담지 Pt 촉매의 분산도 결정을 위한 새로운 기법

김문현, M. Albert Vannice*, 이주헌
대구대학교 건설환경공학부, 펜실베이니아 주립 대학교 화학공학과*

A Novel Titration Technique for Determination of Surface Metal Density in Supported Pt Catalyst

Moon Hyeon Kim, M. Albert Vannice*, Joo-Heon Lee
Department of Architectural, Civil and Environmental Engineering, Daegu University,
Department of Chemical Engineering, The Pennsylvania State University*

INTRODUCTION

A fundamental concern in metal-catalyzed industrial petroleum and chemical reactions is the surface density of the metal in supported catalysts; consequently, the number of surface metal atoms needs to be determined to provide an answer to this important question. The most sensitive and reliable methods for obtaining the dispersion of metals involve 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, and another technique is the titration of an adsorbed species using another gas molecule, as in the case of the titration of adsorbed oxygen by H_2 [1].

One approach to alleviate and avoid incomplete monolayer formation by immobile dissociative O_2 adsorption as well as bulk oxidation is the chemisorption of O atoms *via* the dissociative adsorption of N_2O under specified conditions, as first employed by Stone and coworkers to characterize metallic Cu surfaces [2]. UHV studies of N_2O on single crystals of Cu, Ni, Pt, Rh, Ru, and W have been conducted, and N_2O was found to adsorb very weakly on Cu, Ni and Pt at low temperatures. At higher temperatures, dissociative N_2O adsorption occurred on Re and Rh filaments, but Avery found no dissociation of N_2O on Pt (111) surface [3].

Although N_2O decomposition kinetics have been examined on Pt filaments and wires, we could find no studies of dissociative N_2O adsorption on Pt at higher temperatures and pressures; therefore, this study was devoted to measure O coverages established by N_2O decomposition and to compare them with those obtained by the chemisorption of O_2, H_2, and CO. This approach will lead to other ways to determine Pt dispersion (fraction exposed), once the adsorption stoichiometry for oxygen on Pt *via* this reaction is known.

EXPERIMENTAL

SiO_2 (Davison 57, 220 m^2/g) was ground to a 60/80 mesh and calcined at 773 K for 4 h in flowing O_2 at 1.5 L/min. Silica-supported Pt catalyst containing 0.78% Pt was obtained by an ion exchange method. A stainless steel high vacuum system giving a dynamic vacuum below 10^{-7} Torr was used for the adsorption and titration of probe molecules on the catalyst. Gravimetric measurements of the adsorption of O atoms *via* N_2O decomposition at 363 K on 0.78% Pt/SiO_2 catalyst were conducted using a Perkin-Elmer TGS-2 thermogravimetric system with an instrumental sensitivity of 0.1 µg. Details of such a catalyst preparation and system have been given elsewhere [4]. All catalysts were pretreated *in situ* in a chemisorption using one of the procedures: Pretreatment I, reduction at 673K for 1 h in flowing H_2, and Pretreatment II, adsorptive decomposition of N_2O at 363K on the reduced sample. Before using all gases, Ar, H_2, O_2 (MG Ind., 99.999%), CO (Matheson, 99.99%) and N_2O (BOC, Medical Grade, 99.9%) were purified by flowing them through moisture traps and Oxytraps (Alltech Asso.); however, Ar used for gravimetric system was specially cleaned to an impurity level less than 1 ppb using an Aeronex GateKeeper purifier (Model 400 K, Supelco).

In situ DRIFTS studies were conducted using a Mattson Research Series 10000 spectrometer coupled with a Harrick Scientific DRA diffuse reflection cell. The sample after either pretreatment I or II was first scanned at 300 K to obtain an interferogram which was used as a background for Fourier transforming the sample spectra. Following this, a gas mixture of 10% CO in He 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 a 30-min purge with pure He. Details for this DRIFTS system and spectra-collecting procedures have been provided elsewhere [4,5].

RESULTS

0.78% Pt/SiO_2 underwent pretreatment II and then the hydrogen titration, designated to H_2-N_2O titration, was conducted; the value was around 34.1 μmole H_2/g, as shown in Table 1. The conventional H_2 titration value for oxygen chemisorbed at 300K (H_2-O_2 titration) is also given. The total H_2 uptake on this catalyst was 11.5 μmole H_2/g. All oxygen on the Pt surfaces was irreversibly adsorbed. The irreversible CO uptake at 300 K is also listed in Table 1. A typical set of isotherms is shown in Figure 1. In an independent gravimetric measurement of "O" atoms chemisorbed *via* N_2O decomposition at 363 K, the net weight gain was 2.6 μg, corresponding to an "O" uptake of 23.6 μmol/g.

