JOURNAL OF CATALYSIS 2, 149–151 (1963)

NOTE

Enhancement of Catalytic Properties of Gold for H_2–D_2 Exchange

In spite of the numerous investigations of the isotopic exchange of hydrogen on metallic surfaces (*1–4*) the mechanism of this reaction has not been established unequivocally. As pointed out by Sachtler and DeBoer (*5*), the role of chemisorption in the catalyzed H_2–D_2 exchange reaction may be elucidated by selecting gold as the catalytic surface. The activation energy is relatively high for dissociative chemisorption of hydrogen on gold. However, the energy barrier may be circumvented by exposing the solid to atomic hydrogen (*6*).

In our experiments a comparison was made between the rate of hydrogen–deuterium exchange on a gold surface previously exposed to atomic hydrogen ("treated" surface) and a similar surface not treated in this manner. Equimolar mixtures of H_2 and D_2 were employed in contact with gold foil* (with an estimated geometric surface area of 500 cm^2/g). Three pieces of foil weighing a total of 24 mg were placed in each of four Pyrex reaction vessels, consisting of a bulb with a volume of about 10 cc, and provided with a stopcock at one end. The same gold samples were used throughout the study. Initially the bulbs containing the foil were heated to about 600°K and evacuated to a pressure less than 10^{-6} mm Hg (diffusion pump and liquid nitrogen trap) for about 3 hr. The bulbs were filled with hydrogen to a total pressure of 70×10^{-3} mm Hg at room temperature. In two of the reaction vessels an electrodeless discharge was excited by means of a 14 mc r.f. field for a period of 2 hr. Two additional reaction vessels were used for control experiments. Subsequently all four reactors were evacuated, the H_2–D_2 mixture (1:1) admitted at a total pressure of about 40 mm Hg, and the whole assembly placed in a furnace preheated to temperatures from 300° to 575°K. After a suitable reaction time (*7*) (15 min to 16 hr) the product gas was analyzed for HD by means of a mass spectrograph. The results were corrected for the amount of HD found in the original gas mixture which amounted to 0.4% by volume.

The rates of production of HD in the presence of gold as a function of temperature are summarized in Fig. 1. Circles denote the results obtained for the gold surfaces exposed to atomic hydrogen, preceding the exchange experiments, while squares indicate the reference experiment with untreated gold. For the exchange reaction on untreated gold the data may be represented by a curve with an activation energy of $E_1 = 21.5$ kcal/mole, while for the treated gold at $T < 450°K$ an activation energy of $E_2 = 11.0$ kcal/mole is observed (Fig. 1).

To ascertain whether the production of a chemisorbed layer of hydrogen is responsi-

TABLE 1
H_2–D_2 EXCHANGE KINETICS AT 520°K

Condition	Volume % HD/hr
Pyrex glass	2.5 ± 0.5
Gold	8.7 ± 1.4
Gold in argon plasma	10.8 ± 0.2
Gold + hydrogen plasma	26.8 ± 5.0
Gold + hydrogen plasma, followed by heating in vacuum at 615°K for 3 hr	11.8 ± 2.1

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* Cohesive Gold, Handy and Harmon, El Monte, Calif., 99.99% Au.

