Eclética Química

A FTIR STUDY OF THE METAL-SUPPORT INTERACTIONS AND HYDROGEN SPILLOVER ON Pd/TiO$_2$ and Ni/TiO$_2$.

Flávio FACCIN[*]

Fabiana Flores GUEDES[*]

Edilson Valmir BENVENUTTI[*]

Celso Camilo MORO[*]

ABSTRACT: Nickel and palladium dispersed on titania support were submitted to reductive treatment, under hydrogen, at 200 and 500 $^\circ$C. After the reductive thermal treatment the materials were exposed to carbon monoxide (10 Torr) and analyzed in the infrared region. The increasing of the electronic density in the metallic *d* subshell, produced by the reductive thermal treatment, was monitored by the infrared stretching band shift of carbon monoxide adsorbed and it was interpreted as a consequence of the metal-support interactions. The highest effect was observed for Pd/TiO$_2$ system. From the FTIR spectra was also observed that the hydrogen spillover was stronger on Pd/TiO$_2$ than Ni/TiO$_2$ system.

KEYWORDS: metal-support, infrared, titania, carbon monoxide, hydrogen spillover, palladium, nickel

Introduction

The infrared spectroscopy analysis using probe molecules, like carbon monoxide adsorbed on the metal, has been an useful tool on the dispersed metal properties study.[3,5,10,17,19] When the dispersed metal is reduced to high temperature, the electronic density in the *d* subshell should be increased due to the strong metal-support interactions, thus the dispersed metal can promote a stronger back-bonded metal-carbonyl and the CO bond became weaken.[3,7,12] Therefore the carbonyl coordinated

stretching band position change to lower wavenumbers. Consequently the carbonyl band energy position is inversely correlated to the metal electronic density.

The metal-support interactions were reported for the first time in 1978,[24] and it was primarily interpreted as a morphological effect, where the reduced support produces an expansion in its ionic crystal lattice due to the decreasing in the electrostatic attraction, since reduced species are formed.[1,15,20,24] However, electronic interpretations was also made, in this case the metal-support interactions are considered as a charge transference from the reduced support to the dispersed metal.[2,3,11,16,25] This effect produces an increasing in the electronic density in d subshell of the dispersed metal.

The hydrogen spillover mechanism, that consist in adsorption of molecular hydrogen followed its dissociation and migration of the atomic hydrogen from metal to the support bulk, was already reported for metal dispersed materials that present strong metal-support interactions, like Pt/TiO_2.[2,3]

In this work, nickel and palladium were dispersed on titania that is a typical reducible material. Reducible thermal treatments at 200 and 500 $^{\circ}C$ were performed for the materials and the electronic densities in the d subshell of the dispersed metals were compared, using the FTIR analysis of the carbonyl bands. After the thermal treatment at 200 $^{\circ}C$ the materials were also submitted to hydrogen and the spillover mechanism could be also detected by using the FTIR analysis.

Experimental

Synthesis of Pd/TiO$_2$ and Ni/TiO$_2$

Acidified aqueous solutions (0.2 mol.L^{-1}) of $PdCl_2$ and $NiCl_2$ was dropped under constant stirring on to TiO_2 (anatase) (P25 Degussa). The solids was stirred for 2 h and then dried at 110$^{\circ}C$ for 16 hours. The resulting materials were assigned as Pd/TiO_2 and Ni/TiO_2, respectively. The metal quantities added were calculated to obtain a 1.5 % of the metal loading.

Reductive thermal treatment

Self-supporting disks of Pd/TiO_2 and Ni/TiO_2 with an area of 5 cm^2 and a weight of 50 mg were prepared, heated to 200$^{\circ}C$ under vacuum (10^{-3} Torr) for 1 hour and submitted to 200 Torr of oxygen for 1 hour at 200$^{\circ}C$. The oxygen was degassed (10^{-3} Torr) for 1 h at 300$^{\circ}C$. After that, the materials were submitted to 200 Torr of hydrogen at 200$^{\circ}C$ (LTR - low temperature of reduction) or 500$^{\circ}C$ (HTR - high temperature of reduction) for 1 hour, and finally degassed at the temperature of 300$^{\circ}C$ for 1 h under vacuum (10^{-3} Torr).

