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Catalytic decomposition of nitrous oxide on nano sized palladium catalysts: The influence of precursor and the method of preparation

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Abstract

Alumina-supported 1 wt. % Pd catalysts were prepared by the deposition precipitation (DP) and impregnation (IMP) methods. The DP catalysts showed higher activity than those of their IMP analogues for decomposition of nitrous oxide. The DRIFTS analysis revealed preferential formation of partially oxidized Pd^{+1} species on the surface of DP-Cl catalyst. The temperatures at which the peak maxima appeared were higher in the TPR patterns of the DP-Cl catalysts, indicating greater interaction between Pd and alumina leading to formation of cationic Pd species. The high activity of DP-Cl catalyst prepared by DP method was related to the formation of electron deficient Pd sites during the preparation and their occupancy in the octahedral vacancies of alumina.

Keywords: N_2O decomposition; Temperature-programmed reduction; DRIFTS; Pd catalyst.

1. Introduction

Environmental issues such as global warming and ozone layer depletion are now of universal concern. Nitrous oxide (N_2O) is one of the important compounds associated with this concern. The major sources of nitrous oxide are the nylon production (adipic acid) and fertilizer production (HNO_3) units, which are responsible for 23 % of worldwide emissions. Agriculture (fertilizer use, leguminous crops) and to a lesser extent, vehicles equipped with three-way catalysts and fluidized bed combustion processes also contribute to N_2O emission. With a lifetime of 150 years at atmospheric conditions, it also exhibits a global warming potential 310 times that of carbon dioxide. With the increase in concern for environmental degradation, efforts have been made to convert N_2O into N_2 and O_2 [1]. A recent review, [2] classified the different abatement processes for reducing N_2O emissions from nitric acid plants. Catalytic decomposition, by for, is recommended as a good end-of-pipe technology for N_2O conversion.

A large number of catalysts have been tested for the decomposition of N_2O, such as noble metals (Pt, Au, Ru and Rh), pure oxides (NiO, Co_3O_4, CoO, CuO and MgO), mixed oxides (solid solutions, perovskites and spinels) and zeolites exchanged or impregnated with transition metal ions (ZSM-5, ZSM-11, Beta, Mordenite, USY, Ferrierite, exchanged/ impregnated with Fe, Ni, Co, Rh, Ce, Mn, Ru or Pd). These catalysts have been reviewed by Kapteijn et al. [1]. Metal-exchanged ZSM-5 (Cu, Co, Rh, Ru, Fe), calcined hydrotalcite-like materials and supported metal or metal oxides, in particular noble metals such as Ru/Al_2O_3 [3,4,5], and Rh/ZrO_2 [6] are considered important among them. Supported oxides are more effective in practical applications due to the higher dispersion of active sites and the higher specific surface area of the support. In most of the works alumina was used as a support with Pd, Cu, Co, Mn, Rh, Ru, Fe, or Cr as active component [7-13].

The main problem, observed in most of the catalytic systems, was the inhibition of the N_2O decomposition by the strong adsorption of oxygen species produced during the reaction. Palladium generally displays similar catalytic activity as platinum but has better thermal stability and hence is commonly included in automotive exhaust gas purification catalysts [14]. Kazuyoshi et al. [15] investigated the catalytic decomposition of nitrous oxide over alumina-supported Rh, Pd and Pt catalysts in order to select an effective catalyst for the purification of atmosphere in the operating rooms. Masuda et al. [16] studied the Ag–Pd bimetallic catalyst for the removal of NO_x from diesel exhaust gas. A small amount of Pd seems to improve significantly the catalytic activity in practical conditions.

$PdCl_2$ is one of the major precursors, which is commonly employed as a source of palladium in catalyst preparation. The major problem associated with $PdCl_2$ is the presence of surface chloride. Residual chloride ions on the surface are suggested to inhibit the rate of reaction. Hence new methods are being explored to combat the situation. Deposition precipitation method can effectively remove the surface chloride ions. In the present study the performance of nano sized palladium-based catalysts is examined by preparing them adopting the DP-method. An attempt has been made to identify the nature of the active species by characterization of the catalysts using CO chemisorption, XPS, TPR etc. Alumina has been selected as a support to disperse Pd. In order to compare the activity of the DP catalysts in N_2O decomposition, catalysts with the same Pd loading were prepared using palladium nitrate as a precursor and also adopting the impregnation method. A correlation has been made between the activity of catalyst and the nature of Pd site formed.

