Specialty Gases, Semiconductor Grade, 99.999%), H_2 (MG Ind., 99.999%, and Korea Specialty Gases, 99.999%) and CO (Matheson, 99.99%), on 0.78% Pt/SiO_2 was conducted by using a stainless steel high vacuum system, giving a dynamic vacuum below 10^{-7} Torr (1 Torr=133.3 Pa), equipped with a Balzers Type TPU 170 turbomolecular pump (Pfeiffer Vacuum Technol.) backed by an Edwards Model RV12 mechanical pump. Changes in pressure during the volumetric measurements of N_2O, H_2, and CO were detected with a differential pressure gauge (Type 270B, MKS Instr.) connected to a Baratron Type 310CA pressure sensor. A detailed description of such an adsorption system has been provided elsewhere [Na et al., 1993; Dandekar and Vannice, 1998]. Prior to introducing the light gas molecule into the volumetric system, we pretreated the catalyst *in situ* in a chemisorption cell placed in a cylindrical electric furnace using one of the two pretreatment protocols described in Table 1. All gas flow rates in the course of the pretreatment were maintained at 32 cm^3/min by using Tylan Model FC 260 mass flow controllers. All gases used were purified by passing them through commercial moisture traps and oxytraps (Alltech Asso.), except that only moisture traps were employed for N_2O, as described previously [Kim et al., 2001].

An appropriate amount, typically 0.50 to 0.70 g, of the 0.78% Pt/SiO_2 was routinely reduced by using pretreatment I, and first the hydrogen adsorption at 300 K was measured at pressures ranging from 40 to 350 Torr. The titration of oxygen (designated "O" to distinguish it from oxygen *via* O_2 chemisorption) deposited on the Pt surface *via* N_2O decomposition at 363 K was conducted, and this titration reaction is designated "H_2-N_2O titration" as earlier studies [Kim et al., 2001, 2002]. Both total and reversible uptakes for H_2 in those reactions were determined by extrapolating the linear re-

Table 1. Pretreatment protocols for 0.78% Pt/SiO_2

Pretreatment I
    (1) Heat to 673 K at a rate of 4.5 K/min and hold for 1 h in flowing He (760 Torr).
    (2) Reduce in flowing H_2 (760 Torr) for 1 h at 673 K.
    (3) Cool to 648 K in H_2.
    (4) Evacuate at 648 K for 30 min.
    (5) Cool to 300 K and continue evacuation for 1 h at 300 K.
Pretreatment II
    (1) Reheat to 648 K and hold for 15 min in flowing H_2 (760 Torr) after using pretreatment I.
    (2) Evacuate at 648 K for 30 min.
    (3) Cool to 363 K in vacuum.
    (4) Expose to 10% N_2O (76 Torr) in a He flow at 363 K for 30 min.
    (5) Evacuate at 363 K for 30 min.
    (6) Cool to 300 K and continue evacuation for 1 h at 300 K.

gions, occurring from 150 to 350 Torr, of the isotherms to P=0 to correct for adsorption on the support, as described elsewhere [Benson and Boudart, 1965; Wilson and Hall, 1970]. After the initial reduction, all other adsorption measurements at 300 K were also preceded by either pretreatment I or II. The O monolayer by adsorbing O_2 at 300 K on the Pt surface was titrated with H_2 *via* the standard titration reaction, designated as "H_2-O_2 titration," to allow comparison with the H_2-N_2O titration. Adsorption of CO at 300 K on the oxidized Pt_s *via* pretreatment II, *i.e.*, CO-N_2O titration, was conducted with subsequent measurement of CO uptakes on a clean surface. The dual isotherm technique used by Yates and Sinfelt [1967] was used to determine CO irreversibly adsorbed on the Pt surface at 300 K.

The adsorption of "O" atoms *via* N_2O decomposition at 363 K on the Pt catalyst was gravimetrically conducted by using a Perkin-Elmer TGS-2 thermogravimetric system with an instrumental sensitivity of 0.1 μg, as described earlier [Dandekar and Vannice, 1998]. An appropriate amount of the catalyst (*ca.* 7 to 20 mg) was loaded into the sample-holding pan and reduced *in situ* at 673 K for 1 h in a mixture of 30% H_2 in Ar flowing at a rate of 60 cm³/min according to pretreatment I. The catalyst after cooling to 363 K was exposed to a flowing mixture of 10% N_2O in Ar for 30 min and then a flow of pure Ar to remove N_2O reversibly accommodated on the catalyst. The net weight gain due to the "O" atoms on Pt was determined by subtracting the initial weight from the final one. Essentially the same manner as that for measuring an "O" uptake *via* the N_2O decomposition was used for CO adsorption at 300 K on the catalyst after pretreatment II to clarify surface chemistry regarding the volumetric CO-N_2O titration reaction. All gases used were purified in a fashion similar to that described above, but Ar was specially cleaned to an impurity level less than 1 ppb by passing it through an Aeronex GateKeeper purifier (Model 400 K, Supelco). Details of such gravimetric measurement procedures used here were given in our previous work [Kim et al., 2001].

A Mattson Research Series 10000 spectrophotometer, coupled with a Harrick Scientific DRA DRC (diffuse reflection cell) attaching three NaCl windows, was employed for *in situ* DRIFTS measurements. After a sample (*ca.* 100 mg) of 0.78% Pt/SiO₂ was loaded into the DRC and initially underwent pretreatment I, it was scanned at 300 K to obtain an interferogram as a background for Fourier transforming the sample spectra. Following this, a gas mixture of 10% CO (76 Torr) in Ar was passed through the cell for 30 min at 300 K and a second interferogram was taken in the presence of CO; then a final spectrum was collected after the DRC was purged with pure Ar for 30 min. The catalyst, on which oxygen had been chemisorbed by either pretreatment II or I following exposure to 10% O_2 in Ar at 300 K, underwent the procedures similar to that described above. Spectra of CO adsorbed at 300 K on either of these oxidized surfaces were compared with those for CO on these surfaces that had been exposed to 45% H_2 in an Ar flow at 300 K. Each interferogram in the presence and absence of CO at 300 K was Fourier transformed by using a background which had been collected prior to introducing the CO. All interferograms were recorded with a 4-cm⁻¹ resolution and a scan number of 1000. Details of such a DRIFTS system and spectra-collecting protocols have been provided earlier [Klingenberg and Vannice, 1999; Huang et al., 2000; Kim et al., 2001, 2002].

