JOURNAL OF CATALYSIS **98**, 513–521 (1986)

Metal-Catalyzed Reactions of Methylamine in the Presence of Hydrogen

G. MEITZNER, W. J. MYKYTKA, AND J. H. SINFELT

Corporate Research Science Laboratories, Exxon Research and Engineering Company,
Annandale, New Jersey 08801

Received July 29, 1985; revised November 12, 1985

Rates of formation of various products obtained from methylamine in the presence of hydrogen have been determined over a number of metals supported on silica. The metals included ruthenium, rhodium, palladium, rhenium, osmium, iridium, platinum, and gold. Ammonia and methane were observed as products on all of the metals investigated. Dimethylamine was formed in significant amounts over all the metals except rhodium. Various other products were also observed on certain metals. With regard to the kinds of products formed, the results of the present work are in excellent agreement with previously published results on catalysts in the form of metal films. In addition to extending the earlier work on metal films to supported metals, the present work includes data on several additional metals as well. When the present results are combined with our earlier reported results on ethane hydrogenolysis, we are able, for a common series of metals, to compare patterns of variation of catalytic activity for the hydrogenolysis of carbon–carbon and carbon–nitrogen bonds. Such a comparison is of interest in the general question of the catalytic specificity of metals.

INTRODUCTION

Metal-catalyzed reactions of the carbon–nitrogen bond in aliphatic amines have been studied previously by several groups of workers (*1–7*). When mixtures of methylamine and hydrogen were contacted with various metals, the most common reaction products were ammonia, methane, and dimethylamine (*3*, *6*, *7*). Small amounts of products such as trimethylamine, acetonitrile, ethylenimine, and C_2–C_4 hydrocarbons have also been observed. Data on rates of formation of the most common products have been reported for a number of different metals, including many of the Group VIII metals (*3*, *6*, *7*). The published work includes studies with catalysts in the form of metal films (*3*, *6*), and in some cases metal powders or blacks (*1*, *2*, *7*).

Recently, we have extended this work to supported metal catalysts and have obtained data on several additional metals as well. We have been interested in defining more completely the way in which catalytic activity varies from one metal to another. The approach is very similar to one we took earlier in studies of the hydrogenolysis of ethane to methane (*8–14*). With the results of the present investigation on methylamine and our earlier results on ethane hydrogenolysis, we are able, for a common series of metals, to compare patterns of variation of catalytic activity for the hydrogenolysis of carbon–carbon and carbon–nitrogen bonds. This type of comparison is of interest in the general question of the catalytic specificity of metals.

EXPERIMENTAL

Apparatus and Procedure

Reaction rates were measured in a flow system at atmospheric pressure. The reactor consisted of a vertical stainless-steel tube, approximately 30 cm in length and 1.0 cm in diameter, surrounded by a small furnace. The catalyst was used in the form of 40/60 mesh particles diluted with ground Vycor beads of the same particle size. In a

0021-9517/86 $3.00

typical run, 0.2 g of catalyst was diluted with 0.5 g of the ground Vycor. The diluted catalyst occupied a space approximately 1.3 cm in length and was located halfway between the inlet and outlet of the reactor. It was supported on an 80 mesh stainless-steel screen which was held in place by a 3-mm axial thermowell which extended upward through the screen into the catalyst bed. The tip of the thermowell, which contained an iron–constantan thermocouple, was located at the center of the catalyst bed. Reaction in the presence of the Vycor alone was shown to be negligible throughout the range of temperatures employed in this work. The same was true for the silica carrier used in the catalysts.

The reactant gases, methylamine and hydrogen, were diluted with helium and passed downflow through the catalyst bed. A total gas flow of 1 liter per minute was used throughout. The flow rates of the methylamine, hydrogen, and helium were metered separately prior to mixing of the gases in a section of stainless-steel tubing leading to the reactor. By appropriate control of the flow rates, the partial pressures of the reactants could be maintained at the desired values. In a given run, the mixture of methylamine, hydrogen, and helium was passed over the catalyst for a period of 5 min, at which time the reactor exit gas was sampled for chromatographic analysis. The flow of methylamine was then discontinued, after which a flow of hydrogen and helium was maintained over the catalyst for a period of 15 min prior to another run.

