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Hydroprocessing Catalysis by Supported Ruthenium Sulphide

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Ruthenium sulphide catalysed hydrodenitrogenation (HDN) of quinoline and hydrodesulphurization (HDS) of benzothiophene were studied using a batch autoclave (cold filled with 3448 kPa of hydrogen), at 350/400°C and 300/350°C, respectively. Ruthenium from various precursors—[Ru Cl_3xH_2O], $[Ru_3(CO)_{12}]$, $[Ru(NH_3)_6]^{3+}$—was supported on Y-zeolite and γ-Al_2O_3, and then sulphided. The catalysts were highly active for HDN but not for HDS by comparison with a conventional Ni–Mo/Al_2O_3 formulation. The results were attained with metal loadings (~5%) much lower than those used in conventional hydroprocessing catalysts. Physical combination of the most active catalyst, ruthenium sulphide supported on Y-zeolite, with sulphided nickel molybdate on alumina resulted in a catalyst system with greatly enhanced activity for HDN. © 1986 Academic Press, Inc.

INTRODUCTION

Sulphide catalysts were first employed more than 50 years ago in German coal-liquefaction processes. Since then, catalysts based on transition metal sulphides have been developed into relatively sophisticated systems for the hydroprocessing of petroleum fractions. The catalysts usually employed are Co- and Ni-promoted Mo or W supported on alumina or silica-alumina and are used to remove sulphur and nitrogen and to hydrocrack petroleum feedstock (*1*); these are not, however, particularly effective at high nitrogen levels (*1*, *2*). The anticipated run-down of petroleum feedstocks will require the hydroprocessing of heavier fractions of crude oil as well as an increase in the use of alternative fuel sources such as coal-derived liquids and shale-oil. These feedstocks contain larger amounts of sulphur, oxygen, nitrogen, and metals, so there will be a need for new catalysts with higher activity, selectivity, and resistance to deactivation than the currently used systems.

Traditionally, the support used for hydroprocessing catalysts is an amorphous metal oxide such as alumina or silica–alumina on which the catalytically active metals are placed by impregnation with a solution of a metal salt or, more recently, via low-valent organometallic precursors, to afford highly dispersed metal particles (*3–5*). Despite the extensive use of zeolites in catalysis, there has been little work carried out on their application to hydrotreating processes. The sparse patent literature (*6*) and reports (*7*, *8*) on the subject are concerned mainly with HDS. Zeolites have many desirable features, which include high surface area, shape selective capability, and the ability to produce high dispersion of metals; these should be as applicable to hydrodenitrogenation as they are to other areas of catalysis (*9*).

Ruthenium and its compounds have wide ranging application in both heterogeneous and homogeneous catalysis (*10*). Longstanding catalytic uses of ruthenium metal on refractory oxide supports include methanation (*11*, *12*), Fischer–Tropsch synthesis of hydrocarbons (*5*, *13*, *14*), and steam reformation of methane (*15*). Ruthenium dispersed in the cages of zeolites has also been applied to these processes (*16-19*) as

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well as to hydrogenation (*20*), the water gas shift reaction (*21, 22*) and hydroformylation of ethylene (*23*). Surprisingly, the potential of supported ruthenium as a hydroprocessing catalyst has attracted little attention. A recent study (*24*) of the HDS activity of unsupported transition metal sulphides yielded periodic maxima (or volcano plots), with ruthenium displaying greater activity than the sulphides of either of the classical hydroprocessing metals, molybdenum and tungsten, and carbon-supported ruthenium has also been investigated (*24a*).

In this paper we present the results of a study of the hydrodenitrogenation (HDN) activity (for quinoline) and the hydrodesulphurization (HDS) activity (for benzothiophene) of a number of ruthenium-based catalysts. Quinoline and benzothiophene are models for the organic sulphur and nitrogen material present in raw oils (*25*). Two supports, amorphous γ-Al_2O_3 and crystalline Y-zeolite, were impregnated with various precursor materials—$[RuCl_3xH_2O]$, $[Ru_3(CO)_{12}]$, and $[Ru(NH_3)_6]^{3+}$—and the resulting catalysts were sulphided (H_2/H_2S or H_2/CS_2) for the HDN/HDS investigation. The activities of the prepared catalysts were compared with that of a commercial Mo/Ni-based catalyst under the same experimental conditions. A preliminary account of some of this work has been published (*26*).