RESULTS

0.78% Pt/SiO₂ was subjected to pretreatment II thereby depositing the "O" atoms onto the Pt surfaces *via* dissociative N_2O adsorption at 363 K and the extent of "O" coverage of the Pt was determined by the H_2-N_2O titration; the value was around 34.1 μmol H_2/g, as shown in Table 2. CO_{irr} coverage *via* the volumetric CO-N_2O titration was 23.3 μmol/g and increased significantly compared to that on the reduced Pt_s, as listed in Table 2. The conventional H_2 titration value for oxygen chemisorbed *via* O_2 adsorption at 300 K is also included to compare with that established from the H_2-N_2O titration. The total hydrogen uptake on this Pt catalyst was 11.5 μmol

Table 2. Adsorption of N₂O at 363 K and H₂, O₂ and CO at 300 K on 0.78% Pt/SiO₂

Pretreatment	Gas uptake (μmol/g)								Surface site density[a]				Crystallite size, d_p (nm)[b]
	Volumetric						Gravimetric		$\dfrac{H_{tot}}{Pt_{tot}}$	$\dfrac{O_{tot}}{Pt_{tot}}$	$\dfrac{CO_{irr}}{Pt_{tot}}$	$\dfrac{"O"_{irr}}{Pt_{tot}}$	
	H₂-N₂O titr.	H₂	O₂[c]	CO	H₂-O₂ titr.	CO-N₂O titr.	"O"[d]	CO-N₂O titr.					
	Tot.	Tot.	Tot.	Irr.	Tot.	Irr.	Irr.	Irr.					
II	34.1								0.57				2.0
I		11.5							0.58				2.0
I			10.4							0.52			2.2
I				17.6							0.44		2.6
I					31.9				0.53				2.1
I							23.6					0.59	1.9
II						23.3					0.58		2.0
I								25.4			0.63		1.8

Note. No CO_{irr} uptake on bare SiO₂ after any pretreatment.

[a]Assuming H/Pt_s=O/Pt_s=CO/Pt_s=1.

[b]Assuming d_p (nm)=1.13/D, where D is H_{tot}/Pt_{tot}, O_{tot}/Pt_{tot}, CO_{irr}/Pt_{tot}, or "O"_{irr}/Pt_s.

[c]No reversible adsorption.

[d]"O" uptake *via* dissociative N₂O adsorption at 363 K.
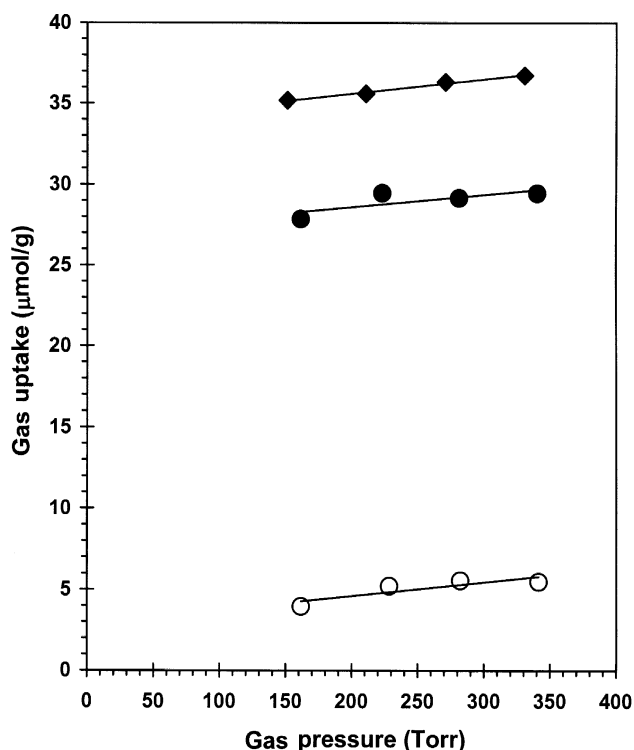
Fig. 1. Titration isotherms on 0.78% Pt/SiO₂ after pretreatment II: (●, ○) CO-N₂O titration; (◆) H₂-N₂O titration. Open and closed symbols are the respective total and reversible uptakes at 300 K.
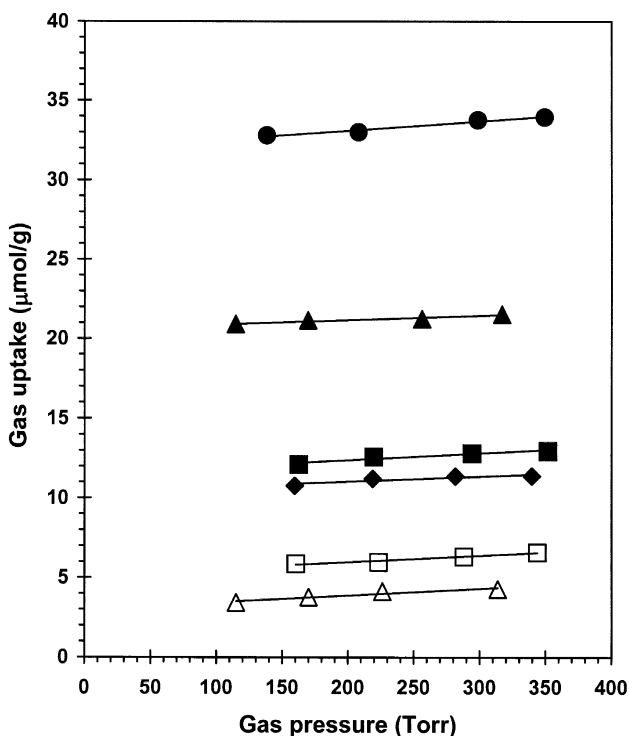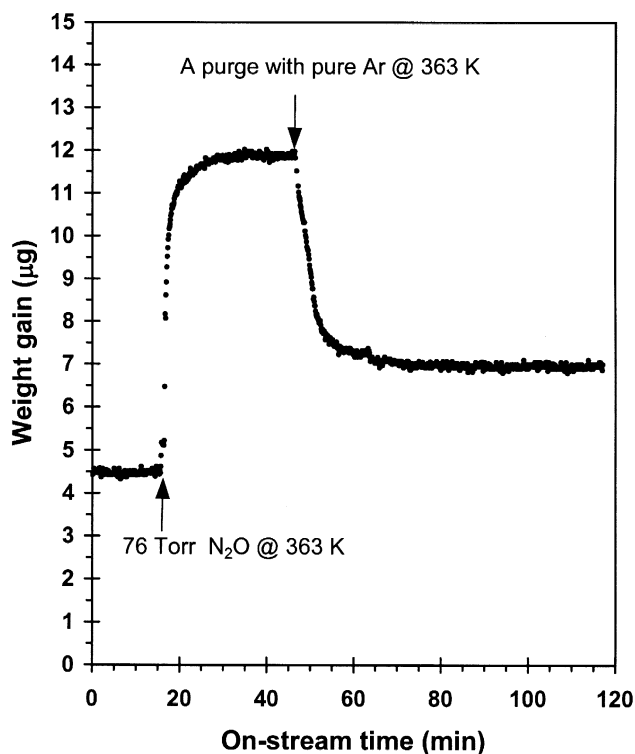

