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Surface Reactivity of Supported Gold

II. Hydrogen Transfer Between Benzene and Cyclohexane

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The rate of redistribution of ^{14}C between benzene and cyclohexane has been investigated over supported Au catalysts, in the temperature range 200 to 250°C, partial pressures of $\sim$0.2 atm, and total pressure 1 atm. The catalyst variables studied were the Au concentration, 0.3 to 5 wt %, and the catalyst support, Al_2O_3, MgO. Two methods of catalyst preparation were employed. In one, Au particles were formed by low temperature ($\sim$100°C) chemical reduction, while in the second method by thermal decomposition of the Au salt at higher temperatures. Diameter of the Au particles ranged between 40 to $>$1600 Å depending upon the type of support and preparative method. From the experimental results the reaction rate constant and the analytical relation between the ratio cyclohexane/benzene and reaction rate were determined. Rate constants of the order of $(1 \text{ to } 10) \times 10^{-6}$ [mole/g(cat)sec] were calculated. The analytical relation between the cyclohexane/benzene ratio and the reaction rate was found to change for values of the ratio $\approx$3.

The extent of the available metal surface per weight of metal was found to influence the reaction rate constant. This intrinsic surface effect was detected under conditions such that the molecular mean free path of reactants and products was large in relation to the diameter of the metal particle. It is suggested that whenever particle size and molecular free path are of the same order of magnitude, surface effects do not lend to easy detection.

The general picture of the reactivity of surfaces of finely dispersed Au toward hydrogen and oxygen is compared.

Recent investigations have disclosed that Au surfaces display considerable reactivity toward oxygen in the temperature range 300 to 400°C (*1*). The effect was observed by studying the rate of oxygen transfer between CO and CO_2 catalyzed by supported Au. In these studies the contribution of thermodynamic and kinetic factors to the Au–oxygen interaction was analyzed and the influence of experimental variables (preparative procedure, concentration of adsorbed oxygen, nature of catalyst support) upon surface reactivity was examined. In view of these results it appeared of interest to expand the studies to hydrogen transfer steps to derive similar information on the Au–hydrogen interaction under experimental conditions approaching those of conventional catalytic hydrogenations. There are no literature reports on direct studies of the interaction between supported Au and molecular H_2 or hydrogen containing species. The H_2–D_2 reaction has been studied on Au foils (*2*) and wires (*3*). Supported Au has been employed in studies on the oxidation of H_2 (*4*), and a variety of hydrogenation reactions has been investigated on Au in film, wire, and foil form. These investigations suggested the presence of an interaction between hydrogen and Au surfaces. However, details about this interaction, and the experimental conditions that influence it were only indirectly gleaned.

The role of physical and chemical factors upon the reactivity of the surface may be uncovered more directly if surface reaction steps are studied individually and not as they appear simultaneously in a net conversion reaction. In previous reports from this laboratory (*5, 6*), the usefulness of the hydrogen transfer reaction between benzene (BE) and cyclohexane (CHA) for unraveling details of the interaction of catalytic surfaces with hydrogen donor and acceptor molecules was pointed out and demonstrated in the case of noble metal catalysts. It was then decided to employ this transfer reaction to perform a similar analysis of the reactivity of Au surfaces towards hydrogen. The rate of hydrogen transfer was determined by following the redistribution of isotopic carbon between BE and CHA, namely:

$$^{*}C_6H_6(g) + C_6H_{12}(g) \rightarrow C_6H_6(g) + {}^{*}C_6H_{12}(g), \quad (1)$$

where g refers to the gas phase and *C is a ^{14}C atom. At catalytic surfaces it may be assumed that reaction (1) takes place by a sequence of two surface reaction steps:

$$^{*}C_6H_6(g) + 6\ H(s) \rightarrow {}^{*}C_6H_{12}(g), \quad (1a)$$

$$C_6H_{12}(g) \rightarrow C_6H_6(g) + 6\ H(s). \quad (1b)$$

The rates of reaction steps (1a) and (1b) are similar, since reaction step (1b) is the backward stage of reaction step (1a) and reaction (1) formally establishes a chemical equilibrium. Consequently, the rate of the individual surface transfer steps (1a) and (1b) is directly obtainable by following the rate of reaction (1).