EXPERIMENTAL

Materials. Synthetic Na–Y-zeolite (SK–40) was from Union Carbide, Linde Division. γ-Al_2O_3 purchased from Merck, had a surface area (BET method) of 124 m^2 g^{-1}. $[RuCl_3 \cdot xH_2O]$ was purchased from Johnson Matthey Ltd. and $[Ru_3(CO)_{12}]$ and $[Ru(NH_3)_6]^{3+}$ were prepared by literature methods (*27, 28*). The commercial catalyst, BASF M8-21 (MoO_3 ~ 15 wt%, NiO ~ 3 wt% on Al_2O_3), was donated by BASF (Australia). The quinoline and benzothiophene were purchased from Aldrich and used as received.

Catalyst preparation. Na–Y was stirred overnight twice with 1 *M* NH_4Cl, washed chloride free, then oven dried at 80–100°C to give NH_4–Y.

The NH_4–Y and γ-Al_2O_3-supported catalysts were prepared by stirring aqueous solutions (0.5 litre of 0.002 *M*) of $[Ru(NH_3)_6]^{3+}$ and $[RuCl_3 \cdot xH_2O]$ with the support (2 g) overnight. The resulting solids were then air-dried (80°C). The $[Ru_3(CO)_{12}]$-based catalysts were prepared by impregnating the support (2 g) with a solution of the carbonyl (0.211 g) in benzene, then stirring overnight under an atmosphere of nitrogen. The solvent was evaporated in a stream of nitrogen. Catalyst samples were sulphided before use by heating a heptane slurry at 350°C for 3 h in the presence of sulphur (introduced as a H_2/H_2S mixture, or H_2/CS_2). The ternary metal catalyst system was prepared by physically mixing equal weights of sulphided nickel molybdate with RuNY prepared as above.

HF digested samples of the catalysts were analysed for ruthenium by atomic absorption spectroscopy (Table 1), using a GBC-901 instrument.

X-ray diffraction (XRD) patterns of the sulphided samples were obtained using a Siemens D500 diffractometer with nickel-filtered Cu*Kα* radiation.

Transmission electron microscopy (TEM) was carried out with a JEOL 100 CX instrument.

TABLE 1

Composition of Catalysts

Catalyst precursor	Support	Designation	Metal (wt%)
$[Ru(NH_3)_6]^{3+}$	Y-zeolite	RuNY	3.33
$[Ru_3(CO)_{12}]$	Y-zeolite	Ru(CO)Y	2.30
$[RuCl_3 \cdot xH_2O]$	Y-zeolite	RuClY	5.17
$[Ru(NH_3)_6]^{3+}$	γ-Al_2O_3	RuNγ	3.99
$[Ru_3(CO)_{12}]$	γ-Al_2O_3	Ru(CO)γ	4.86
$[RuCl_3 \cdot xH_2O]$	γ-Al_2O_3	RuClγ	4.29
MoO_3, NiO	Al_2O_3	BASF M8-21	~10; ~3

The X-ray photoelectron spectra for the sulphided catalysts were measured with a V.G. ESCALAB-5 spectrometer using Al$K\alpha$ X rays (1486.6 eV) and an anode run at 150 W. The binding energies were referenced to the Al $2p$ line of the zeolite at 74.3 eV.

Gas chromatographic analyses were carried out on a Varian Model 3700 gas chromatograph (flame ionization detector) equipped with a 25 m × 0.2 mm i.d. vitreous silica capillary column wall-coated with SE-54, programmed from 40°C (1 min) to 280°C (hold) at 10° min^{-1}. Detector response factors were determined by injecting known quantities of compounds of interest. Compound identities were confirmed by gas chromatography/mass spectroscopy analyses carried out on a Hewlett–Packard Model 5995A machine equipped with a 50 m × 0.2 mm i.d. vitreous silica WCOT SE-30 column.

