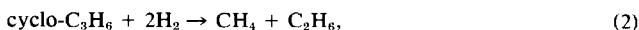
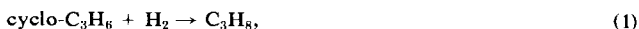


Cyclopropane Hydrogenation on Ru and Ru-Au Catalysts

S. GALVAGNO,¹ J. SCHWANK, AND G. PARRAVANO²*Department of Chemical Engineering, University of Michigan, Ann Arbor, Michigan 48109*

Received March 30, 1979; revised July 23, 1979

The rate of reaction between cyclopropane and hydrogen was measured in a flow system on unsupported Ru, Ru/SiO₂, and Ru/MgO. The effect of the addition of Au to Ru/MgO was also investigated. The temperature was in the range 30–170°C; partial pressures were 0.01 ≤ P_{cp} ≤ 0.1 atm, 0.1 ≤ P_{H₂} ≤ 0.5 atm; and total pressure was 1 atm. The reaction proceeded via three different routes, namely:



At low temperatures (<110°C), only reactions (1) and (2) took place. At higher temperatures (>110°C), reaction (3) was also detected. Ruthenium particle size and presence of Au on the surface were found to have a strong influence on reaction (3), while reactions (1) and (2) were unaffected. It is suggested that, on Ru, reactions (1) and (2) have the same intermediate or they require a surface site having the same geometry.

INTRODUCTION

Recent studies on supported bimetallic Au-Ru catalysts indicate interactions between the metal components, and furthermore, between the metals and the support (1, 2). Although gold and ruthenium are practically immiscible in the bulk (3), the existence of metal-metal interactions in dispersed Au-Ru preparations is not unexpected. Indeed, in bimetallic systems, which do not form bulk alloys, a formation of bimetallic clusters is possible as demonstrated, e.g., for the Cu-Ru system (4, 5). Generally the surface of a bimetallic sample is enriched with the element having the lower heat of sublimation (6). Therefore, in systems containing a group IB metal and a group VIII metal, the group IB metal should have a tendency to segregate at the surface, at least in the absence of a strong

chemisorptive interaction between the group VIII component and the gas phase. This was verified experimentally in the case of, e.g., Cu-Ni (7, 8), Au-Pt (9, 10), Ag-Pd (11), and Cu-Ru (5).

However, this tendency of group IB segregation was not confirmed for a series of MgO-supported Au-Ru catalysts. On the contrary, an infrared study of CO adsorption (1) and a study of CO/CO₂ exchange, including a detailed characterization of these samples by different techniques (2), indicate an enrichment of ruthenium at the cluster surface.

There are two objectives of this study. First, a further investigation of these Au-Ru samples seemed appropriate using a ruthenium-catalyzed hydrogen transfer reaction for which gold was inactive. As test reaction the hydrogenation and hydrogenolysis of cyclopropane were selected. Several investigators have studied this reaction on a number of metals, most extensively on supported nickel and platinum catalysts. Gold promotes no significant hydrogenation or fragmentation of cyclopropane. Ac-

¹ On leave from the G. Donegani Research Institute, Novara, Italy. To whom all correspondence should be addressed.

² Deceased on April 1, 1978.

tually, a temperature of 375°C was necessary to initiate an isomerization of *gem*-dialkylcyclopropane on gold films (12). Ruthenium, however, gives a fragmentation of cyclopropane to methane and ethane, in addition to the hydrogenation yielding propane (13, 14). In view of these facts, the cyclopropane molecule seemed a good candidate for probing the surface of the bimetallic Au–Ru catalysts. Presence of gold at the cluster surface should suppress the probably more geometrically “demanding” fragmentation reaction, analogous to the effect of copper on the activity and selectivity of nickel (15, 16).

Second, the study provides more detailed kinetic data concerning the reaction between cyclopropane and hydrogen on ruthenium. As a matter of fact, the actual reaction mechanisms are still debatable and there is, to date, no definite answer to the question, whether the fragmentation and the hydrogenation of cyclopropane occur via one common intermediate or via different adsorbed species.

