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The Specific Activity of Technetium, Rhenium, Ruthenium, Platinum, and Palladium in Catalytic Reactions of Benzene with Hydrogen

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The specific activities of technetium, rhenium, ruthenium, platinum, and palladium catalysts supported on silica and γ-alumina at a concentration of 1% have been studied for the reactions of benzene with hydrogen in the temperature range of 100–235° by the microreactor chromatographic pulse method. The surface areas of the metals were determined by selective hydrogen chemisorption at 20° and by the X-ray line-broadening methods. The measurements on ruthenium, platinum, and rhenium powders of known surface areas were applied to determine the metal site areas effectively occupied by one hydrogen atom.

Both technetium and rhenium reveal a catalytic activity in hydrogenation of benzene to cyclohexane. At sufficiently high temperatures, both metals, like ruthenium, are also catalysts in benzene hydrogenolysis, resulting in aliphatic C_1–C_6 hydrocarbons. The specific activities of metals for hydrogenation and hydrogenolysis decrease in the order: $Ru > Pt > Tc \approx Pd > Re$ and $Ru > Tc > Re$, respectively. The apparent activation energies are 7–11 kcal/mole for hydrogenation and 29–32 kcal/mole for hydrogenolysis. Rhenium, ruthenium, platinum, and palladium supported on γ-alumina were found to be less active as compared with the same metals on silica carrier, but the maximum difference was only a nearly twofold change in specific activity. The activity and selectivity of technetium appear to be distinctly dependent on the nature of the support.

In discussing the results the factors determining the catalytic activities of the metals are mainly considered, e.g., the extent and strength of hydrogen adsorption, the mode of bonding of the benzene molecules, and the role of the carrier.

INTRODUCTION

The possibility of displaying the specific catalytic properties of technetium was pointed out by some authors (*1, 2*), but no appropriate experimental work has been done so far. The available data on the catalytic activity of rhenium in benzene hydrogenation are rather scarce (*3*). According to these data, the benzene ring cannot be hydrogenated in the presence of rhenium up to 250° while above this temperature it decomposes to methane. Recent experiments have shown, however, that this metal is the catalyst in the dehydrogenation of cyclohexane (*4, 5*) and of disproportionation of cyclohexene (*5*). The high activity of ruthenium in benzene hydrogenation is well known (*6, 7*). On the other hand, it has been found recently (*8*) that ruthenium is a highly active catalyst for hydrogenolysis of cyclohexane to aliphatic hydrocarbons.

In this work the catalytic hydrogenation of benzene was investigated in the wide temperature range of 100–235° over technetium, rhenium, and ruthenium, the results being compared with those obtained for typical catalysts of this reaction, i.e., platinum and palladium. The metals sup-

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ported on silica and γ-alumina at a concentration of 1% were used. The investigations were carried out using the microreactor chromatographic pulse method, which is especially suitable when the product distribution is to be examined or the activity of different catalysts is to be compared. Some preliminary kinetic data could also be obtained with this technique.

The measurements of hydrogen chemisorption at 20° on ruthenium, platinum, and rhenium powders of known surface areas permitted comparison of their surface coverages by the hydrogen. Similar measurements on the catalysts, combined with X-ray determinations of the average crystallite sizes were used in estimating the surface areas of the supported metals and enabled the comparison of their specific activities.

EXPERIMENTAL

The following materials were used in catalyst preparation: ammonium pertechnetate (Oak Ridge National Laboratory, Oak Ridge, Tennessee), ammonium perrhenate (Biddle Sawyer & Co.), ammonium chlororuthenate ("Analar"), chloroplatinic and chloropalladic acids, the latter being obtained from the Pt and Pd powders (Johnson & Matthey). Silica and γ-alumina calcined at 700° during 10 hr were used as carriers; their grain size was below 0.2 mm; BET surface area, 210 and 200 m^2/g; and magnetic mass susceptibility, -0.35×10^{-6} or -0.38×10^{-6}, independent of temperature and field strength. The spectral analysis of the carriers showed only trace amounts of the following impurities: Ca, $<10^{-2}\%$; Al, Ti, $<10^{-3}\%$; Cu, Ag, $\sim 10^{-4}\%$ in silica; and Ca, $<10^{-2}\%$; Mg, $<10^{-3}\%$; Si, Cu, $\sim 10^{-4}\%$ in γ-alumina.

The catalysts were prepared by impregnating the weighed amounts of silica or γ-alumina with an appropriate volume of an 0.1 *M* water solution of the metal compound followed by drying at 60° for 20 hr. The reduction of the catalysts was carried out in a hydrogen stream at temperatures which were gradually increased, at a controlled rate, up to 700° during 10 hr. Then the samples were cooled in a hydrogen stream to room temperature. A similar procedure was applied to pure carriers using distilled water instead of solutions of metal compounds.

The samples for the hydrogen chemisorption measurements, weighing 3–7 g, were transferred into the suitable glass vessel, which was sealed to the BET vacuum apparatus. The trap cooled by liquid nitrogen protected the sample against grease and mercury poisoning. After evacuation at room temperature the sample was alternately treated with hydrogen at about 100 mm Hg and evacuated at 10^{-6} mm Hg at 400°. The treatment with hydrogen and the following evacuation was repeated five times during 10 hr. The same procedure was applied to metal powders (Johnson & Matthey) and to pure carriers. The chemisorption of hydrogen was measured at five pressures up to about 200 mm Hg with the accuracy of 2×10^{-6} moles. The BET surface areas of metal powders were determined from the adsorption isotherms of nitrogen at 77°K. Prior to measurements, the sample was kept in a nitrogen atmosphere at about 100 mm Hg at room temperature for 20 hr, then cooled to 77°K and finally evacuated quickly to 10^{-3} mm Hg, to prevent, as far as possible, the influence of nitrogen chemisorption. The results of the surface areas of pretreated samples were reproducible within 2%. It was established for ruthenium and rhenium powders that such measurements gave the values of the surface areas, which were lower by about 50% than those obtained for the samples reduced in hydrogen and evacuated at 400° without pretreatment with nitrogen.

