

In situ deposition of silver and palladium nanoparticles prepared by the polyol process, and their performance as catalytic converters of automobile exhaust gases

F. Bonet^a, S. Grugeon^a, R. Herrera Urbina^{b,*}, K. Tekaiia-Elhsissen^a, J.-M. Tarascon^a

^a *Université de Picardie Jules Verne, Laboratoire de Réactivité et de Chimie des Solides UPRES-A6007, 80039 Amiens, France*

^b *Universidad de Sonora, Departamento de Ingeniería Química y Metalurgia, 83000 Hermosillo, Sonora, Mexico*

Abstract

In situ deposition of silver particles onto alumina and palladium particles onto mixed Ce–Zr oxides has been achieved upon chemical reduction of the corresponding metal species (AgNO_3 and PdCl_2) by ethylene glycol in the presence of polyvinylpyrrolidone. The support oxide powders were found to keep their crystalline structure and morphology after treatment with hot ethylene glycol while the BET surface area decreased after metal deposition. Microprobe maps obtained from energy dispersive X-ray analysis revealed a homogeneous distribution of metal nanoparticles on the surfaces of alumina and of the mixed Ce–Zr oxides. Supported silver and palladium were tested as catalytic converters of simulated exhaust automobile gases. The catalytic activity of silver-loaded alumina powder catalyst for CO and hydrocarbon oxidation as well as NO and NO_x reduction, was found to be higher than that of a reference silver catalyst. Palladium-loaded mixed Ce–Zr oxides powder catalyst showed a similar performance to that of a reference palladium catalyst as a three-way catalyst converter. © 2002 Éditions scientifiques et médicales Elsevier SAS. All rights reserved.

Keywords: Silver; Palladium; In situ deposition; Three-way catalysts; Ethylene glycol

1. Introduction

Noble metal nanoparticles are currently used in a wide variety of scientific and technical fields because they possess specific and remarkable properties. Due to their high proportion of surface vs. core atoms, the reactivity of these materials is significantly superior to coarse particles making them ideal candidates for catalytic applications. Among the many noble metals nanoparticles currently used in catalysis, those of silver and palladium deposited onto different substrates are used for catalytic conversion of gas molecules present in the emissions of automobile exhaust gases. Silver loaded catalyst has been widely studied and patented. But to our knowledge, such catalyst has been not industrially used for this kind of application until now. Catalytic converters are essential in today's automobiles because they reduce the concentration of such pollutants as hydrocarbon gases, CO and nitrogen oxides in engine emissions into the environment.

The performance of catalytic converters depends on the characteristics of both the support and active metal catalyst. The method used to synthesize the finely divided metal catalyst as well as the way it is deposited onto the substrate are also important factors that determine the catalytic activity of catalytic converters. Bera et al. [1] synthesized metal nanoparticles onto Al_2O_3 by a combustion method, and tested them as catalysts for CO oxidation and NO reduction. Alumina-supported silver has been tested as catalyst for the selective reduction of NO by higher hydrocarbons [2].

Because of its excellent thermal stability, palladium is widely used as active catalyst for hydrocarbon and CO oxidation in three-way catalytic converters. Ce/Zr mixed oxides have also good thermal properties, and can withstand high operating temperatures. In addition, ceria provides oxygen for thorough hydrocarbon and CO oxidation under rich conditions [3]. Ce/Zr mixed oxides substrates are therefore good supports for three-way catalytic converters. Palladium supported on Al_2O_3 and $\text{Al}_2\text{O}_3/\text{CeO}_2$ is also a good catalyst for CO and C_3H_6 oxidation [4].

The polyol process, a well-known method used for monodisperse metal powders synthesis in our laboratory,

* Correspondence and reprints.

involves redox reaction between a metallic compound and a liquid polyol (generally ethylene glycol), and in some cases a surfactant (such as polyvinylpyrrolidone (PVP)) may be used to avoid particle sintering. Following the principles of this method, Kurihara et al. [5] have deposited different metallic films onto various substrates, and Ayyappan et al. [6] have achieved the reduction of nickel acetate and silver nitrate into montmorillonite. Recently, Sales et al. [7] have prepared alumina-supported Ag, Pd and Ag–Pd particles by the polyol process, and tested them as catalysts for the hydrogenation of hexa-1,5-diene.