Table 1. Adsorption of N_2O at 363K and H_2, O_2 and CO at 300K on 0.78% Pt/SiO_2

Pretreatment	Gas uptake (μmol/g) at 300K						Dispersion[a]			d_p (nm)[b]
	Vol.					Grav.	H_{tot}	O_{tot}	CO_{irr}	
	H_2-N_2O titr.	H_2	O_2	CO	H_2-O_2 titr.	'O'[c]	Pt_{tot}	Pt_{tot}	Pt_{tot}	
	Tot.	Tot.	Tot.	Irr.	Tot.	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

[a] Assuming H, O and CO are adsorbed per one Pt_s.

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

[c] 'O' uptake *via* N_2O decomposition at 363K.

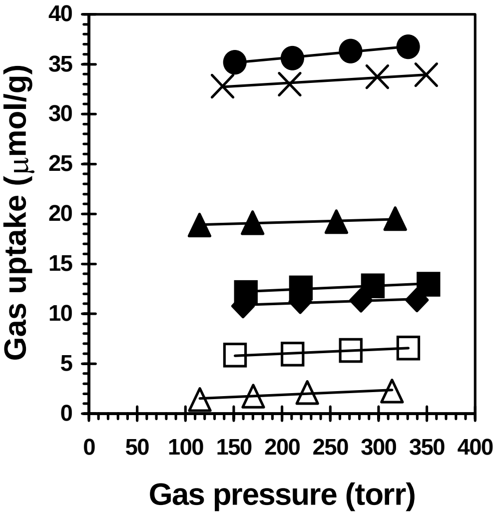

Figure 1. Adsorption isotherms on 0.78% Pt/SiO_2 after either pretreatment II or I: (●) H_2 titration-N_2O; (■, □) H_2 adsorption; (▲, △) CO adsorption; (◆) O_2 adsorption; (×) H_2 titration-O_2. Open and closed symbols are the respective total and reversible uptakes at 300K.

Spectra taken after CO adsorption on a catalyst surface covered by “O” atoms *via* N_2O decomposition on 0.78% Pt/SiO_2 at 363 K using pretreatment II are shown as a function of exposure time in Figure 2. After 0.5 min in flowing 10% CO (76 Torr) in He at 300 K, peaks at 2487, 2341, 2186 and 1827 cm^{-1} appeared along with a strong peak at 2076 cm^{-1} with a weak shoulder at 2091 cm^{-1}. All bands were unchanged in their position and intensity after a 30-min exposure, except for the 2341 cm^{-1} peak that decreased with time, and a 30-min purge with pure He at 300 K left all bands except that at 2341 cm^{-1} and caused shift of the 1827 cm^{-1} to 1815 cm^{-1}. No peaks were detected with pure SiO_2.

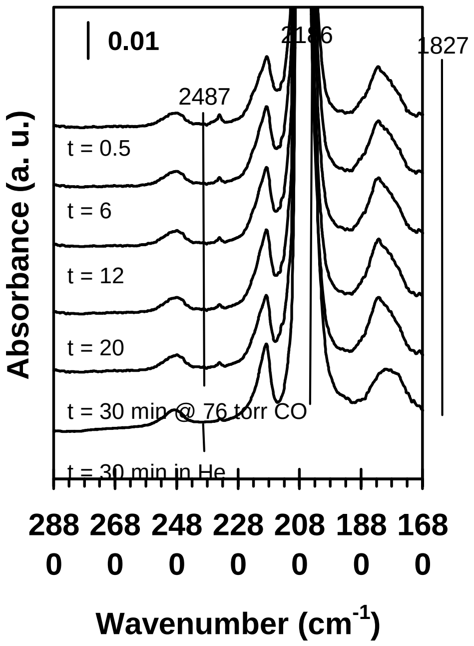

Figure 2. DRIFTS spectra of CO adsorbed at 300K on 0.78% Pt/SiO_2 after pretreatment II.

IR spectra of CO adsorbed on 0.78% Pt/SiO_2 after different pretreatments were provided in Figure 3. CO adsorption on a clean Pt surface after pretreatment I gave, after purging, a very strong peak at 2076 cm^{-1} with a shoulder at 2085 cm^{-1} and a very weak band near 2488 and 1779 cm^{-1}, as shown in Figure 3a. When the sample was exposed to N_2O at 363 K, titrated with a flow of 45% H_2 in He at 300 K, then exposed to CO in flowing He, bands at 2486, 2086, 2073 and 1778 cm^{-1} were observed after purging, as seen in Figure 3b. No peak around 2185 cm^{-1} was indicated with the clean and H-covered surfaces.