The samples for X-ray line-broadening studies were prepared immediately after the reduction and evacuation procedure described above. The specimens were in cylindrical form of 0.5-mm diameter, a dioxane solution of collodion being used as a binder. The X-ray diffraction patterns were obtained using the TuR VEM 60 apparatus and 114.6-mm camera. Filtered copper radiation was used, the exposure time being 16 hr. The line profiles were obtained by employing a Zeiss microphotometer.

In the technique used for testing the activity, similar to that described by Kokes, Tobin, and Emmett (*9*), the microreactor was connected directly to the Perkin-Elmer 116 E gas chromatograph. The chromatograph consisted of a 2 m long column packed with 27.7% di-2-ethylhexylsebacate +10% sebacic acid on Celite and of the platinum thermal conductivity cell connected to the Kipp-Micrograph BD 2. The chromatographic column and the catharometer were kept at 85°. Electrolytic grade hydrogen was used both as a reactant and carrier gas at an inlet pressure of 1.7 atm; the flow rate of 80 cm^3/min was controlled at the detector exit with a soap-bubble meter. The reactor consisted of a Pyrex glass U-tube of inside diameter 8 mm; the catalyst samples weighing 0.005–1.00 g (eventually diluted to 1 g with the carrier) were uniformly mixed with 2 g of glass capillaries; the packing was held in place by a porous glass diaphragm. Thus, the standard flow conditions were preserved in all experiments. The slugs of benzene vapors diluted with hydrogen were admitted into the catalyst bed with the aid of a gas injection valve connected to the benzene saturator maintained at 20°. The doses of the volume 0.25 cm^3 contained about 3.5×10^{-6} moles of benzene. The residence time of the benzene wave in the reactor was about 30 sec. This corresponded to a molar ratio of benzene to hydrogen of about 1:700 at the applied flow rate. Thus, the reaction was carried out at a considerable excess of hydrogen.

The catalyst was preheated in the reactor in the hydrogen stream at 400° during 10 hr, and after cooling to the highest reaction temperature of 235° it was pretreated with few (*4–5*) doses of benzene. After such procedure the activity of the catalyst was determined at both decreasing and increasing temperatures, the determination being repeated at least twice at each temperature, The elution time was 15 min. In that time 80–90% of the benzene dose passed through the apparatus and was registered on chromatograms either in unreacted form or as the reaction products, in the order: CH_4, C_6H_{14}, cyclohexane (cyclohexene), and benzene, the retention time of benzene being 11 min. A time interval of 30–40 min between individual tests, necessary for changing the catalyst temperature and sweeping out the residue of hydrocarbons from the previous experiment, was applied.

The chromatographic separation of hydrocarbons was good, except that of methane, ethane, and propane. The components were identified by comparing their retention times with those of pure substances or by applying mass spectrometry. The samples for mass spectrometry were collected in appropriate glass traps immersed in liquid nitrogen. The composition of the effluent was determined from the relation $x_i = f_i P_i / \Sigma f_i P_i$, where x_i is the weight fraction of a component i and P_i, its peak area on the chromatogram. On the basis of preliminary tests the factor f_i was assumed to be 1 for benzene and cyclohexane, and 0.8 for aliphatic hydrocarbons. The contents of individual hydrocarbons in the effluent were reproducible within 10% at each temperature.

RESULTS

Adsorption of Hydrogen—Surface Area of Metals

The determination of the surface area of supported platinum from selective chemisorption of hydrogen has been discussed by various authors (*10, 11*). The method has also been extended to some other metals like nickel, cobalt (*12*), ruthenium, rhodium, and iridium (*13*). The investigations presented here show that with the exception of palladium, the same method can be applied to the supported metals used in this work, including rhenium, on which the chemisorption of hydrogen was recently established (*14*)*, and technetium, for which no adsorption data have been known so far. The adsorption on palladium catalysts was not measured because of the solubility of hydrogen in palladium.

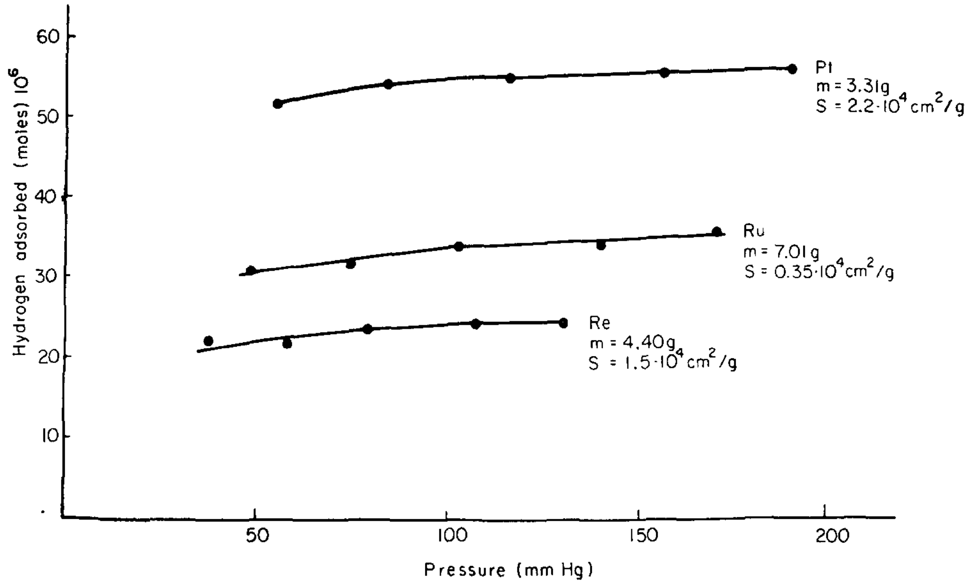

FIG. 1. Adsorption isotherms for hydrogen at 20° on metal powders.