In the present paper, we report the results of in situ deposition of silver nanoparticles onto alumina and palladium nanoparticles onto a mixture of Ce–Zr oxides using the polyol process. As-received oxide substrates, ethylene glycol-treated substrates and metal-loaded substrates were characterized by scanning electron microscopy, X-ray diffraction, and BET surface area determinations. Metal-loaded oxide substrates were also characterized by energy dispersive X-ray analysis. Supported palladium and silver were tested as catalytic converters of simulated automobile exhaust gases.

2. Materials and methods

2.1. Materials

Alumina and mixed Ce–Zr oxides powders were used as substrates. The BET specific surface area of the as-received powders had the following values: $156 \text{ m}^2 \text{ g}^{-1}$ for alumina and $18.3 \text{ m}^2 \text{ g}^{-1}$ for the Ce–Zr oxides mixture. All chemicals used were reagent grade materials. Ethylene glycol was purchased from Prolabo. The metal compounds used to synthesize colloidal metals were silver nitrate (Aldrich) and palladium chloride (ABCR). In order to avoid particle sintering and aggregation, polyvinylpyrrolidone (PVP) (Aldrich, molecular weight = 10 000) was used as protective agent.

2.2. Methods

The procedures previously described for the synthesis of unsupported silver particles [8] and palladium particles [9] were used for in situ deposition of silver nanoparticles onto alumina and palladium nanoparticles onto Ce–Zr oxides in ethylene glycol–PVP solutions. The experimental procedure was as follows. A given amount of the substrate powder was added to an ethylene glycol–PVP–metal precursor solution at room temperature, and agitated with a magnetic stirrer. The initial metal content (in wt.% of the catalyst) in solution was 1% for alumina-supported silver and 0.5% and 5% for mixed Ce–Zr oxides-supported palladium. Then, the suspension was heated up to the desired temperature (120°C for silver and 100°C for palladium) at a rate of 1°C min^{-1} , and allowed to react at this temperature during one hour. At the end of the reaction time, the preparation

was rapidly cooled to room temperature with tap water. The powder thus obtained was separated from the supernatant by centrifugation, and subsequently washed several times with water and acetone in order to remove the organic phase. After each washing step, the solids were also separated from the liquid by centrifugation. Afterwards, the metal-loaded powder catalyst was dried in a furnace at 55°C under air.

The reactivity of the oxide substrates in ethylene glycol–PVP solutions was investigated by conducting “blank tests” under the same conditions as those of metal particle deposition, and characterizing the resulting solid products.

2.3. Characterization

As-received substrates as well as those treated in hot ethylene glycol–PVP solutions and the metal-loaded substrates were characterized by X-ray powder diffraction with a Philips PW 1710 diffractometer using $\text{Cu } K_\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) and a diffracted-beam monochromator. A Philips Field Emission Gun (FEG) XL-30 Scanning Electron Microscope (SEM) was used for microscopy observation of catalyst powders. Energy dispersion X-ray (EDX) microanalysis was used for silver and palladium detection on the surfaces of the substrate powders using an Oxford Link-Isis analyzer coupled to the FEG probe. By means of the mapping facility, EDX was also used to determine the distribution of metal particles on the surface of metal-loaded substrates, and to provide information about the homogeneity of the metal deposition procedure. Transmission electron microscopy (TEM) observations were performed on a Philips CM 12 in order to measure the metal particles size.

Measurement of the specific surface area of powder catalysts was carried out with a Micrometrics Gemini II 2370 surface area analyzer by nitrogen physisorption at 77 K following the multi-point BET technique. Chemical analyses of metal-loaded substrates were performed at the analytical laboratory of the CNRS to verify the final metal content of the powder catalysts.

2.4. Catalytic tests

The catalytic activity of silver and palladium-loaded powders was compared to reference test catalysts loaded with the same metal amounts. Prior to the tests, polyol catalysts and reference samples were aged under similar conditions. In order to point out the influence of the deposition method, the evaluation of the catalytic activity was achieved under similar conditions for each test, which involved heating the catalyst under a gas flow similar in composition to automobile exhaust gases.

