

Catalytic reduction of N₂O by H₂ over well-characterized Pt surfaces

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Abstract—A 0.65% Pt/SiO₂ catalyst has been prepared using an ion exchange technique and extensively characterized prior to being used for continuous catalytic N₂O reduction by H₂ at very low temperatures, such as 363 K. The supported Pt with a high dispersion of 92% gave no presence of O atoms remaining on an H-covered Pt, based on *in situ* DRIFTS spectra of CO adsorbed on Pt, after either N₂O decomposition at 363 K or subsequent exposure to H₂ for more than 1 h; thus the residual uptake gravimetrically observed even after the hydrogen titration on an O-covered surface is associated with H₂O produced by introducing H₂ at 363 K onto the oxidized Pt. Dissociative N₂O adsorption at 363 K on Pt was not inhibited by the H₂O_(ad) on the silica surface but not on Pt, as acquired by IR peaks at 3,437 and 1,641 cm⁻¹, in very consistent with the same hydrogen coverage, established via H₂-N₂O titration on a reduced Pt, as that revealed upon the titration reaction with a fully wet surface on which all bands and their position in IR spectra for CO are very similar to that obtained after H₂ titration on a reduced Pt. Based on the characterization using chemisorption and *in situ* DRIFTS and TPD measurements, the complete loss in the rate of N₂O decomposition at 363 K after a certain on-stream hour, depending significantly on N₂O concentrations used, is due to self-poisoning by the strong chemisorption of O atoms on Pt, while the presence of H₂ as a reductant could readily catalyze continuous N₂O reduction at 363 K that is a greatly lower temperature than that reported earlier in the literature.

Key words: Catalytic N₂O Reduction, Supported Pt, Chemisorption, DRIFTS, Global Warming

INTRODUCTION

Nitrous oxide (N₂O), commonly known as laughing gas, has been recognized as a strong greenhouse gas with CO₂ and CH₄ [Crutzen, 1971; Kramlich and Linak, 1994], and chronic exposure of humans to N₂O even at very low concentrations has been known to cause miscarriages in an early gestation period, liver disorder, kidney trouble, cancer, troubles of the nervous system and so on [Geraci, 1977; Mattia, 1983]. N₂O is released from natural sources, such as microbial action in soils and oceans, and anthropogenic sources, including adipic acid production via HNO₃ oxidation, circulating fluidized bed combustions, automotive exhaust emissions, nitric acid synthesis and the use of anesthetic in medical operating rooms of hospitals [Centi et al., 1999; Doi et al., 2001; Perez-Ramirez et al., 2003]. N₂O possesses about 20 and 300 times the respective global warming potentials (GWP) for CH₄ and CO₂ and has approximately a 150-year lifetime in the atmosphere [Kroeze, 1994; Centi et al., 1999]. N₂O emitted at ground level can be advected slowly upward and entered into the stratosphere, thereby being the principal natural source of stratospheric NO which can substantially destroy the ozone layer in the stratosphere [Crutzen, 1971; Kramlich and Linak, 1994]. Therefore, anthropogenic N₂O emissions need to be reduced by using appropriate, efficient control technologies because of the unhealthy effect on humans and the global environmental problems.

An industrial effort to lower N₂O emissions is strongly associated with its emission legislation that does not exist at present even in highly industrialized countries but will be made in the near future,

and technological approaches for reducing N₂O emissions from the major anthropogenic sources may depend significantly on the conditions under which N₂O is removed and on the infrastructure consisting of the emission processes. Catalytic abatement technologies, *i.e.*, direct decomposition and reduction by appropriate reductants, are available for controlling N₂O emissions from a variety of industrial processes. As extensively reviewed by Kapteijn et al. [1996], catalytic decomposition has been a very attractive way to remove N₂O from various anthropogenic sources mentioned above. ZrO₂-supported CoO-NiO catalysts with small amounts of precious metal ingredients are commercially used for the decomposition of N₂O from adipic acid production plants from which very high N₂O concentrations, typically 20-40%, are released; however, these deN₂O catalysts are not sufficient to be applied for removing N₂O in nitric acid production processes having N₂O concentrations relatively as low as 0.05-0.5% [Riley and Richmond, 1993; Kapteijn et al., 1996; Perez-Ramirez et al., 2003]. A Co-exchanged MFI zeolite has been proposed to be very active for stoichiometric N₂O decomposition under a simulated condition for nitric acid industries [Li and Armor, 1992], while Kannan and Swamy [1993] have reported a higher activity of Ni-, Co- and Cu-based hydrotalcites for N₂O decomposition at temperatures ranging 423 to 583 K, in comparison with that obtained for Cu-, Co- and Rh-MFI catalysts. About 95% N₂O removal activity has been obtained at 730 K when an Rh/Al₂O₃ catalyst was employed to directly decompose N₂O in a flue gas, containing 4,000 ppm CO, 400 ppm NO and 1,000 ppm SO₂, of fluidized bed combustion [Dann et al., 1995], but a positive role of CO and NO in this decomposition reaction may not be excluded. Zeng and Pang [1997] observed 95% N₂O removal at 673 K with a Ru/Al₂O₃ catalyst for the decomposition of N₂O in a tail gas of Nylon

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66 synthesis, but the catalytic conversion decreased to ca. 30% in the presence of 4% H₂O. Supported Rh metals in N₂O decomposition have given a strong dependence on supports used; for instance, Rh/USY containing 2 wt% Rh exhibits 90% N₂O conversion at 523 K, while less than 15% conversion is indicated for Rh/La₂O₃ even at 663 K [Yuzaki et al., 1998]. When a mixture of 60 ppm N₂O with air to model a typical condition of medical operating rooms was used for evaluating catalytic performance of Al₂O₃-supported Pt, Pd and Rh metals, 5 wt% Rh showed the highest activity but a decrease in activity at low temperatures appeared in the presence of ethanol [Doi et al., 2001].

Catalytic N₂O reduction has been intensively investigated with various catalysts, particularly metal ions-exchanged zeolites, to overcome the requirement of high temperatures for achieving competitive activity in N₂O decomposition. A Co-MgO catalyst gives a steady-state activity for N₂O reduction with NH₃ and C₂H₆ at 570 K, but the activity decreases asymptotically with time, depending on N₂O pressures used, because of the strong adsorption of oxygen atoms on the catalyst surface via N₂O decomposition [Aika and Oshihara, 1996]. Pophal et al. [1997] have studied selective catalytic reduction of N₂O by C₃H₆ over Fe-MFI-88 and Cu-MFI-122 in the presence of 5% O₂, where the numbers next to the zeolite structure code represent the extent of the ion exchange expressed in percentage. The Fe-MFI catalyst has 50% of N₂O conversion at 600 K which is usually defined as a light-off temperature, and the conversion rate increases with temperature, while the Cu-MFI is completely inactive for this N₂O reduction reaction at that temperature. It is of particular interest for us to yield that the Fe-MFI possesses almost zero activity at 600 K in the absence of C₃H₆ (N₂O decomposition), and that a reaction temperature around 720 K is required to obtain light-off performance with the Fe-MFI in the decomposition. Therefore, these results indicate that C₃H₆ as a reductant facilitates N₂O removal reaction at much lower temperatures. Similarly, significant enhancements in N₂O removal activity in the presence of CO, C₃H₈, and CH₄ have been reported for Fe-exchanged MFI zeolites, depending on the kinds of reductants and their feed concentrations used [Perez-Ramirez et al., 2003, 2004; Perez-Ramirez and Kapteijn, 2004]. When Fe-BEA catalysts with different Fe contents has been used for N₂O reduction by NH₃ with O₂, the exchange level of Fe ions little affects the activity of the Fe-BEA catalysts at all temperatures covered, which has been very similar to that revealed for N₂O removal reaction without NH₃, and a light-off temperature of ca. 660 K is obtained with all the Fe-BEA catalysts, although the decomposition catalysis exhibits much lower performances, such as less than 5% N₂O conversion [Guzman-Vargas et al., 2003]. This represents that the extent of the decomposition of N₂O over the catalysts could be accelerated by using NH₃ because this reductant would be readily reacted with surface oxygen atoms adsorbed upon the decomposition, thereby giving turnover sites for N₂O removal reaction.