Catalyst testing. Quinoline HDN experiments were carried out in a 70-cm^3 autoclave (Parr Model 4742), operated in the batch mode. The autoclave was loaded with the reactants in a glass liner (quinoline (1 g); catalyst (0.100 g); CS_2 (0.030 g)) in a slurry with *n*-heptane (15 ml) as carrier. Carbon disulphide was added to maintain the catalyst in the sulphided state. The autoclave was flushed with nitrogen, cold-filled to 3448 kPa hydrogen pressure, then heated, with stirring, to the required temperature (350 or 400°C). At these temperatures the pressures were approximately 6600 and 10,300 kPa, respectively. After reaction the autoclave was cooled and flushed with nitrogen, and the contents were analysed. Total time from switch-on to switch-off was 5 h. Under these conditions only moderate nitrogen removal occurred so changes in product distribution could be monitored readily. A similar procedure was followed for the benzothiophene HDS experiments, although lower temperatures (300 and 350°C) were used and different operating pressures (8300 and 9600 kPa) were reached.

RESULTS AND DISCUSSION

Catalyst Characterization

The ruthenium loadings obtained from the various precursors ranged from 2.30 to 5.17 wt% and are given in Table 1. Color of the sulphided catalysts varied from dark brown to black.

An XRD examination of the catalysts before and after use showed that the crystallinity of the zeolites was maintained under the reaction conditions given above. XRD of the catalysts in the sulphided state revealed crystalline ruthenium sulfide in only one case, RuNγ, which exhibited the RuS_2 (laurite) 111(w), 200(s), and 311(s) diffraction peaks. Examination of the broadening of the 200 and 311 peaks indicated a mean crystallite size of 60 Å (using the simple Scherrer equation with $K = 1$). Although care must be taken when using XRD information to predict crystallite size limits, (*29*), this suggests that the size of any crystallites in the other catalysts must fall well below this value. TEM imaging and selected area diffraction of specimens of RuNγ revealed clusters of crystallites of ruthenium sulphide and confirmed the XRD findings for this catalyst. The ruthenium sulfide was not on the support but formed a separate phase. On none of the other catalysts could distinct particles of ruthenium sulphide be detected in the TEM with either imaging or diffraction. From our experience with metallic clusters examined with this microscope, an upper limit of 10 Å was set for the size of any ruthenium sulphide present.

Thus both XRD and TEM methods indicated that, with the exception of RuNγ, in all catalysts the ruthenium sulphide was dispersed as aggregates composed of only a few molecules at most.

Information on the location of the ruthenium was obtained by X-ray photoelectron spectroscopy of the zeolite-supported catalysts. The technique was used to measure the Ru to Si ratio; a comparison of this with the theoretical value indicates whether the

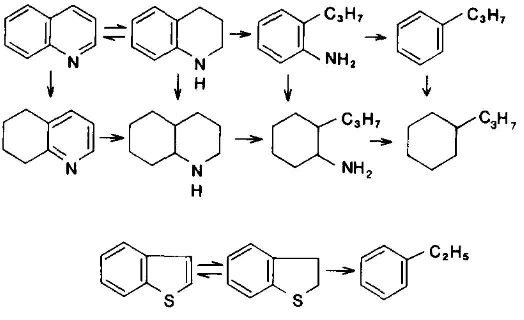


FIG. 1. Reaction networks for HDN of quinoline and HDS of benzothiophene.