3. Results and discussion

3.1. Reactivity of powder substrates in hot ethylene glycol–PVP solutions

A material selected as substrate for in situ metal deposition in ethylene glycol must be insoluble in this solvent, inert towards the formation of glycolate compounds, and electrochemically stable towards ethylene glycol reducing power in the range of working temperatures required to synthesize the desired metal particles. To test whether or not the selected substrates meet these requirements, they were first treated in ethylene glycol–PVP solutions under the same conditions of metal particles deposition.

X-ray powder diffractograms of as-received substrates and of the solids recovered from the blank tests are almost identical for each oxide powder, clearly showing that their original crystal structure is preserved after treatment in hot ethylene glycol–PVP solutions. According to these results, alumina and the mixture of Ce–Zr oxides are chemically inert in ethylene glycol under the conditions of silver and palladium nanoparticles deposition. Scanning electron micrographs of as-received powders and of solids recovered from the blank tests reveal no change in the morphology of alumina and of the mixed Ce–Zr oxides. Alumina and the mixed Ce–Zr oxides can therefore be used as substrates for the preparation of metal-loaded powder catalysts by the polyol process.

Table 1 lists the BET specific surface area of as-received substrates used in this research work as well as those treated in the blank experiments and those loaded with silver and palladium nanoparticles. In the case of the blank test

products, the original surface area decreases as follows: 12.3% for alumina and 12.6% for Ce/Zr mixed oxides. These results could be explained by the adsorption of organic molecules (PVP or EG) at both the external and internal surfaces of the substrates which may interfere with N_2 adsorption during the BET measurement.

3.2. Characterization of metal-loaded substrates

3.2.1. Silver-loaded alumina

According to the X-ray powder diffractograms shown in Fig. 1, which can be indexed as γ - Al_2O_3 according to the JCPDS #29-0063, the crystalline structure of as-received alumina is also preserved after in situ deposition of colloidal silver. The specific surface area of silver-loaded alumina (listed in Table 1) has almost the same value as that of the as-received alumina powder. Although treatment of the original substrate in hot ethylene glycol–PVP solutions reduces its specific surface area, the presence of colloidal metal onto silver-loaded alumina compensates the reduction of the initial specific surface area associated to solvent and polymer molecules adsorption. The distribution of silver on the surface of alumina is shown in Fig. 2, which presents EDX mapping revealing a homogeneous metal deposition onto the substrate. Elemental chemical analysis of silver-loaded alumina, listed in Table 2, indicates that its silver content is smaller than the initial silver in solution: 0.59% as opposed to 1% initially added. The poor deposition of silver onto alumina is confirmed by the orange color of the supernatant obtained after centrifugation, indicating the presence of colloidal silver in solution. Sales et al. [7] also found that silver poorly deposited onto alumina, and

Table 1
BET specific surface area of as-received substrates, ethylene glycol treated substrates and metal loaded substrates

Powder substrate	As-received ($m^2 g^{-1}$)	Treated with ethylene glycol ($m^2 g^{-1}$)	Metal-loaded ($m^2 g^{-1}$)
Alumina	156	137	150
Mixed Ce–Zr oxides	18.3	16	16.8

