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Hydrogenolysis of Methyl Chloride on Metals

Metal-catalyzed hydrogenolysis reactions of carbon–halogen bonds have received less attention than hydrogenolysis reactions of carbon–carbon bonds. The information available is about equally divided between results of investigations on evaporated metal films (*1–4*) and on more conventional metal catalysts (*5–9*). In this note we report results of a study on the hydrogenolysis of methyl chloride over a number of metals supported on silica. The products of the reaction are methane and hydrogen chloride. Somewhat earlier, a similar study was completed for the hydrogenolysis of the carbon–carbon bond in ethane (*10, 11*), and, more recently, for the hydrogenolysis of the carbon–nitrogen bond in methylamine (*12*). Establishing activity patterns for the hydrogenolysis of these different types of bonds provides useful information regarding the specificity of metal catalysts for this important class of reactions.

Reaction rates were measured in a flow system at atmospheric pressure. The reactor was a horizontal Pyrex glass tube approximately 75 cm in length, with an internal diameter of 0.9 cm. It was 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 size. In a 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. Before and after the catalyst section, there was a small section (about 0.6 cm long) of 40/60 mesh ground Vycor followed by quartz wool. The remainder of the reactor tube (about 35 cm at either end) was filled with inert ceramic beads about 0.16 cm in diameter, which were held in place by quartz wool plugs at both ends. An axial glass thermowell (3 mm in diameter) containing a Chromel–Alumel thermocouple extended into the center of the catalyst charge.

The gas stream contacting the catalyst contained methyl chloride, hydrogen, and a helium diluent. A total gas flow of 1 liter per minute was used throughout. The exit of the reactor was connected to a vent through a section of polypropylene tubing from which a fixed volume of gas could be drawn through a Dräger tube (Devco Engineering Inc., Fairfield, N.J.) for analysis of hydrogen chloride. A bromphenol blue indicator in the tube undergoes a color change from blue to yellow on contact with hydrogen chloride. The concentration of HCl is determined from the length of the zone undergoing the color change. The reactor exit was also connected through a section of Monel metal tubing to a Hastelloy valve used for taking a sample for analysis with a Hewlett–Packard Model 5840 gas chromatograph. In a given run, the mixture of methyl chloride, 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 methyl chloride was then discontinued, after which a flow of hydrogen was maintained over the catalyst until the next reaction period.

The metals investigated as catalysts included Ru, Rh, Pd, Ag, Re, Os, Ir, Pt, and Au, all dispersed on silica. In all cases the metal content of the catalyst was 1 wt%. The preparation of the catalysts, except for the one containing silver, has been described previously (*12*). The silver catalyst was prepared in the same manner, with the use of an aqueous solution of silver nitrate

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for the impregnation step. After a sample of catalyst was charged to the reactor, it was contacted with a stream of hydrogen at 725 K to ensure that the metal was reduced.

Values of metal dispersion (ratio of surface atoms to total atoms in the metal clusters or crystallites) were 0.5, 0.6, and 0.8, respectively, for the Ru, Os, and Pt catalysts, and 1.0 for the Rh, Ir, and Re catalysts. The values for the Pd, Ag, and Au catalysts were 0.1, 0.2, and 0.02, respectively. For all of the catalysts except the one containing silver, the dispersion values and the methods used to determine them have been reported previously (*12*). In the case of the silver catalyst, the value was estimated from the crystallite size obtained from X-ray diffraction line broadening.

Data were obtained on the temperature dependence of the rate r_0 of hydrogenolysis of methyl chloride at methyl chloride and hydrogen partial pressures of 0.030 and 0.20 atm, respectively. The partial pressure of the helium diluent was 0.77 atm. The rates were obtained at conversion levels in the approximate range of 0.04 to 10%. For the platinum catalyst, data were obtained over a wider range of conversions, extending to levels as high as 30%. The apparent activation energy E and the preexponential factor r_0' in the equation, $r_0 = r_0' \exp(-E/RT)$, were obtained for each of the catalysts. The units of r_0 and r_0' are molecules per second per metal surface atom. Values of E and $\log r_0'$ are given in Table 1 for the various metal catalysts (log designates common logarithm, i.e., to the base 10).

Catalytic activities of the metals are compared in Fig. 1, where they are shown in relation to the positions of the metals in the periodic table. The activities shown in the figure are derived from reaction rates at a temperature of 521 K, expressed as molecules of methyl chloride hydrogenolyzed per second per surface metal atom. The rates were calculated from the kinetic parameters in Table 1. The temperature of 521 K was chosen for the comparison because it was within the range of temperatures investigated for all of the metals. Consequently, no extrapolation of rate data was necessary.