Based on the previous discussion for earlier studies on the direct N₂O decomposition and reduction by reductants over various catalysts, metal ions-exchanged zeolites possess very weak tolerance for N₂O decomposition in the presence of H₂O vapor [Zeng and Pang, 1997; Pophal et al., 1997], and oxygen atoms accommodated strongly on the surface of metals and their oxides and metal-exchanged zeolites via N₂O decomposition should be desorbed to gen-

erate reaction sites and this surface mechanism usually requires high temperatures, such as 600-780 K, depending on the kinds of catalysts used [Pophal et al., 1997; Satsuma et al., 2000; Schay et al., 2002; Perez-Ramirez et al., 2003]. To overcome the retardation of the reaction rate and increase slow reaction rate under steady state due to such strong oxygen adsorption, either reaction temperatures can increase or some reductants can be introduced, as discussed previously. If appropriate reductants such as CO, CH₄, NH₃, C₃H₆ and C₃H₈ are used together, temperatures for achieving light-off performances could be appreciably lowered, by 180 K or less, but are still higher than 550 K, depending significantly on catalysts and reductants and their concentration used [Cunningham and McNamara, 1990; Dann et al., 1995; Guzman-Vargas et al., 2003; Perez-Ramirez et al., 2004; Nobukawa et al., 2004]. Only an earlier study has been reported for catalytic reduction of N₂O by H₂ over 4.9 wt% Cu/Al₂O₃ at temperatures greater than 450 K [Dandekar and Vannice, 1999], and we are not aware of such data for supported Pt in the literature. Recently, we first investigated dissociative N₂O adsorption on a Pt/SiO₂ catalyst at 363 K and 76 Torr N₂O in either He or Ar [Kim et al., 2001, 2002]. The monolayer coverage of chemisorbed oxygen on metallic Pt surfaces via the N₂O decomposition is slightly greater than that established by O₂ chemisorption at either 300 or 363 K but the same as that obtained by H₂ chemisorption, and this oxygen is completely titratable using H₂ at 300 K, as designated by "H₂-N₂O titration" reaction. Therefore, this study was conducted to transpose our titration technique to catalytic N₂O reduction by H₂ as a reductant at very low reaction temperatures, such as 363 K, which is much lower, by 200 K, than those required for obtaining light-off N₂O conversions using metal ions-exchanged zeolites and supported metals and their oxides in the earlier reports.

EXPERIMENTAL

1. Catalyst Preparation

SiO₂ having a surface area of 480 m²/g (Davisil, Grade 634) was ground to a 60/80 mesh size and used for preparing a supported Pt catalyst. Prior to loading the Pt onto the SiO₂, it was calcined at 773 K for 4 h in flowing O₂ (Prexair, 99.999%) at 200 cm³/min. A 0.65% Pt/SiO₂ catalyst was obtained by an ion exchange method. The calcined SiO₂ was first brought into an NH₄OH solution with a pH value of 9.8, and then an aqueous solution of Pt(NH₃)₄Cl₂ (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 NH₄OH solution to it. Details of such procedures regarding the ion exchange technique have been described elsewhere [Benesi et al., 1968; Kim et al., 2001].

2. Gravimetric H₂-N₂O Reaction

The adsorption of O atoms via dissociation of N₂O (Korea Speciality Gases, Semiconductor Grade, 99.999%) at 363 K on the 0.65% Pt/SiO₂ catalyst was gravimetrically conducted with a Perkin-Elmer TGS-2 thermogravimetric system with an instrumental sensitivity of 0.1 µg. An appropriate amount of the catalyst (ca. 3 to 10 mg) was loaded into the sample-holding pan and reduced *in situ* at 673 K for 1 h in flowing a mixture of 50% H₂ in He (Prexair, 99.999%) at a rate of 60 cm³/min. The catalyst after cooling to 363 K was exposed to a flowing mixture of 1,000 ppm N₂O in He for 30 min and then to a flow of pure He for sufficient hours to remove N₂O re-

versibly accommodated on the catalyst. The net weight gain due to the O atoms on surface Pt metals, Pt_s, was determined by subtracting the initial weight from the final one, and finally 1,000 ppm H₂ in He was fed onto the oxidized Pt_s at 363 K. All gases used here were purified by flowing them through commercial moisture traps and oxytraps (Alltech Asso.), except that only a moisture trap was employed for N₂O. Details of such gravimetric measurement technique have been given in our earlier work [Kim et al., 2001].

3. *In situ* DRIFTS Measurements

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 0.65% Pt/SiO₂ was loaded into the DRC, it underwent pretreatment protocols consisting of (a) heating to 673 K and holding for 1 h in flowing pure He; (b) reducing in flowing pure H₂ for 1 h at 673 K; (c) cooling to 648 K in the H₂; (d) purging at 648 K for 30 min in flowing pure He; and (e) cooling to either 363 or 300 K and continuing purge for 1 h at either temperature. All gas flow rates during the pretreatment were maintained at 50 cm³/min using Brooks Model 5850E and MKS Type 1179A mass flow controllers.

The sample itself after the pretreatment was scanned at either 363 or 300 K to obtain a background interferogram for Fourier transforming the sample spectra. Following this, a flowing mixture of either 1,000 ppm H₂ or N₂O in He was introduced into the cell for 30 min at 363 K and a final interferogram was recorded after a 30-min purge with He. These sample spectra were compared with that obtained after consecutive N₂O decomposition and H₂ titration at 363 K on a sample of the reduced catalyst. To obtain spectra of CO adsorbed at 300 K on 0.65% Pt/SiO₂ after different surface reactions, a gas mixture of 1,000 ppm CO (Matheson, 99.99%) in flowing He was used, and *in situ* DRIFTS spectra for CO on the oxidized Pt surfaces were collected with those for CO on the surfaces that had been exposed to 1,000 ppm H₂ in a He flow at 363 K. Each interferogram was Fourier transformed by using a background which had been collected before desired reactions or introduction of the CO. All interferograms were recorded with a 4-cm⁻¹ resolution and a scan number of 1,000. 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].

4. Temperature Programmed Desorption (TPD)

A U-shaped tubular reactor placed in a temperature-controllable electric furnace was employed to collect *in situ* TPD spectra for 0.65% Pt/SiO₂ following different pretreatments. A 300-mg sample was reduced in a fashion similar to that used for the IR measurements and was cooled to 363 K at which the sample was exposed to 1,000 ppm N₂O in He at a flow rate of 30 cm³/min to deposit O atoms on Pt_s, and then the oxidized sample was heated to 873 K at a ramping rate of 10 K/min under a flow of pure He at a rate of 30 cm³/min for desorbing the O atoms on Pt_s. TPD spectra were also collected for the catalyst after H₂ and CO titrations of the oxygen coverage established by N₂O decomposition at 363 K on a reduced sample. During each experiment, the effluent gases were monitored at 32 and 17 amu for the respective O₂ and H₂O using an on-line, computer-controlled OmniStar GSD 301 O₂C quadrupole mass spectrometer (Pfeiffer Vacuum Technol.).