Fig. 3. Gravimetric measurement for dissociative N₂O adsorption at 363 K on 0.78% Pt/SiO₂ reduced at 673 K.

H₂/g. Uptake values were very reproducible even with different samples and there was no difference in gas uptakes between repeatedly-pretreated and single-pretreated sample, which consistently agrees with previous results [Kim et al., 2001]. A typical set of isotherms is shown in Figs. 1 and 2.

The extent of "O" deposition on 0.78% Pt/SiO₂ via N₂O decomposition at 363 K was gravimetrically determined. For this, the catalyst sample was subjected to pretreatment II in the gravimetric system. A measurable weight change appeared when 10% N₂O was additionally introduced in a flow of pure Ar, as shown in Fig. 3. The net weight gain due to the "O" coverages on the Pt surface was 2.6 μg, corresponding to an "O" uptake value of 23.6 μmol/g when using Eq. (2). The gravimetric measurement of CO uptake at 300 K on the Pt following N₂O decomposition at 363 K gave about 5.8 μg, as seen in Fig. 4, that can be an estimate of 25.4 μmol CO_{irr}/g with an assumption of complete titration of "O" atoms on Pt_s by CO at 300 K. No accommodation of atomic oxygen via N₂O decomposition at 363 K was found with bare SiO₂ in an earlier gravimetric measurement [Kim et al., 2001]. Adsorption of CO at 300 K on pure SiO₂ clearly obeyed Henry's Law, with no CO_{irr} adsorption occurring and less than 1 μmol/g of total uptake at 300 Torr CO and 300 K [Kim et al., 2001]. In addition, there were no appreciable Pt peaks in an XRD measurement with the catalyst that had been pretreated by using the same protocols as that employed for the adsorption measurements.

In situ DRIFTS spectra taken after CO adsorption at 300 K on an "O"-covered surface obtained *via* N₂O decomposition at 363 K on 0.78% Pt/SiO₂ using pretreatment II are shown as a function of exposure time in Fig. 5. After a 0.5-min exposure in flowing 10% CO (76 Torr) in Ar at 300 K, peaks at 2,487, 2,341, 2,186 and 1,827
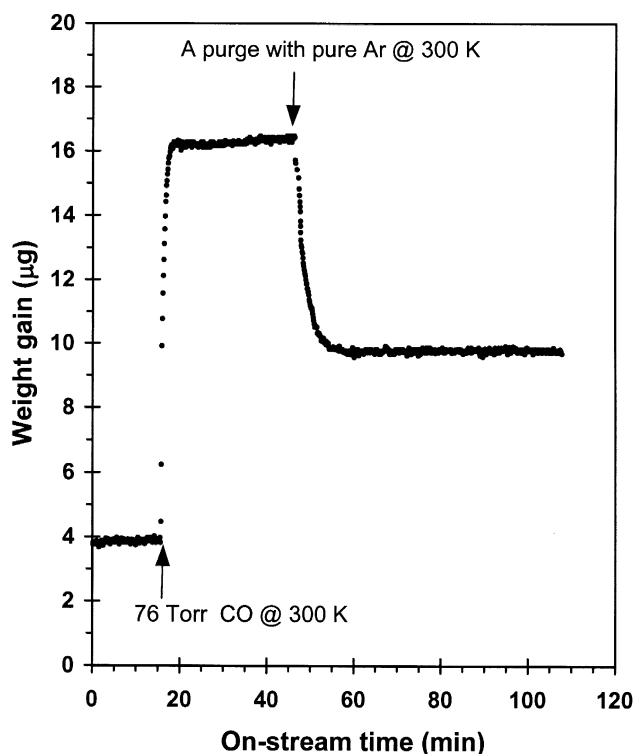

Fig. 2. Adsorption isotherms on 0.78% Pt/SiO₂ after pretreatment I: (■, □) H₂ adsorption; (▲, △) CO adsorption; (◆) O₂ adsorption; (●) H₂-O₂ titration. Open and closed symbols are the respective total and reversible uptakes at 300 K.

Fig. 4. Gravimetric measurement for CO adsorption at 300 K on 0.78% Pt/SiO₂ following pretreatment II.