2. Experimental
2.1. Catalysts preparation
In the deposition – precipitation method the support Al_2O_3 was first dispersed into an aqueous solution of 1 wt.% $PdCl_2$ or $Pd(NO_3)_2$. To this solution 1 M Na_2CO_3 was slowly added until the pH of the mixture reached 10.5. The suspension was then maintained at the same pH for 1h during the precipitation process. The resulting solid was filtered. In the case of chloride precursor ($PdCl_2$), the mass was washed with deionized water several times, after precipitation, until no chloride ion was detected

by silver nitrate solution. Catalysts were also synthesized by conventional impregnation (IMP) of Al_2O_3 with an aqueous solution of metal precursor containing 1 wt.% metal following the wet impregnation method. All the catalysts were then calcined at 500 ^{o}C for 5 h in air. The catalysts were designated as DP-Cl, DP–N, IMP –Cl, IMP–N where DP and IMP refer to deposition–precipitation and impregnation methods respectively, Cl and N refer to the chloride and nitrate precursors of Pd, respectively.

2.2. Characterization of catalysts
Adsorption Measurements

The specific surface area of the catalyst samples were estimated using the N_2 adsorption at –196 ^{o}C by the single-point BET method using a Micromeritics Plus Chemisorb 2700 instrument. Before measurements, the samples were oven-dried at 393 K for 12 h and flushed in situ with He gas for 2 h. Room temperature CO chemisorption was carried out on a pulse adsorption apparatus. In a typical experiment, the catalyst was first oxidized in a 10 % O_2 /He mixture at 300 ^{o}C for 30 minutes and subsequently reduced in a 10% H_2/He mixture under similar conditions flushing the catalyst with pure He in between. The CO adsorption capacity was then obtained by the number of pulses required to saturate the surface.

DRIFTS experiments were performed with an FT-IR (Digilab excalibur series) equipped with an MCT detector and a high-pressure, high-temperature DRIFTS cell (Harrick) fitted with KBr windows allowing to record spectra at different temperatures under controlled atmosphere. The cell was connected to a flow reaction system at atmospheric pressure. The temperature was monitored through a thermocouple in direct contact with the sample. Spectra were acquired at a resolution of 2 cm^{-1}, typically averaging 100 scans. The samples were initially flushed with helium and then were activated at 300 ^{o}C at a ramping rate of 10 ^{o} C / min in a flowing 10 % H_2 -balanced by argon gas mixture. After 1 h the sample was flushed and cooled to room temperature in the flow of helium. The sample was then allowed to adsorb CO by flowing a gas mixture containing 10% CO balanced by helium at a total flow rate of 30 ml / min for 1 h. The spectrum of adsorbed CO was obtained by the difference between the absorbance of the sample after and before absorption of CO.

Powder X – ray Diffraction (XRD) studies

X-ray powder diffraction patterns were obtained with a Siemens D5000 diffractometer, using Cu Kα radiation (1.5406 Å). The measurements were recorded in steps of 0.045 ^{o} with a count time of 0.5 s in the 2Θ range of 2-80 ^{o}. Identification of the phases was made with the help of the Joint Committee on Powder Diffraction Standards JCPDS files.

X – ray photoelectron spectroscopy (XPS)

XPS measurements were conducted with a KRATOS AXIS 165 with a DUAL anode (Mg and Al) apparatus using the MgK$_\alpha$ anode. The non-monochromatized Al-K$_\alpha$ X–ray source (hν = 1486.6 eV) was operated at 12.5 kV and 16 mA. Before

acquisition of the data the sample was out gassed for about 3 h at 373 K under a pressure of 1.0 x 10^{-2} torr to minimize the surface contamination. The XPS instrument was calibrated using Au as a standard. For energy calibration, the carbon 1s photoelectron line was used. The carbon 1s binding energy was taken to be 285 eV. Charge neutralization of 2 eV was used to balance the chargeup of the sample. The spectra were deconvoluted using Sun Solaris based Vision-2 curve resolver. The location and the full width at half maximum (FWHM) value for the species were first determined using the spectrum of pure sample. The location and FWHM of products which were not obtained as pure species were adjusted until the best fit was obtained. Symmetric Gaussian shapes were used in all cases. Binding energies for identical samples were, in general reproducible within $\pm$ 0.1 eV.

Temperature programmed reduction (TPR)

Temperature programmed reduction (TPR) of the catalysts was carried out in a flow of 10 % H_2/Ar mixture gas at a flow rate of 30 ml/min with a temperature ramp of 10 ^{o}C / min. Before the TPR run the catalysts were pretreated with argon at 300 ^{o}C for 2 h. The hydrogen consumption was monitored using a thermal conductivity detector.

