

## Pt/ZnO Catalysts: Spectroscopic and Catalytic Evidences of a Ligand Effect as a Consequence of PtZn Alloying

FLORA BOCCUZZI,\* ANNA CHIORINO,\* GIOVANNA GHIOTTI,\* FRANCESCO PINNA,†  
GIORGIO STRUKUL,† AND ROBERTO TESSARI†

\*Dipartimento di Chimica Inorganica, Chimica Fisica e Chimica dei Materiali, Università di Torino, 10125 Torino, Italy, and †Dipartimento di Chimica, Università di Venezia, 30123 Venezia, Italy

Received March 6, 1990; revised May 31, 1990

The methanation of carbon monoxide with Pt/ZnO catalysts activated at three different temperatures (220, 250, 300°C) is reported. An increase in specific activity that is paralleled by a drop in the CO chemisorption ability is found when the activation temperature is increased. Characterization of the samples with IR and TEM indicates extensive formation of a PtZn alloy already at 220°C. As the activation temperature increases, the spectroscopic data indicate an increased back-donation in the CO antibonding orbitals which seems to be related to a significant ligand effect of Zn in the alloy. It is suggested that other cooperating effects like the stabilization of the intermediate products and a larger hydrogen supply from the alloy during the reaction may play a significant role in the CO methanation. © 1990 Academic Press, Inc.

### INTRODUCTION

The so-called Strong metal-support interaction (SMSI) is still a subject of current interest in the catalysis field.

A great number of papers (1-3) have been published on group VIII metals supported on transition metal oxides including La<sub>2</sub>O<sub>3</sub> and ZrO<sub>2</sub> or TiO<sub>2</sub> and V<sub>2</sub>O<sub>5</sub>, but not many results have been reported on other reducible metal oxide systems. Indeed, a relationship between the oxide reducibility and the extent of SMSI was established some years ago by Tauster and Fung (4) who reported an extensive study of the SMSI properties of Ir supported on several reducible and non reducible oxides.

Recently it has been reported (5) that Pt/ZnO shows a SMSI behavior after reduction in H<sub>2</sub> but at temperatures significantly lower than Pt/TiO<sub>2</sub>. The origin of this interaction has been ascribed (6) to changes in the surface composition of the metal particles from pure Pt to PtZn alloy which produce both a dilution and a ligand effect.

Since the CO hydrogenation reaction has often been used as a probe to investigate

metal-support effects, in this paper we report the results obtained on CO hydrogenation with Pt/ZnO pretreated in H<sub>2</sub> at two different temperatures (250 and 300°C). HRTEM and IR data are also reported with the aim to better understand the nature of the factors that are at the origin of the observed enhancement of CO methanation in the samples reduced at higher temperature.

### EXPERIMENTAL

Pt/ZnO samples were prepared by photo-deposition (6) on commercial ZnO (Kadox 25) as support, with a method that was previously described by Bard (7) for the deposition on TiO<sub>2</sub>. The Pt content was 2.4 wt%.

Chemisorption measurements were performed on fresh samples at 25°C in a flow system with a pulse technique. H<sub>2</sub> (99.999%), CO (99.95%), Ar (99.999%), and He (99.999%) were purified by passage through an oxytrap (Alltech) and molecular sieve filters. O<sub>2</sub> (99.995%) was purified with a molecular sieve trap.

The measurements of CO hydrogenation activity were carried out at atmospheric pressure in a glass flow differential reactor

as previously described (8). The freshly prepared catalyst (0.4 g), diluted in a 1 : 8 ratio with carborundum (60–100 mesh), was activated under a stream (30 ml/min) of H<sub>2</sub>/Ar mixture (2/1) at 220, 250, and 300°C for 2 h before being cooled to the reaction temperature. The reaction conditions were: temperature 220 and 250°C, total pressure 1 atm, CO partial pressure 0.084 atm, H<sub>2</sub>:CO = 3:1. All experiments were duplicated and conversion was in the range 0.1–0.3%. Reactant and product gas concentrations were measured chromatographically using thermal conductivity and flame ionization detectors.

The IR measurements were performed with an infrared cell, equipped with KBr windows, designed to treat the sample *in situ* under vacuum or under controlled and static atmospheres. Pellets were prepared by pressing the powder at 500 mn m<sup>-2</sup>. The spectra were recorded on a FTIR Perkin-Elmer 1760 spectrometer.

