JOURNAL OF CATALYSIS 13, 397–403 (1969)

Isomerization and Dehydrogenation of Butene Catalyzed by Noble Metals and Their Alloys*

S. HENRY INAMI, BERNARD J. WOOD, AND HENRY WISE

From the Solid-State Catalysis Laboratory, Stanford Research Institute,
Menlo Park, California 94025

Received October 11, 1968; revised November 18, 1968

Isomerization and dehydrogenation of butene have been studied on metal catalysts composed of palladium, gold, and their alloys. The isomerization of 1-butene to 2-butene was found to be catalyzed by gold at temperatures of 300° and 400°C in the absence of added hydrogen. In the presence of added hydrogen, some isomerization activity was exhibited also by palladium and palladium-gold alloys. The addition of small quantities of oxygen, however, completely suppressed the isomerization process and led to the formation of butadiene on catalysts containing up to 60 atom % gold. Results of measurements on a hydrogen-porous metal membrane indicate that the rate of isomerization is faster than that of hydrogenation and that both processes depend on the surface density of hydrogen atoms. As a primary step in the isomerization process, the addition of a hydrogen atom is proposed, followed by hydrogen abstraction.

INTRODUCTION

For elucidation of the influence of the solid state on the surface reactivity of metals, the properties of alloys of metals in Groups VIII and IB in the periodic table have been of considerable interest in catalytic research. Studies employing such systems have been concerned principally with hydrogenation of various unsaturated hydrocarbons (*1*). In general the data suggest enhanced or sustained specific activity with the addition of the Group IB metal up to a concentration of 30 to 50 atom % in the alloy and marked changes in the activation energy at alloy compositions corresponding to a filled *d* band (*2–6*). We extended these studies to reactions other than hydrogenation by investigating the isomerization and dehydrogenation of 1-butene catalyzed by palladium, gold, and their alloys.

EXPERIMENTAL DETAILS

The pure metals and their alloys employed in our studies were in the form of microspheres† with a particle diameter range of 44 to 53 μ. The lattice spacings of these alloys as a function of gold content were determined by X-ray diffraction, and the values were in agreement with those reported by Maeland and Flanagan (*7*) (Table 1). A series of analyses with the aid

TABLE 1
LATTICE PARAMETERS OF Pd/Au ALLOYS

Composition (at. % Au)	Lattice parameter, a_0 (Å)	
	Measured	Ref. (7)
0	3.895	3.890
19.5	3.931	3.927
39.5	3.967	3.965
59.5	4.004	4.002
100	4.078	4.078

---

* This work was carried out under the sponsorship of several industrial companies whose support is gratefully acknowledged.

† Microspheres were furnished by Engelhard Industries, Inc., Newark, New Jersey.

TABLE 2
YIELD OF BUTADIENE FROM 1-BUTENE AT 300° AND 400°C

	Butadiene yield[a] (% conversion/g catalyst)									
Catalyst comp. (at. % Pd):	100		80		60		40		0	
Aliquot No.	300°	400°	300°	400°	300°	400°	300°	400°	300°	400°
1	4.5	10.3	4.0	8.0	5.3	—	4.9	9.4	0.8	5.6
2	3.5	6.6	1.5	4.4	1.5	—	3.6	7.0	0.6	4.5
3	2.0	4.9	1.2	3.1	—	—	3.2	4.8	0.6	4.2
4	—	—	—	2.3	—	—	3.5	4.6	—	—
5	—	—	—	1.9	—	—	—	—	—	—
Surface area[b] (cm^2/g)	139		110		102		110		85	

[a] Per pass conversion.
[b] By BET measurement.

of an electron microprobe analyzer suggested little variation from the specified alloy composition.* In addition, surface areas of the catalyst were determined by the BET technique using krypton sorption.