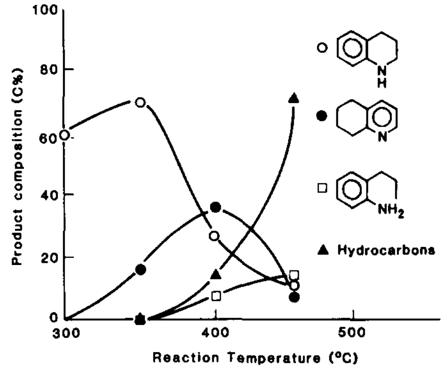


FIG. 2. Change of product composition with reaction temperature for the HDN of quinoline over RuNY.

ruthenium has remained in the zeolite or migrated to the surface (*30*). The measured ratio was considerably larger than the calculated amount, suggesting significant migration to the external surface of the zeolite. However, it follows from the TEM results that this migration is not accompanied by the formation of crystallites of significant size.

Catalyst Activity

The commonly accepted reaction networks for the HDN of quinoline (*31*) and the HDS of benzothiophene (*32*) are shown in Fig. 1. The products observed in the present study were in agreement with these schemes. The reaction products and conversions found for the various catalysts tested in this work are presented in Tables 2 and 3. The variation of product composition with reaction temperature for quinoline HDN over RuNY is shown in Fig. 2. The appearance of small amounts of propane, butane, and pentane in tests carried out at 400°C indicate that some cracking of reaction products occurs at this temperature.

Hydrodenitrogenation Studies

(*a*) *BASF M8-21*. This reference catalyst behaves as expected (*31*). The overall conversion of quinoline was high at both test temperatures. At 350°C the major product was 1,2,3,4-tetrahydroquinoline and little C–N bond scission had occurred. Hydroge-

TABLE 2

Products of HDN of Quinoline over Ruthenium Catalysts

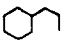
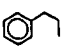
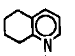
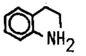
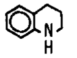
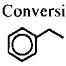
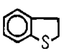
Catalyst	BASF M8-21		RuNY		Ru(CO)Y		RuClY		RuNγ		Ru(CO)γ		RuClγ		RuNY + BASF M8-21
	350°C	400°C	350°C	400°C	350°C	400°C	350°C	400°C	350°C	400°C	350°C	400°C	350°C	400°C	400°C
% Conversion	86	91	88	91	92	88	90	87	95	81	93	77	91	81	96
% 	4	4	—	2	—	3	—	2	—	2	—	2	—	2	6
% 	0.5	1	—	4	—	2	—	1	—	1	—	—	—	1	20
%  N	6.5	25	19	42	2	26	1	27	1	19	5	19	4	19	25
%  NH₂	13	43	—	9	—	19	—	24	—	16	4	5	—	21	22
%  N H	76	19	81	32	98	44	99	36	99	55	90	65	96	52	19
% HCs C_3–C_5	0.5	8	—	11	—	6	—	10	—	7	—	9	—	5	8

TABLE 3

Products of HDS of Benzothiophene over Ruthenium Catalysts

Catalyst	BASF		RuNY		Ru(CO)Y		RuClY		RuNγ		Ru(CO)γ		RuClγ	
	300°C	350°C	300°C	350°C	300°C	350°C	300°C	350°C	300°C	350°C	300°C	350°C	300°C	350°C
% Conversion	57	94	17	83	31	74	36	80	19	75	23	66	21	58
% 	79	96	—	43	7	70	10	57	5	49	17	48	9	59
% 	21	4	100	57	93	30	90	43	95	51	83	52	91	41

nation of the heterocyclic ring is considered to be the first step in most HDN reactions (*2, 31*). At 400°C there was an increase in the amounts of non-nitrogen-containing hydrocarbons while propylaniline was also produced in significant quantities (Table 2). The presence of propylaniline reflects the high stability of anilines with respect to nitrogen removal in comparison to saturated amines.