The micrographs and the selected area electron diffraction patterns were taken with a Jeol 2000 EX electron microscope, equipped with a top entry stage. The powder was ultrasonically dispersed in isopropyl alcohol and the suspension was deposited on a copper grid with a holey carbon film.

## RESULTS AND DISCUSSION

### *Chemisorption and Catalytic Data*

In Table 1 are reported the results of O<sub>2</sub>, CO, and H<sub>2</sub> uptake and the catalytic activity of Pt/ZnO after three different reduction temperatures. While the O<sub>2</sub> chemisorption increases slightly, the CO adsorbed is reduced to about one-fourth with the increase of the reduction temperature from 220 to 300°C. However, a subsequent calcination treatment at 400°C restores the CO adsorption capability after reduction at 250°C. On the other hand, the amount of H<sub>2</sub> adsorbed seems almost unaffected by the reduction treatment and, even more odd, the H/Pt ratios are much smaller than the corresponding CO/Pt.

TABLE I  
Chemisorption and Catalytic Activity Data of Pt/ZnO Samples Reduced at Different Temperatures

Reduction temperature (°C)	O/Pt	CO/Pt	H/Pt	Rate <sup>a</sup> (μmole CH <sub>4</sub> /s × g Pt)	10 <sup>5</sup> × N (μmole CH <sub>4</sub> /s × g.atom Pt) <sup>b</sup>
220	0.040	0.084	0.006	—	—
250	0.048	0.062	0.007	0.018	2.0
300	0.062	0.021	0.008	0.056	17.7
250 <sup>c</sup>		0.060		0.015	1.8

<sup>a</sup> Reaction conditions:  $T = 250^{\circ}\text{C}$ ;  $P = 1 \text{ atm}$ ;  $\text{H}_2/\text{CO} = 3$ ;  $p_{\text{CO}} = 0.084 \text{ atm}$ .

<sup>b</sup> Pt<sub>s</sub> = surface Pt atoms computed from CO chemisorption.

<sup>c</sup> After O<sub>2</sub>, 400°C, 1 h.

When the catalysts were tested in the hydrogenation of carbon monoxide, only methane was observed as a product and the catalytic activity was in any case rather low. If we analyze the results, we observe that a significant enhancement of CO methanation was found on the Pt/ZnO reduced at 300°C with respect to the 250°C reduced sample; moreover the Turnover Number (N) based on the CO chemisorbed showed about a nine-fold increase. Again the original activity is restored after calcining at 400°C and reduction at 250°C. No appreciable conversion was detected at 220°C, at least in our experimental conditions.

In a previous paper (6) from an IR study of CO adsorption on Pt/ZnO systems, it was pointed out that when the sample was reduced in H<sub>2</sub>, the Pt crystallites were converted into a Pt–Zn alloy already at 220°C while at 300°C a surface segregation of Zn occurred, which made the Pt sites almost isolated. In the present work, since the Pt/ZnO did not show any catalytic activity below 250°C, an analysis of the catalytic behavior before the occurrence of the Pt–Zn alloy formation has not been possible. Therefore the comparison of the catalytic behavior at the temperatures considered refers to two different situations in which the Pt–Zn alloy has been already formed, but where the surface composition differs because of the segregation of Zn in the most strongly reduced sample. This seems to re-

flect in the quite large differences observed in the chemisorption and catalytic activity.

### Electron Microscopy Data

Electron micrographs of the Pt/ZnO specimens reduced at 250°C show a quite broad particle size distribution, with a high number of particles with diameters in the 2–10 nm range but also with many particles in the 10–30 nm range (Fig. 1). The most commonly observed shape is a half cubo-octahedron with the basal plane in contact with the support; sometimes a corrosion of the support in the contact region can be noticed (Fig. 1, region \*).

We have observed that the thickness of the thin layer of material visible around some Pt particles grows with the time and intensity of the exposure to the electron beam. This seems to suggest that this layer is primarily a consequence of the electron beam bombardment.