All samples of metal powders of ruthenium, platinum, and rhenium, and of the ruthenium, platinum, technetium, and rhenium catalysts on silica and γ-alumina adsorbed hydrogen at 20° in amounts exceeding the accuracy of measurements by at least several times. Adsorption on samples of pure carriers weighing about 4 g was not noticed. At least 80% of adsorption was instantaneous while slow adsorption became negligible after 30 min. In determining the isotherms, a period of 30–40 min was allowed before reading the equilibrium pressure. The hydrogen uptake above 80 mm Hg was pressure-independent or varied only slightly with increasing pressure. The results obtained for metal powders are shown in Fig. 1. Thus, the amount of hydrogen read from the isotherms at the pressure of 100 mm Hg could be accepted as the saturation value referred exclusively to the adsorption on the metal surface.

The values obtained for metal powders, listed in Table 1, were used in evaluating the metal site area effectively occupied by one atom of adsorbed hydrogen $S_{\mathrm{at\ H}}$ and in estimating the coverage q determining the ratio of adsorbed hydrogen atoms to metal surface atoms, calculated for the three most dense crystallographic planes.

As shown in Table 1, the quantity of hydrogen adsorbed on unit area of rhenium is about 2 and 3 times smaller than that for platinum and ruthenium, respectively. The values of $S_{\mathrm{at\ H}}$ and q indicate that monoatomic coverage of metals (one H atom/one metal surface atom) is acceptable on the assumption that atom configurations of the following crystallographic planes predominate on the surface: the most closely packed (001) plane for ruthenium and the more loosely packed one (110) for platinum. The results obtained for rhenium indicate a coverage which is insufficient for the formation of a monolayer on the three most closely packed planes. When considering the (001) plane exposed on the surface, only one atom of hydrogen could be adsorbed per three surface atoms of the metal.

The saturation amounts of hydrogen obtained for the catalysts were used in evaluating the surface areas S_{ads} of the supported metals. In the calculations it was assumed that one atom of adsorbed hydrogen occupies an area of 6.0, 11.0, and 20.7 Å^2 on ruthenium, platinum, and rhenium, respectively, according to the measurements carried out on metal powders. In the case of technetium, the value of $S_{\mathrm{at\ H}}$ equal to 12.8 Å^2 was assumed, which cor-

TABLE 1

SURFACE COVERAGE OF METAL POWDERS BY HYDROGEN AT 20°

Metal	Lattice structure	Crystallographic plane	Surface area occupied by one metal atom (Å²)	No. of metal atoms per cm²		Adsorption of H_2		$q = \frac{\text{H atoms}}{\text{metal surface atoms}}$	
						$S_{\text{at H}}$ (Å²)	No. of H atoms adsorbed per cm²		
Ruthenium	Close-packed hexagonal	(001)	6.13	16.3×10^{14}	11.8×10^{14}	6.04	16.6×10^{14}	1.02	1.50
		(110)	9.75*	10.3×10^{14}*				1.61	
		(100)	11.25	8.9×10^{14}				1.87	
Platinum	Face-centered cubic	(111)	6.57	15.2×10^{14}	12.6×10^{14}	11.0	9.1×10^{14}	0.60	0.76
		(100)	7.61	13.1×10^{14}				0.69	
		(110)	10.75	9.3×10^{14}				0.98	
Rhenium	Close-packed hexagonal	(001)	6.53	15.3×10^{14}	11.0×10^{14}	20.7	4.8×10^{14}	0.31	0.47
		(110)	10.51*	9.6×10^{14}*				0.50	
		(100)	12.14	8.2×10^{14}				0.59	

* In this case the number of atoms belonging to two sublattices, but lying exactly on the same plane, was taken.

responds to coverage of 0.5 on the most closely packed (001) plane. On this assumption, similar agreement between adsorption and X-ray surface areas was obtained as had been observed for other metals.

The X-ray pattern of ruthenium-silica catalyst showed weak and very diffuse bands corresponding to crystallites of <50 Å size, the latter being the limit of our crystallite-size determinations. The X-ray patterns of other catalysts showed reflections from at least four planes, i.e., (100), (002), (101), (102) of ruthenium, technetium, and rhenium; and (111), (200), (220), and (311) of platinum and palladium. The average crystallite sizes were derived from the width at half-maximum intensities of the 101 line for hexagonal and the 311 line for cubic metals. The Jones corrections were applied as before (*15*). In the calculations, the shape factor of the Scherrer formula of 0.9 was assumed. The results obtained for silica-supported metals could be compared with those derived from the half-width of other visible lines. The agreement was satisfactory.

The adsorption and X-ray results are given in Table 2, the values of the surface areas being expressed in cm² per 1 g of metal. Assuming a spherical form of the crystals, the crystallite size D_{ads} from adsorption data or the metal area S_{roentg} from X-ray data, as shown in the table, were calculated according to the relation

$$D = 6 \times 10^8/S\rho$$

where ρ is the density of the metal in g/cm³.

A particularly high dispersion of ruthenium supported on silica was verified by chemisorption measurements as the surface area of 130×10^4 cm²/g corresponds to crystallites of only 35-Å mean diameter. The surface area of other catalysts estimated from H_2 chemisorption lies in the range of 20×10^4–70×10^4 cm²/g, corresponding to a mean crystallite diameter of 50–145 Å. Good agreement was found between the two methods as applied to silica-supported metals while the surface areas of the metals supported on γ-alumina evaluated from H_2 chemisorption are 1.3–1.6 times higher as compared with those derived from X-ray crystallite sizes. The mean crystallite size of ruthenium and rhenium supported on γ-alumina is distinctly (1.5–2 times) higher as compared with that obtained for these metals supported on silica.