For the catalytic studies the apparatus consisted of a microreactor system (*8*) which permitted injection of aliquots of reactants diluted by He gas. The helium carrier gas flowed at a rate of 60 cc NTP/min in sequence through a multiport injection valve, (Model L-208, Loenco, Inc., Altadena, California), the catalyst bed (contained in a glass reactor), and the gas chromatograph column and detector. The reactant gas mixture (1-butene or 1-butene with added hydrogen or oxygen) flowed through a sample loop (volume of 0.3 to 0.8 cc) connected to the injection valve. When desired, the main carrier gas could be diverted to sweep the reactants contained in the loop into the reactor. The reactor efflux was analyzed by the gas chromatograph, which consisted of a 25-ft column of a 20–80 mixture of 20% diethyl sebacate and 20% bis(methoxyethyl) adipate supported on Chromosorb W (*9*), with a thermistor thermal conductivity cell detector. The absolute pressure in the microreactor during catalysis was 2 atm. Under our experimental conditions the total pressure and the volume of the reactant aliquot passing over the catalyst were kept constant. Consequently the addition of hydrogen or oxygen was accompanied by an equivalent decrease in the volume of 1-butene.

The catalyst (1 g of microspheres) was placed in the cylindrical glass reactor on top of a glass frit and was usually pretreated at reaction temperatures of 300° or 400°C in a stream of oxygen at 1 atm for approximately 1 hr. In some instances it was necessary to preheat the gold sample in oxygen at a temperature of 400°C or greater to activate the catalyst. The reactor was subsequently flushed with helium for a minimum of 0.5 hr at the pretreatment temperature. Control experiments indicated that the empty glass reactor exhibited no catalytic activity under our experimental conditions.

EXPERIMENTAL RESULTS

Three experimental conditions were explored in our catalytic studies with microspheres: (1) the reaction of 1-butene; (2) the reaction of 1-butene in the presence of hydrogen; and (3) the reaction of 1-butene in the presence of oxygen. The behavior of butenes and hydrogen in the presence of a palladium-silver alloy membrane was also investigated, to provide additional insight into the mechanism of isomerization on metal catalysts.

---

* We are grateful to the Applied Research Laboratories of Glendale, California, for supplying these analyses. For the sample examined the nominal composition of the alloy was 55.5 Pd/44.5 Au (in atom %), as compared to 53.5 Pd/46.5 Au by microprobe analysis.

TABLE 3
ISOMERIZATION OF 1-BUTENE TO 2-BUTENE AT 300°C (H_2/1-BUTENE = 1)

Catalyst comp. (at. % Pd):	2-Butene yield[a] (% conversion/g catalyst)			
Aliquot No.	100	60	40	0[b]
1	40	58	73	45
2	24	49	72	51
3	16	—	71	49
4	14	26	61	47
5	11	19	61	39
6	9	—	56	43
7	7	—	—	—
Surface Area[c] (cm^2/g)	139	102	110	85

[a] Per pass conversion.
[b] For Au catalyst H_2/1-Butene ~0.6.
[c] By BET measurement.

Reaction of 1-butene. In the absence of any additional gases, palladium and all alloys containing Pd favored dehydrogenation of 1-butene with butadiene as the primary product. However, the amount of butadiene formed diminished with each subsequent aliquot of reactant passed over the catalyst in the microreactor (Table 2). Most likely the initially high dehydrogenation activity was associated with the existence of an oxide layer formed during the pretreatment in oxygen.

On the other hand, pure gold exhibited pronounced isomerization rather than dehydrogenation activity. Thus we observed conversion of 1-butene to 2-butene (cis and trans isomers in equilibrium ratio) to the extent of 19% to 27% at 300°C without any significant diminution in rate during a series of exposures.

Reaction of 1-butene in the presence of hydrogen. When the sample entering the microreactor was composed of 1-butene to which small amounts of hydrogen had been added, the pure metals and their alloys exhibited isomerization activity at 300°C. But this activity was sustained only for pure gold and for the alloy containing 60 atom % Au. The degree of isomerization and stability of the catalysts are shown in

