JOURNAL OF CATALYSIS 51, 64–71 (1978)

Physicochemical Studies on Silica-Supported Multicomponent Molybdate Catalyst before and after Use in Ammoxidation of Propylene

T. S. R. PRASADA RAO AND P. G. MENON[1]

Research & Development Centre, Indian Petrochemicals Corporation, Ltd.,
Baroda 391346, India

Received September 17, 1976; revised July 25, 1977

A multicomponent molybdate catalyst of the composition 50% $Ni_3Co_5Fe_3BiPK_{0.1}Mo_{12}O_{52.5}$–50% SiO_2 was examined for structural and surface changes before and after its use in ammoxidation of propylene at 480°C for 10 hr. The techniques employed were TG, DTA, X-ray diffraction, ir spectra, ESR, Mössbauer spectra, and ESCA. TG and DTA show that the catalyst is thermally stable up to 1000°C and it does not contain free metal oxides. X-Ray data and ir spectra indicate that Fe, Co, and Ni are present as $Fe_2(MoO_4)_3$, β-$CoMoO_4$, $NiMoO_4$, and Bi, as $Bi_2O_3 \cdot MoO_3$ and $Bi_2O_3 \cdot 3MoO_3$, respectively, in the fresh catalyst (I), while $Fe_2(MoO_4)_3$ is reduced to $FeMoO_4$ in the used catalyst (II). Mössbauer and ESR spectra show that Fe exists in the Fe^{3+} state in I and in the Fe^{2+} state in II, the latter also being in two different chemical environments. ESCA reveals the existence of Co, Mo, Ni, Fe, Bi, Si, O_I, and O_{II} in the surface layer of I; the surface concentrations in II differ markedly: Mo, Bi, Fe, and O_{II} increase and Co, Ni, Si, and O_I decrease upon exposure of the catalyst to ammoxidation conditions.

INTRODUCTION

The industrial catalysts for ammoxidation of propylene are generally based on bismuth phosphomolybdate (*1*, *2*), uranium–antimony oxide (*3*, *4*) and bismuth–iron–molybdate (*5*). In recent years, however, more active and selective multicomponent catalysts containing Ni, Co, Fe, Bi, P, K, and Mo on silica support were described in patents (*6*, *7*) for oxidation and ammoxidation of propylene. In view of the commercial significance of the above catalysts, their physicochemical and structural properties were studied extensively. Batist *et al.* reported such studies on supported and unsupported bismuth molybdate and bismuth phosphomolybdate catalysts (*8*, *9*). Structural aspects of the U–Sb-oxide system were studied by Grasselli and Suresh (*10*). Batist *et al.* (*11*), Daniel and Keulks (*12*), and Noterman *et al.* (*13*) carried out detailed studies on the Bi–Fe–Mo system. Recently Wolfs and others from Eindhoven (*14*–*17*) published the structural properties of various multicomponent molybdate catalysts with the general formula $Me_a^{II}Me_b^{III}Bi_cMo_dO_e$, in which Me^{II} was Ni, Co, Mg, or Mn, and Me^{III} was Fe, Cr, Al, or Ce, and the influence of the various cations on the activity and selectivity for oxidation of butene. Their studies were all on unsupported catalysts. Industrially used catalysts are usually supported on silica (about 50% by weight in the catalyst). Therefore

---

[1] To whom correspondence should be sent at the present address: Laboratorium voor Petrochemische Techniek, University of Gent, Krijgslaan 271, 9000 Gent, Belgium.

0021-9517/78/0511-0064$02.00/0

we undertook the physicochemical characterization of a multicomponent catalyst containing Ni, Co, Fe, Bi, K, P, and Mo on silica support. We aimed our studies primarily at investigating (a) whether these elements in this catalyst are present as their respective oxides or molybdates, (b) the structural properties of the compounds existing in the system, (c) the valency state and coordination of the cations, and (d) the physicochemical and surface changes which take place after exposing the catalyst to the ammoxidation reaction. The physicochemical techniques employed in the present studies were X-ray diffraction, TG, DTA, ir spectroscopy, ESR, Mössbauer spectroscopy and electron spectroscopy for chemical analysis (ESCA).

