JOURNAL OF CATALYSIS **141**, 1–8 (1993)

Reactivity of Pt/Al_2O_3 and $Pt–CeO_2/Al_2O_3$ Catalysts for the Oxidation of Carbon Monoxide by Oxygen

I. Catalyst Characterization by TPR Using CO as Reducing Agent

C. SERRE,* F. GARIN,†,[1] G. BELOT,* AND G. MAIRE†

**Peugeot S.A./E.R., 18 Rue des Fauvelles, 92250 La Garenne Colombes, France; and †Laboratoire d'Etudes de la Réactivité Catalytique des Surfaces et Interfaces (LERCSI), URA 1498 CNRS, Institut Le Bel, ULP, 4 Rue Blaise Pascal, 67070 Strasbourg Cedex, France*

Received February 7, 1992; revised October 2, 1992

Ceria, platinum, and platinum–ceria catalysts supported on γ-alumina have been characterized by temperature-programmed reduction (TPR) using CO as reducing agent. In all cases, CO disproportionation was found to be negligible. Nevertheless, a small CO_2 TPR signal was detected on the γ-alumina support at tempratures higher than 673 K, and has been attributed to the water–gas shift reaction between gaseous CO and the hydroxyl groups of the alumina surface. The comparison between the CO-TPR spectra of CeO_2/Al_2O_3 and $Pt–CeO_2/Al_2O_3$ has revealed that platinum induces a downscale shift on the temperature of the ceria reduction peak. Two possible interpretations of this platinum–ceria interaction are proposed: (i) a C–O bond weakening when CO is adsorbed on platinum particles and (ii) a decrease of the Ce–O bond strength for ceria localized near platinum.

INTRODUCTION

The catalysts used in the field of automobile exhaust depollution are basically composed of precious metals supported on a γ-alumina washcoat containing ceria. The use of ceria is partly due to its oxygen storage capacity, which is related to the reducibility of CeO_2.

Temperature-programmed reduction (TPR) is very well adapted to study this particular property and has already been extensively applied on bulk (*2–5*) or supported (*2, 4, 6*) ceria, with (*2–6*) or without (*2, 5, 6*) precious metals. Nevertheless, most of these studies have been performed by the "classical" TPR, i.e., by using hydrogen as reducing agent, whereas ceria reducibility related to carbon monoxide seems to be of prime importance in the oxygen storage mechanism, when performed in a real exhaust pipe which contains about three times more CO than hydrogen.

Since carbon monoxide has been very seldom used as reducing agent (*7, 8*), this paper is devoted to the study of the influence of platium on the reducibility of CeO_2 by CO, as primary characterization of γ-alumina supported Pt and/or Ce catalysts. The catalytic behaviour of these catalysts will be presented in Part II of this work for the oxidation of CO by O_2 (*1*).

EXPERIMENTAL

Preparation of the catalysts. The catalysts have been prepared by wet impregnation of γ-alumina pellets (purchased from Rhône–Poulenc: specific area, 206 m^2/g; pore volume, 0.54 cm^3/g; and mean particle size, 2 mm) with aqueous solutions of $Ce(NO_3)_3$ for ceria and H_2PtCl_6 for platinum. The $Pt–CeO_2/Al_2O_3$ catalysts have been obtained by successive impregnations, of ceria first, followed by the impregnation of plati-

---

[1] To whom correspondence should be addressed.

0021-9517/93 $5.00

num. After each impregnation step, the samples are calcined for 2 h at 673 K in air. The catalyst compositions have then been analyzed by atomic absorption (Service Central du CNRS, Vernaison, France). Their characteristics are: 14.5% CeO_2 for CeO_2/Al_2O_3, 2.13% Pt for 2% Pt/Al_2O_3, and 1.99% Pt–14.2% CeO_2 for 2% Pt–14.5% Ce/Al_2O_3.

Temperature-programmed reduction. The TPR characterization has been performed on 4.72 g of catalyst, under 1.5% CO/He (vol%), with a constant flow rate of 100 cm^3/min and from room temperature (RT) to 973 K (heating rate: 10 K/min). The treatment procedure performed on the catalyst is described in Fig. 1. After each step, the sample is kept for 1 h at 973 K under the indicated gas composition. Then the reactor is purged at 973 K by pure helium before cooling, in order to eliminate all species weakly adsorbed on the surface of the catalyst.