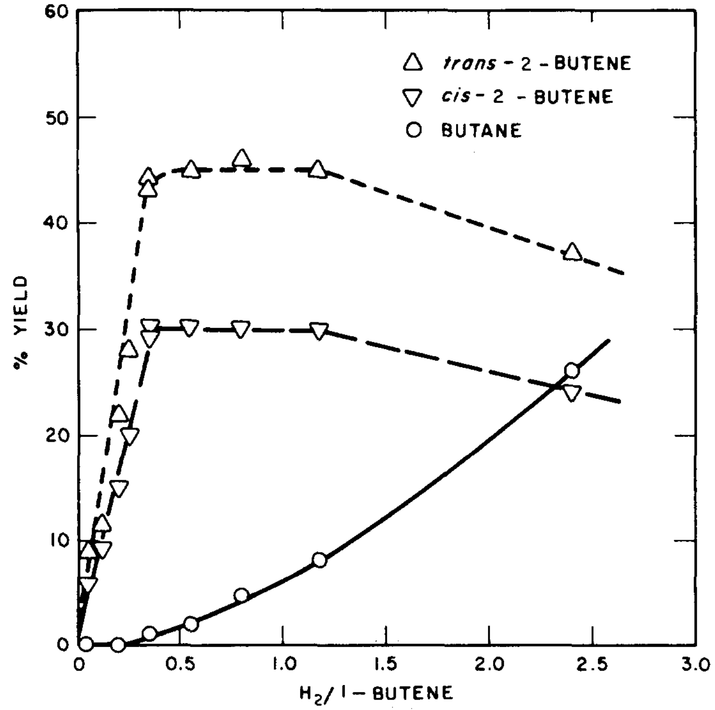

FIG. 1. Hydrogen dependence of isomerization and hydrogenation of 1-butene on 40 Pd/60 Au (atom percent) alloy catalyst.

Table 3. Of special interest is the catalytic activity of the alloy containing 60 atom % gold. As can be seen from the data presented in Fig. 1 this catalyst exhibited high isomerization activity in the presence of small concentrations of added hydrogen. As a matter of fact at a ratio $H_2/C_4H_8 = 0.3$ the isomer yield for this alloy exceeded by almost a factor of 2 that observed for pure gold. At higher relative hydrogen concentrations this catalyst favored the formation of butane (Fig. 1), in contrast to all the other catalysts examined, including 100 Pd, 80 Pd/20 Au, 60 Pd/40 Au, and 100 Au. For the Pd-containing catalysts this lack of ability to hydrogenate the olefin is undoubtedly due to the high absorption rate of hydrogen into the bulk of the microspheres.

Reaction of 1-butene in the presence of oxygen. The addition of small amounts of oxygen to the butene completely eliminated isomerization activity. The reaction products were butadiene, carbon dioxide, and water. The results of the oxidation and oxidative dehydrogenation of 1-butene as a function of gold content at a ratio of O_2/1-butene = 1 are summarized in Table 4. The data show that the specificity for butadiene formation is markedly enhanced by the presence of gold in the alloy catalyst.

TABLE 4

OXIDATION AND OXIDATIVE DEHYDROGENATION OF 1-BUTENE (O_2/1-BUTENE = 1)

Catalyst composition (atom % Pd)	Catalyst surface area[a] (cm²/g)	% C_4H_8 Converted[b]		C_4H_6/CO_2 (mole ratio)	
		300°C	400°C	300°C	400°C
100	139	14.0	24.0	0.23	0.18
80	110	12.0	21.0	0.25	0.23
60	102	8.4	20.0	0.63	0.25
40	110	5.6	17.6	0.63	0.24
0	85	3.6	14.0	0.31	0.10

[a] By BET measurement.

[b] Per pass per gram of catalyst.

Experiments with palladium-silver membrane catalyst. The preceding studies were complemented by two experiments on a catalyst that differed both in composition and form from the microspheres, but that permitted the role of sorbed hydrogen in the butene isomerization reaction to be evaluated. Such a catalyst is a hydrogen-porous membrane* situated in a reactor so that hydrogen can be supplied to or removed from the catalytic surface by diffusion through the body of the metal.

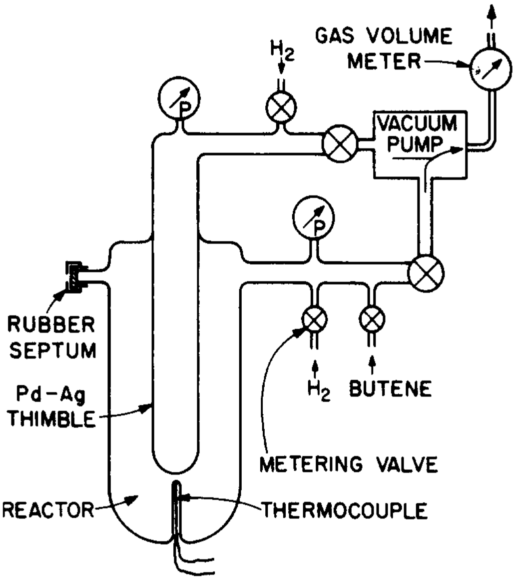

FIG. 2. Schematic diagram of apparatus with hydrogen-porous membrane catalyst.