The lattice fringe spacings observed in many particles are 3.6 Å (Fig. 1, insert a) and exceed the largest Pt and ZnO interplanar spacings (2.26 and 2.81 Å, respectively) while they are quite close to the 3.51 Å spacing of the (001) planes in the  $\delta$ -PtZn intermetallic compound (JCPDS 6-0604). The presence in this sample of the  $\delta$ -PtZn phase is confirmed by the selected area microdiffraction patterns of regions of the sample where mainly only one large metallic particle is present. In fact well-defined and ordered spots corresponding to the (110), (111), and (113) diffractions of this phase have been detected.

The selected area diffraction of the samples treated at 300°C shows extra spots ( $d = 5.2$  Å) that might be related to another PtZn phase, with a different Pt/Zn ratio. However, this cannot be identified with any of the many different Pt/Zn phases reported in the literature (JCPDS 23-466, 12-612, 23-1311). Extra spots or satellite spots can be produced in alloys by different phenomena such as composition fluctuations, antiphase domains, or dislocation arrays. These phenomena are more likely to explain our extra

spots, since some disorder, dislocations (see Fig. 1, region □), and local changes in contrast are also evident in the region reported in insert a.

### IR Data

In Fig. 2 are shown the transmission spectra of Pt/ZnO reduced in pure H<sub>2</sub> at 220, 250, and 300°C (curves *a*, *b*, and *c*). The three spectra are almost coincident in the high-frequency range while they diverge at low frequencies. It appears evident, therefore, that by reduction at high temperature a monotonic absorption growing toward low frequencies is produced (see insert). This absorption can be interpreted as due to the interaction of the free electrons in the ZnO conduction band with the IR radiation. We observe that this absorption is almost absent in the mildly reduced Pt/ZnO samples (9) while it is very strong in pure ZnO treated in the same way (10).

The absence of the free electron absorption in the mildly reduced Pt/ZnO samples was interpreted as due to an electron transfer from the semiconductor conduction band to the metal (9) as a consequence of the difference in the Fermi level of the two phases (Pt  $\approx$  5.7 eV, ZnO<sub>red</sub>  $\approx$  4.2 eV).

The gradual growth of the free electron absorption at increasing reduction temperatures indicates that an increase of the Fermi level of the metallic phase occurs as a consequence of these treatments. It has been shown previously (6) that after the H<sub>2</sub> treatment at 220°C the metal particles are no longer made of pure Pt but are alloyed with Zn. The Zn work function is 4.33 eV, a value very close to the depth of the shallow donor levels of ZnO (4.24–4.37 eV) (10). Changes in the work function of the PtZn alloys are not known at the moment; however, a recent study of the NiPt alloy by PAX (11) showed that at low Ni content an abrupt reduction of the work function of Pt occurred and the alloy showed a work function very close to the Ni one. At increasing Ni contents, a further smooth reduction was observed.