The Hydrogenation and Hydrogenolysis of Benzene

In the reaction of benzene and hydrogen over platinum and palladium catalysts cyclohexane was the only reaction product. Over ruthenium, technetium, and rhenium catalysts at temperatures above 130–200°,

TABLE 2

SURFACE AREA OF SUPPORTED METALS

	Adsorption data						X-Ray data	
		H_2 adsorbed at 20° and 100 mm Hg						
Catalyst	Catalyst weight (g)	moles/ (sample)	(moles/g catalyst)	(atoms/g metal)	S_{ads} (cm²/g metal)	D_{ads} (Å)	D_{roentg} (Å)	S_{roentg} (cm²/g metal)
1% Ru/silica	2.95	52.8×10^{-6}	17.9×10^{-6}	21.5×10^{20}	130×10^4	35	—	Amorph.
1% Pt/silica	3.42	11.6×10^{-6}	3.4×10^{-6}	4.1×10^{20}	45×10^4	60	55	50×10^4
1% Tc/silica	3.16	12.3×10^{-6}	3.9×10^{-6}	4.7×10^{20}	60×10^4	85	95	55×10^4
1% Pd/silica	—	—	—	—	—	—	145	35×10^4
1% Re/silica	5.70	7.1×10^{-6}	1.2×10^{-6}	1.4×10^{20}	30×10^4	95	100	30×10^4
1% Ru/γ-alumina	2.63	25.3×10^{-6}	9.6×10^{-6}	11.6×10^{20}	70×10^4	70	90	50×10^4
1% Pt/γ-alumina	3.60	14.9×10^{-6}	4.2×10^{-6}	5.0×10^{20}	55×10^4	50	95	30×10^4
1% Tc/γ-alumina	2.85	10.6×10^{-6}	3.7×10^{-6}	4.5×10^{20}	60×10^4	85	125	40×10^4
1% Pd/γ-alumina	—	—	—	—	—	—	165	30×10^4
1% Re/γ-alumina	5.94	4.7×10^{-6}	0.8×10^{-6}	1.0×10^{20}	20×10^4	145	190	15×10^4

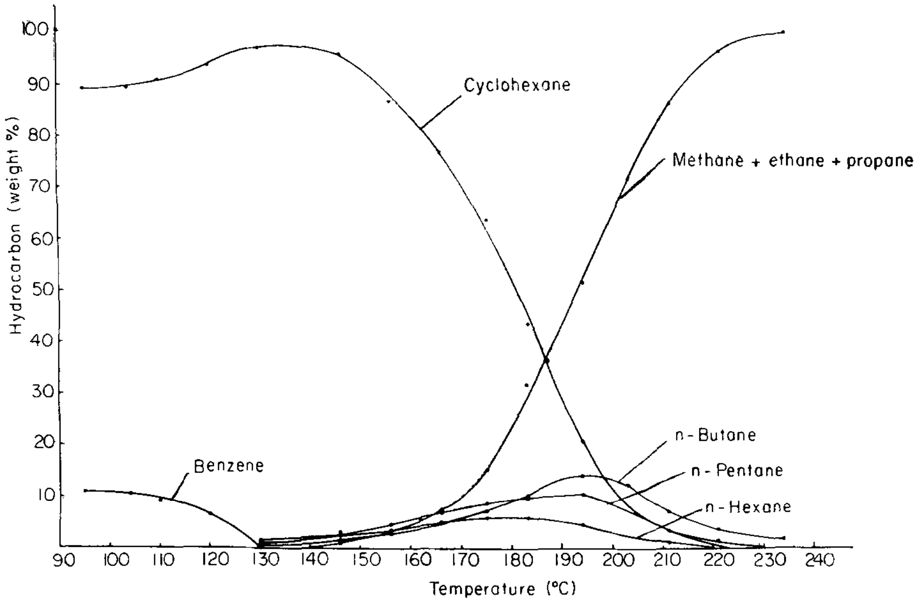

FIG. 2. Variation of product composition with temperature over 0.1 g of ruthenium/silica catalyst.

normal saturated aliphatic C_1–C_6 hydrocarbons were also formed as the products of hydrogenolysis.

Figure 2 shows the product distribution obtained over 0.1 g of silica-supported ruthenium catalyst which was found to be most active for both hydrogenation and hydrogenolysis reactions. Using this catalyst, small amounts of normal alkanes, mainly hexane, in addition to cyclohexane, were formed already at 130° (100% conversion). With increasing reaction temperature the yield of cyclohexane decreased and the yield of aliphatic hydrocarbons increased, reaching maxima for hexane, pentane, and butane at temperatures of 180°, 190°, and 195°, respectively. Above 200° methane, ethane, and propane were the main reaction products. On less effective catalysts the maximum yields of cyclohexane and of individual aliphatic hydrocarbons appeared at higher temperatures. Trace amounts of cyclohexene could be detected in reaction products formed over γ-alumina-supported ruthenium and technetium below 150°.

The Specific Activity and Kinetic Data

The specific activities of the metals were determined at low conversion levels (about 25% total conversion at 235°) by use of appropriate amounts of catalysts. They were expressed as the rates of total conversion A, of hydrogenation A_1, and of hydrogenolysis A_2 in moles per cm² per second from the relation (*16, 17*)

$$A, A_1, A_2 = \frac{\alpha, \alpha_1, \alpha_2}{m_{\text{cat}} S_{\text{Me}}} \frac{n_b}{\tau}$$

where α, α_1, α_2 are fractions of benzene converted in total, to cyclohexane, or to aliphatic hydrocarbons, respectively; m_{cat} is the weight of the catalyst in grams; S_{Me}, the metal surface area in cm² per gram of the catalyst (determined for palladium from X-ray data and for other metals from hydrogen adsorption); and n_b, the dose of benzene in moles passing the catalyst bed in the time of τ seconds. At constant benzene dose, and under standard flow conditions we obtain the corresponding specific activities of metals a, a_1, a_2

$$a, a_1, a_2 = \frac{\alpha, \alpha_1, \alpha_2}{m_{\text{cat}} S_{\text{Me}}}$$

The temperature dependence of a_1 or a_2 may also be applied for determination of the apparent activation energies of the reactions.