5. Volumetric H₂-N₂O Reaction

The adsorption of N₂O and H₂ on 0.65% Pt/SiO₂ 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 were detected by 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 [Kim et al., 2001, 2002]. Prior to introducing the gas molecules into the volumetric system, a sample of an appropriate amount, typically 0.3 to 0.5 g, of the 0.65% Pt/SiO₂ catalyst was reduced *in situ* in a Pyrex chemisorption cell placed in a cylindrical electric furnace using the same pretreatment protocols as that employed for the *in situ* DRIFTS measurements, except for the use of evacuation instead of the He purge at either 363 or 300 K. Then the O monolayer on Pt_s via N₂O decomposition at 363 K was titrated at 300 K with H₂ under pressures ranging from 40 to 350 Torr [Kim et al., 2001, 2002]. Substantially, the hydrogen adsorption at 300 K on the catalyst after reduction was measured to allow a comparison with the H₂-N₂O titration. Both total and reversible uptakes for H₂ in those reactions were determined by extrapolating the linear regions, occurring from 100 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]. All gases used were purified in a fashion similar to that described for the gravimetric measurements.

6. Catalytic N₂O Decomposition and Reduction

Activity measurements were conducted isothermally at 363 K as a function of time on stream in a continuous flow fixed-bed type U-shaped Pyrex reactor placed in a bottom-capped cylindrical electric furnace. Typically, 0.4 g catalyst was placed above a quartz wool plug in the Pyrex reactor and was routinely reduced *in situ* in a fashion analogous to that described for the DRIFTS measurements, prior to being used for the catalytic N₂O reduction at 363 K. The temperature of the reactor during each experimental run was monitored with a K-type thermocouple above the catalyst bed, and was held constant at 363±0.2 K with a PID temperature controller (Hanyoung NP200). A typical gas mixture consisting of either 200-800 ppm N₂O in He or 1,000 ppm N₂O and 1,000 ppm H₂ in He at a total flow rate of 500 cm³/min, corresponding to a gas hourly space velocity (GHSV) of ~30,000 h⁻¹, was passed over the catalyst bed for activity measurements of N₂O decomposition and reduction at 363 K. Blank runs, conducted with the reactor filled with only the quartz wool plug, gave negligible decomposition of N₂O up to 873 K. The product gases were analyzed by using an on-line, computer-controlled Shimadzu 2010 gas chromatograph equipped with a thermal conductivity detector and a Porapak Q column and a molecular sieve 13x column (Alltech Asso.) for the respective N₂O and N₂ separations from the effluent gases. The N₂ concentration produced via N₂O removal reaction in the absence and presence of H₂ was used for verifying the material balance. The extent of the conversion of N₂O in the decomposition and reduction was evaluated based on the N₂O concentration in the up- and downstream.

RESULTS

The 0.65% Pt/SiO₂ catalyst reduced at 673 K gave a measurable

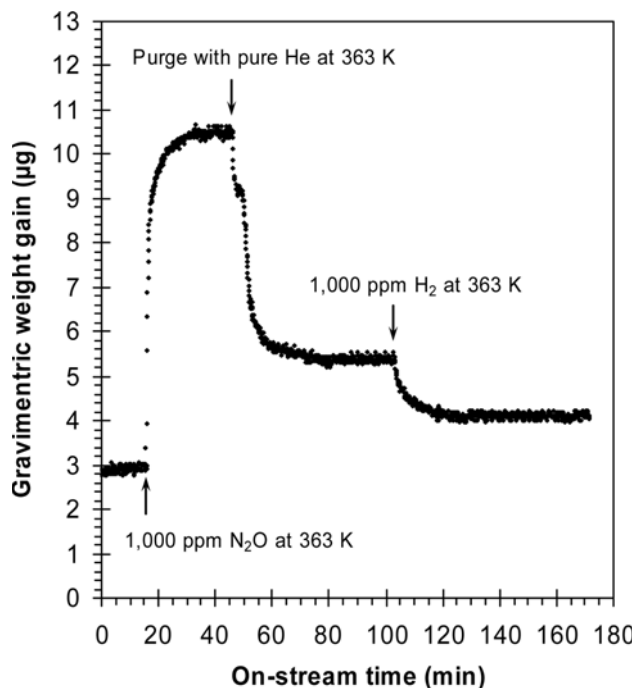


Fig. 1. Gravimetric measurements for dissociative N₂O adsorption at 363 K on 0.65% Pt/SiO₂ after reduction at 673 K followed by H₂ adsorption at 363 K on the oxidized surface.

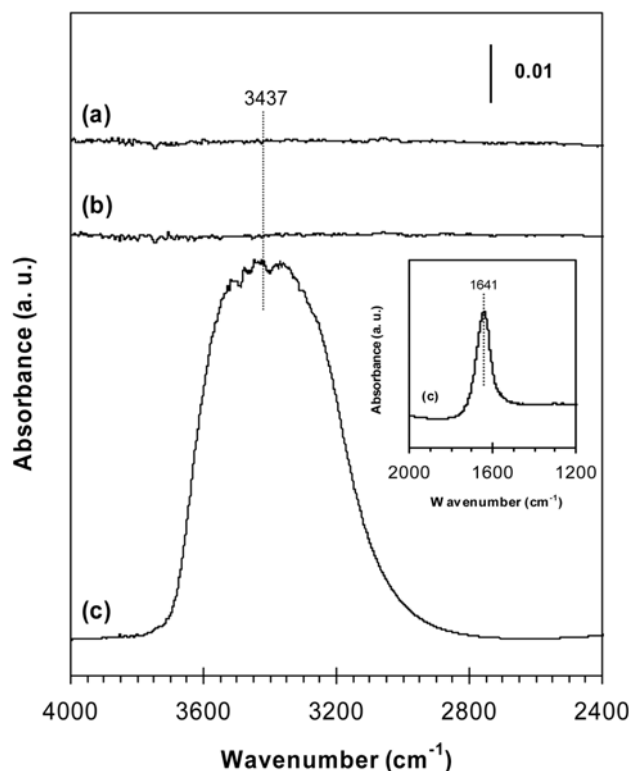


Fig. 2. *In situ* DRIFTS spectra for 0.65% Pt/SiO₂ after reduction at 673 K followed by: (a) H₂ adsorption at 363 K; (b) dissociative N₂O adsorption at 363 K; (c) dissociative N₂O adsorption at 363 K, then H₂ titration at 363 K. Inset: a peak by a deformation mode of H₂O adsorbed on SiO₂ in spectrum (c). All spectra were taken after a 30-min purge with He at 363 K.

weight change when introducing 1,000 ppm N₂O in a flow of He at 363 K, as shown in Fig. 1, and the net weight gain due to the O coverage on Pt, via the N₂O decomposition was ~ 2.5 μg , corresponding to an O uptake value of 30.4 $\mu\text{mol/g}$ based on our earlier studies [Kim et al., 2001]. Consecutive exposure of the O-covered Pt surface to 1,000 ppm H₂ in He at 363 K exhibited decrease in the weight with time and finally had a residual weight of ~ 1.3 μg that may not be associated with untitratable O atoms on Pt, based on the previous titration reaction at 300 K [Benson and Boudart, 1965; Kim et al., 2001]. No accommodation of atomic oxygen upon N₂O decomposition at 363 K was found for the bare SiO₂, as reported in an earlier gravimetric measurement [Kim et al., 2001]. The adsorption of H₂ at 363 K on the pure SiO₂ clearly obeyed Henry's Law, no H₂ adsorption occurring, but H₂O could be accommodated on SiO₂ even at such temperature [Benson and Boudart, 1965; Kim et al., 2001] and the H₂O might give the residual weight.