Fig. 6. *In situ* DRIFTS spectra of CO adsorbed at 300 K on 0.78% Pt/SiO₂ after different pretreatments and a purge with Ar: (a) after pretreatment I; (b) after pretreatment II following H₂ titration at 300 K by flowing 45% H₂ (340 Torr) in Ar.
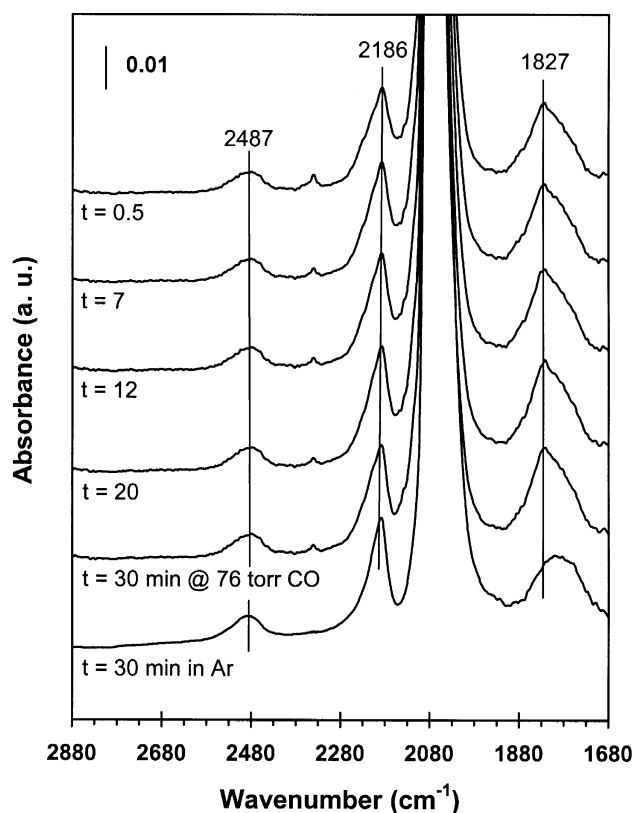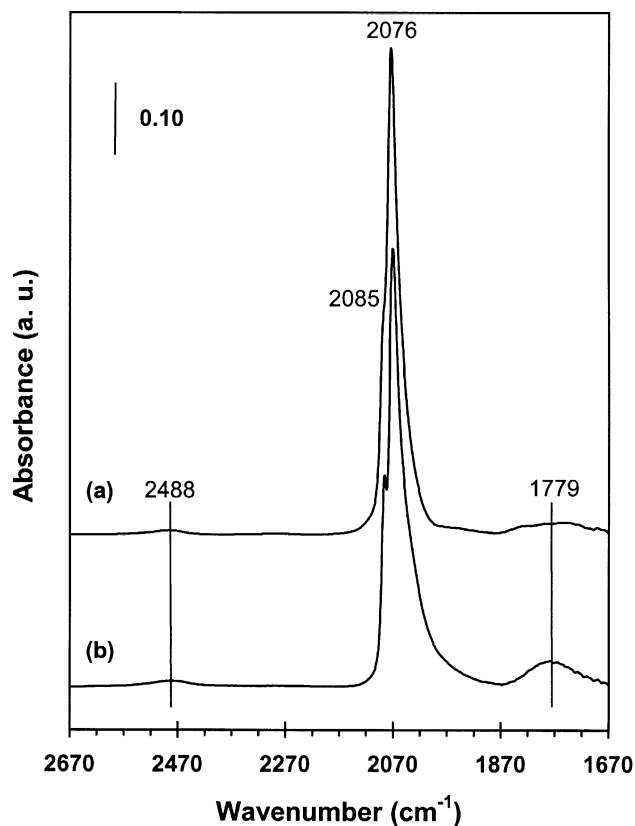

Fig. 5. *In situ* DRIFTS spectra of CO adsorbed at 300 K on 0.78% Pt/SiO₂ after pretreatment II. Spectra were taken both as a function of exposure time under a pressure of 76 Torr CO and after a 30-min purge with Ar.

cm^{-1} appeared along with a predominant band at 2,076 cm^{-1} and a weak shoulder at 2,091 cm^{-1}. The latter two bands are not apparently marked in Fig. 5, because of magnification of less intense peaks; however, their position is quite similar to that given later in Fig. 6. All bands were unchanged in their position and intensity after an exposure of 30 min, except for the 2,341 cm^{-1} peak that decreased with time. A 30-min purge with pure Ar at 300 K retained all bands but that at 2,341 cm^{-1} and caused downwards shift of the 1,827 to 1,815 cm^{-1}; therefore, the principal difference in these spectra is the dependence of the 2,341 cm^{-1} band intensity on time as well as its disappearance with the Ar purge. No peaks were detected with pure SiO₂ [Kim et al., 2002]. These time-dependent spectra indicate that the "O" atoms established by dissociative N₂O adsorption at 363 K can react with gas-phase CO during the titration, although a very small amount of Pt_xO species is still left on the Pt surface. It is of particular interest to note that these spectra are very similar to that taken with a reduced sample following O₂ chemisorption at 300 K.

Spectra of CO adsorbed on 0.78% Pt/SiO₂ after different pretreatments are provided in Fig. 6. Adsorption of CO at 300 K on a clean Pt surface after pretreatment I gave, when purged with a flow of pure Ar, a very strong peak at 2,076 cm^{-1} with a shoulder at 2,085 cm^{-1} and weak bands near 2,488 and 1,779 cm^{-1}, as shown in Fig. 6(a). After the sample was exposed to 76 Torr N₂O at 363 K and titrated with a flow of 45% H₂ in Ar at 300 K, exposure to 10% CO in an Ar flow following a 30-min purge with pure Ar at 300 K ex-

hibited bands at 2,486, 2,086, 2,073 and 1,778 cm^{-1}, as shown in Fig. 6(b). No peak near 2,185 cm^{-1} was indicated with the clean and H-covered Pt surface. The principal distinctive point between spectra (a) and (b) is that not only could the band around 1,779 cm^{-1} be enhanced with the H-covered surface, but the 2,085 cm^{-1} band for bridging CO on Pt$_s$ was also indicated more clearly. However, the spectrum for CO adsorbed on the Pt surface after H$_2$ titration of the oxygen chemisorbed at 363 K represents that all chemisorbed oxygen could be removed and H$_2$ titration using N$_2$O can successfully evaluate the surface metal density in this supported Pt catalyst.