Activity measurements

The catalytic decomposition of N_2O was carried out in a fixed-bed reactor. A fresh catalyst ($\approx$ 0.5 g) was diluted with the same size and amount of quartz powder and loaded in the reactor for each run. Prior to the catalyst testing, the catalysts were pretreated at 300 ^{o}C for 1 h in a flow of hydrogen to activate and stabilize the catalysts. The total flow rate used was 60 ml min^{-1} (yielding a gas hourly space velocity of 7,200 h^{-1}). After the catalyst had attained steady state over a period of 2 h at each temperature, the effluent gas was analyzed by a micro gas chromatograph (Varian CP-4900 TCD) using a molecular sieve 5A column (for the analysis of O_2, N_2) and a poraplot column (for that of N_2O).

The catalytic activity was evaluated in terms of conversion (X) of N_2O gas according to the following equation

$$X_{N2O} = (C_{N2O\ in} - C_{N2O\ out}) / C_{N2O\ in} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Where $C_{N2O\ in}$ & $C_{N2O\ out}$ are concentrations of N_2O at the inlet and outlet of the reactor respectively.

3. Results and discussion

The XRD patterns of palladium catalysts are presented in Fig.1. Even though not very sharp, the XRD patterns displayed peaks (2θ: 33.9, 54.8, and 60.5^{o}) due to the presence of PdO. The Patterns showed broad peaks at 2θ: 36.5, 39.5, 46 and 67° of Al_2O_3 also indicating that the support is poorly crystalline.
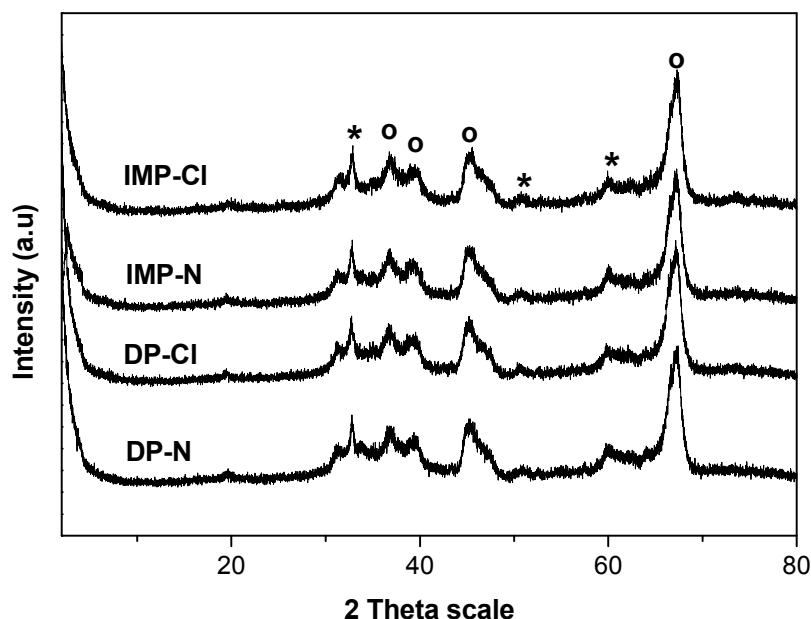
Fig. 1. XRD patterns of Pd/ Al_2O_3 catalysts. (*) PdO and (o) Al_2O_3.

The BET surface area and CO chemisorption results of the catalysts prepared by different preparation methods and using different Pd precursors are summarized in Table 1. The specific surface area of Al_2O_3 support was found to be 195 m^2/g. Among all the catalysts, the DP–Cl exhibited the highest surface area of 181 m^2/g. The DP–N catalyst recorded the lowest surface area of 147 m^2/g. The decrease in the BET surface area of the Pd supported catalysts is presumably a result of the plugging of the pores by crystallites of palladium oxide.

It can be seen from Table 1 that the DP-Cl and IMP-Cl catalysts have a palladium dispersion of 60.2, and 26.0 %, respectively, whereas for DP-N and IMP-N catalysts the dispersion values are 7.0 and 6.0 % respectively. The DP catalysts exhibited better dispersion than the IMP catalysts. These results are in accordance with the data presented by Shen et al. [17] and Rajesh et al. [18]. An experiment conducted to determine CO uptake on Al_2O_3 support alone revealed no significant adsorption, after reduction at 300 ^{o}C. The catalysts prepared from chloride precursor of Pd showed higher dispersions compared to their nitrate analogues. An interesting observation that can be made from the chemisorption results is that the catalysts prepared from the nitrate precursor showed almost similar dispersions irrespective of the nature of preparation method. Thus, influence of palladium precursor and the method of preparation are very clear. Chloride precursors are known for their interaction with the hydroxyl groups present on the surface of alumina leading to a good distribution of the metallic particles [20] thereby giving high dispersions. On the other side, lack of interaction with OH groups by nitrate precursors would promote coalescence of Pd particles.

Table 1 Physico-chemical properties of the Pd/ Al$_2$O$_3$ catalysts prepared from different preparation method and precursors.