(*b*) *Zeolite-supported catalysts.* Transition metals are generally introduced into zeolites by cation exchange or by adsorption of low-valent organometallic complexes. The readily available ruthenium sources are [$RuCl_3 \cdot xH_2O$], [$Ru(NH_3)_6]^{3+}$, and [$Ru_3(CO)_{12}$]. Ruthenium ion exchange into zeolites is considered to be more suitably carried out using [$Ru(NH_3)_6]^{3+}$ than [$RuCl_3 \cdot xH_2O$] and there have been extensive studies of this system (*33*). In the present work all the ruthenium compounds have been introduced into the NH_4^+ form of Y-zeolite. Under test conditions the residual NH_4^+ ions decompose to give the proton form of Y-zeolite. Table 2 shows that at 350°C the zeolite-based catalysts are more active than the commercial catalyst for hydrogenation but not for HDN. Quinoline conversions are high but the products are mainly hydrogenated quinolines; no C–N bond scission has occurred. At 400°C there are increased amounts of the product of hydrogenation of the nonheterocyclic ring of quinoline, and products of C–N bond breaking, i.e., propylaniline and non-nitrogen-containing compounds, are produced in quantities similar to those obtained with the commercial catalyst. RuNY , in particular, compared very favourably with the commercial catalyst in its conversion of quinoline and its C–N bond-breaking ability (Fig. 2), but the other zeolite catalysts were also highly active. Under more forcing conditions (450°C, 13,800 kPa) the most active catalyst, RuNY, gave non-nitrogen-containing material in excess of 70%, compared with 60% for the commercial catalyst. The product mixture obtained is more complex, with considerable cracking and isomerization taking place at this temperature and pressure.

(*c*) *γ-Alumina-supported catalysts.* The traditional carrier for hydroprocessing catalysts is an amorphous solid such as alumina or silica–alumina. Catalytically active metals are usually placed on these acidic supports by impregnation with a solution of metal salt. Impregnation via low-valent organometallic precursors also provides active catalysts (*3, 4*). In this study we have used both methods to disperse ruthenium on γ-alumina. Of the catalysts, only RuNγ did not show good Ru dispersion. The XRD of RuNγ showed some bulk ruthenium sulphide, and this was confirmed by the observation of crystalline clumps in the transmission electron micrographs. These catalysts gave products similar to those for the zeolite-based catalysts with the superior hydrogenation ability of the ruthenium catalysts again being evident. At 350°C quinoline conversion was high, but the product was almost exclusively 1,2,3,4-tetrahydroquinoline. At 400°C some C–N bond cleavage occurred, but the alumina-based catalysts proved less active than the zeolite catalysts and the commercial catalyst.

(*d*) *Ternary-metal catalyst.* Physical combination of RuNY with sulphided nickel molybdate on alumina gave a catalyst with greatly enhanced activity for HDN (Table 2). The maximum activity was obtained with a 1 : 1 mixture and was greater than that of either of the component catalysts. Overall quinoline conversion was increased and there was a significant increase in the amount of non-nitrogen-containing material produced. The high activity of the catalyst system was also displayed in hydroprocessing tests carried out on shale oil when nitrogen removal and hydrocracking levels were obtained which were superior to those from a range of commercial catalysts (*34*).

Examination by XRD and TEM of the used ternary metal catalyst did not reveal any changes to which the promotion in activity could be attributed. Delmon and coworkers have carried out extensive studies on the preparation of promoted Co–Mo HDS catalysts by mechanical mixing of the two phases (*35*). Their remote control theory attributes the enhanced activity to the close contact of MoS_2 with Co_9S_8, and a similar mechanism may apply in the ruthenium-based catalyst. An alternative model for the promotion of HDS activity of supported and unsupported Co(Ni)–Mo catalysts has been developed by Topsøe *et al.* (*36*). They have identified the presence of the Co(Ni) promoter atoms in a Co(Ni)–Mo–S phase in these catalysts and correlated the catalytic activity with the amount of Co(Ni) present in the phase. The formation under reaction conditions of such an active phase in our catalyst (involving Ru–Mo–Ni–S) cannot be discounted as our characterisation methods would not detect it. A further possibility is that a conventional bifunctional mechanism is operating in our system, with the superior hydrogenating ability of ruthenium (Table 2) increasing the availability of 1,2,3,4-tetrahydroquinoline for HDN. The origin of the promotion effects in the ruthenium-based catalyst is being studied (*37*).