IR analysis

The disks of materials were analyzed in the infrared region, *in situ*. The IR cell [9] was connected to a greaseless vacuum line in which the system could be submitted to carbon monoxide or hydrogen, with pressure control. The equipment used was a Shimadzu, model 8300. The spectra were obtained

with a resolution of 2 cm^{-1}, with 150 scans.

Results and Discussion

It was already related that reducible supports, like titania, after being submitted to HTR treatment (500 $^{\circ}$C), undergo a partial reduction.[1,15,20,21,24] In the titania case, TiO_{2-x} species were detected and sometimes the presence of the Ti-alloys with the dispersed metal were allowed and this behavior is attributed to the metal-support interactions.[14,20] However at low temperature of reduction (200 $^{\circ}$C), the reduction of the titania support was not evident. On the other hand, group 10 metal salts, can be easily reduced to metallic state under high and also under low temperature of reduction.

Considering that changes in the metal electronic density in the *d* subshell can be detected by infrared band shift of the carbon monoxide adsorbed, the electronic metal-support interactions could be observed by this technique. The spectra of Pd/TiO$_2$, submitted to 10 Torr of carbon monoxide are shown in the Figure 1. The spectrum 1a was obtained after reduction at low temperature (LTR). The band at 2100 cm^{-1} is due to the linear carbonyl stretching band coordinated to metallic particles,[3,12] the band at 1984 cm^{-1} was attributed to m-CO species,[3,10] while the band at 2187 cm^{-1} was assigned to carbon monoxide physically adsorbed.[10] After reduction at high temperature (500 $^{\circ}$C) the Pd/TiO$_2$ spectrum shows a linear and m-CO band position shifts to lower wavenumber, 2096 and 1976 cm^{-1}, respectively (Figure 1b). This is an evidence that palladium is in a more reduced state, *i.e.*. the *d* subshell of palladium shows an increase in the electronic density, that produces a stronger back-bonded carbonyl bond with consequent weakness of the C-O bond. This increasing in the electronic metal density is possible due to the strong metal-support interactions that produce a charge transference from the reducible support to the dispersed metal. After HTR treatment there is a m-CO band area decreasing in relation to the LTR treatment (see Table 1). The m-CO / linear-CO infrared band area ratio decreasing is an evidence that the HTR treatment do not produces the metal particles agglomeration, and the electronic metal density can be only explained taking into account the metal-support interactions. Thus this spectral feature is also an evidence that strong metal-support interactions occur, since the metal particles agglomeration are inhibited by the interactions with the support.[22]
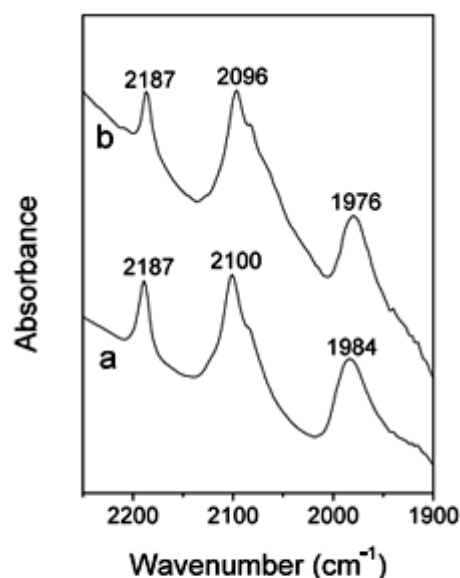
Figure 1: FTIR absorbance spectra of Pd/TiO$_2$ exposed to 10 Torr of carbon monoxide. a) reduced at 200 °C; b) reduced at 500 °C. With the same scale.

Table 1: μ-CO / linear-CO infrared band area ratios.

Treatment	Pd/TiO$_2$	Ni/TiO$_2$
LTR[a]	0.63	0.24
HTR[b]	0.42	0.55

[a] = Reduced in 200 Torr of hydrogen at 200°C;
[b] = Reduced in 200 Torr of hydrogen at 500°C.