Catalyst	Surface area (m^2/ g)	CO uptake (Ncc / g)	Dispersion (%)	Specific metal area (m^2/ g)	Particle size (A^o)	Cl/Pd ratio obtained by XPS analysis
Al$_2$O$_3$	195	-	-	-	-	-
DP-Cl	181	1.2	60.2	2.68	18	0.79
IMP-Cl	167	0.55	26.0	1.16	43	1.58
DP-N	147	0.14	7.0	0.6	69	-
IMP-N	154	0.13	6.0	0.5	78	-

The temperature programmed reduction profiles obtained on the Pd/Al$_2$O$_3$ catalysts are shown in Fig.2. The IMP-Cl, IMP-N and DP-N catalysts exhibited reduction peaks at 120 ^{o}C, whereas that of DP-Cl catalyst exhibited reduction peak at 135 ^{o}C. The TPR profiles did not display the characteristic negative peak in the temperature range of 50–130 ^{o}C. The negative peak appears due to the decomposition of β-PdH [19]. β-PdH formation is normally accompanied by the presence of larger Pd particles in the catalyst. This observation also reveals that the bulk particles are not formed, as revealed by the CO chemisorption data. The low temperature peak obtained in all the catalysts is due to the reduction of less strongly interacted PdO species. The high temperature reduction peak observed in the range 300-450 ^{o}C may be due to the subsurface hydrogen. In the case of DP-Cl catalyst the reduction peak was obtained at 135 ^{o}C relatively at higher reduction temperatures than those of IMP catalysts. As reported by Shen et al. [17] the PdO particles formed by strong interaction on the metal-support interface are more resistant to reduction.

The XPS spectra of the unreduced and reduced DP–Cl and IMP–Cl catalyst are shown in Fig. 3 and Fig. 4, respectively. The Pd 3d$_{5/2}$ binding energy for unreduced DP–Cl catalyst was recorded as 338.5 eV. The XPS analysis of reduced DP–Cl catalyst revealed that the Pd 3d$_{5/2}$ binding energy decreased to 336.5 eV. It seems that in unreduced catalyst, Pd is in a highly oxidized state or there is a complete surface oxidation of Pd that gives rise to higher binding energy values. The binding energy of Pd 3d$_{5/2}$ for metallic Pd is reported to be 335.0 eV in literature [21]. In reduced DP–Cl catalyst the shift of Pd 3d$_{5/2}$ binding energy to higher value of 336.5 eV compared to that of metallic Pd suggests the existence of cationic Pd or Pd with a valency close to 1+. Shen et al [22, 23] also observed a higher Pd 3d$_{5/2}$ binding energy than metallic Pd for catalyst synthesized by DP method. In the DP method of catalyst preparation the formation of palladium hydroxide takes place on the surface of alumina and a chemical binding such as Pd–O–Al can be formed at the interface between Pd and Al$_2$O$_3$ during the consequent calcination and reduction steps. As

Al_2O_3 is an interacting support, the strong contact between the Pd particle and alumina causes electron transfer from Pd to Al_2O_3 leading to the formation of cationic Pd on the surface which is reflected in the increased binding energy on the outer electron shells of the metal. Zhang and Beard [24] also suggested that Pt clusters anchored to Lewis acid sites in alumina form $Pt_n(Al)O_3$ structure which contributes to electron deficient character of the platinum particles.
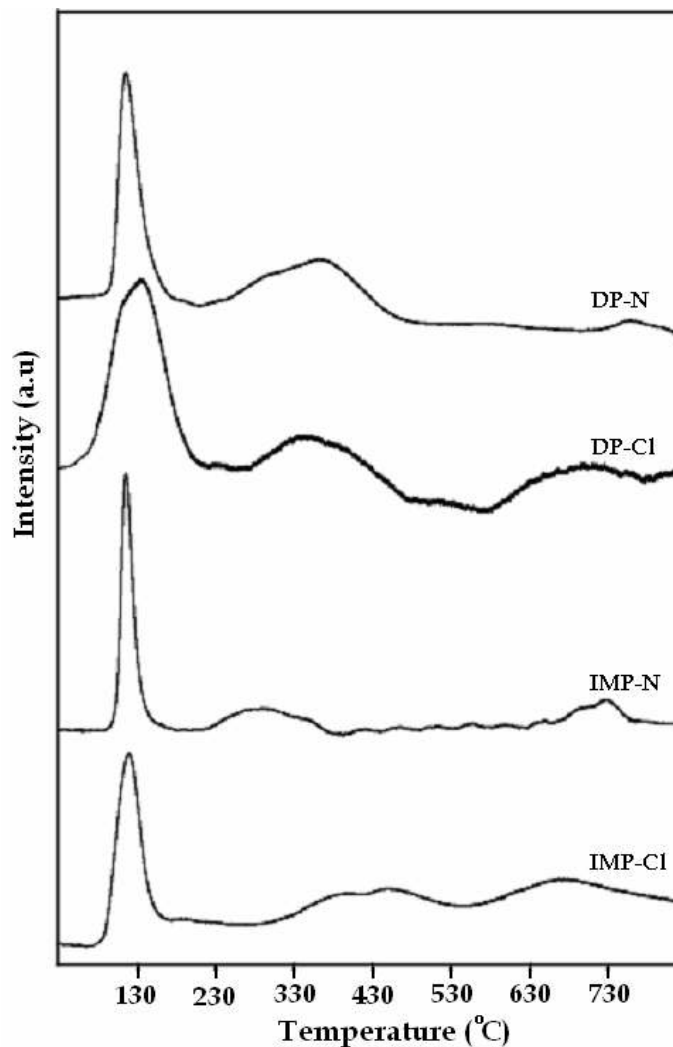