EXPERIMENTAL METHODS

A detailed account of the experimental procedure has been published previously (*6*) including the preparation of the Au catalysts (*1*). Only a brief summary will be presented here.

Supported Au catalysts were prepared from $HAuCl_3 \cdot 3H_2O$ (reagent grade). The preparation procedure consisted in the reduction at ~100°C of the Au salt present in a water suspension of the support (reagent grade Al_2O_3, MgO) by addition of enough 3% oxalic acid solution. The precipitation was followed by repeated washing, drying, and finally heating at ~350°C, 0.1 Torr for 2 hr. In a second procedure, the impregnated support was dried under IR lamp and heat treated at 350°C under conditions of gas pressure and time similar to those employed in the first preparation. A few catalysts were prepared from $KAu(CN)_2$ following the thermal decomposition method. The characterization of the catalysts was carried out by means of X-ray diffraction and electron microscope observations. As already reported (*1*), satisfactory agreement between Au particle size, determined by X-ray line broadening and by direct observations of electron micrographs, was obtained. Some pertinent conclusions from this analysis are reported in Table 1.

TABLE 1
CHARACTERISTICS OF SUPPORTED Au CATALYSTS

Au (wt %)	Support	Preparation method[a]	Particle diam (Å)
0.3	Mgo	CR	40 ± 20
0.7	Mgo	CR	50 ± 20
2.0	Al_2O_3	CR	>1600
2.0	Al_2O_3	TD	>1600
2.0	MgO	TD	1290 ± 60
5.0	MgO	CR	150 ± 13

[a] CR, chemical reduction; TD, thermal decomposition.

The results show a large difference in particle size for the MgO supported preparations depending upon the method of preparation. In a previous communication (*1*), it was argued that the difference was a consequence of the relative extent to which two processes developed during the genesis of the catalyst. If the formation of Au nuclei occurred at low temperature, growth of the former by sintering would not easily occur at $<0.25\ T_m$ (~350°C) and the final particle size was small. T_m is the Tamman temperature for Au (1336°K). Conversely, the decomposition of the salt at higher temperature formed directly large nuclei, possibly through diffusion of the undecomposed or partly decomposed salt to the nucleation site in the solid matrix. Au–Al_2O_3 prepared by chemical reduction, however, showed a particle size in the same range of that observed for similar preparations obtained by thermal decomposition. It is difficult to suggest well-founded reasons for this difference. It seems that the fundamentally different texture between the compact, low area, well crystallized MgO and the open structure, high area, poorly crystallized Al_2O_3 might have been responsible for altering the relative rates of nucleation and growth of the Au particles.

The surface area of Al_2O_3 was 201 m^2/g, and of MgO, 18 m^2/g. Reagent grade hydrocarbons were employed and high purity He was used as a carrier, and further purified by passage through a charcoal trap kept at liquid N_2 temperature.

The rate of reaction (1) was studied in a flow system which permitted the feeding to the reactor of a mixture of CHA + BE + *BE + He at a total pressure of 1 atm. Separation of the CHA from the BE fraction in samples obtained from the exit stream was accomplished by an in line gas chromatograph. The radioactive content of the hydrocarbon fractions was ascertained by liquid scintillation counting techniques. From this information, the rate coefficient, k_c, for reaction (1) was calculated (*6*), k_c is defined by the rate expression for reaction (1a) (or (1b) or (1)):

$$-\frac{1}{w}\frac{dp_{*\mathrm{BE}}}{dt} = k_c p_{*\mathrm{BE}} - k'_c p_{*\mathrm{CHA}}, \qquad (2)$$

where w is the catalyst weight. Integration and rearrangement of Eq. (2) yields:

$$k_c = \frac{\dot{V}}{wRT}\,\frac{1}{1+\dfrac{1}{\beta}}\,\ln\frac{1}{(1-\alpha)}, \qquad (3)$$

where $\dot{V}$ is the total volumetric flow rate at room temperature and atmospheric pressure and the reaction conversion $\alpha = p_{*\mathrm{CHA}}/(p_{*\mathrm{CHA}})_e = (1+\beta)\delta/\beta$, where the suffix e refers to equilibrium conditions and $\delta = p_{*\mathrm{CHA}}/(p_{*\mathrm{BE}})_0$.

