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Study of the Pretreatment Chemistry and Thermal Stability of Zirconia Supported Ru–Pt Catalysts

Juan R. González-Velasco,[1] Miguel A. Gutiérrez-Ortiz, José A. González-Marcos,
Pavol Pranda,[2] and Pavol Steltenpohl[3]

Departamento de Ingeniería Química, Facultad de Ciencias, Universidad del País Vasco/EHU, Apartado 644, 48080 Bilbao, Spain

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The behavior of zirconia supported Ru and/or Pt catalysts in conditions of TPReduction and pulse chemisorption is studied. In order to understand the process of precursor decomposition, several catalysts prepared by either (co)adsorption or (co)impregnation methods and treated in air or nitrogen are investigated by DSC, MS, and by IRS. A possible adsorption path of Ru(NO)(NO$_3$)$_3$ over zirconia and its subsequent decomposition during catalyst conditioning is discussed. Stabilization of supported ruthenium in the presence of platinum due to formation of bimetallic cluster was observed, especially when the catalyst was prepared by adsorption. © 1999 **Academic Press**

Key Words: **ruthenium; platinum; adsorption; impregnation; zirconia; bimetallic; thermal stability; precursor decomposition; IR; TPR; DSC; MS.**

INTRODUCTION

The supported catalysts with more than one noble metal have attracted attention since the 1970s. From that time a great effort to understand and to describe their role in environmental protection, particularly in the control of automotive emissions, has been made.

Bimetallic catalysts containing platinum and ruthenium have been successfully characterized by using several techniques which include selective chemisorption and selective CO–O_2 titration (1), temperature-programmed desorption (2), infrared spectroscopy (3), and differential scanning calorimetry (4, 5). The more commonly used supports, such as alumina, silica, or cellulose-based carbon fiber paper (6–11) interact strongly or weakly with metal precursors depending on their ionic form during the catalyst preparation. The ruthenium precursors have been mainly $RuCl_3 \cdot 3H_2O$, $Ru(NH_3)_6Cl_3$, ruthenocene, and $Ru(NO)(NO_3)_3$ (1–3, 6, 8, 11–13). The former two Ru precursors form cations in water solution (6, 7), and $Ru(NO)(NO_3)_3$ can change its ligands depending on the nitric acid solution concentration giving rise to neutral, anionic, or cationic complexes of general formula $[Ru(NO)(H_2O)_x(NO_3)_{5-x}]^{x-2}$ (14). As platinum precursors, $H_2PtCl_6 \cdot 6H_2O$, $Pt(NH_3)_4(NO_3)_2$, and $Pt(NH_3)_2(NO_2)_2$ have been used (1–3, 6, 8, 11, 12). In aqueous solution, hexachloroplatinic acid undergoes hydratation and hydrolysis and behaves like a poor acid with $pK_a = 3.8$ (15), whereas $Pt(NH_3)_4(NO_3)_2$ and $Pt(NH_3)_2(NO_2)_2$ form cations.

However, not only do the interactions between support and metal precursor play an important role and influence the final properties of the catalyst; so does the pretreatment chemistry. Alerasool and González (7) showed that coimpregnation of silica by aqueous solution of $Pt(NH_3)_4(NO_3)_2$ and $Ru(NH_3)_6Cl_3$ followed by reduction in hydrogen leads to the formation of highly dispersed bimetallic particles. Pretreatment in oxygen prior to reduction leads to phase separation, the formation of oxidized ruthenium species being suspected to be the underlying reason leading to this phenomenon. Zou and González (8) confirmed this supposition by CO chemisorption and EDAXS. Similar effects have been reported by Lin *et al.* (16) and Pearce *et al.* (17) for catalysts prepared by liquid phase adsorption of $Ru(NH_3)_6Cl_3$ over alumina and Y zeolites, respectively.