EXPERIMENTAL METHODS

(a) *Fresh catalyst.* The method of preparation of the catalyst was similar to that reported by Wolfs (*14*) with some alterations to incorporate silica, potassium, and phosphorus.

Initially silica gel was precipitated from sodium silicate solution (25.39 g of Na_2SiO_3 in 250 ml of distilled water) by the addition of 200 ml of 1 *N* HCl, filtered, and washed thoroughly till it was free of chloride ions. Hot solutions (100°C) of $Ni(NO_3)_2 \cdot 6H_2O$ (3.79 g in 100 ml of water), $Co(NO_3)_2 \cdot 6H_2O$ (6.32 g in 100 ml of water), $Bi(NO_3)_3 \cdot 5H_2O$ (2.11 g in 100 ml of water, containing 5 ml of concentrated HNO_3), and $Fe(NO_3)_3 \cdot 9H_2O$ (5.27 g in 50 ml of water) were added slowly to the silica gel while stirring. Then 0.43 g of H_3PO_4 (85%) and KNO_3 solution (44 mg in 50 ml of water) were also added. After stirring for 60 min, powdered MoO_3 (7.51 g) was added very slowly. Vigorous stirring was continued for another 45 min; then 5 *N* NH_4OH was added until the pH was 5. A brownish precipitate was formed. Further heating (100–110°C) with stirring was continued until the water evaporated and a viscous slurry with a pH of 3–4 was obtained. The slurry was dried at 110°C for 15 hr; then it was powdered and calcined at 320°C for 5 hr and at 520°C for 5 hr. All the reagents used were of analytical reagent grade. The chemical composition of the catalyst thus prepared corresponds to the formula 50% $Ni_3Co_5Fe_3BiPK_{0.1}Mo_{12}O_{52.5}$, and the rest, 50% SiO_2. Surface area of the catalyst (BET-N_2 method) was 194 m^2/g. A sample of this catalyst was also heated at 600°C for 24 hr; this is referred to as the heat-treated sample.

(b) *Used catalyst.* The catalyst prepared as described in section (a) was tested for its activity and selectivity in a continuous-flow reactor made of stainless steel. About 5 g of catalyst was taken. Tests were carried out at atmospheric pressure with a feed ratio of $C_3H_6/NH_3/\text{air} = 1/1.5/11$. The feed rate was 200 ml/min and the reaction temperature was 480°C. The reactants and products were analyzed (*18*) by on-line gas chromatography. After attaining a steady state the test was continued for 10 hr and the average of test results indicated that the catalyst had good activity and selectivity (85% total propylene conversion and 75% selectivity). After this activity test the catalyst was taken out of the reactor and physicochemical studies were carried out on this used catalyst (exposed to air during handling). The surface area of this catalyst was 246 m^2/g.

(c) *Physicochemical measurements.* X-Ray diffraction patterns were recorded using a Philips X-ray diffractometer with a Geiger–Müller counter and Ni-filtered Cu$K\alpha$ radiation. TG and DTA were carried out on a Derivatograph (Paulik–Paulik–Erdey instrument made by MOM, Budapest, Hungary) which gave TG and DTA simultaneously. α-Al_2O_3 heated to 1250°C was used as reference material for DTA. The heating rate was 10°C/min. Infrared spectra were recorded using the KBr disk method on a Perkin–Elmer grating spectrometer. Mössbauer spectra were obtained at 300°K using a ^{57}Co source. The isomer shifts were measured taking Fe as standard. Electron spin resonance spectra of the samples were taken at 77°K on a Varian E400 X-Band unit, using DPPH as the internal calibrant. ESCA measurements were made at 300°K on a DuPont 650B electron spectrometer with a Mg anode operated at 5 mA and 12 kV. Binding energies of the samples were corrected for sample charging using the C_{1s} line as reference and were reproducible to ±0.3 eV. The measured intensity (counts per second, cps) of the peaks of photoelectron spectra of all the elements were normalized using the standard intensities compiled by Swingle and Scofield (*19*).