From expression (2) it is clear that generally $k_c = f(\beta)$ where $\beta = (p_{\mathrm{CHA}}/p_{\mathrm{BE}})$. The analytical expression may be formulated (*6*) as

$$k_c = k\beta^{\pm m}, \qquad (4)$$

where k is the reaction rate constant and m = constant over a large range of values of β. The experimental results on the rate of reaction (1) were obtained in the temperature range 200 to 248°C, and $10^{-1} \leq \beta \leq 10^2$. The catalysts were not subjected to hydrogen or oxygen pretreatment. Generally, experimental measurements were carried out after 2 to 3 hr from startup and the catalysts showed constant and reproducible activity for periods of time up to 2 to 3 days of continuing operation.

EXPERIMENTAL RESULTS

From the experimental observations, values of k_c were calculated according to Eq. (3). Typical results at 205°C for Au(2 wt %)–Al_2O_3 are plotted in Fig. 1 as a function of β. The results correspond to $\alpha \sim \leq 25\%$. Similar observations on catalysts supported on MgO are presented in Fig. 2. Results in the temperature range 200 to 248°C on Au (5 wt %)–MgO prepared by chemical reduction are shown in Fig. 3, while in Fig. 4 we report observations on Au (0.7 wt %)–Al_2O_3 obtained from $KAu(CN)_2$. No catalytic activity for reaction (1) was detected on pure Al_2O_3 and MgO at temperatures $\leq$450°C. In all cases, it was possible to fit the experimental results with Eq. (4). However, two main slopes were generally recognized in the logarithmic plots. From the slope of the plots of log k_c versus log β the value of the exponent m in Eq. (4) was determined.

DISCUSSION

The activity of supported Au to catalyze reaction (1) indicates the presence of an interaction between CHA, BE, and Au surfaces at the experimental conditions employed in the reported experiments. It seems reasonable to assume that the preponderant product of this interaction is adsorbed hydrogen, and that hydrogen containing hydrocarbon fragments occur at much lower concentrations and may be neglected in the formulation of the adsorption equilibrium. At the temperature of the experiments the values of β employed corresponded, through the CHA–BE equilibrium [reactions (1a) and (1b)], to $10^{-4} \leq p_{H_2} \leq 10^{-2}$ Torr. It is likely that no bulk compound between Au and H_2 was stable at these conditions and that the interaction studied was confined to the surface layer. The correct formulation of the equilibrium reaction is difficult for lack of independent information on the structure of the Au–H surface layer. We shall assume that the layer contained Au–H groups of variable composition formally expressed by:

$$C_6H_6(g) + \frac{1}{m} AuH_{6m}(s) \rightleftharpoons C_6H_{12}(g) + \frac{1}{m} Au(s), \quad (5)$$

where $0 > m \geq 1$.

For most of the runs the reaction isotherms (Figs. 1 to 4) showed a change of slope at $\beta \approx 3$. It may be speculated that this effect indicates in a rudimentary fashion the presence of sigmoidal isotherms. The values at very low β were difficult to obtain because of experimental difficulties with accurate measurements at low surface coverages. The intermediate portion of the isotherms is linear over a wide range of β's, while the decreasing slope at $\beta \sim >3$ indicates the approaching of surface saturation.

Despite the absence of quantitative information on the adsorbate concentration at the operative surface, it seems reasonable to assume that it was low and that surface saturation did not reflect physical crowding of adsorbate species and the insurgence of lateral interaction effects. Thus, repulsion forces among the adsorbate species do not seem to have played a significant role in the change of the value of m. This is also consistent with the observation that the change in slope of the isotherms is rather insensitive to temperature. These conclusions suggest that the adsorption process resulted in the formation of patchy layers of Au–H compound with a characteristic structure, and that variations in m reflected the stabilization of different structures.