The apparatus, which is similar to that used in an earlier study (*10*), is shown in Fig. 2. The butene isomer is admitted to the reactor, which is heated to 300°C by a surrounding furnace. Under these conditions, even with the interior of the palladium-silver alloy thimble evacuated, both 1-butene and *trans*-2-butene are perfectly stable for at least several hours. (The contents of the reactor are sampled with a gas-tight syringe, inserted through the rubber septum, and are analyzed by gas chromatography.)

When hydrogen is supplied to the catalytic surface by admitting the gas to the interior of the thimble to a pressure of 1 atm, the butene in the reactor begins to react rapidly. The effect of supplying, and later removing, hydrogen from the reactor by way of diffusion through the membrane

---

* Palladium-silver hydrogen purification alloy supplied by J. Bishop & Co., Malvern, Pennsylvania.

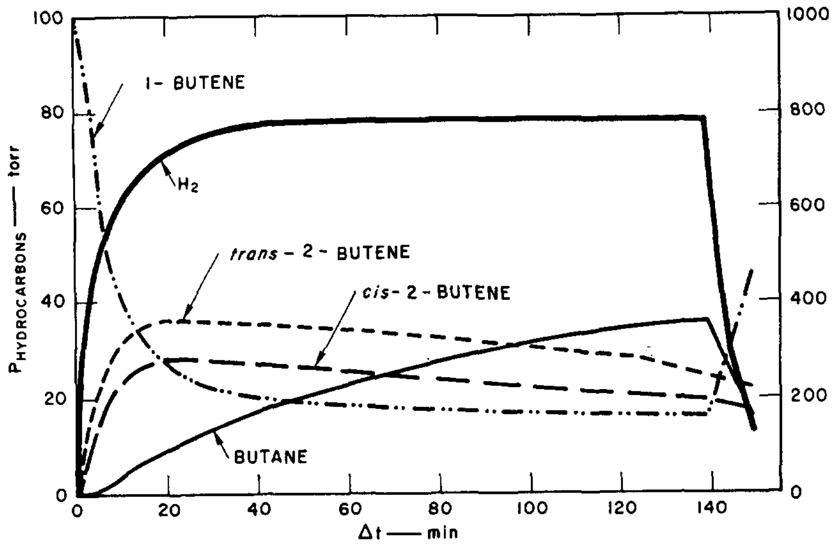

Fig. 3. Reactions of 1-butene and hydrogen on Pd-Ag alloy membrane at 330°C.

is shown in Fig. 3 for 1-butene and in Fig. 4 for *trans*-2-butene.

The data displayed in Figs. 3 and 4 show clearly that when a small quantity of hydrogen is supplied to the catalyst surface, isomerization proceeds rapidly relative to hydrogenation. As the hydrogen pressure increases, however, the hydrogenation reaction overtakes the isomerization reactions and becomes dominant. In a steady-state experiment, in which hydrogen was supplied to the reactor through a metering valve at the same rate as it was pumped out through the membrane, it was established that hydrogenation commenced when the hydrogen pressure exceeded 400 torr.

Removal of hydrogen by diffusion through the membrane results in rapid dehydrogenation of butane, but when all hydrogen has been removed, the composition of the reactor remains "frozen." Once this state has been attained, the catalyst is totally inactive. Indeed, it behaves as if poisoned, for even the addition of hydrogen to the reactor through the metering valve will not restore activity. The catalyst can be regenerated only by diffusing hydrogen onto the catalyst surface through the mem-