In situ DRIFTS spectra for 0.65% Pt/SiO₂ after different surface reactions were collected to verify the adsorption of H₂O, produced upon H₂-N₂O titration at 363 K, on the support surface, as shown in Fig. 2. All the catalysts reduced at 673 K as well as exposed subsequently to 1,000 ppm N₂O at 363 K gave no infrared absorption bands in the fundamental stretching vibrations of OH groups and molecular H₂O bound weakly to the surface of SiO₂ (Fig. 2a and 2b). After H₂ adsorption on an oxidized Pt, obtained via N₂O decomposition at 363 K on the catalyst, following a 30-min exposure in flowing pure He at 363 K, a very broad, intense peak centered around 3,437 cm⁻¹ appeared (Fig. 2c), and as indicated in the inset of Fig. 2 a peak at 1,641 cm⁻¹ was visible. The 3,437 cm⁻¹ band was tentatively assigned to an OH stretching of hydrogen-bonded molec-

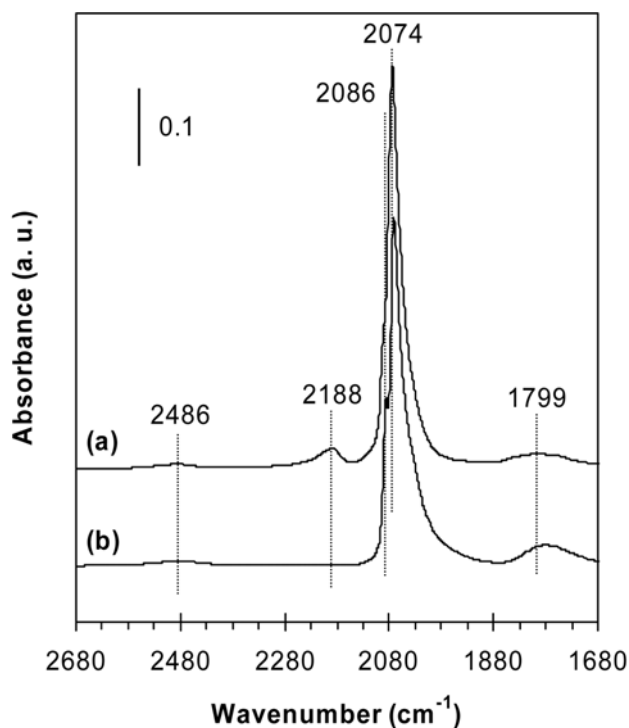


Fig. 3. *In situ* DRIFTS spectra of CO adsorbed at 300 K on 0.65% Pt/SiO₂ after (a) dissociative N₂O adsorption at 363 K and (b) subsequent H₂ adsorption at 363 K. All spectra were taken after a 30-min purge with He at 300 K.

ular H_2O , which had been produced during the reaction between H_2 and O atoms on Pt_s . The $1,641\text{ cm}^{-1}$ peak could be due to a bending mode of the molecular H_2O adsorbed on the silica support [Orcel et al., 1986; Fanning and Vannice, 1993; Kim and Lee, 2004]; therefore, the principal difference in these spectra is the presence of the $3,437$ and $1,641\text{ cm}^{-1}$ bands after H_2 titration of the O atoms on Pt_s .

To independently determine whether the residual weight gain in the gravimetric measurements results from untitratable oxygen atoms or not, *in situ* DRIFTS spectra of CO adsorbed at 300 K on either an O-covered surface established via the decomposition reaction of 1,000 ppm N_2O in He at 363 K on 0.65% Pt/SiO_2 reduced at 673 K or subsequent exposure to 1,000 ppm H_2 at 363 K are shown in Fig. 3. After a 30-min exposure of the oxidized Pt_s to a flow of 1,000 ppm CO in He at 300 K, peaks at $2,486$, $2,188$ and $1,799\text{ cm}^{-1}$ appeared along with a predominant band at $2,074\text{ cm}^{-1}$ and a very weak shoulder at $2,086\text{ cm}^{-1}$ (Fig. 3a). The surfaces with H coverage, which had been obtained by admitting 1,000 ppm H_2 in He at 363 K for 30 min to the oxidized Pt surfaces, gave peaks at $2,482$, $2,086$, $2,071$ and $1,779\text{ cm}^{-1}$ but no band around $2,188\text{ cm}^{-1}$ (Fig. 3b). No peaks for CO adsorbed on any surfaces were detected with pure SiO_2 , as reported earlier [Kim et al., 2002]. Thus these spectra indicate that the oxygen atoms chemisorbed even on a highly dispersed Pt_s as for this sample would react completely with H_2 at that temperature.

Fig. 4 shows *in situ* TPD spectra for 0.65% Pt/SiO_2 after the catalyst surface was modified not only by exposing the reduced sam-

ple to 1,000 ppm N_2O in flowing He at 363 K, but also by titrating the oxidized surface with a flow of 1,000 ppm H_2 in He at 363 K. The reduced sample (Fig. 4a) possessed no desorption peaks for both O_2 and H_2O at temperatures ranging from 363 to 873 K, as expected, while after exposure to the N_2O flow for 30 min followed by a He purge, the surface covered by the chemisorbed oxygen at 363 K gave a predominant oxygen desorption peak at 730 K along with a bump at 703 K and a weak peak at 821 K, as displayed in Fig. 4b. The desorption spectrum for the catalyst after H_2 and CO titration of the oxygen chemisorbed at 363 K is shown in Fig. 4c and 4d. After purging, only a single peak at 396 K was observed with the oxidized sample following the H_2 titration at 363 K (Fig. 4c), and when CO adsorption on the O-covered surface was conducted at 363 K prior to ascending temperature a peak at 821 K appeared, as given in Fig. 4d. In either case, the catalyst surface established by the titrations gave no peaks near 703 and 730 K.

The 0.65% Pt/SiO_2 catalyst underwent pretreatment protocols similar to that described upon the infrared measurements, thereby depositing the O atoms onto Pt_s via dissociative N_2O adsorption at 363 K. The extent of the O coverage on the Pt_s was determined by H_2 titration reaction at 300 K; the uptake value was ca. $46.1\text{ }\mu\text{mol/g}$ based on total H_2 adsorption, as listed in Table 1. The conventional H_2 chemisorption at 300 K is also measured to compare with that obtained from the H_2 - N_2O titration. The total hydrogen uptake on this reduced Pt sample was $15.3\text{ }\mu\text{mol/g}$, giving a Pt_s value of $30.6\text{ }\mu\text{mol/g}$ based on an assumption of a 1 : 1 correspondence between adsorbed H and Pt_s as widely accepted in the literature [Benson and Boudart, 1965]. These H_2 uptake values were very reproducible even for different samples, in excellent agreement with previous results [Kim et al., 2001], and the pure SiO_2 , which had been reduced at 673 K, gave no H_2 adsorption uptake at 300 K. A typical set of isotherms is shown in Fig. 5.