DISCUSSION

Variation in adsorption stoichiometries of gas molecules on metal surfaces is closely related to the coordination environments that are of particular interest to be mainly discussed in this paper. Coverages of hydrogen on large Pt crystallites are widely accepted to be H/Pt$_s$ stoichiometries near unity [Vannice et al., 1970; Freel, 1972], while H/Pt$_s$ values greater than one have been reported for very small Pt particles highly dispersed on a variety of supports [Mears and Hansford, 1967; Freel, 1972; Candy et al., 1980; Humblot et al., 1998]. The latter behavior has been explained by inquiring hydrogen spillover, metal-support interactions, and low coordination metal sites. Near 300 K, both oxygen and CO monolayer coverages are consistently lower than that for hydrogen [Freel, 1972; Frennet and Wells, 1985; Wells, 1985]. Incomplete saturation of oxygen, compared to hydrogen, is primarily due to an immobile monolayer formation and/or a lower adsorption capacity on very small Pt crystallites and clusters [Vannice et al., 1970; Wilson and Hall, 1970]. Not only could CO coverages on metal surfaces depend on the crystal plane and mode of its accommodation, but adsorbate-induced rearrangements, i.e., surface reconstruction, also create the complicity of surface stoichiometries in CO adsorption [Barteau et al., 1981; Behm et al., 1983].

Keeping in mind these adsorption phenomena depending on metal surface structures, a main focus in this paper is the relationship between surface chemistry and surface stoichiometries of the titration reactions on Pt$_s$ having different surface coordination. The probe gas uptakes on the 0.78% Pt/SiO$_2$ catalyst give very consistent results with previous studies. The Pt dispersion indicated is in the range of 0.52 to 0.59, corresponding to crystallite sizes of 1.9 to 2.1 nm by using the correlation, d$_p$ (nm)=1.13/D, given in Table 2. It may be very difficult to be distinguished easily from the background of silica itself by XRD, which is consistent with our measurements. The O and CO$_{irr}$ coverages are lower than that based on total H atoms established via H$_2$ adsorption at 300 K. This would be due to the formation of bridged-bonded O and CO$_{irr}$ on Pt$_s$ sites. One half of the coverage based on the total hydrogen uptake is reversible, in good agreement with previous studies of Pt dispersed on SiO$_2$ and Al$_2$O$_3$ [Palmer and Vannice, 1980; Sen and Vannice, 1991]. The "O" coverage value at 300 K, whether determined volumetrically or gravimetrically, is essentially equal to the H$_{tot}$ coverage, indicating the occurrence of Eq. (2) during N$_2$O decomposition at 363 K, thereby forming a saturated "O" monolayer that could be stoichiometrically titratable using hydrogen at 300 K as described by Eq. (3), which is consistent with the earlier discussion with a 0.81% Pt/SiO$_2$ [Kim et al., 2001]. The titration reaction of "O" atoms via N$_2$O decom-

position at 363 K consistently gives an oxygen monolayer formation greater than that formed by O$_2$ chemisorption at 300 K. Such a major difference in surface chemistry of oxygen chemisorption via N$_2$O and O$_2$ could result from the site pair requirement for immobile oxygen dissociation which does not exist for N$_2$O; therefore, the volumetric oxidation and reduction of the Pt surfaces via the CO-N$_2$O titration reaction gives readily consistent coverages with the earlier H$_2$-N$_2$O titration technique. This surface reaction, combined consecutively with Eq. (2), is expected to be a stoichiometry of:

$$Pt_sO + 2CO_{(g)} \rightarrow Pt_sCO + CO_{2(g)}. \tag{4}$$

The titration reaction, when measured gravimetrically with a given sample size, predicts a weight gain of 5.2 μg if only Eq. (4) occurs, and the extent of CO irreversibly adsorbed on Pt$_s$ after N$_2$O decomposition at 363 K is somewhat greater than that acquired by the volumetric CO-N$_2$O titration. This indicates that the following process during CO adsorption on the "O"-covered surfaces could also occur:

$$Pt_sO + CO_{(g)} \rightarrow Pt_sO\text{-}CO. \tag{5}$$

If it is assumed for only a single reaction given in Eq. (5) to be probable, the net weight gain expected is shown to be ca. 12.2 μg; therefore, Eq. (4) is predominant in the course of the titration. In either case, the net change in volume is a CO$_{ad}$/Pt$_s$ ratio of unity because of no significant adsorption of CO$_2$ produced. Consequently, the consecutive use of the chemisorption of oxygen via the decomposition of N$_2$O on Pt$_s$ following CO titration is an alternative approach to evaluate the Pt dispersion, in addition to the earlier H$_2$-N$_2$O titration technique.

Prior to using this supported Pt for catalytically reducing N$_2$O by either H$_2$ or CO at low temperatures, surface-oriented information regarding the titration reaction of chemisorbed oxygen with the gas molecule at 300 K could be successfully induced from DRIFTS spectra of CO on both clean (reduced and evacuated) and "O"-covered Pt surfaces. Based on earlier IR and EELS studies of CO adsorption on reduced Pt surfaces [Eischens et al., 1954; Shigeishi and King, 1976; Froitzheim et al., 1977; Bare et al., 1984; Barshad et al., 1985; Greenler et al., 1985; Hayden et al., 1985; Wells, 1985; Haaland, 1987; Gardner et al., 1990; Solymosi and Knozinger, 1990; Liotta et al., 1996; Hadjiivanov, 1998; Kim et al., 2001], the CO absorption bands, i.e., 2,486±2, 2,341, 2,186, 2,088±3, 2,076 and 1,803±24 cm^{-1}, observed in the presence and absence of CO at 300 K (Figs. 5 and 6) can be assigned. The peak near 2,486 cm^{-1} band is assigned to be a combination mode of C-O and Pt$_s$-C symmetric stretching vibrations in on-top Pt$_s$-CO species [Bare et al., 1984]. The band near 2,341 cm^{-1} results from a very weak interaction between CO$_2$, created during reduction of the oxygen-covered Pt surface by gas-phase CO, and SiO$_2$ [Solymosi and Knozinger, 1990; Liotta et al., 1996]. The 2,186 cm^{-1} band represents CO adsorbed on oxidized Pt surface sites [Barshad et al., 1985; Balakrishnan et al., 1990; Hadjiivanov, 1998]. The 2,088 and 2,076 cm^{-1} bands indicate linearly adsorbed CO on metallic Pt$_s$ atoms having different coordination numbers, while the band around 1,803 cm^{-1} corresponds to multi-coordinated (bridge-bonded) CO on metallic Pt$_s$ [Eischens and Pliskin, 1958; Greenler et al., 1985; Hayden et al., 1985; Venus et al., 1988; Gardner et al., 1990].