Hydrodesulphurization Studies

(*a*) *BASF M8-21.* With this catalyst nearly 100% conversion of benzothiophene was achieved at 350°C; the major product (96%) was ethylbenzene, so essentially most of the organic sulphur had been extruded. At 300°C HDS activity was not as high and some dihydrobenzothiophene was formed. Although styrene has been observed as a product of the HDS of benzothiophene (*32*) we found no evidence for its presence.

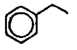
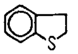
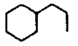
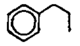
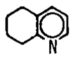
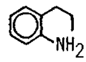
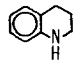
(*b*) *Ruthenium catalysts.* The ruthenium catalysts are much less active for the HDS reaction than for HDN. The catalysts showed far lower HDS conversions than the commercial catalyst at both 300 and 350°C, and the zeolite-supported species were only marginally more active than the alumina-supported (Table 3). Not only were the conversions much lower over the ruthenium catalysts, but a large percentage of the products consisted of dihydrobenzothiophene. Thus the extent of hydrogenolysis was also considerably less than that effected by the commercial catalyst.

Competitive HDS and HDN Reactions

It is generally accepted (*1, 38*) that nitrogen removal is more difficult than sulphur extrusion and any catalyst that is active for nitrogen removal is normally highly active for desulphurization. Therefore the large difference observed in this work in the activity of the ruthenium catalysts for HDN as compared to HDS implies a preference of these catalysts for denitrogenation over desulphurization. To test this hypothesis a one-to-one mixture (0.500 g of each) of the nitrogen and sulphur heterocyclic compounds was subjected to the standard test (at both temperatures) over RuNY. The results are presented in Table 4. At 350°C there is a high conversion of quinoline both in the mixture and in isolation, although the

TABLE 4

Competitive Reaction of Quinoline plus Benzothiophene over RuNY[a]

	350°C	400°C
% Conversion quinoline	99 (88)	94 (91)
% Conversion benzothiophene	39 (83)	77 (100)
% HCs C_3–C_5	— (—)	17 (30)
% 	40 (43)	82 (81)
% 	60 (57)	18 (—)
% 	1 (—)	10 (2)
% 	— (—)	6 (4)
% 	4 (19)	31 (42)
% 	— (—)	13 (9)
% 	95 (81)	30 (32)

[a] Figures in parentheses are results of reaction of individual components over RuNY.

conversion consists mainly of hydrogenation and not hydrogenolysis. There is a marked decrease in the conversion of benzothiophene in the mixture in comparison with the single component result, and this decrease is accompanied by a decrease in the relative amount of sulphur extrusion. At 400°C the percentage conversion of quinoline is again similar in both cases, although C–N bond scission appears to be enhanced in the mixture. There is a large decrease in the benzothiophene conversion in the mixture compared with the 100% sulphur removal observed in the single component test. The decrease in overall conversion is accompanied by a decrease in sulphur removal, as is observed in the 350°C run.

These results appear to confirm the hypothesis that the ruthenium catalysts exhibit a preference for nitrogen removal over sulphur, and so are more selective for nitrogen hydrogenolysis than the classical hydroprocessing catalysts. However, it is well established (*39*, *40*) that there are mutual interactions between the catalytic HDS and HDN (over Mo-based catalysts) of mixtures containing both sulphur and nitrogen. These interactions result in a reduction of HDS activity in the presence of basic nitrogen compounds. The possibility that this inhibition has occurred over the ruthenium catalyst cannot be discounted so the apparent preference for nitrogen removal exhibited in the mixed feedstock tests is not clear-cut.