The chromatograph used for the product analysis was a Hewlett–Packard Model 5880 GC with two 3-m glass columns (2 mm i. d.) connected in series. The columns were packed with 60/80 mesh Carbopack B impregnated with 4% Carbowax 20M plus 0.8% KOH. They were obtained from Supelco, Inc., Bellefonte, Pa. The columns were operated at a temperature of 50°C with a flow rate of 33 $\text{cm}^3\ \text{min}^{-1}$ of helium carrier gas. Components of the exit gas which were routinely analyzed with the chromatograph included methylamine, methane, dimethylamine, trimethylamine, ammonia, and ethylenimine. Products were generally identified on the basis of retention time data obtained with pure compounds. The identification of ethylenimine in a chromatogram was made with the aid of a mass spectrometer analysis of the components eluting from the column. The chromatographic analysis for ammonia was less satisfactory than for the other components. Consequently, the exit gas from a run was continuously monitored with an infrared analyzer (Beckmann Instruments Model No. 8650-9900-5000) to obtain more reliable data on the amount of ammonia present.

The apparatus and procedure employed for measurements of hydrogen and/or carbon monoxide chemisorption isotherms on the catalysts have been described elsewhere (*10*). The isotherms were measured at room temperature.

Materials

The metals investigated as catalysts in this work included Ru, Rh, Pd, Re, Os, Ir, Pt, and Au, all dispersed on silica. In all cases the metal content of the catalyst was 1 wt%. The silica employed as the carrier was Cab-O-Sil HS5 (300 m^2/g surface area), obtained from the Cabot Corporation, Boston, Mass. Each catalyst was prepared by a simple impregnation procedure in which the silica was contacted with an aqueous solution of a suitable precursor of the metal. The amount of impregnating solution was approximately 2.2 ml per gram of silica. The metal precursors used in the preparation of the various catalysts were: ruthenium trichloride, rhodium trichloride, palladium nitrate, perrhenic acid, chloroosmic acid, chloroiridic acid, chloroplatinic acid, and chloroauric acid. The concentration of the precursor in solution was chosen to give the desired amount of metal in the final catalyst. After the impregnation step, the material was dried overnight in air at 380 K, and then contacted with flowing hydrogen for 2 h at 725 K to reduce the metal precursors. The resulting metal catalyst was purged with helium and cooled to room temperature. It was then passivated by controlled exposure to air and stored in a closed container until needed. After a sample of catalyst was charged to the reactor or adsorption cell, it was again contacted with hydrogen at 725 K to ensure that the metal was reduced.

The methylamine used in the experiments was obtained from the Matheson Company. It contained 1.5% dimethylamine, along with traces of ammonia and trimethylamine. In a determination of the rate of formation of dimethylamine, a correction was made for the amount introduced with the methylamine. The hydrogen used in the experiments had a nominal purity of 99.999%.

RESULTS

Metal Dispersion Data

Values of metal dispersion, defined as the ratio of surface atoms to total atoms in the metal clusters constituting a catalyst, are commonly determined from chemisorption experiments. For all of the catalysts except the rhenium and gold catalysts, metal dispersions were estimated from data on the chemisorption of hydrogen or carbon monoxide at room temperature. The dispersion of the gold was estimated from a determination of crystallite size by X-ray diffraction line broadening, while that of rhenium was assumed on the basis of the total absence of rhenium lines in a diffraction pattern and on the basis that EXAFS data on other similarly prepared rhenium catalysts indicated coordination numbers as low as three (*15*). Values of metal dispersions for all of the catalysts are summarized in Table 1.

TABLE 1

Metal Dispersion Data on the Catalysts

Catalyst[a]	Metal dispersion
Ru	0.5[b]
Rh	1.0[b]
Pd	0.1[c]
Os	0.6[b]
Ir	1.0[b]
Pt	0.8[b]
Re	1.0[d]
Au	0.02[e]

[a] The catalysts consisted of metal clusters supported on silica. The metal constituted 1.0% of the total catalyst mass.

[b] Estimated from hydrogen chemisorption data.

[c] Estimated from carbon monoxide chemisorption data.