RESULTS AND DISCUSSION

The physicochemical characteristics of the fresh and heat-treated (600°C) catalysts were practically identical. Hence only the results for the fresh and used catalysts are given here and the discussion is also confined to them.

X-Ray and Infrared Results

The *d* values of the lines in the X-ray pattern of the fresh catalyst and the relative intensity values, I_{rel} (in brackets), of these lines are as follows: 2.01 (6), 2.24 (8), 2.30 (6), 2.44 (5), 2.65 (20), 2.79 (22), 2.88 (12), 2.95 (8), 3.13 (22), 3.26 (26), 3.33 (100), 3.48 (14), and 3.86 (24). Comparison of these lines with the patterns for different molybdates published by Erman *et al.* (*20*), Batist *et al.* (*8*), Fagherazzi and Pernicone (21), and Wolfs (*14*) indicates that Fe, Co, and Bi are present in the catalyst as $Fe_2(MoO_4)_3$ (*d* = 2.65, 2.88, 2.95, 3.48, and 3.86); β-$CoMoO_4$ (*d* = 2.24, 2.30, 2.44, 2.79, and 3.33); $Bi_2O_3 \cdot 3MoO_3$ (*d* = 2.01, 2.79, and 3.26); and $Bi_2O_3 \cdot MoO_3$ (*d* = 3.13), respectively. Wolfs (*14*) and Wolfs and Batist (*15*) reported the presence of these molybdates in an unsupported multicomponent molybdate catalyst also.

X-Ray patterns of fresh and used catalysts are almost similar except for the following changes: the intensity of the lines at (a) *d* = 2.30, 2.44 (β-$CoMoO_4$), and 3.13 ($Bi_2O_3 \cdot MoO_3$) increased; the lines at (b) *d* = 3.48, and 3.86 decreased; and the lines at *d* = 2.88 and 2.95 [$Fe_2(MoO_4)_3$] disappeared. Earlier, Batist *et al.* (*9*) found that in silica-supported $Bi_9PMo_{12}O_{52}$ catalyst the Erman phase ($Bi_2O_3 \cdot 2MoO_3$) decomposed to $Bi_2O_3MoO_3$ (2/1) and $Bi_2O_3 \cdot 3MoO_3$ (2/3) on carrying out olefin oxidation on the catalyst for 26 and 50 hr and ammoxidation for 1 year. In the multicomponent molybdate catalyst investigated by us, the 2/1 and 2/3 phases of bismuth molybdate are present in the initial catalyst itself and do not undergo any structural transformation during ammoxidation.

Infrared spectra of fresh and used catalysts show the following bands (b = broad, s = strong, and m = medium):

Fresh (cm^{-1})	Used (cm^{-1})
1100 (b)	1100 (b)
945 (s)	945 (s)
830 (m)	—
—	790 (m)
710 (m)	710 (m)

The band at 1100 cm^{-1} is due to Si–O, while that at 945 cm^{-1} can either be due to a metal–terminal oxygen bond (*22*) or be specific for $CoMoO_4$ (*23*). The band at 830 cm^{-1} is reported (*11*) to be characteristic for $Fe_2(MoO_4)_3$. The bands at 945 and 830 cm^{-1} have also been assigned to $Bi_2O_3 \cdot 3MoO_3$ and $Bi_2O_3 \cdot MoO_3$ by Trifirò *et al.* (*24*). Hence it is difficult to make exact assignments based only on the infrared bands to identify individual molybdates. The band at 790 cm^{-1} has been assigned (*25*) to β-$FeMoO_4$. The disappearance of the 830 cm^{-1} band and the emergence of a new band at 790 cm^{-1} in the spectrum of the used catalyst may thus be taken only as an indication of the reduction of Fe^{3+} to Fe^{2+} during the ammoxidation reaction, which is, however, further confirmed by the X-ray, Mössbauer, and ESR results. The bands characteristic of free MoO_3 and