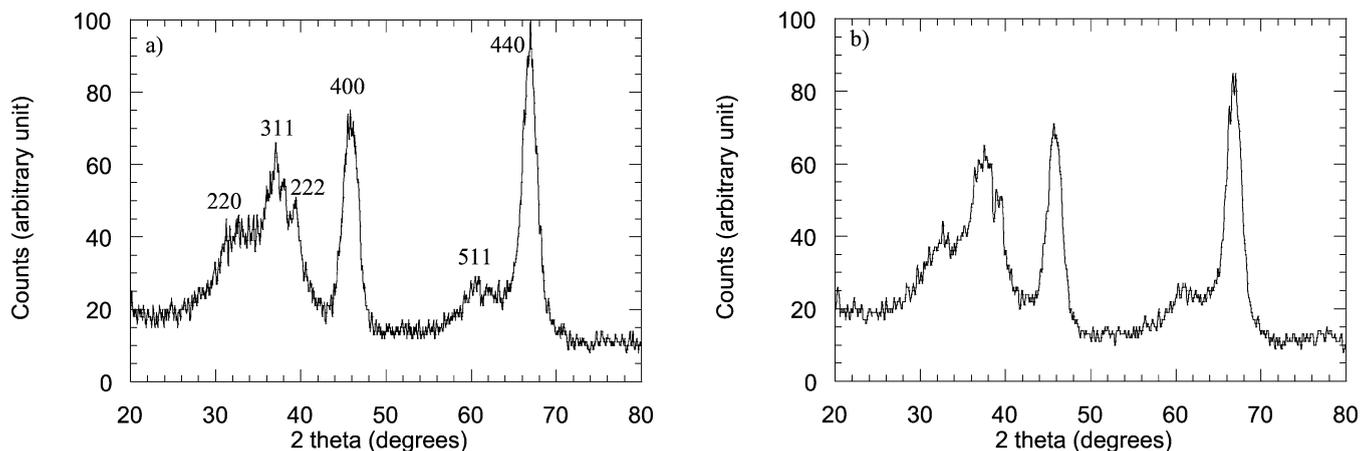


Fig. 1. X-ray powder diffractograms of (a) as-received alumina, and (b) silver-loaded (0.6 wt.%) alumina.

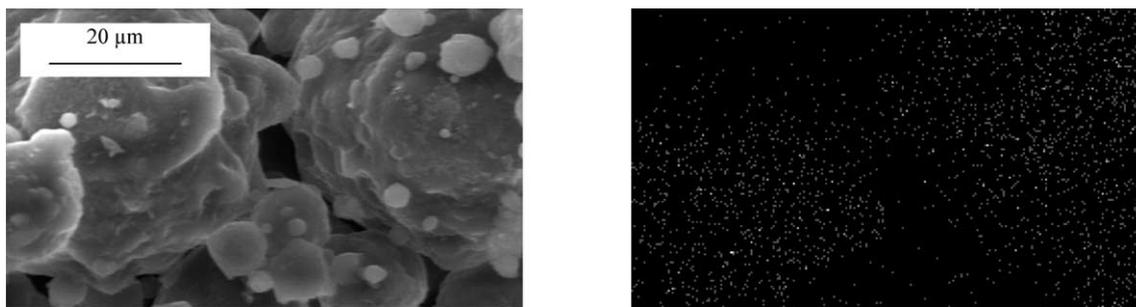


Fig. 2. SEM micrograph and X-ray map of silver-loaded (0.6 wt.%) alumina.

Table 2
Elemental chemical analysis of silver and palladium loaded substrates

Metal/substrate	Metal initially added (wt.%)	Final metal content (wt.%)
Ag/alumina	1.0	0.59
Pd/mixed Ce–Zr oxides	5.0	4.58
	0.5	0.47

attributed it to an incomplete reduction of silver cations at the temperature used for in situ deposition, namely 55 °C. Since the final reaction temperature used in this work for loading silver onto alumina is 100 °C, the reduction of AgNO₃ may be complete after one-hour deposition period. Another possibility to understand the poor silver loading could be due to the presence of PVP. As described by Zhang et al. [10], this surfactant is strongly adsorbed onto silver particles preventing aggregation. According to the observation of Sales et al. [7], silver particles first appear in solution and then deposit onto alumina. Herein, the presence of PVP adsorbed onto silver may prevent the adhesion of metal particles in solution to the substrate. This could explain the poor loading of metal onto the oxide and why the orange color of the supernatant. Furthermore, TEM observations reveal the presence of 15 nm particles onto the alumina powder, that is to say a similar size than the particles obtained without the substrate [9]. These results indicate that the particles appear first in solution as reported by Sales et al. [7] and therefore their formation is controlled by the amount of precursor and PVP, and that the substrate does not interfere with the particle nucleation–growth mechanism, for example, acting as a growth support.