[d] Assumed on the basis of X-ray diffraction data and EXAFS data on similarly prepared rhenium catalysts.

[e] Estimated from a determination of crystallite size by X-ray diffraction line broadening.

In those cases where metal dispersion was estimated from chemisorption data, the measured adsorption isotherm was extrapolated back to zero pressure to obtain the value of the amount adsorbed to be used in the determination of metal dispersion. The isotherms exhibit only a small pressure dependence over the range of pressures used to obtain the data. The small pressure dependence is associated with a weakly bound fraction of the total adsorption. A more strongly bound fraction, which accounts for most of the adsorption measured, is taken up by the metal at equilibrium pressures very much lower than those corresponding to the measured isotherm. A more detailed discussion of the use of chemisorption data for estimating metal dispersions is given elsewhere (*16–18*). The values in Table 1 which were estimated from hydrogen chemisorption data were based on an adsorption stoichiometry of 1 hydrogen atom per surface metal atom (*16*), except for iridium, for which a value of 2 was assumed (*17, 19, 20*). The adsorption stoichiometry for carbon monoxide on palladium was assumed to be one molecule per surface metal atom.

Reaction Rate Data

In general, data on the reactions of

methylamine in the presence of hydrogen over the various metal catalysts were obtained over the approximate range of conversions 0.1 to 10%. For the platinum and gold catalysts, the range was extended to 15 and 25%, respectively. More than 90% of the data used in the determination of reaction rates was obtained at conversion levels lower than about 5%. Ammonia and methane were observed as products for all the metal catalysts investigated. Dimethylamine was a significant product for all the metals except rhodium. With the palladium catalyst, trimethylamine was an additional reaction product. In the case of the rhenium and gold catalysts, the reaction products included ethylenimine (C_2H_4NH).

For the Group VIII metals rhodium, palladium, iridium, and platinum, the method used for the analysis of the reaction products was successful in accounting for virtually 100% of the conversion of methylamine. However, for the Group VIII metals ruthenium and osmium, and also for rhenium, approximately one third of the converted methylamine was not accounted for in our routine analysis of reaction products. This fraction was found to consist largely of acetonitrile, which has a much higher boiling point and longer retention time than the other products routinely analyzed by the gas chromatograph. At the low concentrations at which the acetonitrile appeared in the reactor effluent gas, the peak due to this product was broadened to such an extent that it was indistinguishable from the baseline signal due to the carrier gas. The nature of the product was determined by diverting reactor effluent over a sufficiently long period of time to a cold trap (dry ice–isopropanol). After the more volatile components in the trapped material were removed by vaporization, a sample of the liquid remaining in the trap was injected into the gas chromatograph. Because the concentration of the acetonitrile was very high in the sample admitted to the chromatograph, a very distinct peak was observed in the chromatogram at the expected retention time.

In the case of the gold catalyst, at conditions giving a total methylamine conversion of 3%, approximately 15% of the converted methylamine was not accounted for. The nature of this fraction was not investigated directly, but the data suggested that the carbon-to-nitrogen ratio in this unaccounted-for fraction was close to one. It seems possible that this fraction may have consisted primarily of hydrogen cyanide.

We did not see any indication of loss of carbon to the catalysts in our experiments. There was no visual evidence for the presence of carbonaceous deposits. Furthermore, no increase in catalyst mass was detected at the ends of the runs. In general, catalytic activity remained constant during a run. Consequently, the analysis of the rate data on the various metal catalysts was straightforward. A nonvarying level of catalytic activity is essential for a reliable comparison of reaction rates on different metals and for the determination of the kinetic parameters characteristic of a reaction on a given metal.

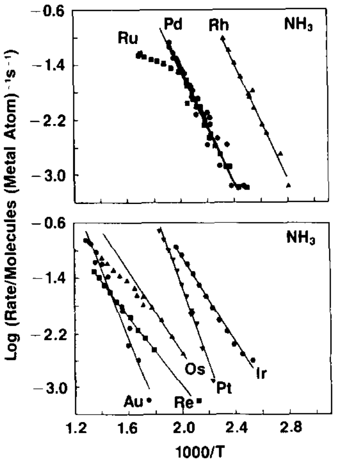

FIG. 1. Temperature dependence of the rate of formation of ammonia from methylamine in the presence of hydrogen over various metals supported on silica. The rates, expressed as molecules formed per second per metal atom in the catalyst, were obtained at methylamine and hydrogen partial pressures of 0.030 and 0.20 atm, respectively.