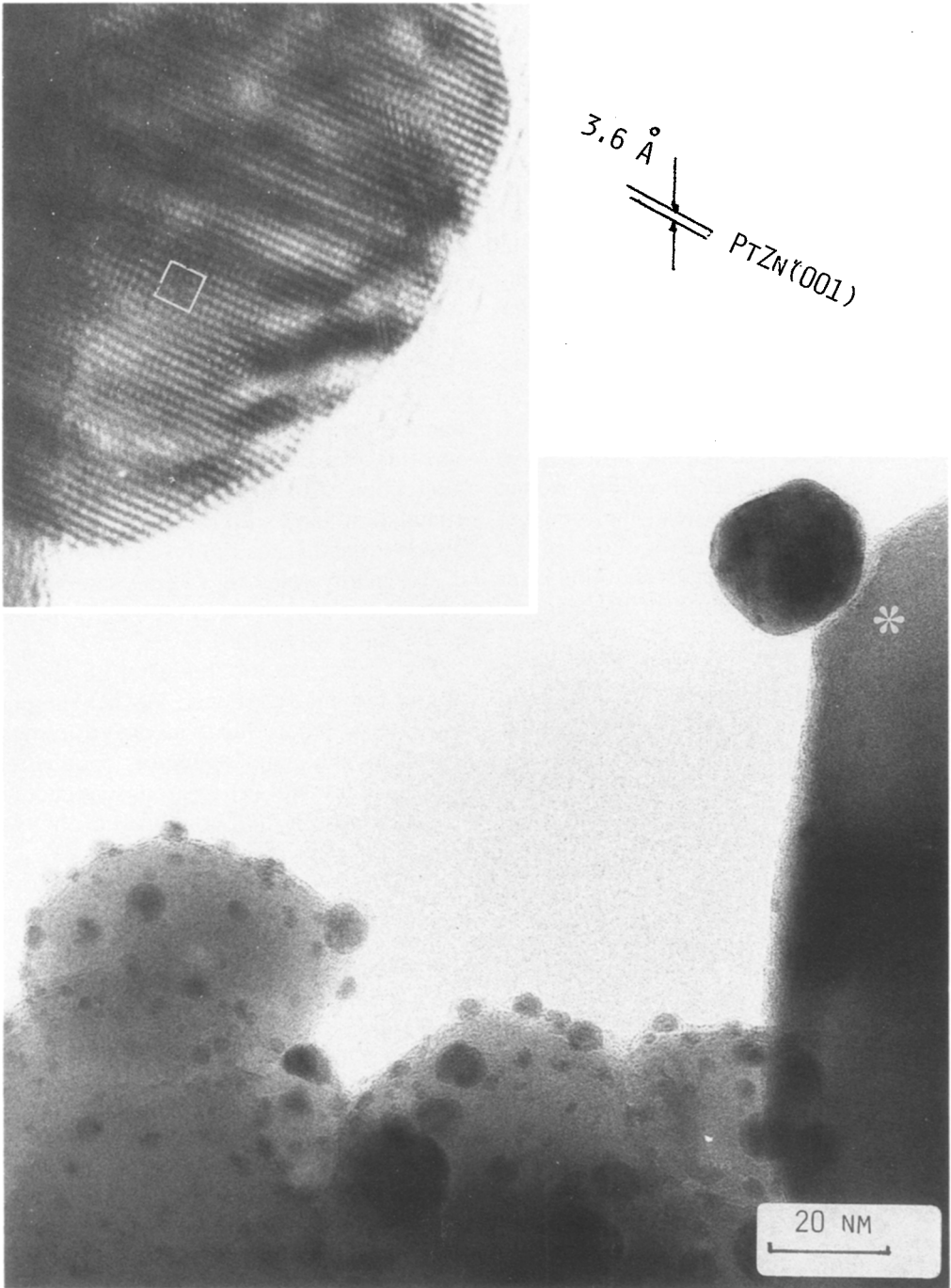


FIG. 1. Photomicrographs of the Pt/ZnO catalyst reduced at 250°C: original magnification  $1 \times 10^5$ ; insert: HRTEM image of a metallic region of the same catalyst; original magnification  $8 \times 10^5$ .

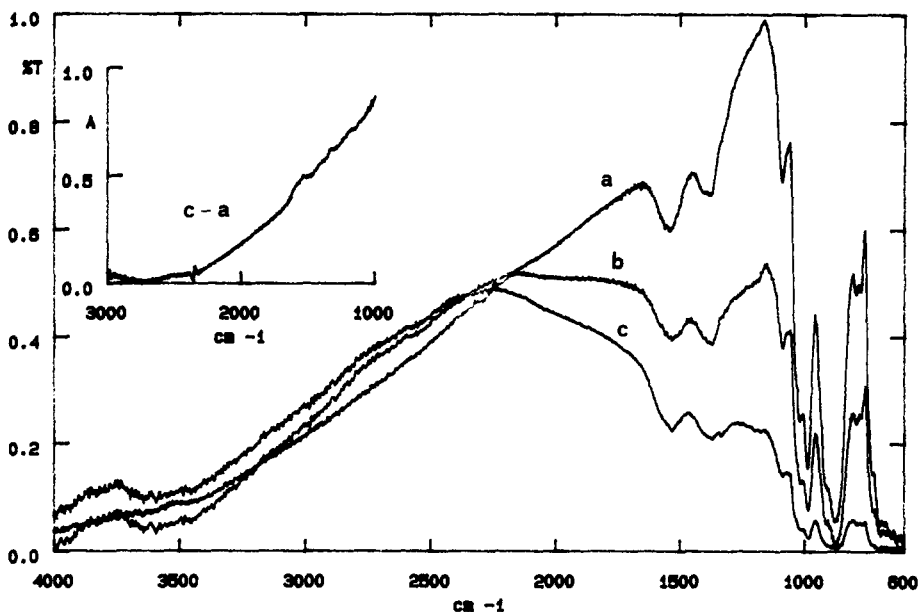


FIG. 2. IR transmission spectra of Pt/ZnO catalysts reduced at different temperatures: (a) 220°C; (b) 250°C; (c) 300°C. Insert: difference in absorbance between (c) and (a).