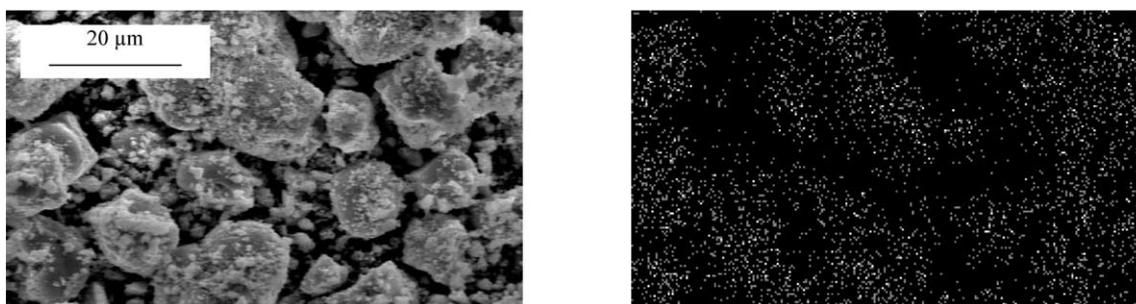


Fig. 3. SEM micrograph and X-ray map of palladium-loaded (0.5 wt.%) mixed Ce–Zr oxides.

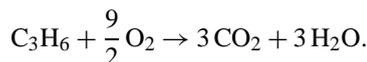
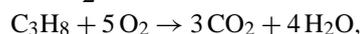
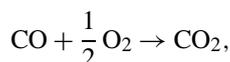
3.2.2. Palladium-loaded mixed Ce–Zr oxides

Palladium deposition onto the mixed Ce–Zr oxides induces a color change of the oxide support from white to grey indicating the presence of metal particles on the surface. As opposed to the results of the silver–alumina system, a clear supernatant was obtained after recovering the palladium-loaded substrate. According to X-ray powder diffraction, palladium-loaded mixed Ce–Zr oxides keep their crystalline structure. Elemental chemical analyses given in Table 2 indicate that the final palladium content of metal-loaded mixed Ce–Zr oxides samples is slightly smaller than the 0.5 wt.% and 5 wt.% palladium initially in solution. Since a colorless supernatant is obtained after separation of the Pd-loaded substrate, it seems that the addition of PVP does not interfere with the deposition of the Pd particles onto the substrate. An X-ray map of the 0.5 wt.% Pd-loaded mixed Ce–Zr oxides is presented in Fig. 3 and shows a homogeneous deposition of the metal on the substrate. Palladium particles can also be observed by TEM, their size ranging from 5 to 10 nm. This polydispersity could be due (i) to the poor dissolution of the precursor in ethylene glycol preventing a uniform particles growth or (ii) to the presence of the substrate acting as a heterogeneous nuclei and disturbing the particles formation.

3.3. Catalytic activity of metal-loaded substrates

Catalytic tests were conducted with alumina-supported silver and mixed Ce–Zr oxides-supported palladium (0.5 wt.%) to determine their catalytic performance as converters of automobile exhaust gases, including CO and hy-

drocarbon molecules (propane and propylene) oxidation to CO_2 , and nitrogen oxides (NO_x) reduction to N_2 . Alumina-supported silver concerns with direct fuel injection applications (DeNOx test) whereas mixed Ce–Zr oxides-supported palladium concerns exhaust gases emitted by classical fuel motors (three-way catalytic converter). The reactions taking place in both applications are the following:



CO, propane and propylene can also be involved in the reduction of NO_x according to the following reactions:



A three-way catalyst should simultaneously oxidize hydrocarbons and CO, and reduce NO_x . Also, in a DeNOx test, a catalyst must show the same trend but the behavior strongly depends on the oxygen content of the gas flow.

3.4. Activity of silver-loaded alumina catalysts

Fig. 4a presents the catalytic activity test results for silver-loaded alumina prepared by the polyol process. For comparison, the catalytic activity of the reference silver–alumina catalyst converter under the same conditions is presented in Fig. 4b. According to these results, the polyol prepared catalyst shows a higher activity for CO and hydrocarbon oxidation, as well as for NO and NO_x reduction. The onset of these processes occurs at temperatures lower than those obtained with the reference catalyst. Maximum CO conversion with the polyol prepared Ag– Al_2O_3 catalyst is about 30% between 400 and 550 °C, whereas it is only about 12% at 550 °C with the reference catalyst. In the case of the polyol prepared Ag– Al_2O_3 catalyst, CO conversion above 550 °C decreases, reaches a minimum at about 610 °C, and then sharply increases up to almost 80% at 700 °C. Hydrocarbon oxidation with the polyol prepared powder catalyst significantly increases from about 15% at 500 °C to 65% at 600 °C. With the reference catalyst, however, only 30% hydrocarbon oxidation is achieved at 600 °C. NO and NO_x reduction with the polyol prepared catalyst reaches a maximum of 20% and 16% at 600 °C, respectively. For the reference catalyst, only 3% NO and NO_x conversion is achieved under the same conditions. The trend, shown by the hydrocarbon oxidation and the NO and NO_x reduction curves obtained with the polyol prepared catalyst, seems to indicate that the reduction of NO and NO_x is associated with the oxidation of propane and propylene up to 600 °C, because the NO_x reduction curves remarkably follow the shape of the hydrocarbons oxidation curve. This is not the case for the curves obtained with the