In the Figure 2 are shown the spectra of Ni/TiO$_2$ material, exposed to carbon monoxide, after reduction at low (LTR) and high temperature (HTR). It can be observed that the Ni/TiO$_2$ material present a very close spectra for both reductive treatment (LTR and HTR). It was interpreted as an absence of metal-support interaction. In the nickel case, the spectra show an additional band in 2128 cm^{-1}. This band was already detected for others authors [4] and it was assigned to linear carbon monoxide coordinated to partially oxidized nickel. After HTR treatment (Figure 2b), the m-CO band area undergoes a increasing when compared with LTR treated samples (spectrum 2a) and it is also an evidence that the metal-support interactions are not significant in this case, since the bridge species are formed preferentially in the agglomerated particle.[22]
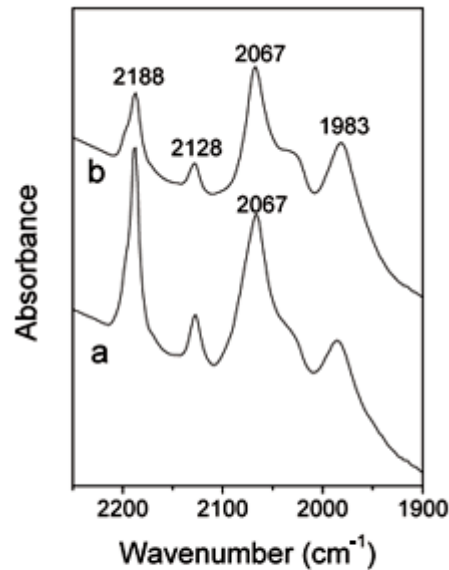
Figure 2: FTIR absorbance spectra of Ni/TiO$_2$ exposed to 10 Torr of carbon monoxide. a) reduced at 200 $^{\circ}$C; b) reduced at 500 $^{\circ}$C. Whit the same scale.

The infrared analysis using carbon monoxide as probing molecule revels that the metal-support interactions are stronger for Pd/TiO$_2$ than Ni/TiO$_2$. This result can be interpreted considering the comparative Fermi level of group 10 metals. Palladium presents a higher Fermi level (4d subshell) while Ni is a 3d element. Therefore, we observe that the detection of the electronic metal-support interactions by FTIR, using carbon monoxide adsorbed, may be influenced by the electronic structure of the metal. For platinum that present the highest Fermi level of group 10 metals, it was already reported that the metal-carbonyl back-bonding is strongly influenced by changes in the electronic density due to the metal-support interactions.[3] However for nickel with the lowest Fermi level, changes in the electronic density due to the metal-support interactions are not detected by using the present technique.

The spectra in the OH stretching region for Pd/TiO$_2$ and Ni/TiO$_2$ submitted to hydrogen at room temperature, after being reduced to 200 $^{\circ}$C (LTR) are shown in the Figure 3. It was possible to observe the band at 3675 cm^{-1} due to n$_{OH}$ of TiOH species. For Pd/TiO$_2$ material, the increasing in the hydrogen pressure produces an another OH stretching broad band with a maximum in ca. 3400 cm^{-1}. This result is a clear indication of the water formation on titania. The water appearance in the material can only be interpreted considering the hydrogen spillover mechanism, where the molecular hydrogen is firstly adsorbed on dispersed palladium and then dissociated in hydrogen atoms, that migrate from surface to the bulk to react with the oxygen species of the titania support.[6,14,18] This effect was not evident in the Ni/TiO$_2$ case.
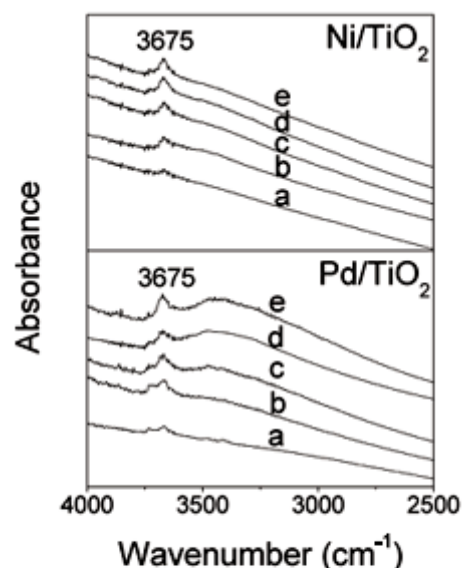
Figure 3: FTIR absorbance spectra in the OH stretching region of the LTR-treated materials after being submitted to hydrogen: a) 10 Torr; b) 22 Torr; c) 50 Torr; d) 100 Torr; e) 200 Torr. With the same scale.

Hydrogen spillover was already reported for platinum dispersed on titania. In platinum case this effect was very strong since electronic defects in the microcrystalline level were noticed.[2,3] Thus we can infer that the spillover effect may be also related with the metal Fermi level and it can be studied by using the FTIR analysis.