CONCLUSIONS

Sulphided ruthenium supported on Y-zeolite or γ-alumina is an active catalyst for hydrodenitrogenation of quinoline. This activity is achieved with metal loadings much lower than those used commonly in commercial hydrodenitrogenation catalysts. The most active catalyst was obtained by ion exchange of $[Ru(NH_3)_6]^{3+}$ into NH_4Y zeolite followed by sulphidation; the alumina-supported catalysts were less effective for C–N bond breaking. Alumina support–metal sulphide interaction has been implicated in a decrease in catalytic activity observed when this support is compared to carbon (*24a*) and a strong correlation has been drawn between electronic structure and catalytic activity of metal sulphides (*24*, *41*). In this work the nature of the active ruthenium–sulphur species has not been established but electronic changes may have occurred, as preliminary studies have indicated that polynuclear species may be present in the zeolite (*42*). Unexpectedly, the high activity of these catalysts for HDN was not reflected in a correspondingly high activity for hydrodesulphurisation. In both single- and mixed-feedstock experiments the ruthenium catalysts displayed a preference for HDN over HDS. A 1 : 1 combination of sulphided ruthenium on Y-zeolite with sulphided nickel molybdate on alumina was extremely active for HDN of quinoline—more so than either of the component catalysts. The reasons for this promotion effect have not yet been established. The HDN of quinoline serves as a model for the HDN of high nitrogen refinery feedstock; work on the upgrading of shale oil, which will be reported elsewhere, confirmed the efficacy of the sulphided ternary metal system for catalytic hydroprocessing.

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REFERENCES

1. Weisser, O., and Landa, S., "Sulphide Catalysts—Their Properties and Applications." Pergamon, Oxford, 1973.
2. Katzer, J. R., and Sivasubramanian, R., *Catal. Rev.-Sci. Eng.* **20,** 155 (1979).
3. Anderson, J. R., Elmes, P. S., Howe, R. F., and Mainwaring, D. E., *J. Catal.* **50,** 508 (1977).
4. Whyman, R., *in* "Transition Metal Clusters," (B. F. G. Johnson, Ed.), p. 545. Wiley, New York, 1980.
5. Okuhara, T., Kobayashi, K., Kimura, T., Misono, M., and Yoneda, Y., *J. Chem. Soc. Chem. Commun.*, 1114 (1981).
6. Gladrow, E. M., and Parker, P. T. (Esso), U.S. Patent 2,967,159 (1981); Pollitzer, E. L. (Universal Oil Products); U.S. Patent 3,730,878 (1973); Gardner, L. E. (Phillips Petroleum Company), U.S. Patent 4,324,647 (1982).
7. Sugioka, M., and Aomura, K., *Prepr. Amer. Chem. Soc. Div. Pet. Chem.* **25,** 245 (1980); Vrinat, M. L., Gachet, C. G., and de Mourgues, L., "Catalysis by Zeolites," p. 219. Elsevier, Amsterdam/New York, 1980; Brooks, C. S., *Surf. Technol.* **10,** 379 (1980).
8. Tait, A. M., Newitt, T. D., and Hensley, A. L. (Standard Oil Co.), European Patent Application EP50911 (1982).
9. Imelik, B., Naccache, C., Ben Taarit, Y., Vedrine, J. C., Coudurier, G., and Praliaud, H., "Studies in Surface Science and Catalysis," Vol. 5. Elsevier, Amsterdam, 1980.
10. Bennett, M. A., and Matheson, T. W., *in* "Comprehensive Organometallic Chemistry" (Sir G. Wilkinson, F. G. A. Stone, and E. W. Abel, Eds.), Chap. 32.9. Pergamon, Oxford, 1982.
11. Dalla Betta, R. A., Piken, A. G., and Shelef, M., *J. Catal.* **35,** 54 (1974).
12. Ferkul, H. E., Stanton, D. J., McCowan, J. D., and Baird, M. C., *J. Chem. Soc. Chem. Commun.*, 955 (1982).
13. Vannice, M. A., *Adv. Chem. Ser.* **163,** 15 (1977).
14. Inoue, M., Miyake, T., Inui, T., and Takegami, Y., *J. Chem. Soc. Chem. Commun.*, 70 (1983).
15. Kikuchi, E., Tanaka, S., Yamazaki, Y., and Morita, Y., *Bull. Japan Pet. Inst.* **16,** 95 (1974).
16. Nijs, H. H., Jacobs, P. A., and Uytterhoeven, J. B., *J. Chem. Soc. Chem. Commun.*, 180 (1979).
17. Leith, I. R., *J. Chem. Soc. Chem. Commun.*, 93 (1983).
18. Audier, M., Klinowski, J., and Benfield, R. E., *J. Chem. Soc. Chem. Commun.*, 626 (1984).
19. Elliot, D. J., and Lunsford, J. H., *J. Catal.* **57,** 11 (1979).
20. Coughlan, B., Narayanan, S., McCann, W. A., and Carroll, W. M., *J. Catal.* **49,** 97 (1977).
21. Verdonek, J. J., Jacobs, P. A., and Uytterhoeven, J. B., *J. Chem. Soc. Chem. Commun.*, 181 (1979); Verdonck, J. J., Schoonheydt, R. A., and Jacobs, P. A., *in* "Proceedings, 7th International Congress on Catalysis, Tokyo, 1980," p. 911.
22. Gustafson, B. L., and Lunsford, J. H., *J. Catal.* **74,** 393 (1982).
23. Jackson, P. F., Johnson, B. F. G., Lewis, J., Ganzerla, R., Lenarda, M., and Graziani, M., *J. Organomet. Chem.* **190,** C1 (1980).
24. Pecoraro, T. A., and Chianelli, R. R., *J. Catal.* **67,** 430 (1981).