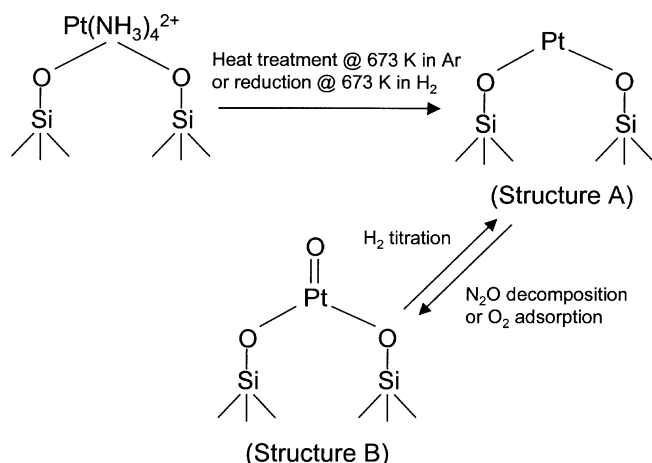CO adsorption at 300 K on an "O"-covered Pt surface (Fig. 5)

Fig. 7. Model structure of Pt$_x$ species isolated onto the silica surface.

obtained *via* N₂O decomposition at 363 K exhibits infrared spectra quite similar to that reported for CO on a variety of silica-supported Pt samples, representatively EUROPT-1 [Wells, 1985] and 0.81% Pt/SiO₂ [Kim et al., 2001]. Only exception to the spectra of CO adsorbed on the oxidized surface is no complete reduction of some Pt surface atoms by gas-phase CO at 300 K, as is evident from the presence of the 2,186 cm^{-1} band. This immediately supports our gravimetric results for CO-N₂O titration reaction that to a very small extent, Eq. (5) occurs subsequently. Introduction of H₂ at 300 K onto this surface readily removes all the surface "O" atoms, thereby completely disappearing the 2,186 cm^{-1} peak and accompanying an increase in intensity of the 2,086 cm^{-1} shoulder as seen in Fig. 6(b). Such behaviors in CO adsorption at 300 K on the oxygen- and hydrogen-covered Pt surfaces suggest that very small amounts of Pt are atomically isolated on the silica surface [Kim and Vannice, 2002], which can be well modeled by the structures shown in Fig. 7. The titration of the oxidized surface at 300 K by H₂ increases the extent of bridge-bonded CO because of an enhancement in a roughened Pt surface. These results indicate that the adsorption of CO at 300 K on an "O"-covered Pt surface *via* N₂O decomposition at 363 K can be adequately described by Eq. (4). Consequently, the surface chemistry represented by Eqs. (2), (4) and (5) is very consistent with our results, acquired from *in situ* DRIFTS and gravimetric measurement techniques, and can be particularly useful to count surface site density in supported Pt catalysts, such as Pt-only and bimetallic Pt-Cu crystallites, when any H spillover occurs. Subsequently, the decomposition of N₂O at low temperatures on a reduced Pt surface, coupled with either Eq. (3) or (4), may be expected to be used to reduce N₂O, which contributes to the overall global warming by 9%, from stationary emission sources; such a potential use of this catalytic process is in progress in another part of this program.

CONCLUSIONS

N₂O is readily dissociated on Pt surfaces at 363 K and pressures around 76 Torr, thereby forming saturated monolayer coverage of chemisorbed oxygen. These "O" atoms accommodated on the surface metals could be completely titrated by CO at 300 K, as by H₂ proposed earlier; thus, these surface reactions are adequately described

by using Eq. (4). The "O" coverage on a 0.78% Pt/SiO₂ catalyst was the same as that established by hydrogen chemisorption at 300 K. H-covered Pt surfaces *via* the hydrogen adsorption at 300 K after N₂O decomposition at 363 K gave the strong linearly-adsorbed CO band at 2,076 cm^{-1} with the weak bridge-bonded CO peak near 1,779 cm^{-1} and this spectrum was quite similar to that established with a clean surface, very consistent with the H₂-N₂O titration reaction. Exposure of "O"-covered Pt surfaces, obtained *via* N₂O decomposition at 363 K, to CO at 300 K and 76 Torr would almost remove the "O" monolayer coverages as indicated by a time-dependent band at 2,341 cm^{-1} due to CO₂ very weakly held on the silica support. A surface model based on the volumetric and gravimetric consecutive titrations is in excellent agreement with *in situ* DRIFTS spectra of CO adsorbed on Pt$_x$. Consequently, the CO-N₂O titration reaction offers an alternative technique to determine a surface site density in supported Pt, and the surface chemistry regarding the H₂- and CO-N₂O titration may be a clue to catalytically reduce N₂O at low temperatures.

REFERENCES

Avery, N. R., "An EELS Study of N₂O Adsorption on Pt (111)," *Surf. Sci.*, **131**, 501 (1983).

Balakrishnan, K., Sachdev, A. and Schwank, J., "Chemisorption and FTIR Study of Bimetallic Pt-Au/SiO₂ Catalysts," *J. Catal.*, **121**, 441 (1990).

Bare, S. R., Hofman, P. and King, D. A., "Vibrational Studies of the Surface Phases of CO on Pt {110} at 300 K," *Surf. Sci.*, **144**, 347 (1984).