The hydrogen adsorption properties of palladium are very known, however these systems are still a very import research field, since they can be used as hydrogen sensors.[8]

Conclusions

The increasing in the electronic density in the *d* subshell, produced by metal-support interactions can be detected by infrared using carbon monoxide as a probe molecule, on Pd/TiO_2, but not on Ni/TiO_2 material. The M-CO back-bonding increasing produced by the metal-support interactions is related to the metal Fermi level. The infrared spectroscopy can be also used to study the spillover hydrogen at room temperature. The hydrogen spillover was detected for Pd/TiO_2, but it is negligible for Ni/TiO_2 material. In the Pd/TiO_2 case the hydrogen presence in the titania bulk was detected by the water appearance, that is related to the hydrogen pressure.

FACCIN, F., GUEDES, F. F., BENVENUTTI, E. V., MORO, C. C. Estudo no infravermelho da interação metal-supporte e do spillover de hidrogênio em Pd/TiO$_2$ e Ni/TiO$_2$. *Ecl. Quím. (São Paulo)*, v.27, p. , 2002.

RESUMO: *Níquel e paládio dispersos no suporte titânia foram submetidos a tratamento redutivo com hidrogênio a 200 e 500 ^{o}C. Após esse tratamento os materiais foram expostos a monóxido de carbono (10 Torr) e analisados na região do infravermelho. O aumento da densidade eletrônica no subnível d do metal, produzido pelo tratamento térmico redutivo, foi monitorado pelo deslocamento da banda de estiramento do monóxido de carbono adsorvido, e foi interpretado como sendo conseqüência da interação metal-suporte. O maior efeito foi observado para o sistema Pd/TiO$_2$. A partir dos espectros no infravermelho, foi possível observar também que o spillover de hidrogênio é mais forte no Pd/TiO$_2$ do que no Ni/TiO$_2$.*

PALAVRAS-CHAVE: *metal-suporte, infravermelho, titânia, monóxido de carbono, spillover de hidrogênio, paládio, níquel.*

References

1   BELTON, D. N.; SUN, Y. M.; WHITE, J. M. Thin-film models of strong metal support interaction catalysts - platinum on oxidized titanium. *J. Phys. Chem.*, v.88, p.1690-1695, 1984.   [Links]

2   BENVENUTTI, E. V.; DAVANZO, C. U. An infrared spectroscopy study of metal-support interaction on Pt/TiO$_2$. The influence of hydrogen adsorption. *Quim. Nova*, v.22, p.674-676, 1999.   [Links]

3   BENVENUTTI, E. V.; FRANKEN L.; MORO, C. C.; DAVANZO, C. U. FTIR Study of Hydrogen and Carbon Monoxide Adsorption on Pt/TiO$_2$, Pt/ZrO$_2$ and Pt/Al$_2$O$_3$. *Langmuir*, v.15, p.8140-8146, 1999.   [Links]

4   BLACKMOND, D. G.; KO, E. I. Carbon-monoxide adsorption as a chemical probe of supported nickel-catalysts - the role of carbonyl formation and support effects. *J. Catal.*, v.94, p.343-352, 1985.   [Links]

5   BOCCUZZI, F.; CHIORINO, A.; TSUBOTA, S.; HARUTA, M. FTIR study of carbon monoxide oxidation and scrambling at room temperature over gold supported on ZnO and TiO$_2$. *J. Phys. Chem.*, v.100, p.3625-3631, 1996.   [Links]

6   CHEN, B.; FALCONER, J. L. Spillover rate from pd to Al$_2$O$_3$. *J. Catal*, v.134, p.737-741, 1992.   [Links]

7   CUNHA, E. V.; FACCIN, F.; MORO, C. C.; BENVENUTTI, E. V. Infrared and X-Ray

Photoelectron Spectroscopy Study of Chloride Effect in Palladium Catalysts. *Quim. Nova*, in the press.   [Links]

8 FAVIER, F.; WALTER, E. C.; ZACH, M. P.; BENTER, T.; PENNER, R. M. Hydrogen sensors and switches from electrodeposited palladium mesowire arrays. *Science*, v.293, p. 2227-2231, 2001.   [Links]

9 FOSCHIERA, J. L.; PIZZOLATO, T. M.; BENVENUTTI, E. V. FTIR thermal analysis on organofunctionalized silica gel. *J. Braz. Chem. Soc.*, v.12, p.159-164, 2001.   [Links]