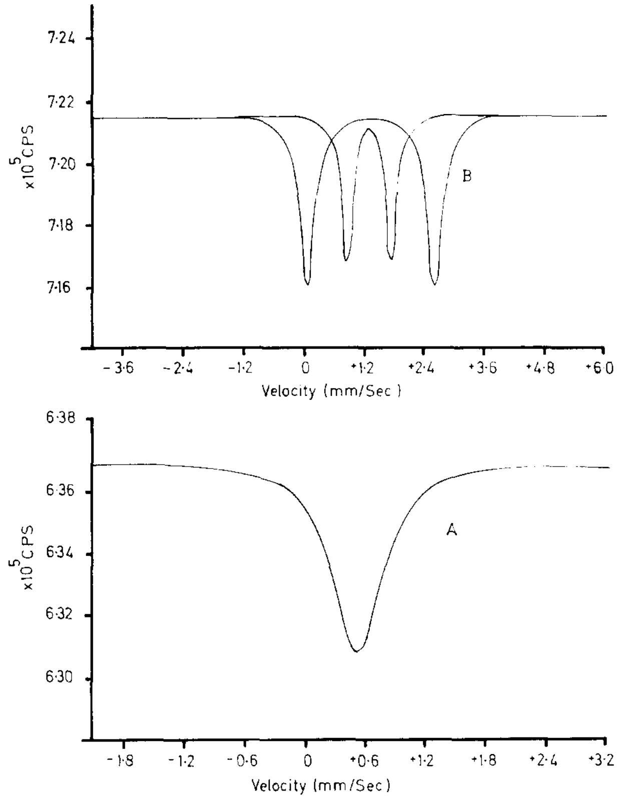

FIG. 1. Mössbauer spectra of fresh (A) and used (B) catalysts.

other metal oxides (*26*) are absent in our catalyst samples.

Thermal Analysis

TG and DTA data did not show any significant thermal changes. The TG curve recorded about 0.8% weight loss in the temperature range of 50–200°C due to loss of residual moisture. Between 200 and 1000°C the TG curve indicated no weight loss and the DTA did not show any exothermic or endothermic effect. This shows that the catalyst is thermally quite stable and no free MoO_3 or other metal oxides are present in it. The thermal behavior of the used catalyst is very similar to that of the fresh one.

Mössbauer and ESR Studies

Mössbauer spectroscopic and ESR studies were carried out to find out the valency state and chemical environment around the iron cations in fresh and used catalysts. Mössbauer spectra are presented in Fig. 1. The spectrum of the fresh catalyst gives a single line with an isomer shift value of 0.43 ± 0.01 mm/sec. No quadrupole splitting is observed. The used catalyst, on the other hand, gives a four-line spectrum with two doublets. Each doublet is attributed to quadrupole splitting. Isomer shift values for the outer and inner doublets are 1.23 ± 0.12 and 1.19 ± 0.12 mm/sec, respectively. A low isomer shift value of 0.43 mm/sec for the fresh catalyst indicates the presence of iron as Fe^{3+}. This is consistent with our findings from X-ray and infrared data that iron is present as $Fe_2(MoO_4)_3$.

The four-line spectrum of the used catalyst with two quadrupole splittings shows that the iron in it is situated at two different chemical sites with different chemical environments. The exact nature of these iron sites is yet to be understood. The larger isomer shift values indicate the presence of iron in the Fe^{2+} state, showing that iron is reduced from Fe^{3+} to Fe^{2+} in the used catalyst. Similar reduction of iron in other iron-containing catalysts has been reported during oxidation of propylene by Wolfs (*14*), of methanol by Pernicone (*27*), and of butene by Pasquon *et al.* (*28*), and during ammoxidation of propylene by Kriegsmann *et al.* (*29*). Hence this seems to be a general phenomenon occurring in iron-containing catalysts during both oxidation and ammoxidation reactions.

The ESR spectrum of the fresh catalyst showed only a moderately broad signal with a g value of 2.016 and a natural line width of 720 G. The g value for $Fe_2(MoO_4)_3$ and $Mg_{9.5}Fe_{1.5}BiMo_{12}O_n$ has been reported to be 2.104 by Wolfs (*14*). The signal with $g = 2.016$ disappeared in the spectrum of the used catalyst indicating that iron was reduced from Fe^{3+} to Fe^{2+}. The used catalyst also gave a weak signal with a g value of 1.926, indicating the presence of Mo^{5+} species (*30*). Divalent ions like Fe^{2+}, Co^{2+}, and Ni^{2+} could not be detected since they give ESR signals only at very low temperatures (4°K). The ESR studies thus corroborate the results obtained from Mössbauer spectra regarding the oxidation state of iron in the fresh and used catalysts.