Figure 2 shows a schematic drawing of the apparatus used for this TPR test. The carrier gas flows through the reference side of the thermal-conductivity detector (TCD is not directly used for TPR characterization but is useful for light-off tests described in Part II (*1*)), whereas the test gas mixture flows successively through the reactor, the TCD, and the two infrared detectors (for CO and CO_2). The trap TR may be connected between the outlet of the reactor and the analysers, in order to trap the water coming out during the first heating. The flow rates are monitored by mass flow controllers. The catalyst is heated with a regulated furnace and its temperature is measured by a thermocouple placed inside the pellets bed.

RESULTS

The TPR curves obtained on the catalysts mentioned above are plotted in Fig. 3.

(*i*) *γ-Alumina*

The TPR spectrum of γ-alumina exhibits a small CO_2 formation (together with a nearly stoichiometric CO consumption) at temperatures higher than 673 K, which increases progressively to a maximum of 6000 ppm CO_2 at 973 K. A further point to note is that this CO_2 signal decreases after successive TPR–TPO cycles. Therefore, it cannot be ascribed either to the reduction of impurities of the support or to the presence of some oxygen in the feedstream, since these two phenomena should be perfectly reproducible after reoxidation.

It seems to us that the only possible reason for this behaviour is the reaction of gaseous CO with the hydroxyl –OH groups remaining on the alumina surface. Indeed, the dehydroxylation of alumina is known to be slow (*9, 10*), and to produce water which is thought to react with CO via the water–gas shift (WGS) reaction.

It is important to keep in mind the existence of this reaction on the support in order to give correct interpretations of the various kinds of phenomena exhibited on the catalysts supported on this alumina.

(*ii*) *14.5% CeO_2/Al_2O_3*

Compared to the support alone, the sample containing 14.5% CeO_2 exhibits a new CO_2 peak, between 573 and 823 K, which is mainly attributed to the reduction of surface oxygen atoms of ceria (by analogy with the TPR results obtained either under hydrogen (*2*) or under CO (*7*)). At higher temperatures, the reduction seems to proceed further, but unfortunately it is impossible to quantify because of the concomitant WGS reaction already observed on pure alumina.

In order to measure the extent of the Boudouard reaction ($2\ CO \rightarrow CO_2 + C$) which would lead to carbon deposition on the surface, the catalysts have been systematically submitted to a subsequent temperature-programmed oxidation (TPO, see Fig. 1). The cumulative amount of CO_2 formed during this treatment is a measure of the extent of carbon atoms deposited during the TPR step. The results of this TPO study are given in Table 1, where they are compared to the amount of CO_2 produced during the TPR characterization. For all samples, we note