The high volatility of ruthenium tetraoxide excludes the use of Pt–Ru catalysts in applications requiring high thermal stability, such as three-way catalytic systems (18). Despite these limitations, bimetallic catalysts consisting of Ru and Pt are intensively studied due to their specific properties (6, 12); e.g., Ru–Pt bimetallic clusters formed over the entire metal composition range have been found to be reasonably stable in oxidizing as well as reducing atmospheres (2, 3). Both active metals are effective catalysts that can be used as catalytic probes. Moreover, ruthenium, as well as platinum, is relatively easy to reduce and shows a well defined chemisorption stoichiometry, although CO chemisorption has some restrictions (1, 19, 20).

The objective of this study is to elucidate the mechanism of ruthenium precursor adsorption over zirconia and its

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[1] To whom correspondence should be addressed.

[2] Present address: Department of Chemical Engineering, State University of New York at Buffalo, Amherst, NY 14260.

[3] Present address: Department of Chemical and Biochemical Engineering, Slovak University of Technology, 812 37 Bratislava, Slovak Republic.

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thermal decomposition and to correlate the nature of prepared supported mono- and bimetallic catalysts with their behavior during characterization.

EXPERIMENTAL

Catalyst Preparation

Zirconia after calcination at 773 K for 4 h with surface area of 71.7 $m^2\,g^{-1}$ and average pore diameter of 10.7 nm obtained from the Norton Company was used as support. As precursors, ruthenium nitrosyl nitrate (Johnson Matthey) and hexachloroplatinic acid (Aldrich) were chosen. The catalysts were prepared either by liquid phase adsorption or impregnation of precursor(s) onto the support.

Adsorption consisted of mixing the precursor aqueous solution(s) (40 $cm^3\,g^{-1}$ of support) with support and stirring for 3 h followed by decantation and washing with distilled water. The resulting mono- or bimetallic catalysts were dried under vacuum at room temperature. The second method, impregnation, consisted of mixing the precursor solution(s) with support and stirring for 10 min and then introducing vacuum at 315 K and evaporating the excess of water. Successive adsorption and impregnation catalysts were prepared by subsequent contact of the support with aqueous solutions of each active metal precursor. No essential differences between catalysts were found if the order of precursor's solutions contact with zirconia support was changed. Further treatment could be necessary depending on the characterization method or measurement applied.

Table 1 shows the metal content of prepared mono- and bimetallic catalysts as determined by colorimetry (Ru) and atomic absorption spectroscopy (Pt).

Procedures

DSC measurements were performed on a Perkin Elmer TGS2 apparatus connected with a Hiden Analytical Model HPR20 quadrupole analyzer. The temperature range of 303 to 773 K, 30 cm^3 of N_2 and H_2 mixture (33% vol. of H_2), a heating rate of 10 K min^{-1}, and 0.02 g of sample were used. Mass spectroscopy (MS) experiments were realized under the same conditions in pure nitrogen.

TABLE 1

Catalyst Active Metal Content and Preparation Method Used

			Active metal content (%)	
Catalyst	Active metal	Preparation method	Ru	Pt
1	Ru	Adsorption	0.88	—
2	Ru	Impregnation	0.44	—
3	Pt	Adsorption	—	0.65
4	Pt	Impregnation	—	0.97
5	Ru + Pt	Coadsorption	0.49	0.58
6	Ru + Pt	Successive Pt–Ru adsorption	0.75	0.68
7	Ru + Pt	Coimpregnation	0.24	0.41
8	Ru + Pt	Successive Ru–Pt impregnation	0.20	0.50

The results of infrared spectroscopy (IRS) were obtained on a Nicolet FT-IR 740 spectrometer in the range from 4000 to 600 cm^{-1}. Samples were prepared by pressing particles of KBr which contained 2–3 wt% of powdered catalyst.

Temperature programmed reduction (TPR) and pulse chemisorption measurements were carried out on an AMI-1 apparatus (Altamira Instruments). TPR results were obtained in the temperature range 303–923 K, with 30 cm^3 N_2 and H_2 mixture (10% vol. of H_2), a heating rate of 30 K min^{-1}, and approximately 0.3 g of previously calcined sample used in each run. Pulse chemisorption experiments consisted of calcination at 573 K for 1 h in He, N_2, or air, reduction at 573 K for 1 h in H_2, catalyst metal surface purification of adsorbed hydrogen at 573 K for 3 h in He, and measurement of the H_2 amount chemisorbed at 298 K. The last two steps were repeated three times.