ESCA Studies

The X-ray photoelectron spectra of the elements detected on the surface of the fresh and used catalysts are shown in Fig. 2. The elements Fe, Co, Ni, Bi, Mo, Si, and O are present on the catalyst surface, but K and P are not detected probably due to their very small concentrations. Comparison with the published binding energy values (*31*) for these elements indicates that Mo is present as Mo^{6+}, Bi as Bi^{3+}, Si as Si^{4+}, Fe as Fe^{3+} or Fe^{2+}, Co as Co^{3+} or Co^{2+}, and Ni as Ni^{2+}. In the case of Fe and Co, whether it is the 2+ or 3+ oxidation state could not be determined since their chemical shift ranges overlap. Two distinct types of oxygen are detected: the higher binding energy (532.6 eV) oxygen, O_I, is associated with the silica support, and the

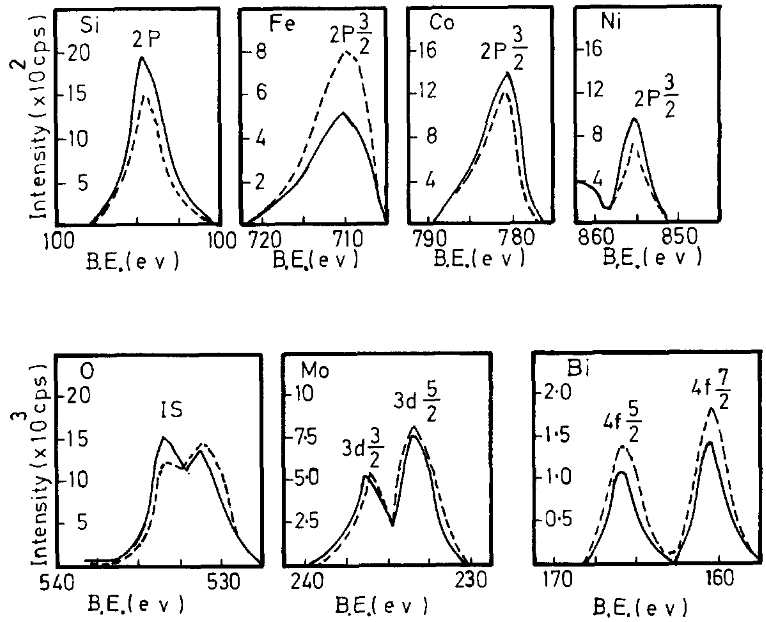

FIG. 2. X-Ray photoelectron spectra of the elements present on the surface of fresh (——) and used (- - - -) catalysts.

lower one, O_{II} (530.4 eV), with metal oxide species.

The ESCA results of Wolfs and coworkers (*14*, *16*, *17*) on unsupported multicomponent catalysts of compositions $Co_8Fe_3BiMo_{12}O_x$, $Mn_8Fe_3BiMo_{12}O_x$, and $Mg_8Fe_{2.5}BiMo_{12}O_x$ are worth discussing here in the context of our results. They found that only Bi, Mo, and O were present on the surface of the above catalysts. After a single sputtering of the surface with Ar^+ ions, they observed that the concentration of Bi and Mo decreased and Fe appeared on the surface. After a second sputtering, Bi disappeared completely from the surface while the concentration of Mo further decreased and those of Fe increased to a significant extent. Based on these ESCA results and on surface area and X-ray studies, Wolfs *et al.* (*14–17*) suggested a shell and core model for the multicomponent molybdate catalysts. In this model, Bi is present as a thin shell of bismuth molybdate on the surface of the catalyst particle while the core of it contains a mixture of $Fe_2(MoO_4)_3$ and $Me^{II}MoO_4$ where Me^{II} = Co, Mg, or Mn. Our ESCA results, however, show that all the elements present in the catalyst (Fe, Co, Ni, Bi, Mo, Si, and O) except K and P are present on the surface of the catalyst. Hence the above shell model proposed by Wolfs *et al.* is not valid in the case of our supported catalyst. Wolfs *et al.* also attributed the high activity and selectivity of the multicomponent molybdate catalysts to their surface structure in which the whole surface of the catalyst particles was covered with so-called active bismuth molybdates. But our studies indicate that such catalysts are still active and selective even when elements like Fe, Co, Ni, and Si are also present on the surface along with Bi and Mo.