If the PtZn alloy work function has a behavior similar to that of the NiPt one, the formation of the alloy can also be related to the population of the ZnO conduction band and the gradual reduction of the IR transparency of the Pt/ZnO samples can be interpreted as due to a gradual increase of the PtZnO work function.

The CO adsorption at room temperature on the Pt/ZnO samples prerduced in H<sub>2</sub> at three different temperatures (220, 250, and 300°C) gives rise to a small change in the overall IR transparency and to a single band at  $\approx 2070$  cm<sup>-1</sup>; no bands in other spectral regions can be detected.

In Fig. 3 are shown the absorption bands of the CO adsorbed at full coverage on the three samples prerduced in pure H<sub>2</sub> at different temperatures (curves *a*, *b*, and *c*): by increasing the reduction temperature, a decrease of the intensity and a redshift of the CO absorption band are observed. The band is ascribed to the CO adsorption on Pt sites present in PtZn surfaces containing different amounts of zinc. After reoxidation and outgassing at 400°C (curve *d*) the CO

absorption gives rise to a stronger and blue-shifted band at  $\approx 2100$  cm<sup>-1</sup> that can be easily assigned to the adsorption on pure Pt particles.

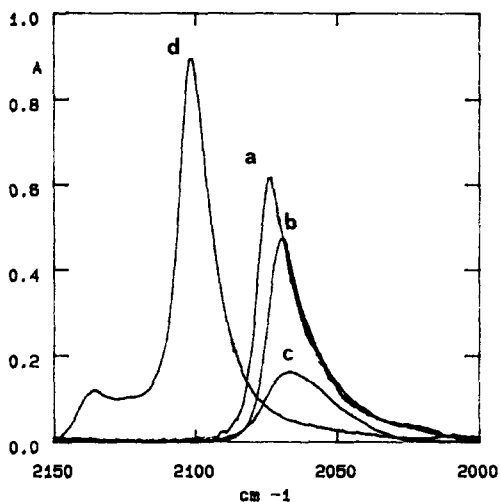


FIG. 3. Absorbance IR spectra of 10 Torr of CO adsorbed at room temperature on differently reduced samples: (a) 220°C; (b) 250°C; (c) 300°C; (d) sample reduced at 300°C reoxidized and outgassed at 400°C.

The large shift of the band is the result of both a dilution and a chemical effect of the alloying. In fact, in a previous paper (6) it has been shown, by comparing the results of the adsorption of a 1 : 1  $^{12}\text{CO}/^{13}\text{CO}$  mixture on samples reduced at different temperatures, that on the sample reduced at 300°C the Pt sites are almost isolated. Moreover the study of a 1 : 9  $^{12}\text{CO}/^{13}\text{CO}$  mixture on the latter sample has evidenced a quite large chemical contribution ( $\approx 20 \text{ cm}^{-1}$ ) to the red shift of the  $^{12}\text{CO}$  band. This chemical effect reveals an increased back-donation from the Pt orbitals to the CO antibonding  $2\pi^*$  levels. This could ease the CO dissociation.

### *Surface Composition and Catalytic Activity*

As a result of a great number of mechanistic studies (12) a general agreement has emerged on the main pathways by which CO undergoes hydrogenation to form  $\text{CH}_4$ . The reaction requires initial CO and  $\text{H}_2$  dissociative chemisorptions: the carbon released then reacts with the adsorbed hydrogen to form  $\text{CH}_4$  while oxygen reacts to form  $\text{H}_2\text{O}$ . The direct cleavage of adsorbed CO involves a stabilization of the intermediate species  $\text{C}_{\text{surf}}$  and  $\text{O}_{\text{surf}}$ .