Fig. 2. TPR patterns of Pd/ Al_2O_3 catalysts.

The Pd $3d_{5/2}$ binding energies for the unreduced and reduced IMP–Cl catalysts are obtained as 338.09 and 338.7 eV, respectively. The peak maxima observed at 338.09 eV for unreduced IMP–Cl catalyst corresponds to $PdCl_2$ as reported by Bozon–Verduraz et al [25]. The peak maximum observed at 338.7 eV for reduced IMP–Cl catalyst indicates the presence of a complex species, $PdCl_4^{2-}$, as well as

PdCl$_2$. The XPS results indicate that alumina supported palladium catalysts synthesized by impregnation method retain chlorine on its surface even after reduction at 300 °C. These results are in accordance with the observations made by Bozon–Verduraz et al [25] that alumina supported Pd catalysts from PdCl$_2$ precursor retained residual chlorine ions in the vicinity of Pd atoms even after the calcination and reduction treatments.
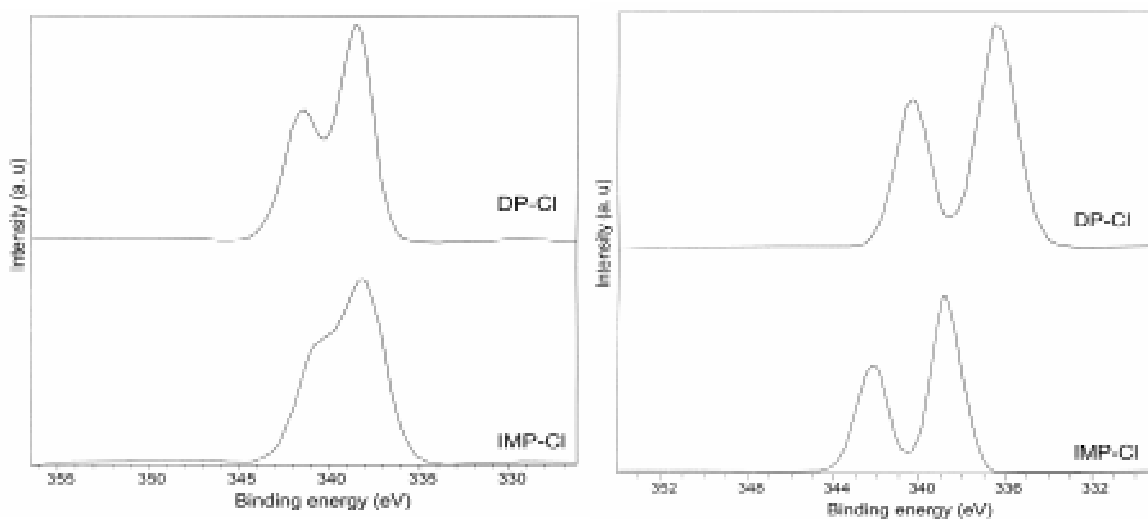

Fig. 3: (a). XPS spectra of non-reduced Al$_2$O$_3$ supported Pd catalysts. **(b).** XPS spectra of reduced Al$_2$O$_3$ supported Pd catalysts.

The activity profiles obtained on the catalysts for the decomposition of N$_2$O are shown in Fig. 5. The conversion plots follow S-shaped curves for all the catalysts. In the case of IMP-N and DP-N catalysts the decomposition started at 300 °C and the complete conversion occurred above 525 °C. The DP-N catalyst showed relatively higher activity than IMP-N at a given temperature. On the IMP-Cl catalyst the decomposition was initiated at 300 °C and the complete conversion occurred above 600 °C, whereas on the DP-Cl catalyst the initiation of decomposition occurred at 250 °C and completed at 500 °C. Thus, the DP-Cl catalyst showed complete conversion relatively at low temperature than that of IMP-Cl catalyst.