RESULTS AND DISCUSSION

Preparation of Supported Ru Precursor and Mechanism of Its Thermal Decomposition

$Ru(NO)(NO_3)_3$ was deposited onto the support surface either by adsorption or by impregnation from aqueous solutions.

During liquid phase adsorption, the surface of zirconia was exposed to the precursor's solution with a pH value lower (in fact it was pH ≈ 2) than that corresponding to its isoelectric point. For zirconia, pH_{IEPS} 8.5 was estimated by titration at constant pH value (21). Under these conditions, protonization of the support surface and hydratation of the ruthenium precursor takes place:

$$(s)\text{–Zr–OH} + H_3O^+ \leftrightarrow (s)\text{–Zr}^+ + 2H_2O,$$

$$Ru(NO)(NO_3)_3 + 2NO_3^- + xH_2O \leftrightarrow [Ru(NO)(H_2O)_x(NO_3)_{5-x}]^{x-2} + xNO_3^-.$$

Then the protonized surface of zirconia is subjected to nucleofillic attack of anions, e.g.,

$$(s)\text{–Zr}^+ + [Ru(NO)(H_2O)_x(NO_3)_{5-x}]^{x-2} \leftrightarrow (s)\text{–Zr–}[O\text{–}NO_2\text{–}Ru(NO)(H_2O)_x(NO_3)_{4-x}]^{x-1}.$$

Another possible adsorption path is the attack of two surface centers, giving rise to species bound to the support surface via OH ··· O bridges:

$$2(s)\text{–Zr–OH} + [Ru(NO)(H_2O)_x(NO_3)_{5-x}]^{x-2} \leftrightarrow 2(s)\text{–Zr–OH} \cdots [O_2\text{–NO–}Ru(NO)(H_2O)_x(NO_3)_{4-x}]^{x-2}.$$

TABLE 2

TPR Measurement of Monometallic Ruthenium Catalysts

Catalyst	Pretreatment	Reduction temperature (K)	H_2 uptake (μmol g_{cat}^{-1})	H_2/Ru molar ratio
1	None	475	745.8	8.56
1	0.5 h, N_2, 423 K	477	560.2	6.43
1	0.5 h, N_2, 573 K	369, 429	344.4	3.96
2	None	468	656.9	15.09
2	0.5 h, N_2, 423 K	451	503.9	11.57
2	0.5 h, N_2, 573 K	349, 437	244.9	5.63

TABLE 3

Reduction Temperature and Heat Liberated during DSC Experiment

Catalyst	Reduction temperature (K)	Liberated heat (kJ mol_{metal}^{-1})
1	461	−1.02
2	468	−4.74
3	464	−0.65
4	467	−0.49
5	421	−1.27
7	430, 460	−4.77

Taking into account the possibility of ligand exchange during liquid phase adsorption, it is very probable that only one NO_3 group, that bounded directly to the support surface either by Zr–O–NO–O–Ru or Zr–OH $\cdots$ O–NO–O–Ru bonds, remains unsubstituted. The evidence for this hypothesis was derived from TPR of adsorbed and impregnated Ru/ZrO_2 catalysts, whose results are presented in Table 2.

The idea of ligand exchange during adsorption procedure becomes clearer considering the reduction of supported ruthenium complexes by hydrogen:

$$(s)\text{–Ru(NO)(H}_2\text{O)}_4\text{(NO}_3\text{)} + 7\text{H}_2 \rightarrow (s)\text{–Ru} + 2\text{NH}_3 + 8\text{H}_2\text{O} \qquad \text{H}_2/\text{Ru} = 7$$

and

$$(s)\text{–Ru(NO)(H}_2\text{O)2(NO}_3\text{)}_3 + 16\text{H}_2 \rightarrow (s)\text{–Ru} + 4\text{NH}_3 + 12\text{H}_2\text{O} \qquad \text{H}_2/\text{Ru} = 16.$$

The suggested precursor reduction scheme was supported by combined TG-MS experiments. During precursor reduction, an increase in intensity of masses 16, 17, and 18 (O and NH_2, OH and NH_3, and H_2O, respectively) was observed, while no changes in intensity of masses 30, 44, and 46 (NO, N_2O and CO_2, and NO_2, respectively) were registered. Measured loss of sample weight corresponded to the amount of NO and $–NO_3$ liberated from the precursor.