TABLE 1

Kinetic Parameters for Methyl Chloride Hydrogenolysis on Silica-Supported Metals

Metal	Temperature range, K	E^a	$\log r_0'^b$
Ru	517–573	16.9	5.1
Rh	462–521	12.5	4.0
Pd	515–572	18.9	6.5
Ag	521–576	20.2	6.1
Re	514–577	17.9	4.5
Os	519–586	18.0	5.4
Ir	479–526	15.1	5.5
Pt	483–533	15.4	6.0
Au	518–604	14.1	4.3

[a] Apparent activation energy, kcal/mole.

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

For the period containing the metals Re, Os, Ir, Pt, and Au, the hydrogenolysis activity increases in the direction of increasing atomic number from rhenium to platinum, but decreases from platinum to gold (lower field of Fig. 1). Since the apparent activation energies for these metals are not very different, the effect of temperature on the comparison of activities is small. Indeed, the order of activities of these metals is unchanged over the whole range of temperatures (462–604 K) encompassed in this investigation.

For the period containing the metals Ru, Rh, Pd, and Ag, the data in the upper field of Fig. 1 indicate a maximum activity for rhodium. The order of activities shown is unchanged over the range of temperatures from 462 to 560 K. However, at temperatures higher than 560 K, the rate of hydrogenolysis on palladium is higher than it is on rhodium, and the position of maximum activity in the upper field of Fig. 1 shifts from rhodium to palladium.

Thus, for the range of temperatures (462–604 K) employed in this investigation, maximum hydrogenolysis activity in the two periods is observed for the metal in the

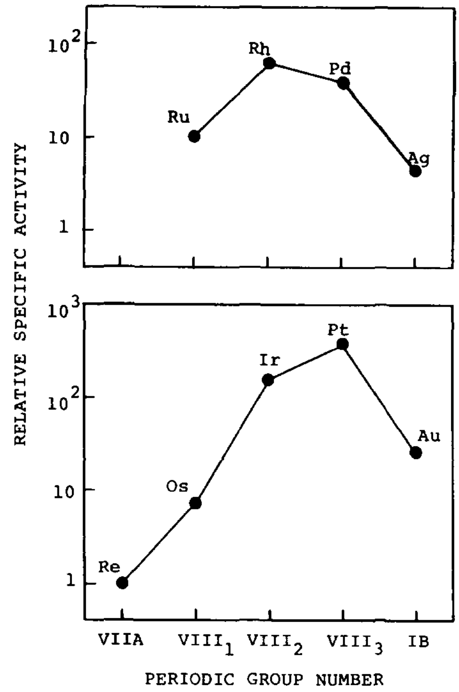

FIG. 1. Pattern of variation of the catalytic activities of metals for the hydrogenolysis of the C—Cl bond in methyl chloride. Activity is defined as the rate of hydrogenolysis per metal surface atom at a temperature of 521 K and at methyl chloride and hydrogen partial pressures of 0.030 and 0.20 atm, respectively.

second or third subgroup within Group VIII. These subgroups are designated as $VIII_2$ and $VIII_3$ in Fig. 1. In this respect, the hydrogenolysis of the carbon–chlorine bond in methyl chloride differs from the hydrogenolysis of the carbon–carbon bond in ethane (*10, 11*), for which the position of maximum activity in these same two periods is displaced to the left relative to the positions of the maxima in Fig. 1. One might expect the difference in the position of the maximum to be related to differences in the strengths of binding of chemisorbed intermediates for the two reactions.

The range of variation of activities of the metals for methyl chloride hydrogenolysis is much smaller than for ethane hydrogenolysis (two vs eight orders of magnitude among the Group VIII metals). The activities of the Group IB metals for ethane hydrogenolysis are so low that rates cannot be measured satisfactorily, even at temperatures somewhat higher than those investigated for the least active Group VIII metals. The situation is clearly very different for methyl chloride hydrogenolysis, for which the activities of silver and gold are within two orders of magnitude of those observed for the most active Group VIII metals.

The fact that the Group IB metals are inactive for ethane hydrogenolysis is attributed to their inability to chemisorb ethane. In contrast, their activity in catalyzing methyl chloride hydrogenolysis is a clear indication of their ability to chemisorb methyl chloride. The ability to form a metal–chlorine bond, as demonstrated by the existence of stable chlorides of the Group IB metals, provides a driving force for the chemisorption of methyl chloride and the associated rupture of the carbon–chlorine bond. The activation of the hydrogen molecule in the reaction of methyl chloride on the Group IB metals is intriguing, since hydrogen chemisorption supposedly does not occur on these metals. Perhaps the chemisorption is assisted by the presence of chlorine on the surface.

In the comparison of catalytic activities in Fig. 1, the possibility that metal dispersion may affect the activity per surface metal atom has been ignored; i.e., the reaction has been treated as if it were structure insensitive. We doubt that metal dispersion has any significant effect on the patterns of variation of catalytic activity in Fig. 1. In this regard, we note that the activity of gold relative to platinum, where dispersion differs by a factor of 40, is not appreciably different from the activity of silver relative to palladium, where the dispersion differs only twofold.

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