Barker, F. G. and Gasser, R. P. H., "The Reaction of Nitrous Oxide with Rhodium," *Surf. Sci.*, **39**, 136 (1973).

Barshad, Y., Zhou, X. and Gulari, E., "Carbon Monoxide Oxidation under Transient Conditions: A Fourier-Transform Infrared Transmission Spectroscopy Study," *J. Catal.*, **94**, 128 (1985).

Barteau, M. A., Ko, E. I. and Madix, R. J., "The Adsorption of CO, O₂, and H₂ on Pt (100)-(5 x 20)," *Surf. Sci.*, **102**, 99 (1981).

Behm, R. J., Thiel, P. A., Norton, P. R. and Ertl, G., "The Interaction of CO and Pt (100). I. Mechanism of Adsorption and Pt Phase Transition," *J. Chem. Phys.*, **78**, 7437 (1983).

Benesi, H. A., Curtis, R. M. and Studer, H. P., "Preparation of Highly Dispersed Catalytic Metals: Platinum Supported on Silica Gel," *J. Catal.*, **10**, 328 (1968).

Benson, J. E. and Boudart, M., "Hydrogen-Oxygen Titration Method for the Measurement of Supported Platinum Surface Area," *J. Catal.*, **4**, 704 (1965).

Berndt, H. and Muller, U., "Determination of the Surface Area of Dispersed Ruthenium by Reactive Nitrous Oxide Chemisorption," *Appl. Catal. A*, **180**, 63 (1999).

Candy, J.-P., Fouilloux, P. and Renouprez, "Hydrogen Adsorption on Platinum Catalysts: Quantitative Determination of the Various Species Population," *J. Chem. Soc., Faraday I*, **76**, 616 (1980).

Dandekar, A. and Vannice, M. A., "Determination of the Dispersion and Surface Oxidation States of Supported Cu Catalysts," *J. Catal.*, **178**,

621 (1998).

Daniel, W. M., Kim, Y., Peebles, H. C. and White, J. M., "Adsorption of Ag, O_2 and N_2O on Ag/Rh (100)," *Surf. Sci.*, **111**, 189 (1981).

Dell, R. M., Stone, F. S. and Tiley, P. F., "The Adsorption of Oxygen and Other Gases on Copper," *Trans. Faraday Soc.*, **49**, 195 (1953).

Eischens, R. P. and Pliskin, W. A., "The Infrared Spectra of Adsorbed Molecules," *Adv. Catal.*, **10**, 1 (1958).

Eischens, R. P., Pliskin, W. A. and Francis, S. A., "Infrared Spectra of Chemisorbed Carbon Monoxide," *J. Chem. Phys.*, **22**, 1786 (1954).

Freel, J., "Chemisorption on Supported Platinum. II. Stoichiometry for Hydrogen, Oxygen and Carbon Monoxide," *J. Catal.*, **25**, 149 (1972).

Frennet, A. and Wells, P. B., "Characterization of the Standard Platinum/Silica Catalyst EUROPT-1. 4. Chemisorption of Hydrogen," *Appl. Catal.*, **18**, 243 (1985).

Froitzheim, H., Hopster, H., Ibach, H. and Lehwald, S., "Adsorption Sites of CO on Pt (111)," *Appl. Phys.*, **13**, 147 (1977).

Fuggle, J. C. and Menzel, D., "XPS, UPS and XAES Studies of the Adsorption of Nitrogen, Oxygen, and Nitrogen oxides on W (110) at 300 and 100 K. I. Adsorption of N_2, N_2O and NO_2/N_2O_4," *Surf. Sci.*, **79**, 1 (1979).

Gardner, P., Martin, R., Tushaus, M. and Bradshaw, A. M., "The Adsorbate-Inducing Lifting of the Pt {100} Surface Reconstruction: IRAS Investigations," *J. Electron Spectrosc. Rel. Phen.*, **54/55**, 619 (1990).

Gasser, R. P. H. and Marsay, C. J., "The Chemisorption of Nitrous Oxide at Low Temperatures by Rhenium," *Surf. Sci.*, **20**, 116 (1970).

Greenler, R. G., Burch, K. D., Kretschmar, K., Klauser, R., Bradshaw, A. M. and Hayden, B. E., "Stepped Single-Crystal Surfaces as Models for Small Catalyst Particles," *Surf. Sci.*, **152/153**, 338 (1985).

Haaland, D. M., "Infrared Studies of CO Adsorbed on Pt/Al_2O_3: Evidence for CO Bonded in 3-Fold Coordination," *Surf. Sci.*, **185**, 1 (1987).

Hadjiivanov, K., "IR Study of CO and H_2O Coadsorption on Pt^{n+}/TiO_2 and Pt/TiO_2 Samples," *J. Chem. Soc.*, *Faraday Trans.*, **94**, 1901 (1998).

Hayden, B. E., Kretschmar, K., Bradshaw, A. M. and Greenler, R. G., "An Infrared Study of the Adsorption of CO on a Stepped Platinum Surface," *Surf. Sci.*, **149**, 394 (1985).

Hoffman, D. A. and Hudson, J. B., "The Adsorption and Decomposition of N_2O on Nickel (100)," *Surf. Sci.*, **180**, 77 (1987).

Huang, S.-J., Walters, A. B. and Vannice, M. A., "Adsorption and Decomposition of NO on Lanthanum Oxide," *J. Catal.*, **192**, 29 (2000).

Humblot, F., Didillon, B., Kepeltier, F., Candy, J. P., Corker, J., Clause, O., Bayard, F. and Basset, J. M., "Surface Organometallic Chemistry on Metals: Formation of a Stable≡Sn(*n*-C_4H_9) Fragment as a Precursor of Surface Alloy Obtained by Stepwise Hydrogenolysis of Sn(*n*-$C_4H_9)_4$ on a Platinum Particle Supported on Silica," *J. Am. Chem. Soc.*, **120**, 137 (1998).

Kim, M. H., Ebner, J. R., Friedman, R. M. and Vannice, M. A., "Determination of Metal Dispersion and Surface Composition in Supported Cu-Pt Catalysts," *J. Catal.*, **208**, 381 (2002).