Data on the temperature dependence of rates of formation of various products from methylamine were obtained at methylamine and hydrogen partial pressures of 0.030 and 0.20 atm, respectively. The partial pressure of the helium diluent was 0.77 atm. In the presentation of the data in Figs. 1–5, the rates are expressed as molecules of product formed per second per atom of metal in the catalyst. With the data on metal dispersions in Table 1, rates per surface metal atom can be obtained.

In Figs. 1, 2 and 3, respectively, data are shown for the rates of formation of ammonia, methane, and dimethylamine. In the upper fields of the figures, the data are for the ruthenium, rhodium, and palladium catalysts. The data in the lower fields are for the rhenium, osmium, iridium, platinum, and gold catalysts. No data are shown for rates of formation of dimethylamine on rhodium in Fig. 3, since the product was not a significant one.

In Fig. 4 the rate of formation of trimethylamine on the palladium catalyst is shown as a function of temperature. Its rate of formation was about an order of magnitude lower than the rate of formation of dimethylamine on palladium. Data on rates of formation of ethylenimine on the rhenium and gold catalysts are shown in Fig. 5.

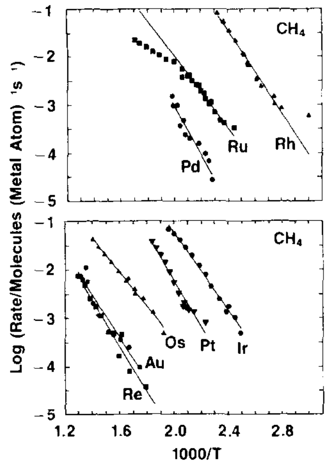

FIG. 2. Temperature dependence of the rate of formation of methane from methylamine in the presence of hydrogen over various metals supported on silica. The definition of rate and the reaction conditions are the same as for Fig. 1.

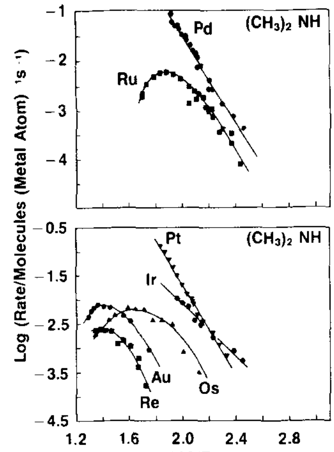

FIG. 3. Temperature dependence of the rate of formation of dimethylamine from methylamine in the presence of hydrogen over various metals supported on silica. The definition of rate and the reaction conditions are the same as for Figs. 1 and 2.

From the data on the temperature dependence of the rates of formation of ammonia and methane given in Figs. 1 and 2, and the data on metal dispersions tabulated in Table 1, values were determined for the apparent activation energy E and preexponential factor r_0' in the equation

$$r_0 = r_0' \exp(-E/RT). \qquad (1)$$

The quantity r_0 is the rate of formation of the particular product at methylamine and hydrogen partial pressures of 0.030 and 0.20 atm, respectively, at absolute tempera-

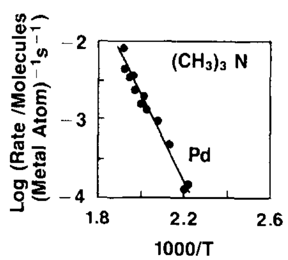

FIG. 4. Temperature dependence of the rate of formation of trimethylamine from methylamine in the presence of hydrogen over palladium supported on silica. The definition of rate and the reaction conditions are the same as for Figs. 1–3.