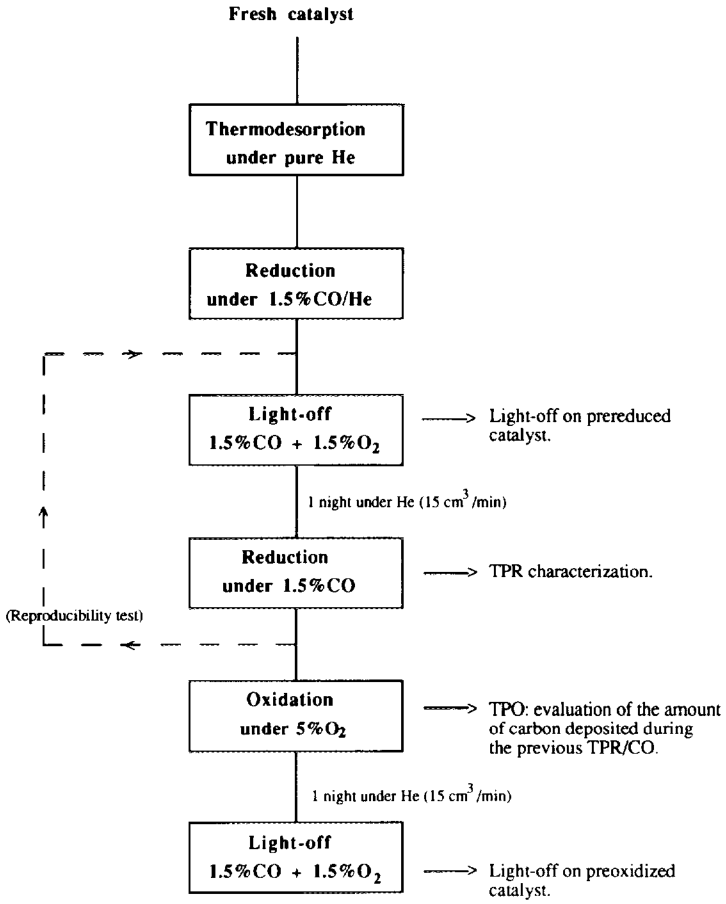

FIG. 1. Treatment procedure used for the TPR characterization of the catalysts. Step 1: thermodesorption aimed to dehydrate the catalyst support. Steps 2 and 3: reductive and oxidative treatments aimed to obtain a reproducible state of the catalyst; note that step 3 is also a light-off test whose results will be discussed in Part II of this work. Step 4: TPR characterization. Step 5: temperature-programmed oxidation (TPO) used to measure the extent of carbon deposition that may occur during the previous TPR under CO. Step 6: light-off test performed on preoxidized catalyst; see Part II of this work.

that the Boudouard reaction is negligible under our operating conditions.

Thus, we may conclude that the TPR spectrum of 14.5% CeO$_2$/Al$_2$O$_3$ is mainly composed of the superposition of a reduction phenomenon (of surface CeO$_2$) and the water–gas shift reaction between CO and H$_2$O coming from the dehydration of the support.

(iii) 2% Pt/Al$_2$O$_3$

Just before the TPR test, the last pretreatment step consists of an oxidation of the catalyst at 973 K under the oxidative mixture 1.5% CO + 1.5% O$_2$/He. At this temperature, platinum oxide is known to be unstable, even under an oxidative atmosphere (*11*). This means that at the beginning of our TPR test the 2% Pt/Al$_2$O$_3$ is already in the metallic form and will not exhibit any CO$_2$ peak due to the reduction of the catalytic phase.

Indeed, the TPR spectrum of this catalyst (Fig. 3c) only shows a small amount of CO$_2$, beginning around 373 K and similar to the spectrum obtained on γ-alumina (Fig. 3a).

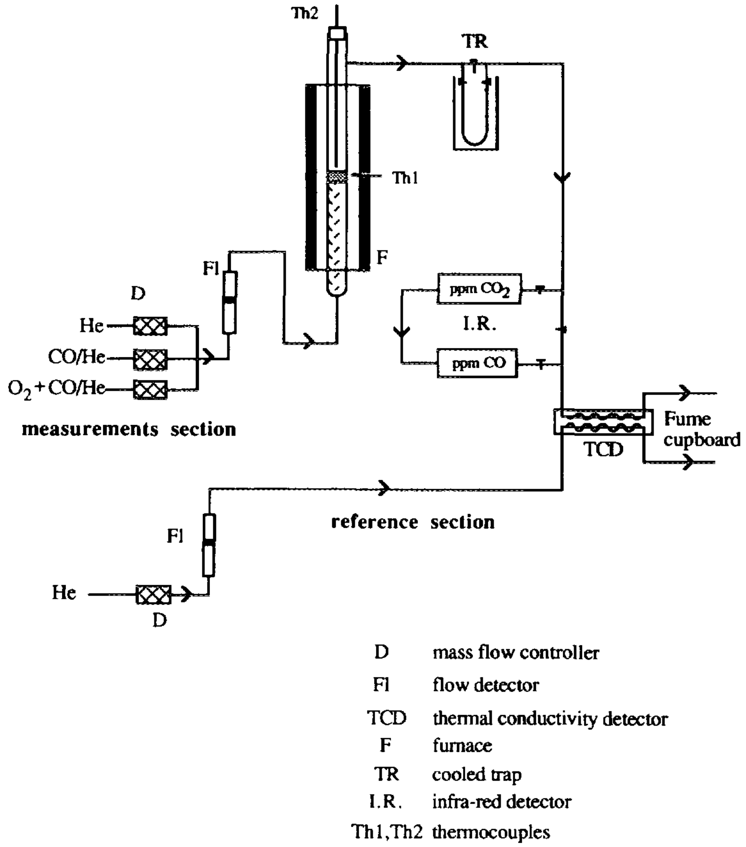

FIG. 2. Schematic drawing of the apparatus used for the TPR characterizations. The experimental conditions are: mass of catalyst, 4.72 g; gas flow, 100 cm^3/min; reducing gas composition, 1.5% CO/He; heating rate, 10 K/min.

This curve seems to be also related to the WGS reaction, owing to the water issued from Al_2O_3 dehydroxylation, this reaction being tentatively catalysed by the platinum present in the sample (the reaction is detectable at higher temperature on pure alumina).