Now we discuss the factors that can make the reaction easier in our 300°C reduced sample. This has shown a methanation activity higher than the 250°C reduced one in spite of the lower CO chemisorption at room temperature. On the other hand the former catalyst shows a slight increase of  $\text{O}_2$  chemisorption. The CO chemisorption data appear to be in line with the characteristic features of  $\text{TiO}_2$ -supported metals in the SMSI state. Among the many explanations (13) that have been proposed to account for this phenomenon, the most widely accepted one (14) suggests the migration of  $\text{TiO}_x$  species onto the metal surface, resulting, on the one side, in similar  $\text{H}_2$  and CO chemisorption decreases and, on the other side giving rise to new active sites at the metal-titania interface for the CO hydrogenation.

The noteworthy feature of the  $\text{H}_2$  chemisorption in this work is the very low cover-

age compared to that obtained with CO. Now a mere site blockage by migration of support suboxides cannot account for such a difference in adsorption behavior. Similar results (15, 16) have been found in chemisorption studies on Pt-Sn and Pt-Pb alloys and two complementary explanations have been suggested: (i) the dissociative chemisorption of hydrogen is likely to require an ensemble of Pt atoms larger than the molecular adsorption of carbon monoxide, and the alloying of platinum would probably reduce the average ensemble size; (ii) alloying Pt with Sn would produce also a strong ligand effect resulting in a drastic lowering of the heat of adsorption of hydrogen.

In the  $\text{TiO}_2$ -supported Pt catalysts the enhanced hydrogenation activity in the SMSI state has been explained (17) with the formation at the Pt- $\text{TiO}_x$  interface of new active sites which could interact with the oxygen of the chemisorbed CO to ease the dissociation. However, we have no IR evidence for the presence of these species. In fact they are expected to have the CO stretching mode in the 1650–1500  $\text{cm}^{-1}$  region (18), while no bands in this region are detected in our case. Analogous behavior in similar Pt/ $\text{TiO}_2$  catalysts has been interpreted by Vannice and Sudhakar (19) by invoking the existence of an IR inactive CO species. However, a CO inactive species can be assumed only if the adsorption occurs parallel to a clean metallic surface; the IR inactivity, in this case, is justified by the screening of the CO dipole moment by the free electrons of the metals. This phenomenon is known as "metal surface selection rule" (20).

On Pt-Ti systems parallel-adsorbed species are theoretically predictable. Actually theoretical calculations (21) of the CO adsorption on (111) and (100) surfaces of the  $\text{Pt}_3\text{Ti}$  alloy predict parallel binding. However, in this case the preference for parallel adsorption is a consequence of a  $\pi$ -CO donation in the almost empty  $d$  orbitals of Ti, while for the PtZn alloy the  $d$  orbitals of Zn are almost full, and therefore the  $\pi$ -CO donation is prevented.

As previously shown, an increased back-donation from the Pt orbitals to the CO antibonding levels can be at the origin of the high methanation activity shown by the sample reduced at 300°C. We suggest that this is related to the decrease in the work function of the metallic particles in the highest temperature reduced samples. In addition, the cleavage of the adsorbed CO on our samples is also favored by a stabilization of the reaction products in the alloy. The O<sub>2</sub> chemisorption parallels the methanation activity; this could suggest that a fraction of the Zn sites on the alloy surface may accept the oxygen atoms produced in the CO dissociation and therefore have an important role in the reaction.

The data here reported seem to suggest that a common explanation of the increased activity of the Pt/ZnO and Pt/TiO<sub>2</sub> catalysts in the SMSI states can be found. Recently (22) some PtTi phases have been identified by HRTEM on high-temperature reduced Pt/TiO<sub>2</sub> samples.

Therefore in the two cases Pt is alloyed with two elements (Zn and Ti) that are characterized by the same work function (4.33 eV) (23), lower with respect to that of pure Pt (5.7 eV) (23). This fact, as previously stated, can make the CO dissociation easier as a consequence of an increased population of the antibonding levels of the CO adsorbed molecules.

In conclusion, on the basis of our analysis we can infer that several cooperating effects can have a role in the CO methanation on Pt supported on reducible oxides as a consequence of alloying effects, in particular an increased back-donation in the CO antibonding orbitals and the stabilization of the reaction products.