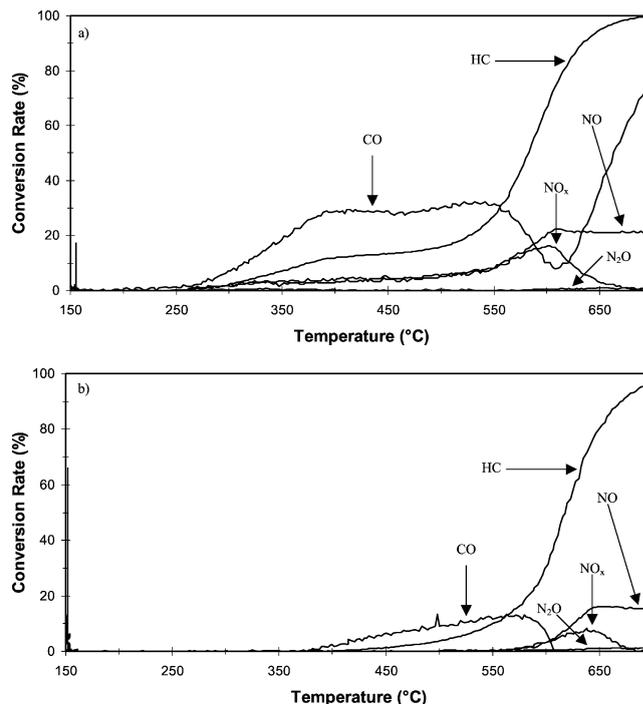


Fig. 4. Conversion of simulated automobile exhaust gases in “DeNOx” conditions as a function of temperature using (a) polyol-prepared silver-loaded (0.6 wt.%) alumina catalyst, and (b) reference silver-loaded alumina catalyst. (The HC term refers to propane and propylene molecules.)

reference catalyst, and one may conclude that NO and NO_x reduction needs higher temperatures and higher oxidation of the hydrocarbon molecules.

3.5. Activity of palladium-loaded mixed Ce–Zr oxides powder catalysts

Fig. 5 exhibits the catalytic activity of palladium-loaded mixed Ce–Zr oxides powder catalysts tested as three-way catalytic converters as a function of temperature under lean conditions, that is to say in the presence of excess O_2 . Due to the presence of O_2 , both catalysts show no activity for NO_x reduction. Comparing the curves of the polyol (Fig. 5a) with reference (Fig. 5b) catalysts, one can see that the polyol catalyst shows a higher catalytic activity for propane conversion, because this process starts at about 275 °C compared to 400 °C with the reference catalyst. The reference catalyst, on the other hand, shows a higher activity for both CO and propylene conversion as indicated by the slope of the corresponding conversion curves. However, the difference between the light-off temperature of both catalysts, $T = 50$, defined as the temperature at which 50% conversion is achieved, is insignificant.