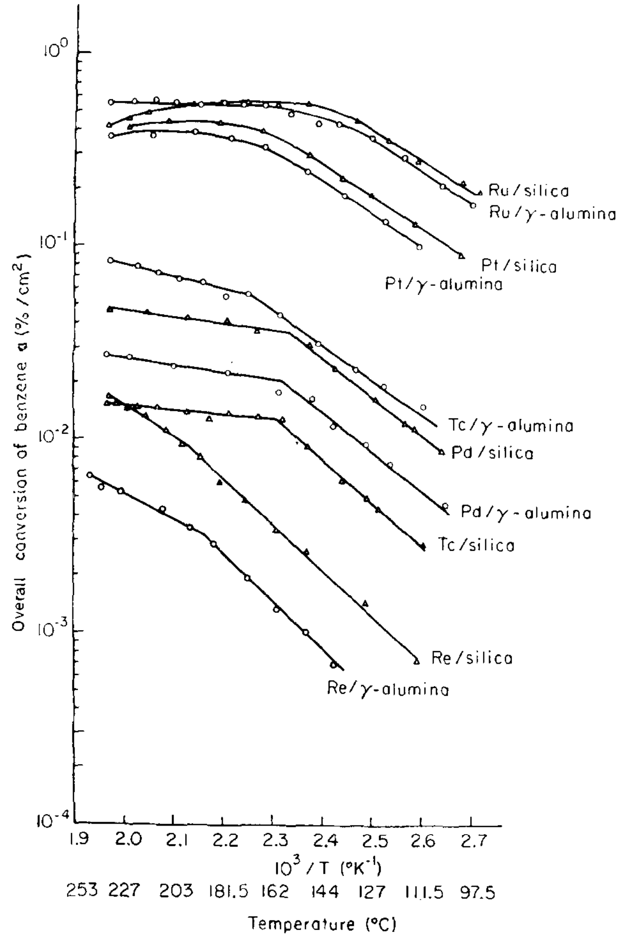

FIG. 3. Arrhenius plots for benzene overall conversion over silica and γ-alumina-supported metals.

The values of a, a_1, and a_2 are shown in the Arrhenius plots in Figs. 3–5. Listed in Table 3 are the apparent activation energies of hydrogenation E_1 and of hydrogenolysis E_2 in kcal/mole, the activities A_1 at 127° and A_2 at 227° and also the pre-exponential factors of Arrhenius equations $A_1{}^0$ and $A_2{}^0$ in moles per cm^2 per second. The selectivities of metals at 227° defined as A_2/A_1 are also given in the table.

In the calculations it was assumed that $\alpha_i = x_i$. This assumption, however, has no effect on the values of E_1 and E_2 in the accuracy limits of 0.5 and 1.0 kcal/mole, respectively. It was further accepted that $n_b = 3 \times 10^{-6}$ moles and $\tau = 30$ sec. The effect of temperature on the retention time, if any, could have been very small for all the catalysts used, and was consequently neglected.

It is evident that ruthenium and platinum exhibit the highest catalytic activity for hydrogenation reaction. Technetium and palladium catalysts are proved less effective while rhenium is found to be the least active catalyst of all. The activities of ruthenium, technetium, and rhenium catalysts in hydrogenolysis decrease in the same order. The apparent activation energies were found to be 7–11 kcal/mole for hydrogenation and 29–32 kcal/mole for hydrogenolysis. The compensation law is approximately fulfilled for hydrogenation, as illustrated in Fig. 6. High activity of ruthenium for hydrogenolysis appears to be related mainly to high value of the pre-exponential factor of the Arrhenius equation.

The activities A_1 of alumina-supported metals were found to be lower than those of the metals supported on silica, but the differences amounted only to 20% for ruthenium and platinum while for palladium and rhenium a twofold decrease was observed. The selectivities of ruthenium and rhenium are independent of the kind of carrier. Only technetium shows different behavior. Its activity for hydrogenation in the case of γ-alumina carrier is higher by about four times and the selectivity lower by six times than in the case of silica-supported catalyst.

The apparent activation energies given in Table 3 refer to the linear low-temperature portions of the Arrhenius plots. It is evident from Figs. 3–5 that all straight lines of log a (or log a_1) vs. $1/T$ show a break at temperatures between 130° for ruthenium on silica and 190° for rhenium catalysts. Above the break temperatures the total conversion of benzene increases only slightly, or does not vary or, after passing the maximum, decreases with increasing temperature. In the case of ruthenium on both silica and γ-alumina carriers, breaks also occur in the Arrhenius plots for hydrogenolysis rate at 170° and 190°, respectively. At these temperatures, the apparent activation energy decreases from 30 to 15 kcal/mole.

The absence of outer and inner diffusion limitations could be shown in the experiments, in which the amounts and the granule sizes of the catalysts were changed. The results obtained for silica-supported platinum, one of the most active catalysts,