The present results closely parallel those recorded in the past for adsorption isotherms of sulfur on Cu and Ag surfaces, measured with $H_2S + H_2$ mixtures (*7*). These investigations bear great similarity to those of the present work. In both instances, the measurements were obtained under conditions of gas–surface equilibrium and this fact is likely reflected in the structure and properties of the surface layer. As pointed out previously (*8a,b*), for these adsorption isotherms the equilibrium constant and free energy become dependent upon the extent of surface coverage (nonideal adsorption). These observations cannot be easily reconciled with a classical Langmuir surface. Furthermore, Eq. (4) may be considered at first sight an approximation for a Langmuir isotherm in an intermediate pressure range. This, however, requires that m decreases progressively from unity to zero as the pressure increases. This is clearly not the behavior shown by the results reported in Figs. 1 to 4, comprising a pressure range of about three orders of magnitude. A more realistic view is to regard the isotherm underlying Eq. (4) of the general type: $\theta = bp^{m'}/(1 + bp^{m'})$ which describes several dissociative adsorptions.

Application of the mass action expression to equilibrium (5) yields:

$$\frac{[AuH_{6m}]}{[Au(s)]} \propto \left(\frac{p_{CHA}}{p_{BE}}\right)^m. \quad (6)$$

Relation (6) is useful for the discussion of surface behavior under limiting conditions of adsorbate concentration. At low adsorbate concentration $[Au(s)] \cong$ const. From Eq. (6) it follows:

$$[AuH_{6m}] \propto \left(\frac{p_{CHA}}{p_{BE}}\right)^m = \beta^m. \quad (7)$$

For the rate-controlling step for reaction (1) [(1a) or (1b)], we shall neglect, as kinetically significant, reaction steps occurring totally in the adsorbed phase. H atom transfer between adsorbed species could reasonably take place at a faster rate than the adsorption–desorption of BE and CHA, and could not be kinetically distinguishable from the adsorption–desorption process. The rate-controlling step for reaction (1) may then be written as:

$$^*C_6H_6(g) + AuH_{6m}(s) \rightarrow {}^*C_6H_{12m}(s) + Au(s). \quad (8)$$

From Eqs. (7) and (8) the rate of reaction (8) is expressed by:

$$\frac{dp_{^*\mathrm{CHA}}}{dt} = k_c p_{^*\mathrm{BE}} = k''[AuH_{6m}]p_{^*\mathrm{BE}} = k\beta^m p_{^*\mathrm{BE}}. \quad (9)$$

Equation (9) is consistent with the experimental results (Figs. 1 to 4).

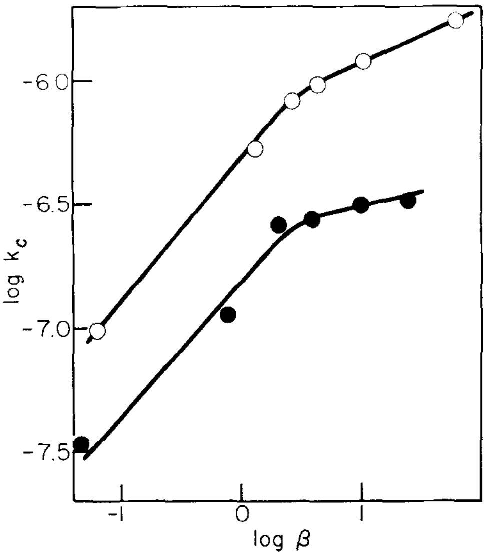

FIG. 1. k_c versus β for reaction (1) catalyzed by Au(2 wt %)-Al_2O_3 prepared by: chemical reduction ○; thermal decomposition ●; 205°C.

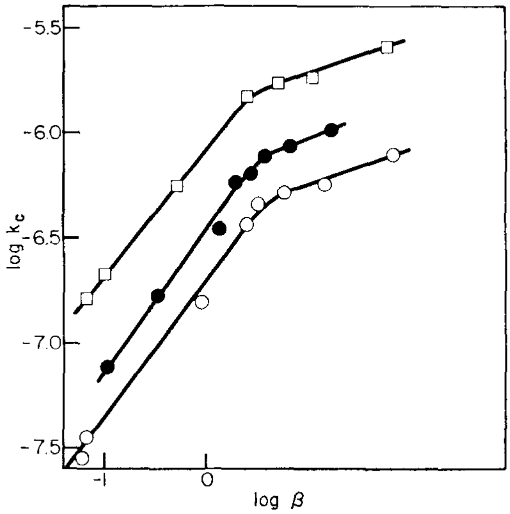

FIG. 2. k_c versus β for reaction (1) catalyzed by Au-MgO prepared by chemical reduction: 0.3wt % Au ○; 0.7 wt % Au ●; 233°C. 2.0 wt % Au prepared by thermal decomposition, 205°C □.