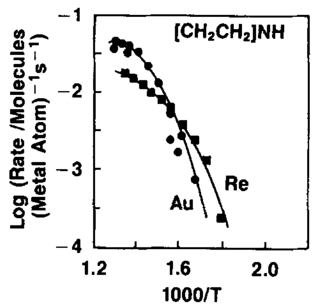

FIG. 5. Temperature dependence of the rate of formation of ethylenimine from methylamine in the presence of hydrogen over rhenium and gold supported on silica. The definition of rate and the reaction conditions are the same as for Figs. 1–4.

ture T. The units of r_0 and r_0' are molecules per second per metal surface atom. Values of E and log r_0' for methane and ammonia formation are summarized in Table 2 for the various metal catalysts (log designates common logarithm, i.e., to the base 10).

Values of apparent activation energies and preexponential factors for the formation of dimethylamine and trimethylamine are given in Table 3 for some of the metal catalysts. For dimethylamine, values are given for palladium, iridium, and platinum. Values are not included for the other metals which catalyzed the formation of dimethylamine, since the Arrhenius plots are not straight lines. For trimethylamine, values are shown for palladium only, since this is the only metal for which the formation of the product was significant.

In Table 4, data on the ratio of dimethylamine to methane in the products are summarized for the various metal catalysts. On palladium and gold, dimethylamine is formed in a much larger amount than methane at the conditions employed in this work. It is also formed in larger amounts on rhenium, osmium, and platinum. On ruthenium and iridium, dimethylamine is formed less extensively than methane. On rhodium, the formation of dimethylamine is insignificant in comparison with methane.

DISCUSSION

With regard to the kinds of products formed from methylamine–hydrogen mixtures, the results of the present work on supported metal catalysts are in excellent

TABLE 2

Kinetic Parameters for Production of Methane and Ammonia from Methylamine on Silica-Supported Metals

		Methane		Ammonia	
Metal	Temperature range (K)	E^a	log $r_0'^b$	E^a	log $r_0'^b$
Ru	402–487	17.1	5.8	18.0	6.7
Rh	357–430	19.6	8.9	19.3	8.8
Pd	398–521	22.9	8.0	18.6	7.7
Re	559–742	21.9	4.1	11.6	2.1
Os	500–710[c]	16.2	3.9	12.9	3.4
Ir	395–510	18.3	6.8	14.1	5.1
Pt	448–544	21.8	7.4	24.9	9.5
Au	572–774	20.2	5.4	23.4	7.6

[a] Apparent activation energy (kcal/mol), determined from the temperature dependence of the rate r_0 of formation of the product in question at methylamine and hydrogen partial pressures of 0.030 and 0.20 atm, respectively.

[b] The common logarithm of the preexponential factor r_0' defined by Eq. (1) in the text. The units of r_0' are molecules per second per metal surface atom.

[c] Temperature range of applicability of kinetic parameters for methane production on osmium; the parameters for ammonia production are applicable over a more limited temperature range, 500–570 K.

TABLE 3

Kinetic Parameters for Production of Dimethylamine and Trimethylamine from Methylamine on Silica-Supported Metals

Metal	Temperature range (K)	Product	E^a	$\log r_0'^b$
Ir	395–510	Dimethylamine	12.3	3.3
Pt	448–544	Dimethylamine	22.0	8.0
Pd	398–521	Dimethylamine	20.2	8.4
Pd	398–521	Trimethylamine	24.4	9.0

[a] Apparent activation energy (kcal/mol), determined from the temperature dependence of the rate r_0 of formation of the product in question at methylamine and hydrogen partial pressures of 0.030 and 0.20 atm, respectively.

[b] The common logarithm of the pre-exponential factor r_0' defined by Eq. (1) in the text. The units of r_0' are molecules per second per metal surface atom.

agreement with previously published results on catalysts in the form of metal films (*3*, *6*). For the metals palladium and platinum, which were common to the earlier investigations on metal films and to our present work on supported metals, the catalytic activities appear to be in reasonable agreement, on the basis that the temperature ranges employed were very similar. On the matter of loss of carbon to the catalyst, however, the present results appear to differ from the results obtained with the metal films. While incorporation of carbon in the metal films was observed, there was no evidence for this in the work on supported metals reported here. Possibly the higher hydrogen partial pressure and higher molar ratio of hydrogen to methylamine employed in the present work may be responsible for the difference.