The ESCA studies on the used catalyst show that the surface of the catalyst contains all the elements that are present on the surface of the fresh catalyst (Fig. 2), but the surface compositions of the elements change very radically. The surface compositions were assumed to be proportional to the normalized intensities of the peaks. The relative changes in the surface composition are shown in Fig. 3. The surface of the used catalyst is enriched with Mo, Bi, Fe, and O_{II} and is depleted of Co, Ni, Si, and O_I. The depletion may probably result when these elements are relatively "buried" as the enriching ones migrate from the interior to the surface of the catalyst particles. The increase in concentration of Fe on the surface is much more than that of Bi and Mo. The significance of this migration of the cations from the bulk to the surface during the ammoxidation reaction must be studied in greater detail. For the present we are only able to report that the surface composition of the catalyst changes radically during the ammoxidation reaction, and hence studies on the catalyst surface in its virgin state do not seem to have much relevance to the realities of the surface under actual reaction conditions. Investigations to understand the implications of these surface changes are in progress in our laboratory.

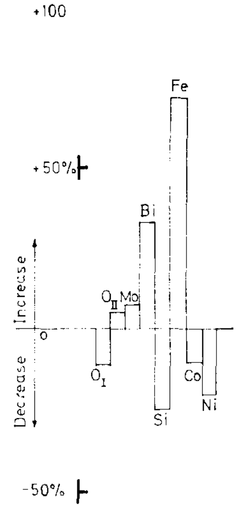

FIG. 3. Percentage change in surface composition of the used catalyst relative to the fresh one, calculated from ESCA results.

TABLE 1

Summary of the Results for the Fresh and Used Catalysts

Technique used	Conclusion	
	Fresh catalyst	Used catalyst
TG and DTA	Free metal oxides absent; thermally stable up to 1000°C	Thermal behavior similar to that of fresh catalyst
X-Ray and ir	Fe, Co, and Ni present as $Fe_2(MoO_4)_3$, β-$CoMoO_4$, and $NiMoO_4$; Bi present as $Bi_2O_3 \cdot MoO_3$ and $Bi_2O_3 \cdot 3MoO_3$	Same as for fresh catalyst except that $Fe_2(MoO_4)_3$ is reduced to $FeMoO_4$
Mössbauer and ESR	Fe present as Fe^{3+}	Fe present as Fe^{2+} in two different chemical environments
ESCA	Co, Mo, Ni, Fe, Bi, Si, O_I, and O_{II} present on the surface	Surface concentrations of Mo, Bi, Fe, and O_{II} increase and those of Co, Ni, Si, and O_I decrease

The conclusions drawn from our studies using the various techniques are summarized in Table 1.

ACKNOWLEDGMENT

We gratefully acknowledge the experimental facilities extended to us by the Regional Research Laboratory, Hyderabad, India, for X-ray diffraction, the National Chemical Laboratory, Poona, India, for infrared spectra, the Indian Institute of Technology, Madras, India, for Mössbauer and ESR spectra, and the DuPont Application Laboratory, Wilmington, Delaware, for ESCA. We thank Dr. J. Prasad for many helpful discussions and Miss Meera Joshipura for her skilled assistance in experiments. The financial support by the Oil Industry Development Board, India, is also acknowledged.