(*iv*) *2% Pt–14.5%* CeO_2/Al_2O_3

As for the 2% Pt/Al_2O_3 catalyst, PtO_2 should not be present after the oxidative treatment at 973 K and thus, the reduction peak of PtO_2 is not present in this TPR spectrum (Fig. 3d; if present it would have appeared at a temperature lower than 473 K (*12*)).

Consequently, the CO_2 signal observed is tentatively ascribed to the reduction of surface CeO_2, as for the TPR spectrum of 14.5% CeO_2/Al_2O_3 in Fig. 3b.

However, we note that this reduction step starts at 413 K on 2% Pt–14.5% CeO_2/Al_2O_3, compared to a higher temperature (553 K) without platinum. This decrease in the reduction temperature of CeO_2 surface by addition of platinum has already been observed by numerous authors working with hydrogen as reducing agent.

DISCUSSION

The most interesting result of these TPR experiments is that platinum is implicated in the reduction of surface ceria, since it enables ceria reduction at lower temperature than without platinum. This phenome-

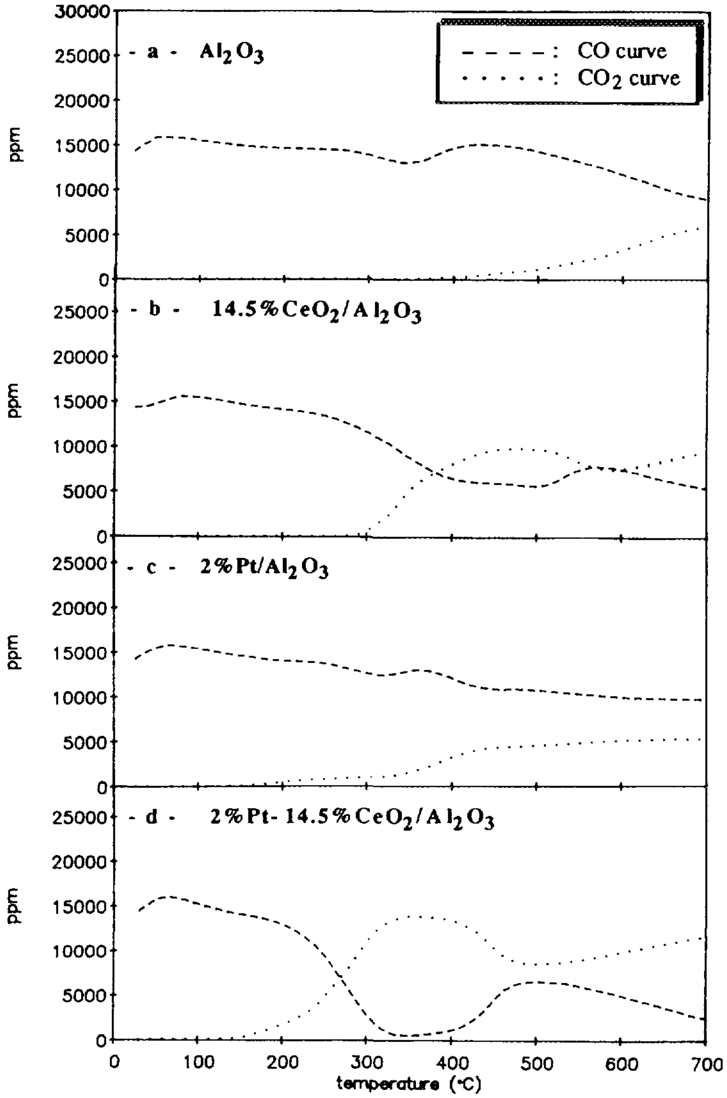

FIG. 3. TPR profiles obtained by reduction of the catalysts by carbon monoxide. The experimental conditions are: mass of catalyst, 4.72 g; gas flow, 100 cm^3/min; reducing gas composition; 1.5% CO/He; heating rate, 10 K/min.

non reveals the presence of an interaction between platinum and ceria, and confirms the results obtained by other authors with TPR performed under hydrogen. In the case of hydrogen reduction, the effect of platinum can be attributed to hydrogen spillover from platinum particles, leading to activated hydrogen atoms which can reduce ceria more easily. This interpretation is that given by Levy and Boudart (*13*) to explain the decrease of WO_3 reduction temperature when platinum is added to tungsten oxide.