The IMP-Cl catalyst was found to be least active among the four catalysts. The two catalysts prepared using nitrate precursor i.e, IMP-N and DP-N exhibited almost identical activity irrespective of method of preparation. The DP-Cl is found to be highly active. Many reports stated that the chloride precursors are less active than nitrate precursors. A similar observation was also made in the present catalyst prepared by impregnation. But, by changing the method of preparation, it is possible to change the less active palladium chloride catalyst into a highly active one. Several authors [17,18] have extensively demonstrated the disadvantages of the surface chloride ions. Mainly, the surface properties of Pd particle are altered by interaction with the residual chloride ion. By adopting the DP method of catalyst preparation, it is

possible to effectively remove the surface chloride species to the maximum extent. The enhancement in the activity of the chloride precursor catalysts by several folds after selective removal of chloride ions is a testimony for the usage of the DP method. This is an important revelation of this work.
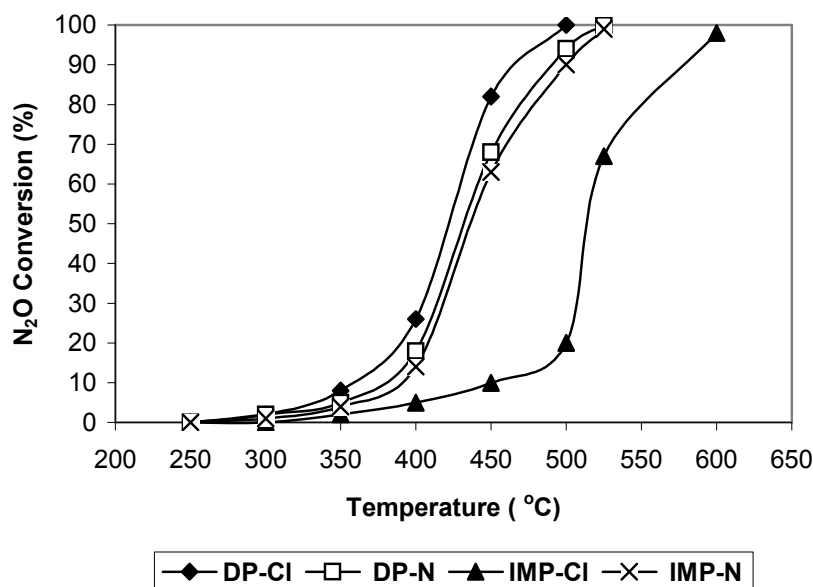

Fig. 4. N_2O Conversion on Pd/ Al_2O_3 catalysts with temperature.

In order to understand the nature of Pd surface species formed during method preparation CO DRIFTS adsorption studies have been carried out. Christoforou et al. [13] proved that partially reduced Rh is responsible for catalytic conversion of N_2O to N_2. In the same way to know the oxidation states of the Pd DRIFTS experiments were conducted using CO as a probe molecule. Fig. 6 shows the infrared spectra of CO adsorbed at room temperature on palladium catalysts. When the catalysts were reduced at 300 °C, five bands were observed on IMP-Cl at 1929, 1973, 2080, 2129 and 2162cm^{-1}, whereas IMP-N showed three major bands at 1934, 1982 and 2077 cm^{-1}. In the case of DP-Cl four major bands were observed at 1938, 1982, 2087 and 2129 cm^{-1} and similarly DP-N catalyst showed three major bands at 1933, 1984 and 2080 cm^{-1}.

The stretching frequency is often an excellent indicator of the way CO binds to the substrate. Linearly adsorbed CO absorbs at frequencies between 2000-2130 cm^{-1}, bridged-bonded CO between 1880-2000 cm^{-1}. Therefore, the IR band at 2070 cm^{-1} can be assigned to linearly bonded CO to Pd^o, and the 1980 and 1930 cm^{-1} bands to bridge-bonded Pd^o to CO. In the IR spectrum for IMP-Cl, additional IR bands assignable to monocarbonyl Pd^{2+}–CO and Pd^{1+}–CO species [26–28] were also observed at 2160 and 2125 cm^{-1}, respectively. Indicating that the surface property of palladium on IMP-Cl prepared from palladium chloride seems to be different from