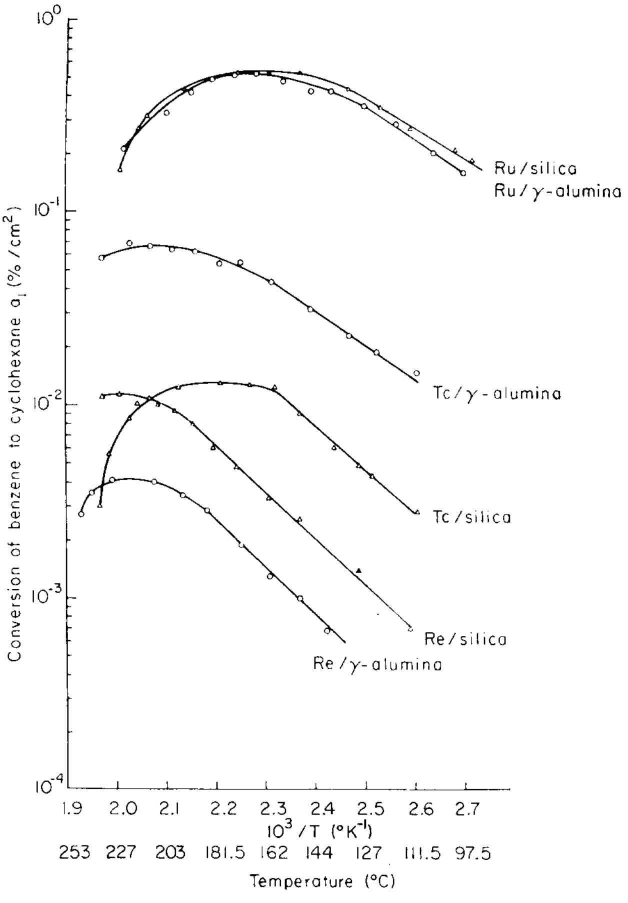

FIG. 4. Arrhenius plots for benzene hydrogenation over silica and γ-alumina-supported metals.

TABLE 3

Catalytic Activity of Metals

		Hydrogenation of benzene				Hydrogenolysis of benzene				
Catalyst	Catalyst weight (g)	Temperature range (°C)	E_1 (kcal/mole)	$A_1(127°)$ (moles/cm^2 sec)	log A_1^0 (moles/cm^2 sec)	Temperature range (°C)	E_2 (kcal/mole)	$A_2(227°)$ (moles/cm^2 sec)	log A_2^0 (moles/cm^2 sec)	Selectivity $A_2/A_1(227°)$
1% Ru/silica	0.005	95–132	7.0	395×10^{-12}	−0.13	132–173	30.0	300×10^{-12}	25	2.2
1% Pt/silica	0.01	100–148	8.0	175×10^{-12}	0.25	—	—	—	—	—
1% Tc/silica	0.3	111–158	11.0	4.6×10^{-12}	2.9	167–235	29.0	8.9×10^{-12}	18	1.5
1% Pd/silica	0.1	106–148	9.5	16×10^{-12}	1.3	—	—	—	—	—
1% Re/silica	0.5	113–191	11.0	1.2×10^{-12}	2.3	206–234	32.0	3.4×10^{-12}	19	0.29
1% Ru/γ-alumina	0.005	97–145	8.0	350×10^{-12}	0.62	145–192	30.0	390×10^{-12}	25	2.4
1% Pt/γ-alumina	0.01	108–165	8.0	142×10^{-12}	0.32	—	—	—	—	—
1% Tc/γ-alumina	0.05	111–171	8.5	20×10^{-12}	0.06	171–234	29.0	16×10^{-12}	19	0.26
1% Pd-γ-alumina	0.25	105–159	9.5	8.4×10^{-12}	1.2	—	—	—	—	—
1% Re/γ-alumina	1.00	140–185	11.0	0.5×10^{-12}	2.0	200–245	32.0	1.1×10^{-12}	20	0.26

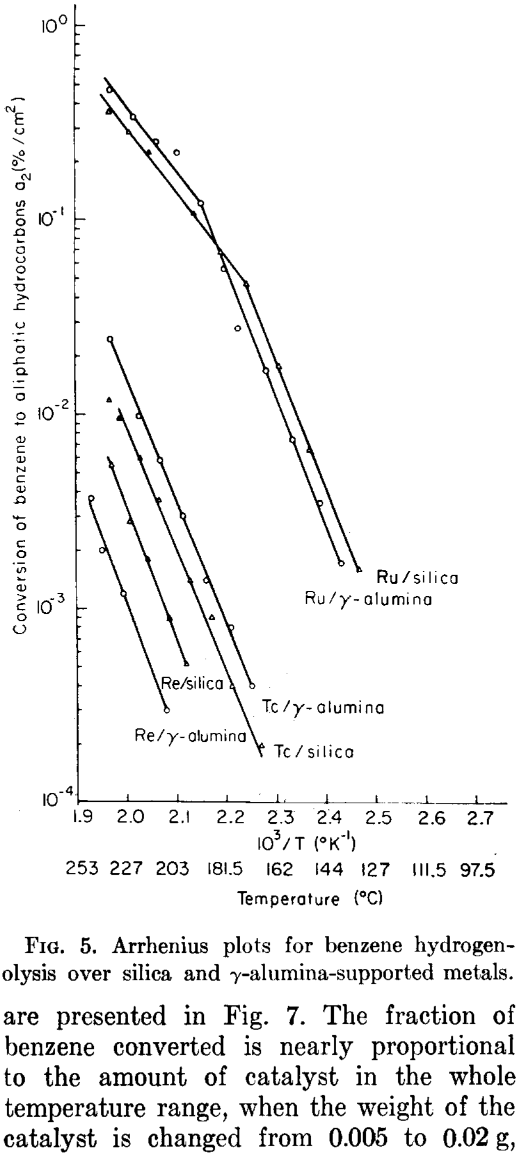

FIG. 5. Arrhenius plots for benzene hydrogenolysis over silica and γ-alumina-supported metals.

are presented in Fig. 7. The fraction of benzene converted is nearly proportional to the amount of catalyst in the whole temperature range, when the weight of the catalyst is changed from 0.005 to 0.02 g, corresponding to an increase of the conversion at 235° from 9% to 36%. It is also evident that the conversion is unaffected by increase in size of catalyst granules from the standard dimensions below 0.2 mm to the range of 0.2–0.5 or 0.5–1.0 mm. The results indicate that even at the highest reaction temperatures the diffusion of the reactants to the outer or inner surface of the catalysts could not be a rate-controlling step.

DISCUSSION

The differences in hydrogen chemisorption on ruthenium, platinum, and rhenium powders at 20° could be connected with various factors depending on the nature of the metal, such as the atomic arrangement on the surface, the specific properties of definite crystallographic planes, the valency of the surface atoms. The simplest explanation may be based on the assumption that the adsorption takes place on the interstitial positions on the surface (*18*) and that on the surface of various metals different proportions of definite crystallographic planes are exposed (*14*). It is remarkable that for rhenium the fractional coverage by hydrogen must be assumed on each of the three most densely packed planes.