EXPERIMENTAL

Materials

Prepurified H₂ and ultra high-purity He were used. H₂ was passed through Pd asbestos at 400°C and He through Cu turning at 400°C. Then both were passed through a molecular sieve trap at liquid N₂ temperature. Also, cyclopropane, CP grade (>99.5%), was passed through a molecular sieve trap kept at room temperature.

Ru/MgO, Au/MgO, and Ru–Au/MgO catalysts were prepared by impregnation of MgO (Carlo Erba, reagent grade, surface area 15 m²/g) with a solution of RuCl₃ · H₂O (Rudi-Pont reagent grade) and H₂AuCl₄ · 3H₂O (Carlo Erba RPE). Approximately 4 ml of solution with an appropriate concentration of metals was employed per gram of support.

After 16 hr the excess water was removed by filtration and the resulting material was dried in air at 110°C. The catalysts

were reduced in flowing H₂ at 300°C for 2 hr, 400°C for 2 hr, and then stored in air.

Ru–SiO₂ was prepared by impregnation of the support (SiO₂, Davison grade 62, surface area 340 m²/g) with an amount of solution slightly greater than the pore volume of the silica gel (1.15 cm³/g). After impregnation the catalyst was dried at 120°C for about 24 hr and reduced *in situ* at 400°C for 2 hr.

Metallic ruthenium was a Ru sponge from Baker. The MgO-supported catalysts have been characterized by infrared spectroscopy (1), wide-angle X-ray scattering, small-angle X-ray scattering, extended X-ray absorption fine structure, X-ray photoelectron spectroscopy, diffuse reflectance spectroscopy, transmission electron microscopy. The results obtained have been previously reported (2).

A summary of the pertinent characterization is reported in Table 1.

Procedure

The reaction rates were measured using helium as diluent in a flow system employing a tubular reactor at atmospheric pressure. H₂, cyclopropane, and He streams were controlled by Nupro valves and metered by orifice flowmeters.

The analysis of the products and reactants was carried out by gas chromatography (HP Model 5750 with flame detector). The peak areas were measured with an HP Model 3380 A electronic integrator. The gc column employed was a 2-m copper tube (6 mm o.d.— filled with silica gel (100–120 mesh) which permitted the separation of CH₄, C₂H₆, C₃H₈, and cyclopropane at 80°C. The reactor contained about 10 to 100 mg of catalyst. It was diluted with 0.3 g of the inert support used in the preparation of the sample under examination. Ru sponge was mixed with ground Pyrex glass.

Since preliminary runs showed a decrease of activity with time (about 20% after 1 hr), the following procedure was used to measure the initial rates. The reactant gases were passed over the catalyst for

TABLE I
Summary of Characterization of Ru and Ru-Au Preparations

Catalyst	Support	Au (atom%)	Total metal, Au + Ru (wt%)	H/Ru	Particle size (Å)
R100	MgO	0	4.44	0.071	71 ^a (129 ^b)
R089	MgO	11	4.29	0.079	77 ^a
R064	MgO	36	4.46	0.100	78 ^a
R010	MgO	90	4.71	0.146	61 ^a
R000	MgO	100	3.46	—	83 ^a
0.6 Ru/SiO ₂	SiO ₂	0	0.6	—	<30 ^a
Ru (Sponge)	—	0	100	0.0009	1000 ^b

^a By transmission electron microscopy.

^b By H₂ chemisorption (H/Ru = 1).

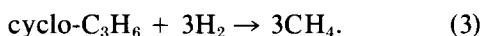
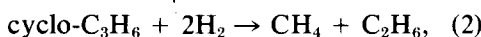
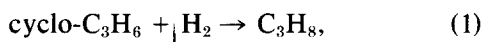
2 min prior to sampling products for analysis. The cyclopropane and helium were then cut out and the hydrogen flow continued for 15 min prior to another reaction period. After four or five runs the catalyst was treated at 350°C in flowing H₂ for 15 min and cooled at reaction temperature in H₂ before another series of measurements were taken.