Further information obtained from DSC measurements confirms the proposed mechanism of Ru precursor binding to the support surface. In the course of reduction, almost five times less heat was liberated from catalysts prepared by adsorption than those prepared by impregnation (see Table 3).

The amount of heat widespread during Ru precursor reduction should be, in our opinion, also attributed to the number of $–NO_3$ groups coordinated to the Ru atom after its incorporation into the support. The increase in heat liberation in the case of impregnated catalyst is related to higher hydrogen consumption, as shown by TPR experiments (see Table 2).

More strong evidence confirming this mechanism is represented in Fig. 1, which shows the MS results of thermal decomposition of the supported Ru precursor. In the case of catalyst prepared by adsorption (Fig. 1a), the relative heights of both NO peaks are almost equal, meaning that

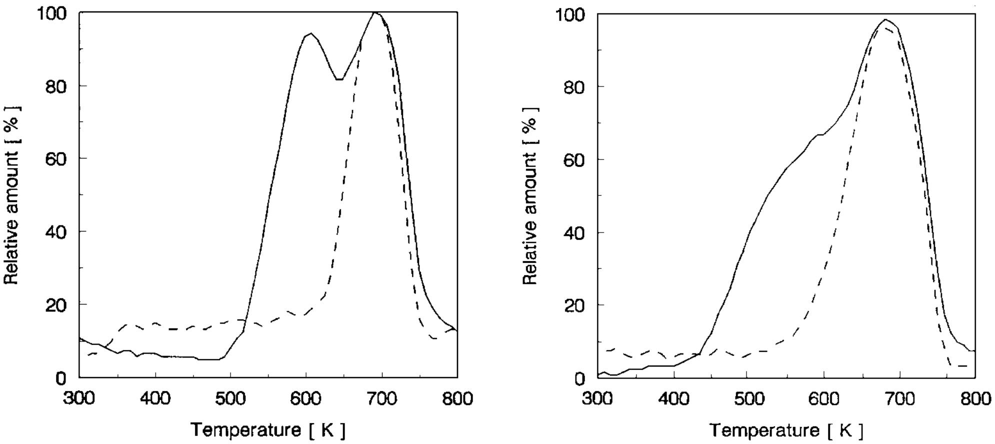

FIG. 1. Decomposition of zirconia supported $Ru(NO)(NO_3)_3$ in the stream of N_2. Released NO (solid line) and O_2 (dashed line) course measured by MS detector. (a) Catalyst 1; (b) catalyst 2.

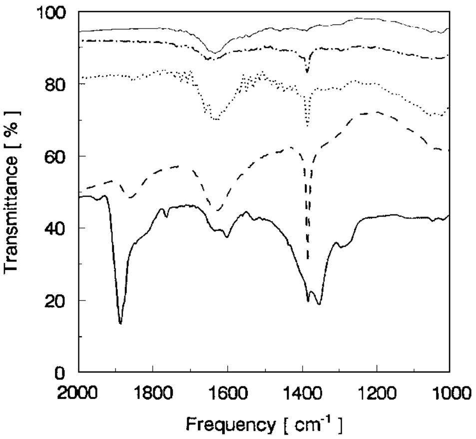

FIG. 2. IR spectra of Ru precursor (solid line) and Ru precursor supported on zirconia: fresh (dashed line) and heated to 623 K (dotted line), 723 K (dotted-dashed line), and 773 K (thin solid line).

the amounts of NO and NO_3 ligands liberated during this experiment are practically the same (as will be discussed later).