#### REFERENCES

1. Tauster, S. J., Fung, S. C., and Garten, R. L., *J. Amer. Chem. Soc.* **100**, 170 (1978).
2. Resasco, D. E., and Haller, G. L., *J. Catal.* **82**, 147 (1983).
3. Baker, R. T. K., Tauster, S. J., and Dumesic, J. A., Eds., "Strong Metal-Support Interactions," ACS Symposium Series, Vol. 298. Amer. Chem. Soc., Washington, D.C., 1986.
4. Tauster, S. J., and Fung, S. C., *J. Catal.* **55**, 29 (1978).
5. Li, W. Z., Chen, Y. X., Yu, C. Y., Wang, X. Z., Hong, Z. P., and Wei, Z. B., in "Proc. 8th Int. Congr. on Catalysis, Berlin," Vol. V, p. 205. Verlag-Chemie, Weinheim, 1984.
6. Boccuzzi, F., Chiorino, A., and Ghiotti, G., *Surf. Sci.* **209**, 77 (1989).
7. Krenth, B., and Bard, A. J., *J. Amer. Chem. Soc.* **100**, 4317 (1978).
8. Dall'Agnol, C., Gervasini, A., Morazzoni, F., Pinna, F., Strukul, G., and Zanderighi, L., *J. Catal.* **96**, 106 (1985).
9. Boccuzzi, F., Chiorino, A., Ghiotti, G., and Guglielminotti, E., *Langmuir* **5**, 66 (1989).
10. Boccuzzi, F., Ghiotti, G., and Chiorino, A., *J. Chem. Soc. Faraday Trans. 2* **79**, 1779 (1983).
11. Fargues, D., Ehrhardt, J. J., Abon, M., and Bertolini, J. C., *Surf. Sci.* **79**, 1779 (1983).
12. Sachtler, W. M. H. in "Proc. 8th Int. Congr. on Catalysis, Berlin," Vol. I p. 151. Verlag-Chemie, Weinheim 1984; Chuang, S. C., Tian, Y. H., Goodwin Jr, J. G., and Wened, I., *J. Catal.* **96**, 396 (1985); Haller, G. L., and Resasco, D. E., in "Advances in Catalysis" (D. E. Eley, H. Pines, and P. B. Weisz, Eds.), Vol. 36, p. 173. Academic Press, New York, 1989.
13. Hermann, J. M., *J. Catal.* **89**, 404 (1984); Koninsberger, D. C., Martens, J. H. A., Prins, R., Short, D. R., and Sayers, D. E., *J. Phys. Chem.* **90**, 3047 (1986); Sanz, J., Rojo, J. M., Malet, P., Munuera, G., Blasco, M. T., Conesa, J. C., and Soria, J., *J. Phys. Chem.* **89**, 5427 (1985).
14. Resasco, D. E., and Haller, G. L., *J. Catal.* **82**, 279 (1984); Sadeghi, J. R., and Henrich, V. E., *J. Catal.* **87**, 279 (1984).
15. Verbeek, H., and Sachtler, W. M. H., *J. Catal.* **42**, 257 (1976).
16. Bastein, A. G. T. M., Toolenaar, F. J. C. M., and Ponc, V., *J. Catal.* **90**, 88 (1984).
17. Vannice, M. A., and Twu, C. C., *J. Catal.* **82**, 213 (1983); Bracey, J. D., and Burch, R., *J. Catal.* **86**, 384 (1984).
18. Sachtler, W. M. H., and Ichikawa, M., *J. Phys. Chem.* **90**, 4752 (1986); Ghiotti, G., Boccuzzi, F., and Chiorino, A., *J. Chem. Soc. Chem. Commun.* 1012 (1985).
19. Vannice, M. A., and Sudhakar, C., *J. Phys. Chem.* **88**, 2429 (1984).
20. Greenler, R. G., *J. Chem. Phys.* **44**, 310 (1966).
21. Mehandru, S. P., Anderson, A. B., and Ross, P. N., *J. Catal.* **100**, 210 (1986).
22. Wang, L., Qias, G. W., Ye, H. Q., Kuo, K. H., and Chen, Y. X., in "Proc. 9th Int. Congr. on Catalysis, Calgary" (M. J. Phillips and M. Ternan, Eds.) Vol. III, p. 1253, 1988.
23. Weast, R. C., Ed. "Handbook of Chemistry and Physics," 66th ed. CRC Press, Boca Raton, FL, 1985.