The electronic conditions of the Au-H bond are difficult to visualize correctly. However, it is conceivable to regard the value of the coefficient m in Eqs. (4) and (7) as an indication of the nature of the surface bonding. Values of m close to 1 correspond to higher H/Au ratios and suggest a weak, delocalized and, possibly, mobile adsorbate, and conversely for values of m close to zero. It was hoped to check

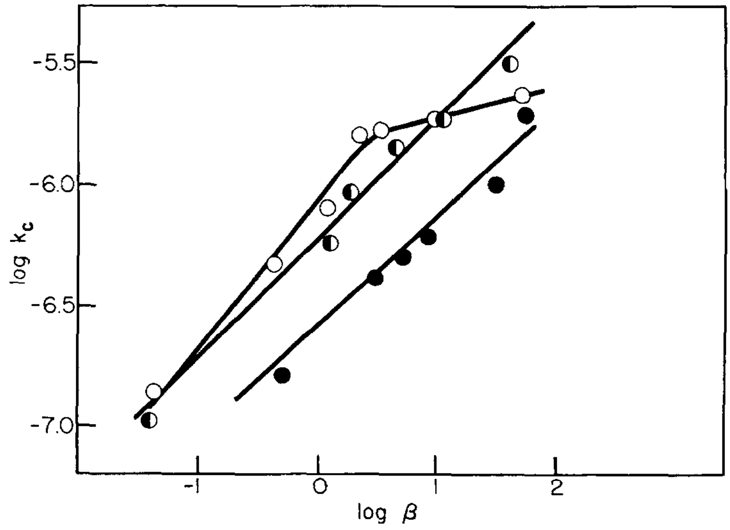

FIG. 3. k_c versus β for reaction (1) catalyzed by Au(5 wt %)-MgO prepared by chemical reduction: 200°C ○; 235°C ●; 248°C ◐.

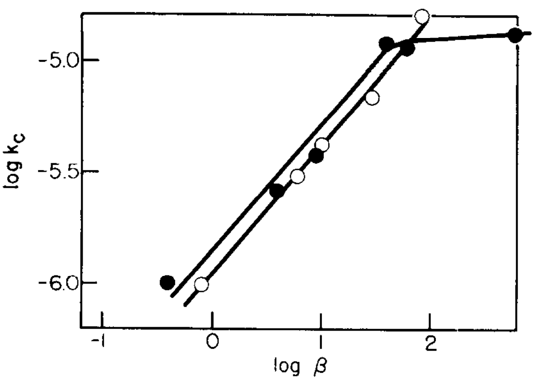

FIG. 4. k_c versus β for reaction (1) catalyzed by Au (0.7 wt %)–Al_2O_3, prepared by chemical reduction of $KAu(CN)_2$: 150°C ○; 233°C ●.

this suggestion by studying the temperature dependence of m. In fact, it was reasoned that if the relation between m and surface bond strength is valid, one would expect $dm/dt > 0$. The experimental results, however, were not too illuminating since little temperature variation for m was found between 200 and 250°C and no definite conclusions could be reached.

From the experimental results, it is possible to derive the influence upon k and m of: (a) the nature of the catalyst support, (b) the method of catalyst preparation, and (c) the concentration of Au. The results on the effect of the support upon m and k are reported in Table 2.

For $\beta \sim <3$, $0.10 \leq m \leq 0.22$ indicating that the surface groups contained on the average 1 H atom/surface Au atom. The hydrogen content of the surface increased by preparing the catalysts by chemical reduction and, to a lesser extent, by substituting MgO to Al_2O_3 as a catalyst support. For $\beta \sim >3$, $0.54 \leq m \leq 0.60$. Differences between supports and preparative procedures are less traceable in this range of β's: on the average 3.5 H atoms/Au surface atom is calculated in all catalysts tested. The effects underlying the results of Table 2 indicate the existence of a coupling between metal and substrate that modify the properties of the metal at the surface. Although the effects are not too large it is remarkable that they take place between two of the most inert materials: MgO and Au. This is a significant conclusion, which should be viewed in the light of recent results obtained from Mössbauer spectroscopy of Au–Al_2O_3 catalysts (*9*). These studies indicated a modification in the *s*-electron density at the Au nucleus by conditions arising from the state of Au atoms in the Al_2O_3 matrix, and suggesting an interaction between the latter and the *d*-electrons of the Au shell.