After desorption of water, the thermal decomposition of supported Ru precursor begins with the breaking of the Ru–NO bond, being the weakest one compared to those of Ru–O and OH $\cdots$ O. In nitrogen flow, this rupture was pronounced by NO liberation starting from about 500 K (Fig. 1a). The NO_3 group, which in our opinion forms the bridge between ruthenium and zirconium atoms, is decomposed to NO and O_2 at temperatures above 620 K, as shown by the released oxygen curve in Fig. 1a. Decomposition of these two bonds passes through maxima at 600 K (Ru–NO) and 680 K (Ru–O–NO_2) and is completed at 700 and 780 K, respectively.

Figure 2 shows the IRS diagrams corresponding to decomposition of ruthenium precursor prepared by adsorption over zirconia. Three main regions of vibrations can be found in the spectra: frequencies in the range 1890–1850 cm^{-1} are associated with linear NO vibrations (22), at about 1640 cm^{-1} they belong to HOH bending or NO tension, and the frequencies close to 1385 cm^{-1} correspond to symmetric vibrations of the NO_3 group (23).

The effect of temperature can be analyzed by comparison of the spectra shown in Fig. 2. The Ru precursor decomposition starts with destruction of the Ru–NO bond. Liberation of NO was completed before 723 K and almost simultaneously the rupture of the Ru–ONO_2 bond began. The symmetric vibrations of NO_3 disappeared only when the temperature was elevated to 773 K.

Compared to Ru/ZrO_2 catalysts prepared by adsorption, the mechanism of Ru deposition over zirconia by impregnation and its thermal decomposition is even more complex. During impregnation, all ligands and ions present in solution were deposited over the support surface. Therefore, the amount of hydrogen consumed during the TPR run (Table 2) and also the amount of heat released during the DSC experiments (Table 3) exceeded the corresponding values for catalyst prepared by adsorption of Ru precursor. Similarly, the NO_3/NO molar ratio measured by MS during thermal decomposition of supported precursor should be equal to or even greater than three, depending on the amount of nitric acid used for modification of the precursor's solution pH. In fact, Fig. 1b shows only one NO peak coinciding with the O_2 release, however, with some shoulders in the position where previously the peak corresponding to NO liberated by Ru–NO bond rupture was situated (see Fig. 1a).

Then similar decomposition paths for both Ru catalysts, with the active phase deposited over the zirconia support by adsorption or by impregnation, could be concluded.

Stability of Ruthenium Catalysts

Stability of fresh, but also reduced, ruthenium catalysts depends strongly on conditions under which calcination or chemical reaction is performed. In an oxidizing atmosphere, ruthenium tetraoxide is formed and due to its volatility the amount of active metal can decrease. Oxidation of supported Ru was also observed in a nonreducing atmosphere (He) during characterization of catalysts by chemisorption (see Table 4, Observation column).

The presence of RuO_4 was observed visually by the change of the catalyst color to yellow. Indirectly, its presence was deduced from the loss of ruthenium in the catalyst samples after calcination. Finally, the formation of ruthenium tetraoxide (mass 165) was registered during combined TG-MS experiments conducted in 21% vol. O_2 in He. The continuous appearence of mass 165 started at 320 K. The possibility of measuring the background data was excluded after an experiment in reducing atmosphere (33% vol. H_2 in He). Under these conditions, no specia with mass 165 were detected. The same experiment was conducted also in pure helium, generally exhibiting the presence of the same specia as observed in the oxidizing atmosphere, including RuO_4.

In order to stabilize Ru/ZrO_2 catalysts, platinum was introduced to form more stable bimetallic clusters with

TABLE 4

Results of Pulse Chemisorption of Catalysts Calcined at 573 K in He

Catalyst	Active metal	H/metal	Observation
1	Ru	0.54	RuO_4
2	Ru	0.44 (0.08^a)	RuO_4
3	Pt	1.30	—
4	Pt	1.05	—
5	Pt + Ru	0.74	—
6	Pt + Ru	0.55	—
7	Pt + Ru	0.34 (0.34^a)	—

[a] Calcination temperature was 723 K.