that on the other catalysts. The IMP-N catalyst did not show formation of any cationic species. Nitrate based precursors are reduced relatively at lower temperatures than that of chloride based precursors. The TPR patterns also reveal that IMP-Cl catalysts showed high reduction temperature than that of IMP-N catalyst. The presence of ionic palladium on the IMP-Cl catalyst is not surprising. The chloride content measured by XPS after reduction at 300 $^{\circ}$C amounted to 1.58% and a part of this quantity could be located in the vicinity of palladium atoms. In the case of the IMP-Cl the high dispersion value should favor (Pd to carrier) electron transfer. At first sight such a transfer could not be involved in the case of IMP-N because of its low dispersion value. The DP-N catalyst also did not show any cationic palladium species on the surface of the catalyst. In the case of DP-Cl catalyst there is a clear formation of Pd^{1+}–CO species at 2129 cm^{-1}. This is due to the fact that the DP-Cl based method of preparation can create strong metal support interactions during the preparation of the catalyst. The high reduction temperature patterns observed in TPR, formation of cationic palladium species and high dispersion values are supporting strong metal support interaction on DP-Cl catalyst.
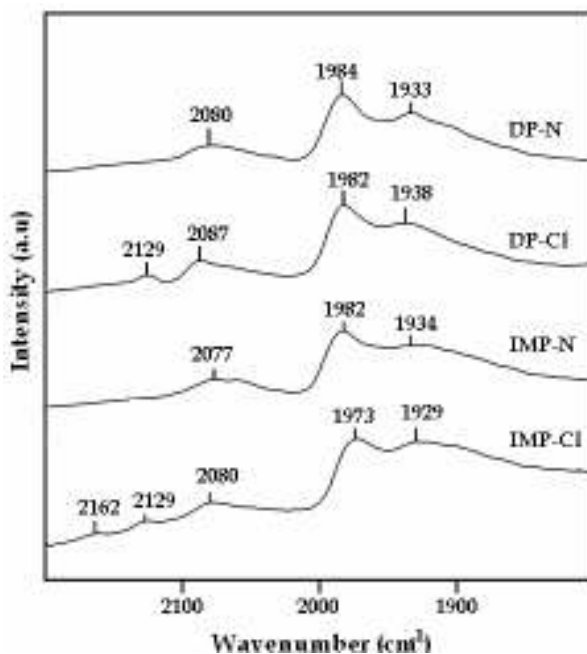

Fig. 5. CO adsorbed DRIFTS spectra on Pd/ Al$_2$O$_3$ catalysts at room temperature.

The differences in the dispersion of the catalysts are related to the nature of species attached to Pd. The metal support interaction is one of the important factors that contribute to the overall dispersion of the catalysts. The Cl/Pd ratio determined by the XPS analysis showed that the catalysts prepared from chloride precursor of Pd, retained a considerable amount of chlorine even after the calcination treatment. The high dispersion of the catalyst from PdCl$_2$ may be attributed to the presence of

interaction of chlorine in H_2PdCl_4 with surface hydroxyl groups on alumina. Several papers reported higher dispersions for catalysts prepared using $PdCl_2$ precursor than those from chlorine–free precursor in the case of Pd/Al_2O_3 catalysts. The authors thought that $PdCl_2$ dissolves in HCl forming $PdCl_4^{2-}$ [32, 33] and an anion exchange reaction proceeds between $PdCl_4^{2-}$ and OH^- groups on the alumina surface that might increase the Pd dispersion [34, 35, 36]. Gaspar and Dieguez [34] studied the dispersion of Pd/Al_2O_3 catalysts with different Pd contents and precursor salts subjecting the final catalysts to reduction – oxidation cycles. The authors reported that the reduction–oxidation cycle resulted in the sintering of all the catalysts except for the 1wt. % Pd catalyst prepared from $PdCl_2$ precursor. The stability of the dispersion was related to the formation of surface complex species like $Pd_xO_yCl_z$. The high dispersion of DP–Cl catalyst than that of IMP-Cl catalyst is due to the formation of palladium hydroxide mainly on the basic sites of Al_2O_3 in the process of DP and a strong chemical bonding, such as Pd-O-Al, occurs at the Pd-support interface during the process of dehydration. This strong interaction inhibits the agglomeration of metal on the surface resulting in a highly dispersed state of Pd. The catalysts prepared from nitrate precursor lends credence to this observation as they showed almost similar value for dispersions, which is related to the facile formation of PdO during the preparation, as palladium nitrate is known to decompose easily at lower temperatures. The lower dispersions of the catalysts from nitrate precursor are due to poor interaction between metal and support.

4. Conclusions

Palladium chloride supported Al_2O_3 catalyst prepared by deposition – precipitation method was found to be highly active among the four catalysts. The Pd catalysts prepared by DP method with chloride precursor provide a convenient approach for the preparation of active catalysts for catalytic decomposition of nitrous oxide reaction. The high activity of DP - Cl catalyst seems to be the manifestation of an active wherein Pd exists in its cationic form.