The activity maintenance profiles for N_2O decomposition at 363 K over 0.65% Pt/SiO_2 reduced at 673 K were measured based on the N_2O conversion to allow an easier comparison between different N_2O feed concentrations, as shown in Fig. 6. As evident from these plots, the conversion of the decomposition was 100% at an initial reaction period, within 5 min on stream, irrespective to N_2O concentration fed; however, the extent of the decrease in activity

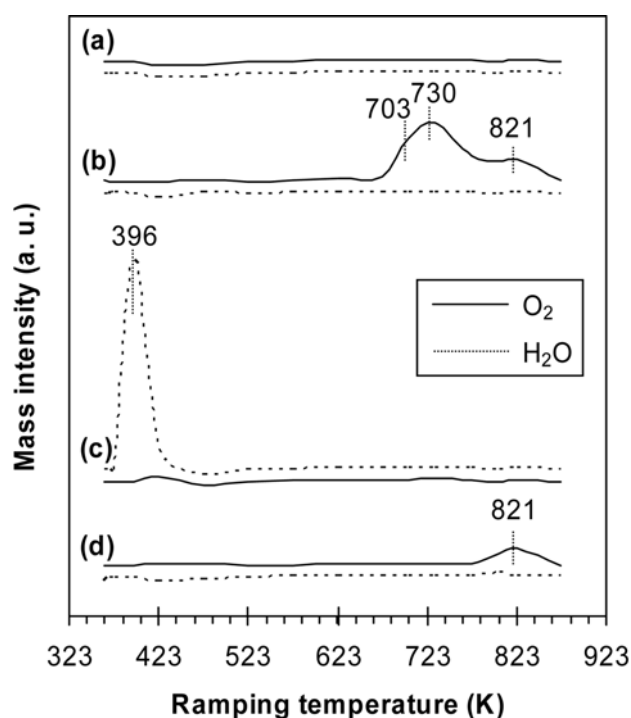


Fig. 4. *In situ* TPD spectra for 0.65% Pt/SiO_2 : (a) after reduction at 673 K; (b) after exposure to 1,000 ppm N_2O in He for 1 h at 363 K; (c) after exposure to 1,000 ppm N_2O in He for 1 h at 363 K following H_2 titration under flowing 1,000 ppm H_2 in He; (d) after exposure to 1,000 ppm N_2O in He for 1 h at 363 K following CO titration under flowing 1,000 ppm CO in He. A 30-min purge with He at 363 K was allowed prior to being ramped up to 873 K.

Table 1. Adsorption of N_2O at 363 K and H_2 at 300 K on 0.65% Pt/SiO_2

Gas uptake ($\mu\text{mol/g}$)			Dispersion based on ^a			
H_2 - N_2O titr.	H_2 tot.	O^c	$\text{H}_{\text{titr.}}-\text{N}_2\text{O}$	$\text{H}_{\text{tot.}}$	O	d_p (nm) ^b
			Pt	Pt	Pt	
46.1	15.3	30.4 ^d	0.92	0.92	0.91	1.2
45.7 ^c			0.91			1.2

Note. No adsorption of H_2 on pure SiO_2 after pretreatment.

^a Assuming $\text{H}/\text{Pt}_s = \text{O}/\text{Pt}_s = 1$.

^b Calculated from d_p (nm) = $1.13/D$, where D is $\text{H}_{\text{tot.}}/\text{Pt}_s$, $\text{H}_{\text{titr.}}/\text{Pt}$ or O/Pt .

^c Atomic O uptake via N_2O decomposition at 363 K measured gravimetrically.

^d At 363 K.

^e On a "wet" Pt surface obtained after N_2O reduction by H_2 at 363 K for 4 h.

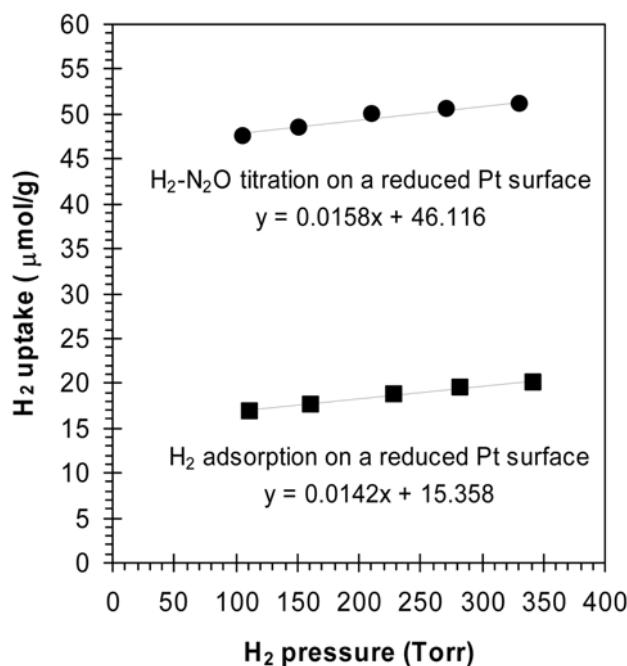


Fig. 5. Adsorption isotherms for H₂ adsorption at 300 K on 0.65% Pt/SiO₂ after either reduction at 673 K or subsequent N₂O decomposition at 363 K.

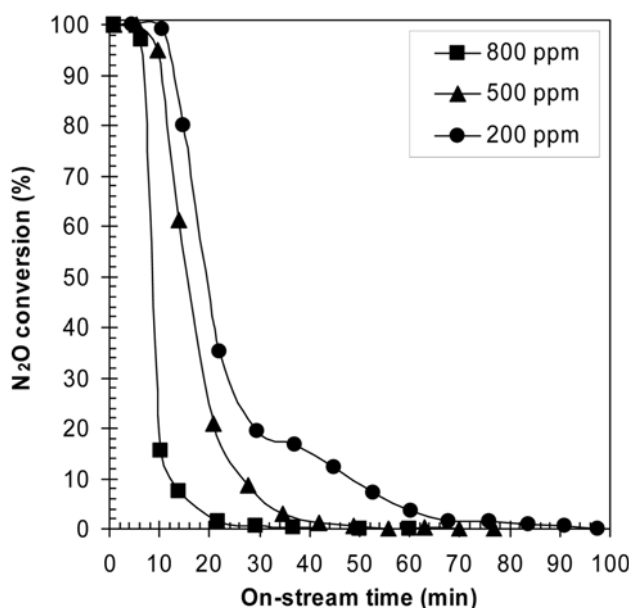


Fig. 6. Conversion profiles of 0.65% Pt/SiO₂ for N₂O decomposition at 363 K as a function of N₂O feed concentration.

was dependent significantly on the concentration. When 800 ppm N₂O was introduced into the reactor, rapid activity loss occurs, i.e., after about 10 min the activity was ca. 16% and finally the reduced catalyst lost its activity completely after 30 min of the continuous operation. During this entire period on-stream, the catalytic activity calculated from the concentration of N₂ produced was equal to that obtained based on the N₂O concentration removed, as expected. In comparison, a slower rate of activity loss was observed for this Pt catalyst with lower N₂O feed concentrations such as 500 and 200

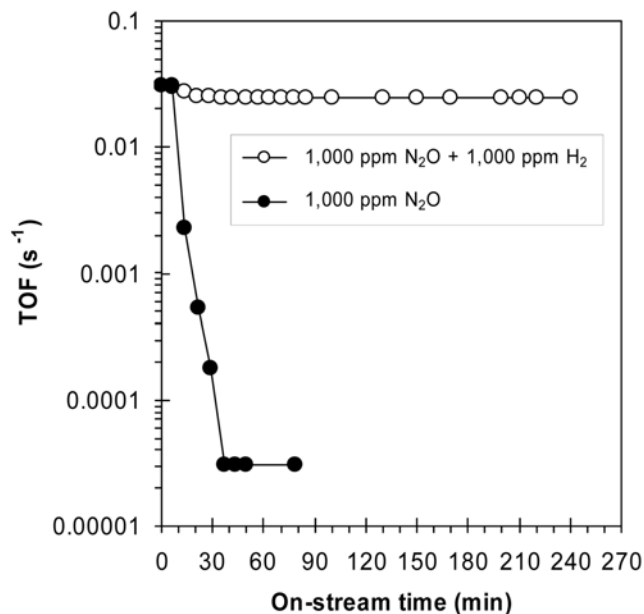


Fig. 7. Turnover frequencies for continuous N₂O reduction in the presence of H₂ at 363 K over 0.65% Pt/SiO₂.

ppm. These results imply that strong chemisorption of O atoms on Pt_s via N₂O decomposition at 363 K caused the activity loss, depending on its concentration, because of difficulty in desorbing such oxygen atoms from the Pt surface at that temperature.