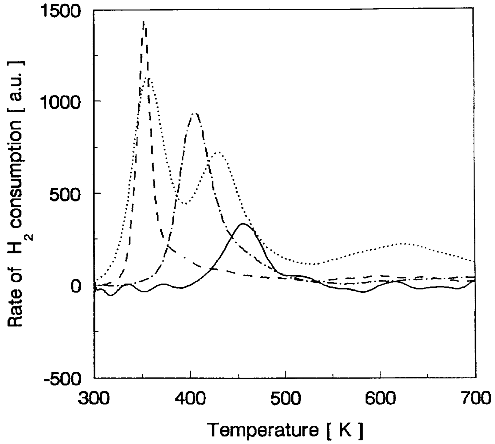

FIG. 3. TPR measurement of zirconia supported catalysts: 1 (dashed line), 3 (solid line), 5 (dotted-dashed line), and physical mixture of monometallic catalysts 1 and 3 (dotted line). All catalysts were calcined at 723 K for 30 min in air prior to the TPR experiment.

dispersed ruthenium (6). The results of TPR experiments shown in Fig. 3 confirm this hypothesis. The data obtained for Ru–Pt catalyst prepared by coadsorption exhibit a single hydrogen consumption peak (408 K) centered between those corresponding to the monometallic catalysts (Ru, 353 K, Pt, 456 K). On the other hand, two maxima were found for the case of catalyst prepared by mixing of the two monometallic catalysts (Ru + Pt, 353 and 431 K).

The influence of the preparation method on bimetallic cluster formation was also studied by DSC. The results of DSC measurement, shown in Fig. 4, unveiled the differences between catalysts prepared by coadsorption and those prepared by coimpregnation.

The reduction temperature of monometallic catalysts prepared by the adsorption and impregnation method, which coincides with minima in curves obtained by the DSC measurement, was situated at about 460–470 K. Only DSC profiles of monometallic catalysts prepared by adsorption are plotted in Fig. 4, being essentially the same as those prepared by impregnation. The curves of bimetallic catalysts contain overlapped peaks. In the profile of catalyst prepared by coadsorption, the species with reduction temperature about 421 K dominate. This peak represents assisted correduction of Ru–Pt clusters as observed previously (4, 5). In the case of impregnated catalyst, exothermic maxima were observed at 430 and 460 K, representing the reduction of Ru–Pt clusters and Pt and/or Ru supported precursors, respectively.

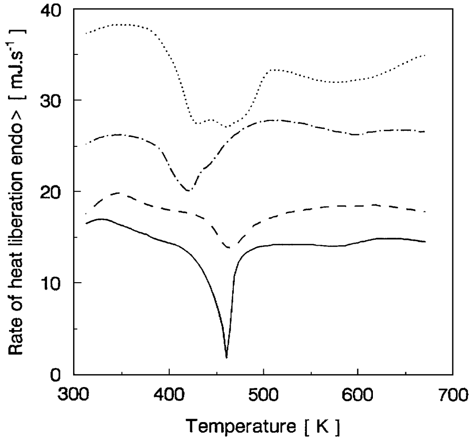

FIG. 4. DSC measurement of zirconia supported catalysts: 1 (solid line), 3 (dashed line), 5 (dotted-dashed line), and 7 (dotted line).

TABLE 5

Influence of Calcination Temperature and Atmosphere on Active Metal Dispersion of Catalyst Prepared by Coadsorption

Temperature (K)	Atmosphere	H/metal	Observation
573	He	0.74	—
423	N_2	0.71	—
423	Air	0.63	RuO_4
573	Air	0.04	RuO_4

Stabilization of ruthenium by platinum via Ru–Pt cluster formation was confirmed by pulse chemisorption experiments. By elevating the calcination temperature from 423 to 723 K, the H/metal ratio of the impregnated Ru/ZrO_2 catalyst decreases sharply due to active metal sinterization and formation of RuO_4. On the other hand, coimpregnated catalyst submitted to the same treatment preserves its dispersion and the presence of volatile ruthenium tetraoxide in the sample was not observed. It should be mentioned that these results were obtained in helium. In an oxidizing atmosphere, phase separation occurred and Ru was reoxidized as shown qualitatively in Table 5.