Nevertheless, this explanation cannot be applied to our own results since carbon monoxide is not dissociated. Therefore, when CO is adsorbed on ceria, one cannot imagine how it could be more activated by a previous adsorption on the precious metal

TABLE I

Quantitatve Measurements of Total CO_2 Amount Desorbed from the Catalyst during the TPR Test and during the Subsequent TPO Test

Catalyst	CO_2 TPR (in mol per g of catalyst)	CO_2 TPO (in mol per g of catalyst)
Al_2O_3	2.5×10^{-4}	0.4×10^{-5}
14.5 % CeO_2/Al_2O_3	6.1×10^{-4}	1.4×10^{-5}
2% Pt/Al_2O_3	3.1×10^{-4}	0.7×10^{-5}
2% Pt–14.5% CeO_2/Al_2O_3	8.0×10^{-4}	1.0×10^{-5}

than by a direct adsorption of gaseous CO on ceria.

This is the reason why we propose two new interpretations which may explain the effect of platinum on the reducibility of ceria by carbon monoxide.

(*i*) *C–O Bond Weakening*

CO adsorption on ceria leads to site blocking by carbonate which limits the extent of reduction, because of its high desorption temperature (*7*, *11*).

When platinum and ceria are present together on the catalyst surface, gaseous CO has the possibility of adsorbing on platinum with a lower adsorption strength than on ceria. The carbon–oxygen bond of CO is then weakened, because of the electronic transfer from the free 5σ doublet of carbon to the empty *d*-orbitals of the metal, and subsequent back-donation of the full *d*-orbitals of platinum to the $2\pi^*$ of carbon (*14*, *15*).

In this situation, CO adsorbed near the Pt–CeO_2 interface will more easily insert an oxygen atom from ceria into its structure, and will quickly desorb as CO_2. A schematic drawing of this reduction mechanism is given in Fig. 4.

This interpretation is similar to the spillover phenomenon, since it is considered that platinum acts as an adsorption activator of the reducing agent (dissociative adsorption for H_2 and molecular adsorption for CO).

(*ii*) *Destabilisation of the Ce–O Bond*

In this interpretation, platinum is considered as modifying directly the ceria properties, decreasing the oxygen–cerium bond strength for ceria located near platinum. Consequently, the CO adsorbed on ceria would be transformed to a less stable carbonate than in the absence of precious metal, and would then desorb as CO_2 at lower temperature, reducing the ceria surface.

This interpretation is supported by previous results obtained in this laboratory (*16*) and by Yu Yao (*17*) who pointed out a charge transfer from metal to ceria, leading to a small increase in the oxidation state of the metal, indicating that cerium is also slightly reduced, leading to a decrease of the Ce–O bond strength (*6*).

The two models proposed explain the fact that the oxygen atoms located at the Pt–CeO_2 interface are easier to reduce than the oxygen atoms of isolated CeO_2.

Nevertheless, the TPR curves (Figs. 3c and 3d) show that it is the *whole* reduction peak which is shifted toward lower temperatures when platinum is added to supported ceria. This result means that platinum exhibits a *long distance* effect on the reducibility of the surface of ceria.

When the temperature reaches the starting point of ceria reduction, only the most easily reducible oxygen atoms, i.e., those at the Pt–CeO_2 interface, will be taken away as CO_2, leaving an oxygen vacancy at the Pt–CeO_2 interface. This first stage of reduction leads to a concentration gradient in oxygen vacancies between the reactive interface and ceria which is far away from platinum. This gradient is a driving force which could enable the progressive diffusion of all reducible surface oxygen atoms towards the interface. At the same time, the oxygen vacancies created at the Pt–CeO_2 interface would migrate in the opposite direction and their surface concentration would increase as a function of the global reduction extent.

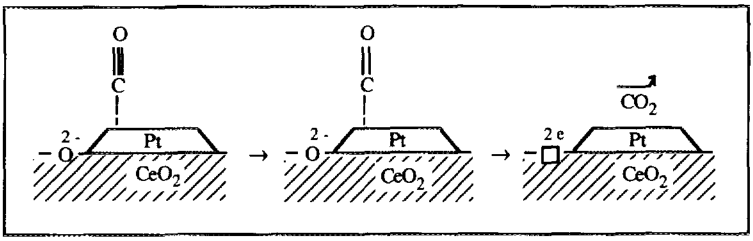

FIG. 4. Schematic drawing of the first proposed mechanism for the interface reduction of ceria by carbon monoxide adsorbed on platinum: model of C–O bond weakening. $-O^{2-}-$, oxygen of ceria; and $\square^{2e}$, oxygen vacancy.