Kemball and Moss (*3*) suggested that the formation of the various products from methylamine involved a common rate-determining step, which they identified with the rupture of the carbon–nitrogen bond. They observed a linear relationship between the logarithm of the preexponential factor and the apparent activation energy for the formation of ammonia on their metal films. We also observe such a relationship (Fig. 6), which may be an indication of a mechanistic feature which is common to the various reactions of methylamine yielding ammonia as one of the products. Such reactions would include hydrogenolysis of methylamine to methane and ammonia, as well as the reactions leading to formation of di- and trimethylamine, acetonitrile, and ethylenimine. The common feature may be a rate-determining step involving the rup-

TABLE 4

Ratio of Dimethylamine to Methane in the Products of Methylamine Conversion on Metal Catalysts

Metal	Temperature (K)	Dimethylamine/methane[a]
Ru	478	0.5
Rh	430	~0
Pd	478	40
Re	573	3
Os	523	4
Ir	478	0.2
Pt	478	3
Au	573	10

[a] At conversion levels lower than about 5%.

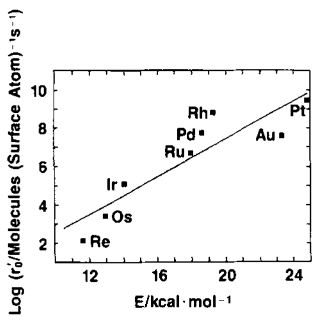

FIG. 6. Relationship between preexponential factors and apparent activation energies for the production of ammonia from methylamine on the various metal catalysts. The kinetic parameters were determined from the temperature dependence of rates of ammonia formation at methylamine and hydrogen partial pressures of 0.030 and 0.20 atm, respectively.

ture of the C—N bond in a surface intermediate formed in the chemisorption of methylamine, as originally suggested by Kemball and Moss (*3*). On the basis of the results in the present paper, we see no reason to alter this suggestion.

In the work on reactions of methylamine reported in this paper, we have been primarily interested in establishing the pattern of variation of catalytic activity from one metal to another. Catalytic activities of the metals for hydrogenolysis of methylamine to methane and ammonia, i.e.,

$$CH_3NH_2 + H_2 \rightarrow CH_4 + NH_3$$

are summarized in Fig. 7. The activities shown in the figure are relative reaction rates per metal surface atom at a temperature of 478 K. Since methane was not observed in some experiments with a silver catalyst at temperatures well above those used for palladium, the activity for silver is indicated to be lower than for palladium. The activity of gold seems high, on the basis of what is commonly expected for this metal relative to the Group VIII metals and rhenium. The possibility that the gold may have been contaminated with catalytically active metals was checked by energy dispersive X-ray fluorescence. The results of the analysis showed that the amounts of Group VIII metal impurities (including Ru, Rh, Pd, Os, Ir, and Pt) were extremely low, less than 10 ppm each. However, if a very active metal such as rhodium were present to the extent of 10 ppm and if it were present entirely at the surface, it could account in large part for the observed activity. Consequently, the activity of the gold should probably be regarded as an upper limit.

Similar results previously reported (*13*, *14*) for hydrogenolysis of ethane to methane, i.e.,

$$C_2H_6 + H_2 \rightarrow 2CH_4$$

are shown in Fig. 8 for comparison. Here the activities for silver and gold are indicated to be much lower than those for palladium and platinum. Methane formation was negligible over these metals, even at temperatures substantially higher than those used with the Group VIII metals.

For both hydrogenolysis reactions, a characteristic pattern of variation of catalytic activity is observed when one proceeds across the periodic table from Group VIIA through the various metals in Group VIII to the metals of Group IB. A maximum is observed within Group VIII, but the position of the maximum is different for the two reactions. For methylamine hydro-

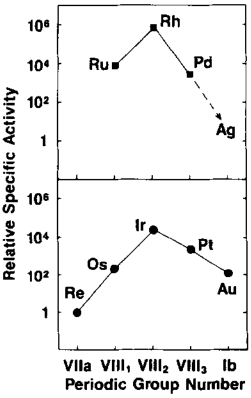

FIG. 7. Pattern of variation of the catalytic activities of metals for the hydrogenolysis of the C–N bond in methylamine. Activity is defined as rate of formation of methane at a temperature of 478 K and at methylamine and hydrogen partial pressures of 0.030 and 0.20 atm, respectively.