The agreement between the surface areas obtained from H_2 chemisorption and X-ray line-broadening data for silica-supported metals indicates the presence of substantial amounts of metal crystallites of rather uniform sizes and sufficiently large to be detected by X-ray diffraction. The divergence between chemisorption and X-ray results for the metals supported on γ-alumina suggests that an appreciable fraction of metal in highly dispersed form not included in the X-ray estimation of crystallite size is present in these catalysts. The higher average crystal diameter of ruthenium and rhenium deposited on γ-alumina as compared with silica indicates a wide range of the crystallite sizes of these metals supported on γ-alumina.

Various authors have pointed out (*6*, *19*) that the dispersion of supported metals in impregnating catalysts may be related to the porous structure of the carrier. Following the suggestions of Dorling and Moss (*19*), one can assume that all the pores contributing to the surface areas of the carriers are filled with metal compound solutions during the impregnation procedure. The differences in the crystallite-size distribution of the metals in two series of catalysts could be explained by assuming that in γ-alumina, in contrast with silica, both micro- and macropores significantly contribute to the surface area and that the small metal particles deposited in micropores cannot undergo extensive recrystallization during the applied slow gradual rise of the reduction temperature.

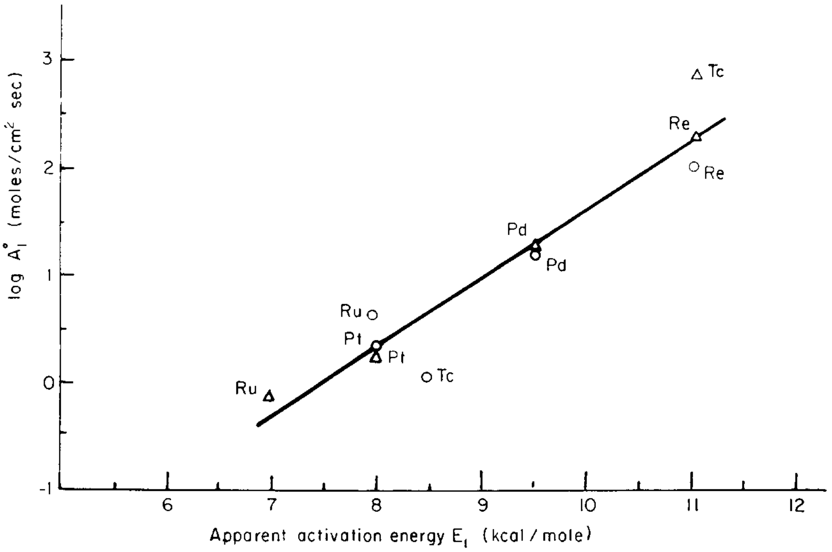

FIG. 6. Compensation effect for benzene hydrogenation over silica and γ-alumina-supported metals; Δ, metal/silica catalysts; O, metal/γ-alumina catalysts.

In discussing the activities it is of interest to consider the factors which may affect the differences in the catalytic action of various metals in hydrogenation and hydrogenolysis of benzene.

The activities for hydrogenation seem to be related to the abilities of the metals to chemisorb hydrogen at room temperature. The sequence of specific activities

$$\text{Ru} > \text{Pt} > \text{Tc} \approx \text{Pd} > \text{Re}$$

is, in the case of ruthenium, platinum, rhe-

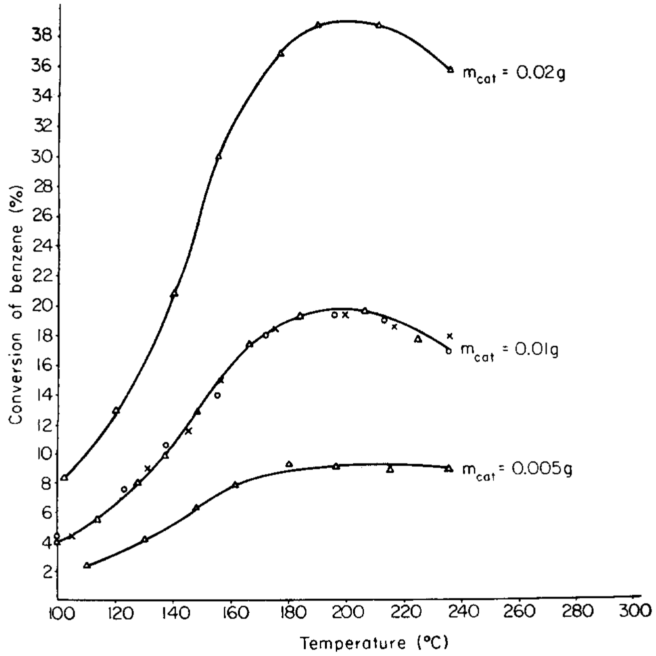

FIG. 7. Conversion of benzene over different amounts (m_{cat}) and granule sizes (a) of platinum/silica catalyst; Δ, a = <0.2 mm; ×, a = 0.2–0.5 mm; O, a = 0.5–1.0 mm.

nium, and presumably technetium, consistent with the extent of hydrogen chemisorption on metal powders at 20°. If the same sequence in adsorption occurs at the reaction temperatures, such correlation is understandable. In the pulse method, in which hydrogen is the reactant and carrier gas simultaneously, cyclohexane is probably formed as a product of a simple or successive bonding of chemisorbed hydrogen atoms to benzene molecules weakly adsorbed on the hydrogenated metal surface. The number of sites active for hydrogen chemisorption should be an important factor determining the reaction rate.