These two interpretations may explain the effect of platinum on the reducibility of ceria by CO. We should not forget the spillover of CO from Pt to CeO_2 as observed by Bond *et al.* (*18*), but when this phenomenon occurs it has been mentioned that the slow step is reoxidation, which is not our case (*1*).

Nevertheless, at temperatures higher than 573 K, the reduction is thought to go further by a mechanism involving the direct adsorption of carbon monoxide on ceria, without any interference of platinum, since this direct mechanism takes place on CeO_2/Al_2O_3 samples.

CONCLUSIONS

—Under the operating conditions used, carbon monoxide disproportionation was found to be negligible for the tested samples.

—It has been shown that the support alone (γ-alumina) was able to oxidize CO to CO_2 from about 773 K, probably via the water–gas shift reaction, owing to alumina dehydration.

This phenomenon is of prime importance since it was also present at high temperature for other catalysts, as a superposition on "real" reduction peaks, thereby preventing good quantification.

—The most interesting result from this TPR/CO study is the decrease of the reduction temperature of surface CeO_2 when platinum is added to supported ceria. Two interpretations of the platinum ceria interaction have been proposed: (i) a C–O bond weakening when CO is adsorbed on platinum particles and (ii) a decrease of the Ce–O bond strength for ceria localized near platinum.

For these two models, platinum acts as a catalyst for the reduction of surface oxygen of ceria, but only for CeO_2 next to platinum. We believe that the remaining ceria is reduced either by a migration process of oxygen atoms and vacancies, respectively, towards and from the reactive Pt–CeO_2 interface, or, at temperature higher than 573 K, by direct adsorption of CO on CeO_2, without any participation of platinum.

REFERENCES

1. Serre, C., Garin, F., Belot, G., and Maire, G., *J. Catal.*, **141**, 1, 1993.
2. Yao, H. C., and Yu Yao, Y. F., *J. Catal.* **86**, 254 (1984).
3. Johnson, M. F. L., and Mooi, J., *J. Catal.* **103**, 502 (1987).
4. Shyu, J. Z., Weber, W. H. and Gandhi, H. S., *J. Phys. Chem.* **92**, 4964 (1988).
5. Harrison, B., Diwell, A. F., and Hallett, C., *Platinum Met. Rev.* **32**, 73 (1988).
6. Yao, H. C., *Appl. Surf. Sci.* **19**, 398 (1984).
7. Badri, A., Lamotte, J., Lavalley, J. C., Laarchir, A., Perrichon, V., Touret, O., Sauvion, G. N., and Quemere, E., *Eur. J. Solid State Inorg. Chem.* **28**, 445 (1991).
8. Kacimi, S., Ph.D. thesis, University of Poitiers, France, 1990.
9. Peri, J. B., *J. Phys. Chem.* **69**, 211 (1965).
10. Tanabe, K., *in* "Catalysis-Science and Technology" (J. R. Anderson and M. Boudart, Eds.), Vol.

2, Chap. V. p. 231. Springer-Verlag, Berlin, Heidelberg, New York, 1981.

11. Li, C., Sakata, Y., Arai, T., Domen, K., Muruya, K., and Onishi, T., *J. Chem. Soc. Faraday Trans.* **85,** 929 (1989).

12. Yao, H. C., Sieg, M. and Plummer, H. K., *J. Catal.* **59,** 365 (1979).

13. Levy, R. B., and Boudart, M., *J. Catal.* **32,** 304 (1974).

14. Vannice, M.A., *in* "Catalysis-Science and Technology" (J. R. Anderson and M. Boudart, Eds.), Vol. 1, Chap. V, p. 139. Springer-Verlag, Berlin, Heidelberg, New York, 1981.

15. Primet, M., Basset, J. M., Mathieu, M. V., and Prettre, M., *J. Catal.* **29,** 213 (1973).

16. Serre, C., Garin, F., Belot, G., Maire, G., and Roche, R., *in* "Catalysis and Automotive Pollution Control II" (A. Crucq, Ed.), Studies in Surface Science and Catalysis, Vol. 71, p. 153. Elsevier, Amsterdam, 1991.

17. Yu Yao, Y. F., *J. Catal.* **87,** 152 (1984).

18. Bond, G. C., Fuller, M. J., and Molloy, L. R., *in* 'Proceedings of the Sixth International Congress on Catalysis" (G. C. Bond, P. B. Wells, F. C. Tompkins, Eds.), Vol. 1, p. 356. The Chemical Society, London, 1976.