DISCUSSION

The present study is to determine the oxygen monolayer coverages obtained by N_2O decomposition and to compare them with coverages by the chemisorption of H_2, O_2 and CO. Near 300 K, both oxygen and CO monolayer coverages are consistently lower than that for hydrogen. The uptakes on the Pt/SiO_2 catalyst studied here give very consistent results with previous studies. The range of indicated dispersion, *ca*. 0.55-0.60, corresponds to crystallite sizes of 1.9-2.1 nm. The hydrogen titration gives very consistent dispersions not only for O_2 chemisorbed at 300 K, but also for the O monolayer formed by N_2O decomposition at 363 K. The latter coverage, whether determined gravimetrically or by H_2 titration, is consistently higher than the former and is essentially equal to the hydrogen coverage. This could be due to the site pair requirement for immobile, dissociative O_2 adsorption which does not exist for N_2O. These results strongly imply that essentially complete monolayer coverage of oxygen is established during N_2O decomposition at 363 K, and the stoichiometric chemisorption of this oxygen on Pt is described by the following reaction,

$$Pt_s + N_2O_{(g)} \rightarrow Pt_sO + N_{2(g)}. \qquad [1]$$

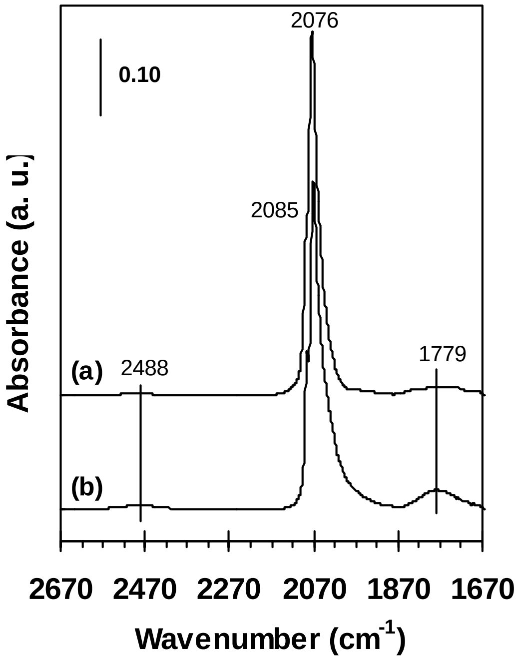

Figure 3. DRIFTS spectra of CO adsorbed at 300K on 0.78% Pt/SiO_2: (a) after pretreatment I; (b) after pretreatment II following H_2 titration at 300 K by flowing 45% H_2 in He.

Based on earlier IR and EELS studies of CO on Pt surfaces [4,6,7], the CO absorption bands observed in this study can be assigned. The 2085 and 2076 cm^{-1} bands indicate linearly adsorbed CO on Pt_s sites of different coordination number [6] while the bands around 1800 cm^{-1} are, after a 30-min purge, related to bridge-bonded CO on sites [6]. The peak near 2488 cm^{-1} is assigned to a combination mode of C-O and Pt_s-C symmetric stretching vibrations in on-top Pt_s-CO species [7]. The band near 2340 cm^{-1} was due to the antisymmetric stretching mode of gas-phase CO_2 created during reduction of the oxygen-covered Pt surface by CO, and the 2186 cm^{-1} band represents CO adsorbed on oxidized surface Pt sites [4,7]. These results coupled with the formation of CO_2 suggest that CO chemisorption at 300 K on an O-covered Pt surface obtained *via* N_2O decomposition at 363 K can be described to be

$$Pt_sO + 2CO_{(g)} \rightarrow Pt_sCO + CO_{2(g)}. \qquad [2]$$

CONCLUSION

N_2O decomposes on Pt surfaces at 363 K and 76 Torr, thereby forming a monolayer of chemisorbed oxygen. The monolayer coverage on a 0.78% Pt/SiO_2 catalyst was the same as that established by hydrogen adsorption. These “O” atoms were completely removed by H_2 titration at 300 K; thus the combination of N_2O dissociation with H_2 titration offers an alternative approach to measure Pt dispersion. After O coverages were established by N_2O decomposition at 363 K, exposure of these Pt surfaces to CO at 300 K removed the oxygen *via* CO_2 formation; when combined with other adsorption techniques, this titration reaction may be a useful approach to individualize surface atoms in supported Cu-based bimetallic Pt systems.

REFERENCES

1. Anderson, J.R.: “Structure of Metallic Catalysts”, Academic Press, NY(1975).
2. Dell, R.M., Stone, F.S. and Tiley, P.F.: *Trans. Faraday Soc.* **49**, 195(1953).
3. Avery, N.R.: *Surf. Sci.* **131**, 501(1983).
4. Kim, M.H., Ebner, J.R., Friedman, R.M. and Vannice, M.A.: *J. Catal.* **204,** 348(2001).
5. Huang, S.-J., Walters, A.B. and Vannice, M.A.: *J. Catal.* **192**, 29(2000).
6. Hayden, B.E., Kretschmar, K. and Bradshaw, A.M.: *Surf. Sci.* **155**, 553(1985).
7. Bare, S.R., Hofman, P. and King, D.A.: *Surf. Sci.* **144**, 347(1984).