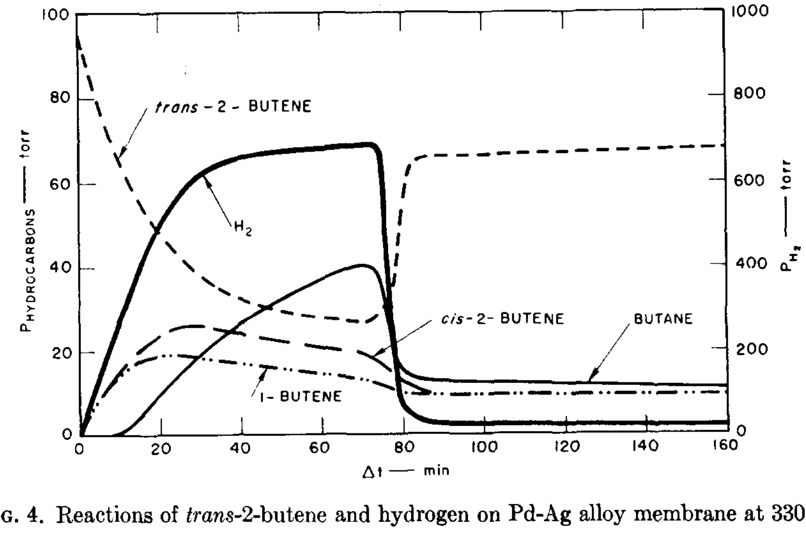

Fig. 4. Reactions of *trans*-2-butene and hydrogen on Pd-Ag alloy membrane at 330°C.

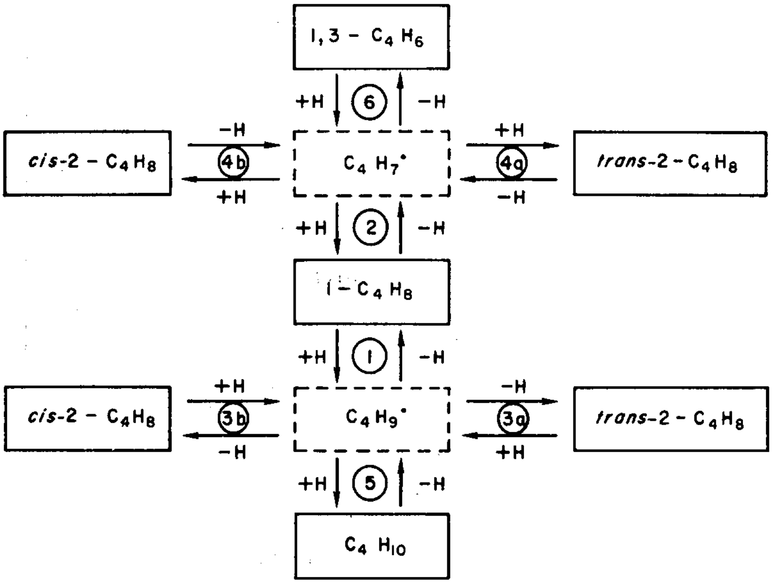

FIG. 5. Reaction mechanisms for 1-butene.

brane. Presumably the olefins sorb on the catalyst surface so strongly that they prevent chemisorption of hydrogen from the gas phase.

DISCUSSION

The experimental results obtained in our measurements offer some insight into the mechanism of catalysis by transition and nontransition metals. In recent years the evidence has been growing that metal surfaces can catalyze nonskeletal isomerization. In particular, Wells and co-workers (*11, 12*) investigated the butene isomer distribution in the hydrogenation of 1,3-butadiene and in the isomerization of 1-butene catalyzed by cobalt. It has been generally accepted that a free-radical mechanism is operative in the presence of a metal catalyst. Basically, the course of the reaction—isomerization, dehydrogenation, or hydrogenation—may be interpreted in terms of chemisorbed hydrogen as the critical intermediate whose lifetime on the solid surface may be governed by such competing processes as abstraction, addition, recombination, and absorption. In Fig. 5 we have shown schematically the various reactions that may be operative in the processes of interest to our study. Note that the isomerization of 1-butene to 2-butene may be formulated by two reaction mechanisms (*13*). The first is an initial hydrogen addition step followed by hydrogen abstraction ("addition–abstraction"), and the second is an initial hydrogen abstraction step followed by hydrogen addition ("abstraction–addition").