On the other hand, the high activity of the metals of Group VIII such as ruthenium and platinum in hydrogenation reactions is usually ascribed to the relatively weak bonding of hydrogen on their surface, since the initial chemisorption heat of hydrogen on these metals amounts only to 26 and 28 kcal/mole [For a review, see ref. (*20*)]. It has been discussed by other authors (*21*) that the high initial chemisorption heat of hydrogen may be unfavorable because of its low reactivity and of blocking the most active sites of the metal by non-reactive species of dehydrogenated hydrocarbon residues or by reaction products. The chemisorption heats of hydrogen on technetium and rhenium are not known. However, according to the theoretical model of the metallic character of the chemisorption bond [Eley, Stevenson, see ref. (*20*)], the initial chemisorption heat should be related to the latent heat of sublimation L_s of the metal. One could expect a rather high value of the initial chemisorption heat of hydrogen on rhenium, since the value of L_s is particularly high for this metal (189 kcal/g atom) as compared with other metals investigated (91–160 kcal/g atom)*. Assuming the above correlation to be valid for rhenium, the low activity of this metal in the hydrogenation of benzene might be connected with a small number of active sites as well as to the comparatively strong adsorption of hydrogen (or benzene) on at least a part of these sites.

The sequence of the catalytic activities of ruthenium, technetium, and rhenium for hydrogenolysis

$$\text{Ru} > \text{Tc} > \text{Re}$$

is consistent with that found for hydrogenation. Platinum and palladium exhibit no activity for hydrogenolysis of benzene in the applied temperature range.

In considering the selectivity pattern of the metals in hydrogenation and hydrogenolysis of hydrocarbons it is commonly assumed (*21, 22*) that the hydrocarbon molecules may be adsorbed in different forms on the metal surface and that different adsorbed species are involved in hydrogenation and hydrogenolysis reactions. As has been postulated by a number of authors (*23, 24*), the hydrogenation of benzene might proceed through the weakly adsorbed π-bonded intermediate. The hydrogenolysis could be connected rather with strong chemisorption, presumably involving the multiple metal–carbon bonds prior to the addition of hydrogens to carbon atoms.

The activities in hydrogenolysis of benzene seem to be related to the electronic properties of the metals. Under the assumption that the electronic structure of the investigated metals is analogous to that of the first row metals (*25*), the order of the activities appears to be consistent with a decrease of the number of unpaired *d* electrons per atom from 2.2 for ruthenium to about 1 for technetium and rhenium, and to 0.6 for palladium and platinum. It is possible that the hydrogenolysis of carbon–carbon bonds depends on the ability of the metals to form multiple metal–carbon bonds and that this ability decreases as the number of unpaired electrons in the metal decreases. Such a correlation is also suggested by decreasing activities of the noble metals on passing from left to right through Group VIII, reported in the literature for hydrogenolysis of cyclohexane (*8*) or ethane (*13*). In these and other hydrogenolysis reactions ruthenium seems to be the most active catalyst. Platinum and palladium are inactive or exhibit a low activity.

The decrease of the activities for hydrogenolysis is consistent with the increase of the nearest neighbor distances of the metals, but only from 2.65 Å for ruthenium to 2.74 Å for rhenium, and to 2.78 Å for platinum. It seems, however, that these small differences in the interatomic distances cannot be responsible for the observed activity differences and are rather of secondary importance as compared with the electronic factor.

Among the factors influencing the activity of supported metals the kind of the carrier should also be considered. A lower activity of the metals supported on γ-alumina as compared with that of the silica-supported metals, at equal selectivity, could be explained by assuming that a part of the surface of the metals supported on γ-alumina does not participate in the reactions. It is possible that the very fine particles contained in micropores, whose occurence was suggested above, are inaccessible for rather large hydrocarbon molecules. A more significant difference in the activity results obtained for palladium and rhenium on both carriers may be ascribed to a relatively small accuracy of the surface area measurements (for palladium from X-ray line-broadening only and for rhenium from small amounts of chemisorbed hydrogen). Thus, it seems justified to conclude that in the case of ruthenium and platinum, and presumably also palladium and rhenium supported on silica and γ-alumina the nature of the carrier affects in the first place the dispersity of the metal and perhaps also the accessibility of its surface for benzene molecules. The activity of the catalysts for hydrogenation and hydrogenolysis of benzene, determined per unit surface area of metal, appears to depend only slightly, if at all, on the kind of the carrier. These conclusions cannot be applied to supported technetium, if the assumptions used in evaluating its surface area were correct. As has been pointed out by other authors (*26*), the effect of the support on the specific activity of the metal may depend on the catalyst as well as on the nature of the reactions.

It has been shown above that the mass-transport limitations were probably of small importance at the conditions prevailing during the activity measurements and therefore cannot be responsible for the occurrence of the breaks in the Arrhenius plots. The breaks occurring in some cases at temperatures as low as 130–140° cannot be also attributed to the back reaction. According to the data of Janz (*27*), the dehydrogenation of cyclohexane could take place under the applied conditions (very high excess of hydrogen, low conversion of benzene) to only a very small extent (maximum of 0.05% at 200° and of 2% at the highest reaction temperature of 235°). It seems that the rate limitations at elevated temperatures are rather of a kinetic nature and could be explained by decreasing surface coverage by benzene and hydrogen, reflected by increase of the reaction orders with respect to the reactants. Also some differences in the surface coverage of various catalysts by the reactants in the temperature range, in which the apparent activation energies were compared (Table 3) might account for occurence of the compensation effect for hydrogenation. Recently, Taylor has pointed out (*28*) the complex nature of the apparent activation energy for the hydrogenation of benzene because of the well-known dependence of the reaction orders on temperature and on reactant partial pressures. A more detailed investigation of the kinetics is necessary for interpreting the course of the Arrhenius plots as well as the mechanism of the reactions studied. Some experimental work in this direction has been started already.

* *Note added in proof.* Recently, a study by K. F. Poulter and J. A. Pryde on the chemisorption of hydrogen on rhenium appeared in the *British Journal of Applied Physics* **1**, Ser. 2, 169 (1968). These authors have found, in agreement with the suggestions given in this paper, a rather high value of 30.5 kcal/mole for the initial heat of adsorption of hydrogen on rhenium.

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