24a. Vissers, J. P. R., Groot, C. K., van Oers, E. M., de Beer, V. H. J., and Prins, R., *Bull. Soc. Chim. Belg.* **93,** 813 (1984).

25. Rollman, L. D., *J. Catal.* **46,** 243 (1977).
26. Harvey, T. G. and Matheson, T. W., *J. Chem. Soc. Chem. Commun.*, 188 (1985).
27. Fergusson, J. E., and Love, J. L., *Inorg. Synth.* **13,** 208 (1972).
28. Bruce, M. I., *in* "Comprehensive Organometallic Chemistry" (Sir G. Wilkinson, F. G. A. Stone, and E. W. Abel, Eds.), Chap. 32.2. Pergamon, Oxford, 1982.
29. Chianelli, R. R., *Int. Rev. Phys. Chem.* **2,** 127 (1982).
30. Pederson, L. A., and Lunsford, J. H., *J. Catal.* **61,** 39 (1980).
31. Gavin, D. G., *RSC Spec. Period. Rep. Catal.* **5,** 254 (1982).
32. Zdrazil, M., *Appl. Catal.* **4,** 107 (1982).
33. Lunsford, J. H., *Stud. Surf. Sci. Catal.* **12,** 1 (1982).
34. Harvey, T. G., Matheson, T. W., Pratt, K. C., and Stanborough, M. S., in preparation.
35. Pirotte, D., Zabala, J. M., Grange, P., and Delmon, B., *Bull. Soc. Chim. Belg.* **90,** 1239 (1981).
36. Candia, R., Clausen, B. S., Bartholdy, J., Topsøe, N.-Y., Lengeler, B., and Topsøe, H., *in* "Proceedings, 8th International Congress on Catalysis," Vol. II, p. 375. Verlag Chemie, Weinheim, 1984.

37. Harvey, T. G., Matheson, T. W., Pratt, K. C., and Stanborough, M. S., unpublished work.
38. Furimsky, E., Erdöl and Kohle-Erdgas, *Petrochemia* **36,** 518 (1983).
39. Satterfield, C. N., Modell, M., and Wilkens, J. A. *Ind. Eng. Chem. Process Des. Dev.* **19,** 154 (1980).
40. Gutberlet, L. C., and Bertolacini, R. J., *Ind. Eng. Chem. Prod. Res. Dev.* **22,** 246 (1983).
41. Harris, S, and Chianelli, R. R., *J. Catal.* **86,** 400 (1984).
42. Oliver, S. W., Smith, T. D., Pilbrow, J. R., Harvey, T. G., Matheson, T. W., and Pratt, K. C., *Inorg. Chim. Acta,* in press.