Acknowledgements

References

[1] Kapteijn, F., Mirasol, J.R. and Moulijn, J.A., (1996) Appl. Catal. B, 9, 25-55.
[2] Pérez-Ramírez, J., Kapteijn F., Schöffel K. and Moulijn J. A., (2003) Appl. Catal. B, 44, 117-151.
[3] Zeng, H.C., Pang, X.Y., (1997) Appl. Catal. B, 13, 113-122.
[4] Wang, X.F., Zeng, H.C., (1998) Appl. Catal. B, 17, 89-99.
[5] Marnellos, G.E., Efthimiadis, E.A., Vasalos, I.A., (2003) Appl. Catal. B, 46, 523-539.

[6] Pinna, F., Scarpa, M., Strukul, G., Guglielminotti, E., Boccuzzi, F., Manzoli, M., (2000) J. Catal, 192, 158-162.

[7] Zeng, H.C., Lin, J., Teo, W.K., Wu, J.C., Tan, K.L., (1995) J. Mater. Res, 10, 545-553.

[8] Li, Y., Armor, J.N., (1993) Appl. Catal. B, 3, 55-60.

[9] Kannan, S., Swamy, C.S., (1994) Appl. Catal. B, 3, 109-116.

[10] Chang, Y.-F., McCarty, J.G., Wachsman, E.D., Wong, V.L., (1994) Appl. Catal. B, 4, 283-299.

[11] Chang, Y.-F., McCarty, J.G., Wachsman, E.D., (1995) Appl. Catal. B, 6, 21-33.

[12] Oi, J., Obuchi, A., Ogata, A., Yagita, H., Bamwenda, G.R., Mizuno, K., (1995) Chem. Lett, 6, 453-459.

[13] Christoforou, S.C., Efthimiadis, E.A., Vasalos, I.A., (2002) Catal. Lett, 79, 137-147.

[14] Parvlescu, V.I., Grange, P., Delmon, B., (1998) Catal.Today, 46, 233-316.

[15] Kazuyoshi, D., Yun, Y.W., Takeda, R., Matsunami, A., Arai, N., Tagawa, T., Goto, S., (2001) Appl. Catal. B, 35, 43-51.

[16] Masuda, K., Shinoda, K., Kato, T., Tsujimura, K., (1998) Appl. Catal. B, 15, 29-35.

[17] Shen, W. J., Ichihashi, Y., Okumura, M. and Matsumura, Y., (2000) Catal. Lett, 64, 23-25.

[18] Gopinath, R., Lingaiah, N., Sreedhar, B., Suryanarayana, I., Sai Prasad, P.S., Obuchi, A., (2003) Appl. Catal. B, 46, 587-594.

[19] Chang, T.C., Chen, J.J., Yeh, C.T., (1985) J. Catal, 96, 51-57.

[20] Rob van Veen, J.A.R., Jonkers, G., Hesselink, H., (1989) J. Chem. Soc, Faraday Trans, 1, 85, 389-413.

[21] Briggs, D., Seah, M.P., Practical surface analysis, in: Auger and X-ray Photoelectron Spectroscopy, Wiley, New York, 2nd Edition, Vol.1 (1990).

[22] Shen, W., Ichihashi, Y., Ando, H., Okumura, M., Haruta, M., Matsumura, Y., (2001) Applied Catal. A, 217, 165-.172

[23] Shen, W., Matsumura, Y., (2000) J.Mol. Catal A, 153, 165-168.

[24] Zhang, Z.C., Beard, B.C., (1999) Appl. Catal A, 188, 229-240.

[25] Bozon-Verduraz, F., Omar, A., Escard, J. and Pontvianne, B., (1978) J. Catal, 53, 126-134.

[26] Vannice, M.A., Wang, S-Y., Moon, S.H., (1981) J. Catal, 71, 152-166.

[27] Daniell, W., Landes, H., Fouad, N.E., Knozinger, H., (2002) J. Mol.Catal. A, 178, 211-218.

[28] Tessier, D., Rakai, A., Bozon-Verduraz, F., (1992) J. Chem. Soc, Faraday Trans, 88, 741-749.

[29] Juszczyk, W., Malinowski, A., Karpinski, Z., (1998) Appl. Catal. A, 166, 311-319.

[30] Lingaiah, N., Uddin, Md. A., Muto, A. and Sakata, Y., (1999) Chem. Commun, 1657-1658.

[31] Gaspar, A.B., Dieguez, L.C., (2000) Appl. Catal A, 201, 241-251.

[32] Ito, K., Ohshima, M., Kurokawa, H., Sugiyama, K., Miura, H., (2002) Catal. Commun, 3, 527-531.

[33] Sivaraj, Ch., Contescu, Cr., Schwarz, J.A., (1991) J. Catal, 132, 422-431.