The subsequent addition of H₂ as a reductant to the feed stream of 1,000 ppm N₂O in He at 363 K produced the turnover frequency (TOF) profile in Fig. 7 for the 0.65% Pt/SiO₂ catalyst after reduction at 673 K, and a TOF value was also measured to track the catalytic decomposition profile without the reductant. In the absence of H₂, a TOF value was about $3.1 \times 10^{-2} \text{ s}^{-1}$ at the initial period on-stream, but it decreased rapidly with on-stream time and was practically zero after 30 min. When 1,000 ppm H₂ existed with the N₂O stream at 363 K, the initial TOF value was still maintained during the continuous reduction even for 4 h. As seen from these activity profiles based on the TOF values as a function of time on-stream, after 30 min the steady-state activity of 0.65% Pt/SiO₂ in the N₂O reduction by H₂ was about 140 times higher than that indicated for N₂O decomposition reaction. No molecular O₂ was detected in the presence of the reductant under the conditions used in this study, suggesting that H₂ efficiently scavenges adsorbed O atoms to form H₂O which may be accommodated on either of Pt_s and SiO₂ or on both all, and this will be further clarified later.

To see if not only could large amounts of H₂O produced during the catalytic N₂O reduction by H₂ at 363 K inhibit the accommodation of N₂O on Pt_s, but the H monolayer on Pt_s was also readily replaced by the O atoms via the N₂O, the catalyst after continuous reduction for 4 h in the chemisorption cell and then exposure to 1,000 ppm N₂O in He at 363 K for 30 min following evacuation for a very short time so as to remove the N₂O mixture was used for H₂ adsorption at 300 K. A total H₂ uptake of 45.7 μmol/g was observed for the hydrogen titration at 300 K of the oxygen coverage on the Pt surface, designated here to “wet” Pt_s to distinguish it from the other Pt surfaces, as listed in Table 1, which is very similar to that indicated for a clean, oxidized Pt surface as revealed in Fig. 5. Thus,

it is clear that the produced water is adsorbed on the silica support but not on Pt, in good agreement with an earlier observation [Ben-

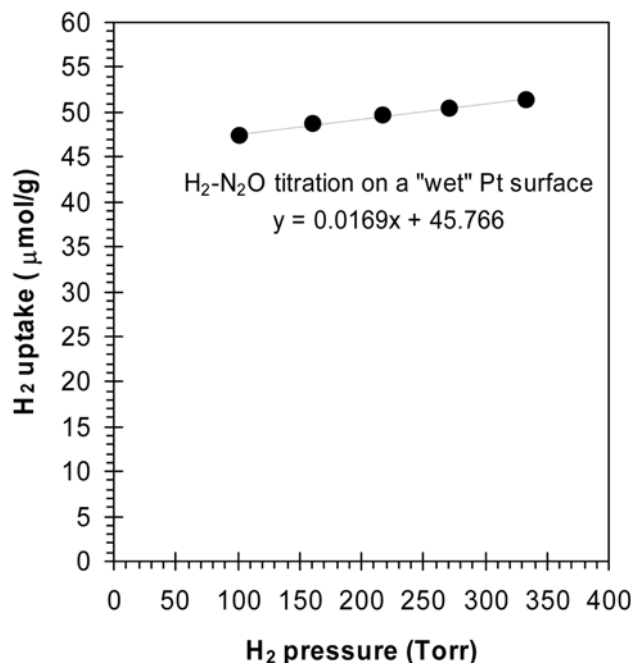


Fig. 8. An adsorption isotherm for H_2 adsorption at 300 K on 0.65% Pt/SiO₂ after continuous N_2O reduction at 363 K in the presence of H_2 for 4 h following dissociative N_2O adsorption at 363 K.

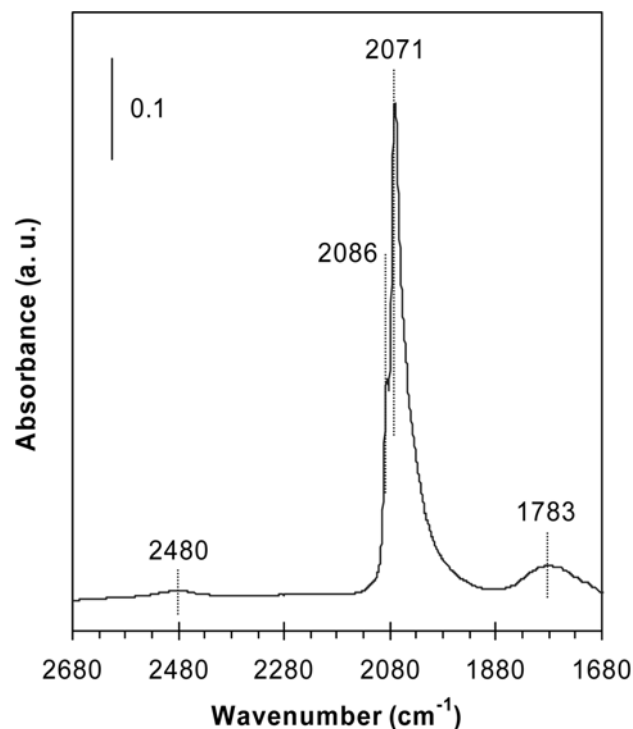


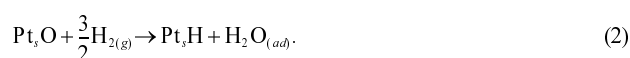
Fig. 9. *In situ* DRIFTS spectra of CO adsorbed at 300 K on 0.65% Pt/SiO₂ after continuous N_2O reduction at 363 K in the presence of H_2 for 4 h following dissociative N_2O adsorption and subsequent H_2 adsorption at 363 K. This spectrum was recorded after a 30-min purge with He at 300 K.

son and Boudart, 1965]. A typical isotherm is provided in Fig. 8.

The adsorption of CO at 300 K on a “wet” Pt, obtained after catalytic N_2O reduction by H_2 at 363 K in the DRC for 4 h on stream, which had been similar to the continuous operation hours allowed upon the activity test in Fig. 7, was of particular interest because of the need to ascertain no suppression of this reaction even over the “wet” Pt. Fig. 9 shows IR spectrum of CO adsorbed on 0.65% Pt/SiO₂ after *in situ* N_2O reduction at 363 K for 4 h in the presence of H_2 . Adsorption of CO at 300 K on the Pt surface gave, when purged with a flow of pure He, a very strong peak at 2,071 cm^{-1} with a shoulder at 2,086 cm^{-1} and weak bands near 2,480 and 1,783 cm^{-1} , and no peak at 2,186 cm^{-1} was indicated with this Pt surface. The position of all these peaks and their relative intensity were very similar to that observed for a Pt surface after a single H_2 - N_2O titration as shown in Fig. 3; therefore, this represents that dissociative N_2O adsorption at 363 K even on such fully “wet” Pt, could occur, thereby continuing catalytic N_2O reduction in the presence of H_2 at that temperature.