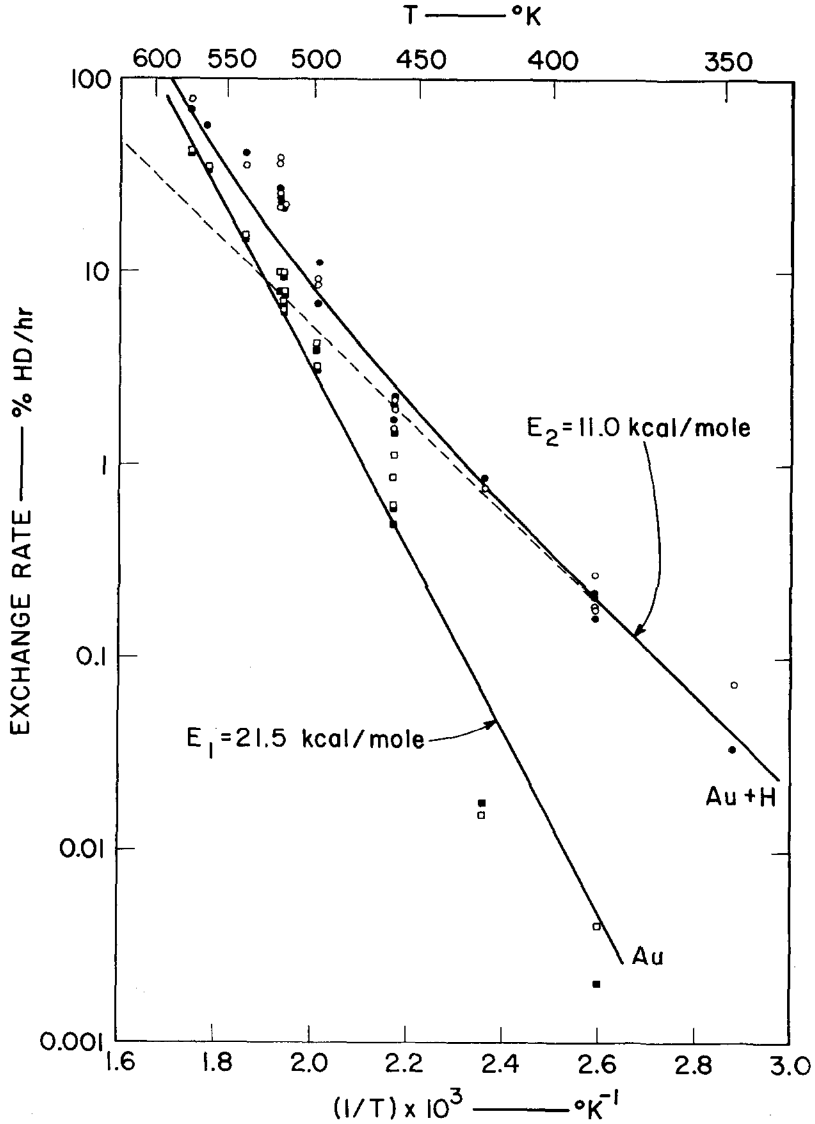

FIG. 1. H_2–D_2 exchange rate on gold as a function of temperature.

ble for this enhanced catalytic activity of gold, several additional experiments were performed. These results are summarized in Table 1. It is apparent that at the temperatures studied the activity of the gold surfaces for the H_2–D_2 exchange reaction is enhanced as a consequence of exposure of the solid to the hydrogen plasma. The fact that an argon plasma does not alter the exchange rate (Table 1) argues against an increased activity due to removal of surface impurities or production of active surface sites as found to occur from bombardment with argon ions (*8*). Furthermore, vacuum heating of a gold surface, previously exposed to the hydrogen plasma, might be expected to clean the gold surface and hence increase the exchange rate. Instead, the rate was decreased due to apparent removal of the chemisorbed layer of hydrogen.*

One may conclude that the exchange re-

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* The fact that chemisorbed hydrogen is so readily removable from a gold surface suggests an endothermic heat of adsorption for this noble metal.

action associated with the low activation energy may proceed by the Rideal-Eley mechanism if the surface is provided with hydrogen adatoms by exposure to the gaseous discharge in hydrogen. However, simultaneously another heterogeneous reaction of higher activation energy takes place which predominates at temperatures in excess of 450°K and which may proceed by some other mechanism, such as the one postulated by Bonhoeffer-Farkas. Indeed, the upper curve shown (Fig. 1) represents the sum of the two exchange rates observed for untreated gold and treated gold.

These results differ from those published in ref. 5 in which was postulated the formation of a chemisorbed layer of hydrogen during the heterogeneous decomposition of formic acid on gold, and in which formation of no HD was observed when D_2 was added to HCOOH during the decomposition. Further experiments are in progress to elucidate in more detail the role of chemisorbed hydrogen on the kinetics of isotopic exchange reactions.

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Received January 10, 1963