Kim, M. H., Ebner, J. R., Friedman, R. M. and Vannice, M. A., "Dissociative N_2O Adsorption on Supported Pt," *J. Catal.*, **204**, 348 (2001).

Kim, M. H. and Vannice, M. A., "Reaction of Chemisorbed Oxygen *via* N_2O Decomposition on Supported Pt Catalyst with CO," to be submitted for publication.

Kim, Y., Schriefels, J. A. and White, J. M., "Adsorption of N_2O on Ru

(001)," *Surf. Sci.*, **114**, 349 (1982) and references therein.

Klingenberg, B. and Vannice, M. A., "NO Adsorption and Decomposition on La_2O_3 Studied by DRIFTS," *Appl. Catal. B*, **21**, 19 (1999).

Liotta, L. F., Martin, G. A. and Deganello, G., "The Influence of Alkali Metal Ions in the Chemisorption of CO and CO_2 on Supported Palladium Catalysts: A Fourier Transform Infrared Spectroscopic Study," *J. Catal.*, **164**, 322 (1996).

Mears, D. E. and Hansford, R. C., "The Stoichiometry for Hydrogen Titration of Oxygen on Supported Platinum," *J. Catal.*, **9**, 125 (1967).

Na, B.-K., Walters, A. B. and Vannice, M. A., "Studies of Gas Adsorption on ZnO Using ESR, FTIR Spectroscopy, and MHE (Microwave Hall Effect) Measurements," *J. Catal.*, **140**, 585 (1993).

Narita, K., Takezawa, N., Kobayashi, H. and Toyoshima, I., "Adsorption of Nitrous Oxide on Metallic Copper Catalysts," *React. Kinet. Catal. Lett.*, **19**, 91 (1982).

Palmer, M. B. and Vannice, M. A., "The Effect of Preparation Variables on the Dispersion of Supported Platinum Catalysts," *J. Chem. Tech. Biotechnol.*, **30**, 205 (1980).

Scholten, J. J. F. and Konvalinka, J. A., "Reaction of Nitrous Oxide with Copper Surfaces: Application to the Determination of Free-Copper Surface Areas," *Trans. Faraday Soc.*, **65**, 2465 (1969).

Sen, B. and Vannice, M. A., "The Influence of Platinum Crystallite Size on H_2 and CO Heat of Adsorption and CO Hydrogenation," *J. Catal.*, **130**, 9 (1991).

Seyedmonir, S. R., Strohmayer, D. E., Geoffroy, G. L., Vannice, M. A., Young, H. W. and Linowski, J. W., "Characterization of Supported Silver Catalysts. I. Adsorption of O_2, H_2, N_2O, and the H_2-Titration of Adsorbed Oxygen on Well-Dispersed Ag on TiO_2," *J. Catal.*, **87**, 424 (1984).

Shigeishi, R. A. and King, D. A., "Chemisorption of Carbon Monoxide on Platinum {111}: Reflection-Absorption Infrared Spectroscopy," *Surf. Sci.*, **58**, 379 (1976).

Shin, E. W., Cho, S.-I., Kang, J. H., Kim, W. J., Park, J. D. and Moon, S. H., "Palladium-Hydrogen Interaction on Supported Palladium Catalysts of Different Metal Dispersions," *Korean J. Chem. Eng.*, **17**, 468 (2000).

Shun, D., Chang, H. S., Park, Y. S., Bae, D.-H. and Jin, G. T., "A Study of Nitrous Oxide Decomposition over Calcium Oxide," *Korean J. Chem. Eng.*, **18**, 630 (2001).

Sinfelt, J. H., "Heterogeneous Catalysis by Metals," *Prog. Solid State Chem.*, **10**, 55 (1975).

Solymosi, F. and Knozinger, H., "Infrared Spectroscopic Study of the Adsorption and Reactions of CO_2 on K-Modified Ph/SiO_2," *J. Catal.*, **122**, 166 (1990).

Song, J. H., Seo, K. W., Mok, Y. I., Park, K. Y. and Ahn, B. S., "Catalytic Hydrogenolysis of CFC-12 (CCl_2F_2) over Bimetallic Palladium Catalysts Supported on Activated Carbon," *Korean J. Chem. Eng.*, **19**, 246 (2002).

Umbach, E. and Menzel, D., "Horizontal and Vertical Configurations of Molecular N_2O on W (110) and Ru (001)," *Chem. Phys. Lett.*, **84**, 491 (1981).

Vannice, M. A., Benson, J. E. and Boudart, M., "Determination of Surface Area by Chemisorption: Unsupported Platinum," *J. Catal.*, **16**, 348 (1970).

Vannice, M. A. and Twu, C. C., "SMSI Effects on CO Adsorption and Hydrogenation on Pt Catalysts. Part II. Influence of Support and Crystallite Size on the Kinetics of Methanation," *J. Catal.*, **82**, 213

(1983).

Venus, D., Hensley, D. A. and Kesmodel, L. L., "High Resolution EELS Measurements of CO Adsorption on Pt/SiO$_2$ Model Catalysts *via* Impact Scattering," *Surf. Sci*., **199**, 391 (1988).

Weinberg, W. H., "A Model Description of the Adsorption and Decomposition of Nitrous Oxide on Clean and Carbon-Covered Platinum Surfaces," *J. Catal*., **28**, 459 (1973).

Wells, P. B., "Characterization of the Standard Platinum/Silica Catalyst EUROPT-1. 5. Chemisorption of Carbon Monoxide and of Oxygen," *Appl. Catal*., **18**, 259 (1985).

Wilson, G. R. and Hall, W. K., "Studies of the Hydrogen Held by Solids. XVIII. Hydrogen and Oxygen Chemisorption on Alumina- and Zeolite-Supported Platinum," *J. Catal*., **17**, 190 (1970).

Yates, D. J. C. and Sinfelt, J. H., "The Catalytic Activity of Rhodium in Relation to Its State of Dispersion," *J. Catal*., **8**, 348 (1967).