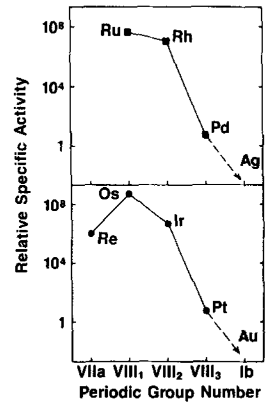

FIG. 8. Pattern of variation of the catalytic activities of metals for the hydrogenolysis of the C–C bond in ethane (*13*, *14*). Activity is defined as rate of conversion of ethane to methane at a temperature of 478 K and at ethane and hydrogen partial pressures of 0.030 and 0.20 atm, respectively.

genolysis, maximum activity is found in the second subgroup ($VIII_2$), i.e., for rhodium and iridium. For ethane hydrogenolysis, however, maximum activity is observed in the first subgroup ($VIII_1$), i.e., for ruthenium and osmium. The maximum for osmium is clear from Fig. 8; a maximum at ruthenium is inferred from auxiliary data not included in the figure (*13*, *14*).

Activity patterns such as those shown in Figures 7 and 8, and their interpretation, are of interest with regard to the general question of the catalytic specificity of metals. It is reasonable to seek an explanation based on the variation in the strength of adsorption of surface species, with possible changes in the nature of the rate-determining step in the reaction, from one metal to another across the periodic table. More detailed studies of the kinetics of methylamine hydrogenolysis on some of the metals, including an investigation of the dependencies of rates on methylamine and hydrogen partial pressures, should be useful in this regard. Studies of this type are currently in progress in our laboratory.

REFERENCES

1. Sabatier, P., and Gaudion, G., *C. R. Acad. Sci., Paris* **165**, 309 (1917).
2. Emmett, P. H., and Harkness, R. W., *J. Amer. Chem. Soc.* **54**, 538 (1932).
3. Kemball, C., and Moss, R. L., *Proc. R. Soc. London, Ser. A* **238**, 107 (1956).
4. Kemball, C., and Moss, R. L., *Proc. R. Soc. London, Ser. A* **244**, 398 (1958).
5. Kemball, C., and Moss, R. L., *Trans. Faraday Soc.* **56**, 154 (1960).
6. Anderson, J. R., and Clark, N. J., *J. Catal.* **5**, 250 (1966).
7. Orita, H., Naito, S., Onishi, T., and Tamaru, K., *Bull. Chem. Soc. Japan* **56**, 3390 (1983).
8. Sinfelt, J. H., *J. Phys. Chem.* **68**, 344 (1964).
9. Sinfelt, J. H., Taylor, W. F., and Yates, D. J. C., *J. Phys. Chem.* **69**, 95 (1965).
10. Sinfelt, J. H., and Yates, D. J. C., *J. Catal.* **8**, 82 (1967).
11. Sinfelt, J. H., and Yates, D. J. C., *J. Catal.* **10**, 362 (1968).
12. Yates, D. J. C., and Sinfelt, J. H., *J. Catal.* **14**, 182 (1969).
13. Sinfelt, J. H., "Advances in Catalysis." Vol. 23, p. 91. Academic Press, New York, 1973.
14. Sinfelt, J. H., *Catal. Rev. Sci. Eng.* **9**(1), 147 (1974).
15. Meitzner, G., Via, G. H., Lytle, F. W., and Sinfelt, J. H., *J. Chem. Phys.* **83**, 353 (1985).
16. Sinfelt, J. H., *Prog. Solid State Chem.* **10**(2), 55 (1975).
17. Garten, R. L., and Sinfelt, J. H., *J. Catal.* **62**, 127 (1980).
18. Sinfelt, J. H., "Bimetallic Catalysts: Discoveries, Concepts, and Applications," pp. 15–17, 22. Wiley, New York, 1983.
19. McVicker, G. B., Baker, R. T. K., Garten, R. L., and Kugler, E. L., *J. Catal.* **65**, 207 (1980).
20. Carter, J. L., McVicker, G. B., Weissman, W., Kmak, W. S., and Sinfelt, J. H., *Appl. Catal.* **3**, 327 (1982).