DISCUSSION

Catalytic activity of supported Pt catalysts in many industrial reactions is associated with the surface metal density (fraction exposed) which can be determined by using the selective chemisorption of probe molecules, such as H_2 , CO and O_2 , on the metal surface, and the titration of an adsorbed species by using another gas molecule, as in the case of the titration of chemisorbed O atoms, via either O_2 adsorption or N_2O decomposition on the metal surface under appropriate conditions, by H_2 [Benson and Boudart, 1965; Vannice et al., 1970; Kim et al., 2001]. The hydrogen chemisorption technique is commonly used to count surface metal atoms, such as Pt, Pd and Rh, on which H_2 around 300 K is accommodated dissociatively with adsorption stoichiometries near unity [Benson and Boudart, 1965; Vannice et al., 1970; Wilson and Hall, 1970], although highly dispersed Pt metals could give surface adsorption stoichiometries near 2 [Candy et al., 1980; Humblot et al., 1998]. The selective chemisorption of O atoms via N_2O decomposition on metallic Cu surfaces with an adsorption stoichiometry of $\text{O}/\text{Cu}_s=0.5$ under specified conditions has been used for decades as a probe to count the number of surface metal atoms in supported and unsupported Cu metals [Dell et al., 1953; Scholten and Konvalink, 1969; Kapteijn et al., 1996]. This dissociative N_2O adsorption technique could be extended successfully to supported Pt and Cu-Pt catalysts for determining the surface density of the metals and the oxygen monolayer coverage obtained by N_2O decomposition at 363 K and 76 Torr could be completely removed by H_2 at 300 K, as first reported by Kim et al. [2001, 2002] to characterize metallic Pt surfaces with O/Pt_s and H/Pt_s of unity according to the following reactions:



In this study, a combination of Eqs. (1) and (2) is of particular interest to continuously catalyze the reduction of N_2O at 363 K in the presence of H_2 ; therefore, our primary focus on a fundamental concern in surface chemistry regarding these reactions is to examine that

Table 2. IR peak assignments for CO chemisorbed on 0.65% Pt/SiO₂ after different surface reactions

Pt surface	Peak position (cm ⁻¹)	Assignment
O-covered Pt _s ^a	2,486	Combination mode of C-O and Pt _s -C in on-top Pt _s -CO
	2,188	On-top Pt _s O-CO
	2,086	On-top Pt _s -CO
	2,074	On-top Pt _s -CO
	1,799	Bridge-bonded CO on Pt _s
H-covered Pt _s ^b	2,482	Combination mode of C-O and Pt _s -C in on-top Pt _s -CO
	2,086	On-top Pt _s -CO
	2,071	On-top Pt _s -CO
	1,779	Bridge-bonded CO on Pt _s
“Wet” Pt _s ^c	2,480	Combination mode of C-O and Pt _s -C in on-top Pt _s -CO
	2,086	On-top Pt _s -CO
	2,071	On-top Pt _s -CO
	1,783	Bridge-bonded CO on Pt _s

^aObtained via N₂O decomposition at 363 K.^bObtained via H₂ titration at 363 K of the surface^a.^cObtained after continuous N₂O reduction at 363 K for 4 h in the presence of H₂.

the H₂O_(ad) would not inhibit the continuous catalytic N₂O reduction at 363 K and that the H coverage, established by Eq. (2), on Pt_s can be readily replaced by O atoms via Eq. (1), using various characterization techniques. Our final interest in practical applications is to see if N₂O can be continuously removed by combining the two surface reactions at much lower temperatures, such as 363 K, compared to that reported earlier for catalytic N₂O reduction by NH₃, CO and hydrocarbons as extensively discussed in the Introduction.

The O coverage acquired gravimetrically by dissociative N₂O adsorption at 363 K on 0.65% Pt/SiO₂ after reduction at 673 K gives very consistent results with the other chemisorption studies. The Pt dispersion indicated for this reduced Pt sample is 0.92, corresponding to a crystallite size of 1.2 nm using the correlation d_p (nm) = 1.13/D, and the hydrogen titration of the O-covered Pt_s reveals a dispersion value in excellent agreement with that based on total H atoms established via H₂ adsorption at 300 K on a reduced Pt_s, as given in Table 1. The O coverage value at 300 K, whether determined volumetrically or gravimetrically, is equal to the H_{ad} coverage acquired by H₂ chemisorption and titration, indicating the occurrence of Eq. (1) during N₂O decomposition at 363 K, thereby causing a saturated O monolayer that could be stoichiometrically titratable using H₂ at 300 K as described by Eq. (2), which is in good agreement with the earlier discussion for a 0.81% Pt/SiO₂ catalyst [Kim et al., 2001]. One-half of the coverage based on the total hydrogen uptake is reversible, which is very consistent with previous studies of Pt metals loaded on SiO₂ and Al₂O₃ [Palmer and Vannice, 1980; Sen and Vannice, 1991; Kim et al., 2001], and H₂ is not adsorbed on solid supports near 300 K [Bae et al., 2004]; thus such reversible behavior in H₂ adsorption is strongly associated with surface features of the support but not with the metal dispersion. The titration reaction of the O atoms chemisorbed on a “wet” Pt surface, that had been established by the reduction of N₂O at 363 K for 4 h over a sample of 0.65% Pt/SiO₂ in the presence of H₂, gives an H uptake value equal to that indicated upon the H₂ titration of a reduced Pt_s following exposure to N₂O at 363 K. Consequently, the residual weight gain after the gravimetric H₂ titration on an oxidized Pt_s via

O monolayer formation by decomposing N₂O at 363 K on the catalyst would be due to the H₂O adsorbed, i.e., H₂O_(ad) in Eq. (2), on the support but not on the metal surface and thus the H₂O_(ad) could not inhibit dissociative N₂O adsorption at 363 K on Pt_s.

A great potential of the surface reaction combining Eqs. (1) and (2) to transpose it to continuous N₂O reduction by H₂ at 363 K over the 0.65% Pt/SiO₂ catalyst is revealed from *in situ* DRIFTS spectra of CO adsorbed on a reduced, O-covered and “wet” Pt_s (Figs. 3 and 9). Based on earlier IR and EELS studies of CO adsorption on reduced Pt surfaces [Eischens et al., 1954; Bare et al., 1984; Barshad et al., 1985; Greenler et al., 1985; Hayden et al., 1985; Wells, 1985; Gardner et al., 1990; Hadjiivanov, 1998; Kim et al., 2001], the CO absorption bands, i.e., 2,483±3, 2,188, 2,086, 2,073±2 and 1,789±10 cm⁻¹, observed after an He purge at 300 K can be assigned, as listed in Table 2. The peak near 2,483 cm⁻¹ band is because of a combination mode of C-O and Pt_s-C symmetric stretching vibrations in CO adsorbed linearly on Pt_s [Bare et al., 1984]. The 2,188 cm⁻¹ band represents on-top CO adsorbed on oxidized Pt surface sites, designated to Pt_sO in Table 2 [Barshad et al., 1985; Balakrishnan et al., 1990; Hadjiivanov, 1998]. The 2,086 and 2,073 cm⁻¹ peaks indicate linearly adsorbed CO on metallic Pt_s atoms having different coordination numbers, while the band around 1,789 cm⁻¹ is associated with 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].