10 GUPTA, N. M.; LONDHE, V. P.; KAMBLE, V. S. Gas-uptake, methanation, and microcalorimetric measurements on the coadsorption of CO and H-2 over polycrystalline Ru and a Ru/TiO2 catalyst. *J. Catal.*, v.169, p. 423-437, 1997.   [Links]

11 ISHIHARA, T.; HARADA, K.; EGUCHI, K.; ARAI, H. Electronic interaction between supports and ruthenium catalysts for the hydrogenation of carbon-monoxide. *J. Catal.*, v.136, p.161-169, 1992.   [Links]

12 KESRAOUI, S.; OUKACI, R.; BLACKMOND, D.G. Adsorption and reaction of CO and H-2 on k-promoted Rh/SiO$_2$ catalysts. *J. Catal.*, v.105, p.432-444, 1987.   [Links]

13 LAMBERT, J. F.; PONCELET, G., FRIPIAT, J. Residual hydrogen in Ni/TiO$_2$ and Pt/TiO$_2$. *Acta Chim. Hungarica*, v.124, p.121-132, 1987.   [Links]

14 LAMBERT, R.; SCHULZEKLOFF, G. Metal-support interaction in a Pt-TiO$_2$ thin-film system - observation of the Pt3Ti phase at 823-K. *Ber. Bunsen. Phys. Chem.*, v.95, p.1479-1481, 1991.   [Links]

15 RESASCO, D. E.; HALLER, G. L. A model of metal-oxide support interaction for Rh on TiO$_2$. *J. Catal.,* v.82, p.279-288, 1983.   [Links]

16 RESASCO, D. E.; WEBER, R. S.; SAKELLSON, S.; MCMILLAN. M.; HALLER, G. L. X-ray absorption near-edge structure evidence for direct metal-metal bonding and electron-transfer in reduced Rh/TiO$_2$ catalysts. *J. Phys. Chem.*, v.92, p.189-193, 1988.   [Links]

17 ROGEMOND, E.; ESSAYEM, N.; FRETY, R.; PERRICHON, V.; PRIMET, M., CHEVRIER, M.; GAUTHIER, C.; MATHIS, F. Characterization of model three-way catalysts - III. Infrared study of the surface composition of platinum-rhodium ceria-alumina catalysts. *J. Catal.*, v.186, p.414-422, 1999.   [Links]

18 ROLAND, U.; SALZER, R.; SUMMCHEN, L. Electronic effects of hydrogen spillover on titania, spillover and migration of surface species on catalysts. *Stud. Surf. Sci. Catal.*, v. 112, p.339-348, 1997.   [Links]

19 RYCZKOWSKI, J. IR Spectroscopy in Catalysis. *Catal. Today*, v.68, p. 263-381, 2001.   [Links]

20 SPENCER, M. S. Models of strong metal support interaction (smsi) in Pt on TiO$_2$ catalysts. *J. Catal*, v.93, p.216-223, 1985.   [Links]

21 TAUSTER, S. J., Strong metal-support interactions, *Acc. Chem. Res.*v.20, p.389-394, 1987.   [Links]

22 TAUSTER, S. J.; FUNG, S. C.; BAKER, R. T. K.; HORSLEY, J. A. Strong-interactions in supported-metal catalysts. *Science*, v.211, p.1121-1125, 1981.   [Links]

23 TAUSTER, S. J.; FUNG, S. C.; GARTEN, R. L. Strong metal-support interactions - group-8 noble-metals supported on TiO_2. *J. Am. Chem. Soc*., v.100, p.170-175, 1978.   [Links]

24 VANDELOOSDRECHT, J.; VANDERKRAAN, A. M.; VANDILLEN, A. J.; GEUS, J. W. Metal-support interaction: Titania-supported and silica-supported nickel catalysts. *J. Catal*., v.170, p.217-226, 1997.   [Links]

25 YOSHITAKE, H.; IWASAWA, Y. Electronic metal support interaction in Pt catalysts under deuterium ethene reaction conditions and the microscopic nature of the active sites. *J. Phys. Chem.*, v.96, p.1329-1334, 1992.   [Links]

*Laboratório de Sólidos e Superfícies – LSS – Instituto de Química – UFRGS – 91501-970 – Porto Alegre – RS – Brasil.