4. Conclusions

The principles of the polyol method have been successfully applied to in situ deposition of silver and palladium

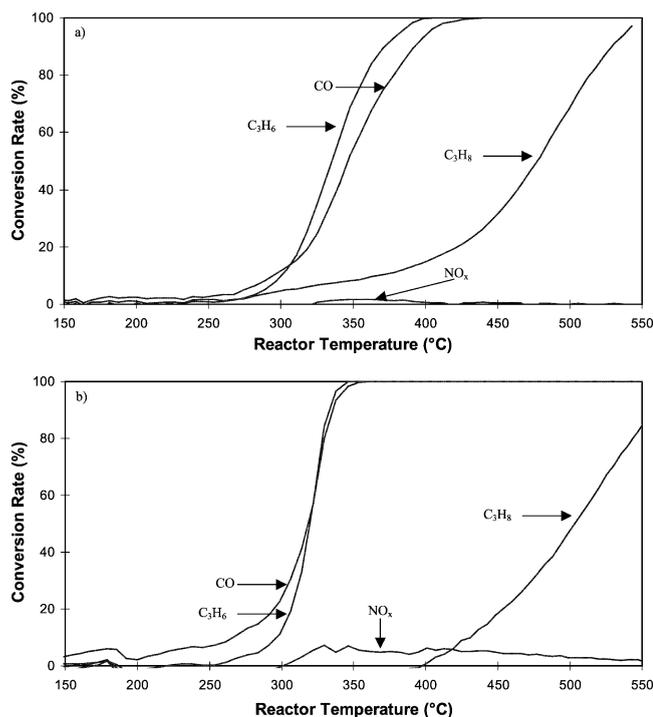


Fig. 5. Conversion of simulated automobile exhaust gases in a three-way catalytic test as a function of temperature using (a) polyol-prepared palladium-loaded (0.5 wt.%) Ce/Zr mixed oxides, and (b) reference palladium-loaded (0.5 wt.%) Ce/Zr mixed oxides catalyst.

nanoparticles onto alumina and mixed Ce–Zr oxides. These substrates were found to be chemically inert towards ethylene glycol under the same reaction conditions used to synthesize unsupported silver and palladium particles. X-ray powder diffractograms reveal that their crystalline structure was also preserved after metal deposition. X-ray maps show a homogeneous distribution of metal particles onto the surfaces of the loaded substrates. The final amount of Pd deposited onto the mixed Ce–Zr oxides was essentially equal to the palladium amount initially present in solu-

tion. In the case of silver deposition onto alumina, however, only 60% of silver in solution is loaded onto the substrate. Alumina-supported silver prepared in ethylene glycol exhibits a catalytic activity as converter of automobile exhaust gases higher than that of a reference sample. The performance of palladium supported onto mixed Ce–Zr oxides as a three-way catalytic converter was found to be similar to the reference catalyst. Due to the variety of metal powders produced by the polyol process and the increase in catalysts demands, this method has potential applications for simple in situ deposition of other metal particles onto different substrate powders.

Acknowledgements

The authors wish to thank Conseil Regional de Picardie and Rhodia for financial support. The authors are grateful to L. Dupont for his help in TEM observations.

References

- [1] P. Bera, K.C. Patil, V. Jayaram, M.S. Hegde, G.N. Subbanna, *J. Mater. Chem.* 9 (1999) 1801–1805.
- [2] K. Shimizu, A. Satsuma, T. Hattori, *Appl. Catal. B* 25 (4) (2000) 239–247.
- [3] M. Jacoby, *Chem. Eng. News* 25 (1999) 36–44.
- [4] Ch.-H. Lee, Y.-W. Chen, *Ind. Eng. Chem. Res.* 37 (4) (1998) 1260–1266.
- [5] L.K. Kurihara, G.M. Chow, P.E. Schoen, *Nanostruct. Mater.* 5 (6) (1995) 607–613.
- [6] S. Ayyapan, G.N. Subbanna, R. Srinivasa Gopalan, C.N.R. Rao, *Solid States Ionics* 84 (1996) 271–281.
- [7] E.A. Sales, B. Benhamida, V. Caizergues, J.P. Lagier, F. Fievet, F. Bozon-Verduraz, *Appl. Catal. A* 2 (1998) 172.
- [8] P.-Y. Silvert, R. Herrera Urbina, N. Duvauchelle, V. Vijayakrisnan, K. Tekaia Elhsissen, *J. Mater. Chem.* 6 (1996) 573–577.
- [9] F. Bonet, V. Delmas, S. Grugeon, R. Herrera Urbina, P.-Y. Silvert, K. Tekaia Elhsissen, *Nanostruct. Mater.* 11 (8) (1999) 1277–1284.
- [10] Z. Zhang, B. Zhao, L. Hu, *J. Solid State Chem.* 121 (1996) 105–110.