TABLE 2

INFLUENCE OF CATALYST SUPPORT AND CATALYST PREPARATION UPON m AND k [Eq. (4)] FOR REACTION (1) CATALYZED BY SUPPORTED Au (2 wt %), 205°C

Catalyst			k^a [mole/ g(cat)sec] × 10^6
Support	Preparation method	m	
Al_2O_3	Thermal decomposition	0.10–0.54	1.6
Al_2O_3	Chemical reduction	0.22–0.56	4.6
MgO	Thermal decomposition	0.13–0.61	8.3

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[a] Referred to unit weight of total catalyst (Au + support).

The effect of Au concentration on the values of k and m for catalysts supported on MgO, prepared by chemical reduction, and tested at 235°C is reported in Table 3.

TABLE 3

INFLUENCE UPON m AND k [Eq. (4)] OF THE Au CONCENTRATION IN Au–MgO CATALYSTS FOR REACTION (1), 235°C

Au (wt %)	m	k [moles/ g(cat)sec] × 10^6	k' [moles/ g(Au)sec] × 10^4
0.3	0.15–0.66	1.82	6.0
0.7	0.19–0.65	3.32	4.7
5.0	0.44	2.50	0.5

The results of Table 3 do not indicate an appreciable influence of the size of the Au particles upon the value of m. A similar result was also obtained for Pt particles up to particle size of ~800 Å (*6*).

The values of k reported in Table 3 may be employed to ascertain whether kinetic effects originating from the extent of metal surface area per unit weight of metal were present. To this end a relation between metal particle size and molecular mean free path will be utilized (*1*). Consider a spherical metal particle of radius r surrounded by a spherical volume element, V_λ, of radius equal to the gas mean free path λ. This element statistically defines all gas molecules that experiment collisions with the particle surface. Thus this volume indicates the gas phase collisional contribution to the reaction rate, while r that of the particle surface area, since the latter is inversely proportional to r. For $\lambda/r \ll 1$ modification of r will not greatly influence the ratio V_λ/r and if an effect of r upon the specific rate of the surface interaction is present, it will not be easily detected. Conversely, if the effect is present, it will be detected for $\lambda/r \gg 1$. The quantitative relation derived previously (*1*) between V_λ, λ, and r is the following:

$$\frac{V_\lambda}{r} = \frac{\lambda}{r} + \left(\frac{\lambda}{r}\right)^2 + \frac{1}{3}\left(\frac{\lambda}{r}\right)^3. \qquad (10)$$

According to the definition of V_λ, the reaction rate constant per unit weight of Au, k', is αV_λ, and Eq. (10) may be used to derive the differential ratio $\partial \ln k'/\partial \ln r = n$.

If the experimental conditions are such that $\lambda/r \ll 1$ and a surface effect is absent, then $n = -1$. Conversely, if it is found $n < -1$, a specific surface influence upon the rate constant is present. To obtain the numerical values of n predicted by the model as a function of r at constant λ, Eq. (10) is differentiated. The result is:

$$n = -\frac{1 + 2\left(\frac{\lambda}{r}\right) + \left(\frac{\lambda}{r}\right)^2}{1 + \left(\frac{\lambda}{r}\right) + \frac{1}{3}\left(\frac{\lambda}{r}\right)^2}. \qquad (11)$$

Equation (11) has been plotted in Fig. 5. The value of the molecular mean free path at 235°C and $p_{\mathrm{BE}} \cong 0.26$ atm is $\approx$1.200 Å. Thus, the experimental results are broadly in the range of $\lambda/r = 30$. Since λ is significantly larger than r, if specific surface effects were present they could be detected and should yield a value of $n \cong -2.90$ (Fig. 5). The values of the logarithm of k' (Table 3) have been plotted in Fig. 6 against the logarithm of the corresponding diameter of the Au particles (Table 1). The slope of the straight line through the points is -2.80. Although the close agreement may be fortuitous, it points to two conclusions. First, *it indicates* that a significant influence of the surface was present in the reported experiments. In previous observations on reaction (1) at Pt surfaces, no large surface effect was detected (*6*). It must be realized, however, that the latter experiments were carried out under experimental conditions for which $\lambda/r \cong 4$. Thus,