All the evidence derived from our measurements points to the "addition–abstraction" mechanism for isomerization and hydrogenation (i.e., steps 1, 3, and 5 in Fig. 5). The onset of isomerization with the transfer of hydrogen through the metal membrane, the promoting effect of small added quantities of hydrogen in the case of the metal microspheres, and the inhibition of catalytic isomerization by small amounts of oxygen [as observed also for cobalt catalyst (*12*)], all indicate the essential role played by chemisorbed hydrogen. Of special interest is the observation that gold in the absence of added hydrogen is able to isomerize 1-butene. On the basis of the foregoing argument we are led to conclude that under our experimental conditions gold is capable of dissociative adsorption of the olefin molecule, thereby providing the chemisorbed hydrogen required for isomerization. Actually, traces of butadiene were

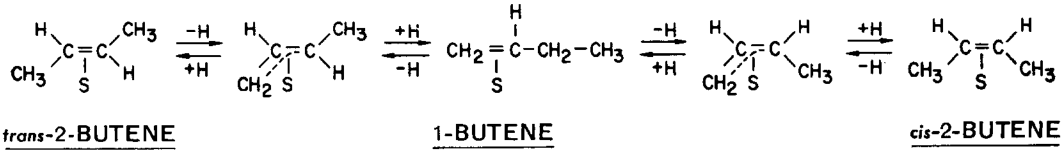

FIG. 6. Butene isomerization by way of π-allylic intermediate.

observed by gas chromatographic analysis among the products resulting from the isomerization of 1-butene on gold. In terms of hydrogen abstraction, the transition metals (such as palladium and the palladium-rich alloys) have properties similar to that of gold. But the difference is to be found in the degree of bonding of the radical formed. In the case of gold a weakly bound intermediate leads to sustained isomerization activity, while in the case of palladium the more strongly bound olefin or intermediate resulting from hydrogen abstraction results in progressive self-poisoning of the surface. In addition, the solubility of hydrogen in palladium causes loss of available surface hydrogen by diffusion into the bulk of the metal catalyst. For the 40 Pd/60 Au alloy, the much lower solubility of hydrogen leads to stable isomerization activity, since bulk absorption ceases to compete for the surface hydrogen.

Further evidence for the "addition–abstraction" mechanism is present in the results obtained with *trans*-2-butene as a starting material in the membrane experiments (Fig. 4). It has been suggested that dissociative adsorption of the monoolefin leads to a π-allylic intermediate (*11, 14*). A consequence of this mechanism is the requirement that the formation of *cis*-2-butene-2 from *trans*-2-butene proceeds by way of 1-butene, as shown by the series of steps given in Fig. 6. Our data (Fig. 4) indicate the simultaneous, rather than sequential, formation of 1-butene and *cis*-2-butene, as would be expected on the basis of the "addition-abstraction" mechanism.

It is of interest that, based on the results of our experimental studies, the non-transition-metal gold exhibits catalytic properties for isomerization superior to those of a transition metal such as palladium.

ACKNOWLEDGMENT

The authors express appreciation to Dr. Hans Gruber for the BET surface area measurements.

REFERENCES

1. BOND, G. C., "Catalysis by Metals." Academic Press, New York, 1962.
2. BOND, G. C., AND MANN, R. S., *J. Chem. Soc.*, p. 3566 (1959).
3. KOWAKA, M., *Nippon Kinozoku Gakkai-si* **23,** 655 (1959).
4. COUPER, A., AND ELEY, D. D., *Discussions Faraday Soc.* **8,** 172 (1950).
5. HALL, W. K., AND EMMETT, P. H., *J. Phys. Chem.* **62,** 816 (1958).
6. CADENHEAD, D. A., AND MASSE, N. G., *J. Phys. Chem.* **70,** 3558 (1966).
7. MAELAND, A., AND FLANAGAN, T. B., *Can. J. Phys.* **42,** 2364 (1964).
8. HALL, W. K., AND EMMETT, P. H., *J. Am. Chem. Soc.* **79,** 2091 (1957).
9. GOLDEN, D. M., EGGER, K. W., AND BENSON, S. W., *J. Am. Chem. Soc.* **86,** 5416 (1964).
10. WOOD, B. J., *J. Catalysis,* in press.
11. WELLS, P. B., AND WILSON, G. R., *Discussions Faraday Soc.* **41,** 237 (1966).
12. JOICE, B. J., ROONEY, J. J., WELLS, P. B., AND WILSON, G. R., *Discussions Faraday Soc.* **41,** 233 (1966).
13. PHILLIPSON, J. J., AND WELLS, P. B., *Proc. Chem. Soc.* (*London*) p. 222 (1964).
14. GAULT, F. G., ROONEY, J. J., AND KEMBALL, C., *J. Catalysis* **1,** 255 (1962).