CONCLUSIONS

Taking into account the results of characterization methods, the possible mechanism of Ru precursor adsorption onto the zirconia surface and its decomposition path has been proposed.

NO_3 ligands were found to form bridges between Ru and surface Zr atoms. The decomposition of ruthenium precursor by temperature begins with the liberation of NO. Later on, the Ru–NO_3 bond also was broken, independently of the preparation method used.

Zirconia supported ruthenium catalysts are thermally unstable and, even under nonoxidizing conditions, formation of volatile ruthenium tetraoxide was observed. Supported ruthenium catalysts exhibiting higher thermal stability have been prepared by introducing a second noble metal, namely platinum. Ru–Pt clusters, easily formed during adsorption of active metal precursors, were responsible for stabilization of ruthenium. However, improvement in stability of metal dispersion was observed only in the case of calcination in a nonoxidizing atmosphere. During calcination in air, phase separation occurs and RuO_4 is formed.

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REFERENCES

1. Miura, H., and González, R. D., *J. Catal.* **74**, 216 (1982).
2. Miura, H., and González, R. D., *J. Phys. Chem.* **86**, 1577 (1982).
3. Ramamoorthy, P., and González, R. D., *J. Catal.* **58**, 188 (1979).
4. Rejai, B., and González, R. D., *J. Catal.* **123**, 98 (1990).
5. Rejai, B., and González, R. D., *J. Catal.* **123**, 113 (1990).
6. Miura, H., Suzuki, T., Ushikubo, Y., Sugiyama, K., Matsuda, T., and González, R. D., *J. Catal.* **85**, 331 (1984).
7. Alerasool, S., and González, R. D., *J. Catal.* **124**, 204 (1990).
8. Zou, W., and González, R. D., *J. Catal.* **133**, 202 (1992).
9. Del Angel, G., Bertin, V., Bosch, P., Gomez, R., and González, R. D., *New. J. Chem.* **15**, 643 (1991).
10. Chakrabarty, D. K., Rao, K. M., Sundararaman, N., and Chandavar, K., *Appl. Catal.* **28**, 69 (1986).
11. Mahmood, T., Williams, J. O., Miles, R., and McNicol, B. D., *J. Catal.* **72**, 218 (1981).
12. Ramamoorthy, P., and González, R. D., *J. Catal.* **59**, 130 (1979).
13. Miura, H., Taguchi, H., Sugiyama, K., Matsuda, T., and González, R. D., *J. Catal.* **124**, 194 (1990).
14. Maya, L., *J. Inorg. Nucl. Chem.* **41**, 67 (1979).
15. Van Den Berg, G. H., and Rijnten, H. Th., *in* “Preparation of Catalysts II” (B. Delmon, P. Grange, P. Jacobs, and G. Poncelet, Eds.), p. 265. Elsevier, Amsterdam, 1979.
16. Lin, Z. Z., Okuhara, T., and Misono, M., *J. Phys. Chem.* **92**, 723 (1988).
17. Pearce, J. R., Gustafson, B. L., and Lunsford, J. H., *Inorg. Chem.* **20**, 2957 (1981).
18. Samsonov, G. V., “The Oxide Handbook,” pp. 26–50. IFI/Plenum, New York, 1982.
19. Kobayashi, M., and Shirasaki, T., *J. Catal.* **28**, 289 (1973).
20. Guerra, C. R., and Schuman, J. A., *Surface Sci.* **7**, 229 (1967).
21. Jirátová, K., *Appl. Catal.* **1**, 165 (1981).
22. Haymore, B. L., and Ibers, J. A., *Inorg. Chem.* **14**, 3060 (1975).
23. Pretch, E., *et al.*, *in*“Tablas para la elucidación estructural de compuestos orgánicos por métodos espectroscópicos,” pp. 218–219. Editorial Alhambra, Madrid 1980.