REFERENCES

1. Idol, J. D., Jr., Standard Oil Co. U. S. Patent 2,904,580. September 15, 1959.

2. Callahan, J. L., Foreman, R. W., and Veatch, F., Standard Oil Co. U. S. Patent 3,044,966. July 17, 1962.

3. Callahan, J. L., and Gertisser, B., Standard Oil Co. U. S. Patent 3,198,750. August 3, 1965.

4. Callahan, J. L., and Gertisser, B., Standard Oil Co. U. S. Patent 3,308,151. March 7, 1967.

5. Dominik, J. G., Presson, R. D., and Wysocki, C. G., U. S. Patent 3,629,148. December 21, 1971.

6. Nippon Kayaku Kabushiki, Kaisha, Tokyo, Japan. Netherlands Patent Application No. 7006454 (1974).

7. (a) The Standard Oil Co., Cleveland, Ohio, German Patent Application No. 2203710 (1972). (b) Sumitomo Chemical Co., Ltd., Osaka, Japan. German Patent Application No. 2133110 (1972).

8. Batist, Ph. A., Bouwens, J. F. H., and Schuit, G. C. A., *J. Catal.* **25**, 1 (1972).

9. Batist, Ph. A., Bouwens, J. F. H., and Matsuura, I., *J. Catal.* **32**, 362 (1974).

10. Grasselli, R. K., and Suresh, D. D., *J. Catal.* **25**, 273 (1972).

11. Batist, Ph. A., van de Moesdijk, C. G. M., Matsuura, I., and Schuit, G. C. A., *J. Catal.* **20**, 40 (1971).

12. Daniel, C., and Keulks, G. W., *J. Catal.* **29**, 475 (1973).

13. Notermann, T., Keulks, G. W., Skliarov, A., Maximov, Y., Margolis, L. Y., and Krylov, O. V., *J. Catal.* **39**, 286 (1975).

14. Wolfs, M. W. J., Doctorate Thesis, Technological University, Eindhoven, The Netherlands, 1974.

15. Wolfs, M. W. J., and Batist, Ph. A., *J. Catal.* **32**, 25 (1974).

16. Wolfs, M. W. J., and Matsuura, I., *J. Catal.* **37**, 174 (1975).

17. Wolfs, M. W. J., and van Hooff, J. H. C., "Scientific Bases for the Preparation of Heterogeneous Catalysts." International Symposium, Brussels, Belgium, Paper No. B3, 1975.

18. Onsan, I. Z., and Trimm, D. L., *J. Catal.* **38**, 257 (1975).

19. cf. Czanderna, A. W., "Methods of Surface Analysis," Vol. 1. Elsevier, New York, 1975.

20. Erman, L. Y., Galperin, E. L., Kolchin, I. K., Dobrazhanskii, G. F., and Chernyshev, K. S., *Zh. Neorg. Khim.* **9**, 1174 (1964).

21. Fagherazzi, G., and Pernicone, N., *J. Catal.* **16**, 321 (1970).

22. Trifirò, F., and Pasquon, I., *J. Catal.* **12**, 412 (1968).

23. Lipsch, J. M. J. G., Doctorate Thesis, Technological University, Eindhoven, The Netherlands, 1968.

24. Trifirò, F., Hoser, H., and Scarle, R. O., *J. Catal.* **25**, 12 (1972).

25. Trifirò, F., Caputo, G., and Villa, P. L., *J. Less Common Metals* **36**, 305 (1974).

26. Nakamato, K., "Infrared Spectra of Inorganic and Coordination Compounds," Wiley, New York, 1964.

27. Pernicone, N., *J. Less Common Metals* **36**, 289 (1974).

28. Pasquon, I., Trifirò, F., and Caputo, G., *Chim. Ind.* **55**, 168 (1973).

29. Kriegsmann, H., Öhlmann, G., Scheve, J., and Ulrich, F. J., "Proceedings, 6th International Congress on Catalysis," London, Paper No. B23, 1976.

30. Peacock, J. M., Sharp, M. J., Parker, A. J., Ashmore, P. G., and Hockey, J. A., *J. Catal.* **15**, 379 (1969).

31. Baker, A. D., and Betteridge, D., "Photoelectron Spectroscopy." Pergamon Press, Elmsford, N. Y., 1972.