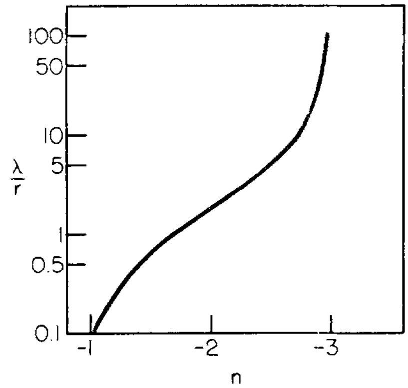

FIG. 5. Plot of $\partial \ln k'/\partial \ln r = n$ as a function of λ/r according to Eq. (11). λ, molecular mean free path (Å); r, diameter of Au particles (Å).

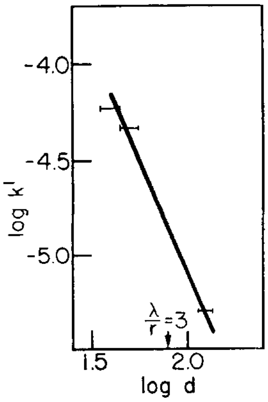

FIG. 6. Plot of log k' versus log d for reaction (1) catalyzed by Au–MgO at 235°C. k', reaction rate constant per unit Au weight; d, diameter of Au particles.

a valid comparison between the results on Au and those on Pt cannot be made unless the results on Pt are taken under a λ/r ratio sufficiently higher than 1. It seems, then, that claims about the presence or absence of a surface effect can only be validly demonstrated under experimental conditions of correct ratio between particle size and molecular free path. In typical investigations on hydrocarbons (molecular diameter ≈ 7 Å) carried out at 200°C and partial pressure of reactant of ~ 0.5 atm over supported metal particles with $r = 40$ Å, the ratio $\lambda/r \cong 14$. In this range the effect may not be easily detected. Despite the lack of sophistication of the model employed and the neglect of several complicating factors (entrainment of metal particles into the matrix, overlapping of critical volumes) the derived relation between λ and r may serve as a useful guide for the discussion of specific surface effects of supported metal catalysts.

The influence of temperature upon the reaction rate was investigated with the catalyst Au(5 wt %)–MgO. In the temperature range 200 to 248°C there was little influence of temperature. A similar effect was previously recorded for supported Pt. Formally, this result shows that $E \cong -\Delta H$ where E is the true activation energy and ΔH the adsorption heat. It is interesting to recall that for the H_2–D_2 exchange reaction on Au wire an apparent activation energy of 7.0 kcal/mole was found (*3*), while on Au foil the value was 13.9 kcal/mole (*2a*).

CONCLUSIONS

It is instructive to compare the surface reactivity of finely dispersed Au for hydrogen, as reported here, with that for oxygen deduced from studies on the oxygen transfer between CO and CO_2 (*1*). In both researches, the individual transfer step between the donor–acceptor couple and the Au surface was studied under conditions of or approaching that of chemical equilibrium. For both oxygen and hydrogen transfers, Au showed measurable activity in the temperature range 200–350°C, and in both cases rate constants of the order of (1 to 10) 10^{-6} [mole/g(Au)sec] were calculated. The two transfer steps, however, had a large difference in the apparent activation energy: ~ 24 kcal/mole for oxygen and ~ 0 for hydrogen. This is related to the variation in affinity of the surface for oxygen and for hydrogen, and to the different energy of the C–O bond in CO_2 and C–H bond in CHA.

Taking into consideration variations in the surface area of Au particles among preparations, there was not a large effect on the reaction rate by the preparation procedure and support; while a specific surface effect was found present in the case of hydrogen for which the rate of reaction was dependent upon the available area per gram of metal. This result was obtained under conditions such that the molecular mean free path was large in comparison to the particle diameter.

Summing up, considerable reactivity towards CO–CO_2 and C_6H_6–C_6H_{12} mixtures can be developed at the surface of Au dispersed upon MgO and Al_2O_3, and this reactivity may be higher than that corresponding to the interaction of Au with molecular O_2 and H_2.

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