We need to particularly acquire that the O atoms via the decomposition reaction of N₂O at 363 K on Pt_s can be removed continuously by the addition of H₂ at 363 K as a reductant. The adsorption of CO at 300 K on a reduced Pt surface following N₂O decomposition at 363 K (Fig. 3) gives IR spectra quite similar to that reported for CO on a variety of silica-supported Pt samples, representatively EUROPT-1 and 0.81% Pt/SiO₂ [Wells, 1985; Kim et al., 2001]. Only an exception to the spectra of CO adsorbed on the oxidized surface is the presence of the 2,188 cm⁻¹ band due to on-top CO on Pt_sO; therefore, this represents no complete reduction of some Pt surface atoms by gas-phase CO at 300 K. Exposure of this surface to H₂ at

363 K readily removes all the surface O atoms, thereby disappearing completely the $2,186\text{ cm}^{-1}$ peak and accompanying an increase in intensity of the $2,086\text{ cm}^{-1}$ shoulder as seen in Fig. 3(b). These spectra for CO adsorbed at 300 K on the O and H-covered Pt, indicate the presence of small amounts of Pt, atomically isolated on the silica surface; however, this type of Pt, existing on the catalyst surface could be also involved with the dissociation of N_2O at 363 K following the removal of the O atoms to H_2O , that is accommodated on the silica surface as discussed previously, when introducing H_2 at 363 K. Titration of the oxidized Pt surface by H_2 gives an increase in the extent of bridge-bonded CO, which is associated with an enhancement of the roughness of Pt,. Consequently, all these results represent that H_2 is a very good titrator of the O atoms on Pt, via N_2O decomposition at 363 K; thus, H_2 can be used as an excellent reductant for continuous catalytic N_2O reduction at 363 K.

The complete removal of the oxygen atoms on Pt, via N_2O decomposition at 363 K, even though some of them could be very strongly chemisorbed on a certain Pt, so as to not be removed upon CO titration, in the presence of H_2 at 363 K is evident from DRIFTS measurements in Fig. 2, which are very consistent with the results in Figs. 4 and 8. Based on the IR results for the 0.65% Pt/SiO₂ catalyst after different surface modifications, and H_2 - N_2O titration reaction conducted gravimetrically and volumetrically, the TPD peaks at 396, 703 to 730 and 821 K in Fig. 4 can be assigned, which strongly supports the continuous catalytic N_2O reduction by H_2 at 363 K. The 396 K peak, which appeared on the catalyst surface after H_2 titration of the oxygen coverage established by dissociative N_2O adsorption at 363 K, is due to the desorption of $\text{H}_2\text{O}_{(\text{ad})}$ on SiO₂ surfaces. The 730 K peak with the 703 K shoulder and the 821 K peak are the O atoms on the respective common and isolated Pt, [Burch et al., 2004]. These TPD results are consistent with that obtained for DRIFTS measurements with 0.65% Pt/SiO₂ after exposure to different probe gases. The oxygen desorption peaks in Fig. 4(b) imply the presence of the oxygen atoms on Pt, with three different coordination environments, in excellent agreement with that (Fig. 3 and Table 2) revealed from IR spectra for CO adsorbed on Pt, with different adsorption modes and oxidation environments, and these O atoms all could be reacted with H_2 to form H_2O as indicated by the 396 K peak in Fig. 4(c), thereby giving consistent results with the previous IR bands that are the $3,437\text{ cm}^{-1}$ OH stretching and the $1,641\text{ cm}^{-1}$ peak due to a deformation mode of $\text{H}_2\text{O}_{(\text{ad})}$ on the silica surface as shown in Fig. 2(c). Consequently, the oxygen atoms chemisorbed on Pt, via N_2O decomposition at 363 K are readily removed by H_2 according to Eq. (2), irrespective of accommodation environment.

The activity profiles obtained for the continuous dissociation of N_2O at 363 K in the absence and presence of H_2 over 0.65% Pt/SiO₂ (Figs. 6 and 7) give very consistent results among themselves and with the previous DRIFTS, TPD, gravimetric and volumetric studies. In the absence of H_2 (thus N_2O decomposition), a decrease in the rate of the N_2O conversion is observed and complete deactivation occurs, depending significantly on the concentration of N_2O being fed (Fig. 6). This is due to self-poisoning with O atoms chemisorbed very strongly on Pt, [Burch et al., 2004], and these oxygen atoms could be desorbed from the Pt surfaces at temperatures greater than 673 K as indicated by *in situ* TPD spectrum in Fig. 4(b). Approximately 773-K temperature may be required in order for N_2O

decomposition reaction to be continuously catalyzed with this Pt/SiO₂ catalyst, as acquired in Fig. 4(b) and (d), if neither of the reductants reported in the literature are employed to facilitate such oxygen removal from Pt,. Thus this represents that most of exhaust streams including N_2O at concentrations of ppm levels should be heated up to the 773 K temperature thereby requiring subsequent heating energy. Therefore, these would motivate the use of appropriate reductants to remove the oxygen atoms on Pt,, i.e., continuous catalytic N_2O removal reaction, at much lower temperatures. The presence of H_2 as an efficient reductant with N_2O plays an excellent role in cleaning up the O atoms chemisorbed strongly on Pt, to produce H_2O during the course of reaction, as revealed in Fig. 7. For all the experiments conducted here, the mass balance for N_2 was greater than 98%, based on the concentration of $\text{N}_{2(\text{g})}$ produced not only upon N_2O decomposition at 363 K, but also upon N_2O reduction with H_2 at 363 K. Consequently, the use of H_2 as a reductant allows the continuous reduction of N_2O at 363 K over the Pt/SiO₂ catalyst and this temperature is dramatically lower, by 230 K, than that reported earlier for N_2O reduction with CO, CH_4 , NH_3 , C_3H_6 and C_3H_8 . This removal reaction can occur without inhibition of the activity due to the presence of $\text{H}_2\text{O}_{(\text{ad})}$ on the silica surface, as confirmed by *in situ* DRIFTS measurements for a fully “wet” surface (Fig. 9).

CONCLUSIONS

A 0.65% Pt/SiO₂ catalyst has a very high dispersion, and the characterization of this Pt surface gives us very consistent results among themselves. A residual uptake is gravimetrically observed after N_2O decomposition at 363 K following exposure to H_2 for more than 1 h, but *in situ* DRIFTS spectra for the catalyst with these reactions at the same conditions give no presence of untitratable O atoms on Pt,. This is associated with the adsorption of H_2O , produced when admitting H_2 onto the oxidized Pt,, on the silica surface but not on Pt,, although exposure of the oxidized Pt surfaces to CO at 300 K represents an IR band at $2,188\text{ cm}^{-1}$ due to add-on CO on Pt₂O. The $\text{H}_2\text{O}_{(\text{ad})}$ acquired by peaks at $3,437$ and $1,641\text{ cm}^{-1}$ could not inhibit dissociative N_2O adsorption at 363 K on Pt, as indicated by the same H uptake, established via H_2 - N_2O titration on a reduced Pt,, as that revealed upon the titration reaction with a fully “wet” surface on which all bands and their position in IR spectra for CO are very similar to that appeared on a H-covered Pt, after single H_2 - N_2O titration.

All these characterization results are in excellent agreement with on-stream activity profiles obtained for continuous N_2O removal reaction in the absence and presence of H_2 . In the absence of H_2 as a titrator, i.e., reductant, the extent of the decomposition of N_2O at 363 K over 0.65% Pt/SiO₂, thereby leaving stoichiometric O coverage on the reduced Pt surface with the release of $\text{N}_{2(\text{g})}$, decreases very rapidly after a certain time on-stream and vanishes completely, depending significantly on the N_2O concentrations used. This activity behavior is because of self-poisoning due to the atomic oxygen chemisorbed strongly on Pt, which could possess three different coordination environments in consistent with *in situ* DRIFTS and TPD results. All the O atoms on such Pt surfaces are readily removed by subsequent feed of H_2 with N_2O ; consequently, this N_2O reduction reaction can be continuously catalyzed at very low temperatures, such as 363 K, that are much lower than that documented earlier.

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