The absence of diffusional limitations was verified by measuring reaction rates at different flow rates and different catalyst grain sizes.

Conversions <15% and generally in the range 0.5–4% were employed. The catalysts were pretreated in a stream of H₂ at 400°C for 2 hr. Reaction rates were determined at a partial pressure of cyclopropane between 0.01 and 0.1 atm and of H₂ between 0.1 and 0.5 atm. The temperature was varied between 25 and 170°C.

RESULTS

In the temperature range used, three reactions with the following overall stoichiometries took place:



Rates were calculated from the relation

$$N = \frac{F}{A_s} \alpha \left[\frac{\text{molecules}}{A_s \times \text{sec}} \right], \quad (4)$$

where F represents the feed rate of cyclopropane in molecules per second, A_s is the number of Ru surface atoms (determined by H₂ chemisorption), and α represents the fraction of consumed cyclopropane.

Percentage selectivity, S , to hydrogenation by reaction (1) [rather than (2) and (3)] was calculated by means of the expression

$$S = \frac{N_1}{N_1 + N_2 + N_3}, \quad (5)$$

where N_1 , N_2 , and N_3 are the rates of conversion of cyclopropane according to reactions (1), (2), and (3), respectively. No reaction was found to take place on the catalyst supports or on the reactor walls. The Au/MgO sample was found to be inactive up to 350°C.

The dependence of reaction rates (1) and (2) on hydrogen and cyclopropane partial pressures was examined at 100°C in the range $0.1 < P_{\text{H}_2} < 0.5$ atm and $0.01 < P_{\text{CP}} < 0.1$ atm. The results on MgO-supported Ru and Ru-Au samples are presented in Figs. 1–4. At $T < 110^\circ\text{C}$, reaction (3) was not detected. The dependence of the rates of reactions (1) and (2) on the partial pressures of the reactants can be expressed in the form of a simple power rate law:

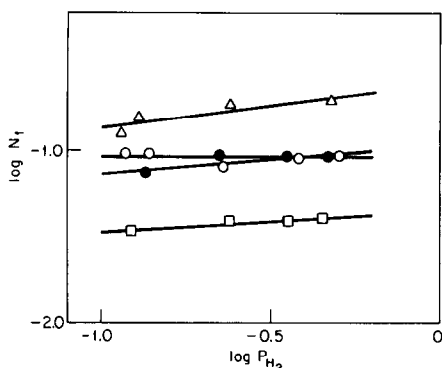


FIG. 1. Rate of C_3H_8 formation through reaction (1): N_1 vs partial pressure of H_2 , P_{H_2} . $T = 102^\circ C$; cyclopropane partial pressure = 0.03 atm. \square , R100; \circ , R089; Δ , R064; \bullet , R010.

$$N = KP_{cp}^n P_{H_2}^m \quad (6)$$

Kinetic orders, n and m , as calculated from the slopes of Figs. 1–4 and other similar graphs, are collected in Table 2. The order of reactions (1) and (2) with respect to cyclopropane partial pressure, n , was found to be similar for all the catalysts investigated regardless of type of support (SiO_2 , MgO , or unsupported Ru), particle size, and presence of Au. The value of n was found to vary between 0.60 and 0.84. Reactions (1) and (2) were approximately the same order in cyclopropane partial pressure. Therefore, no change in selectiv-

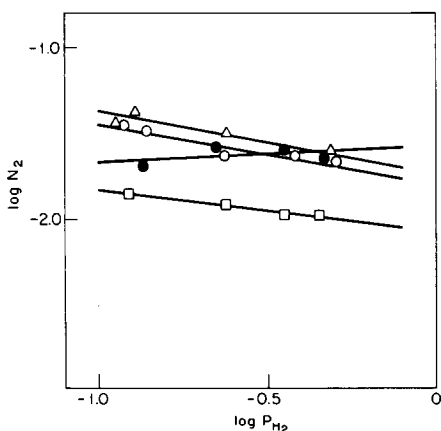


FIG. 2. Rate of C_2H_6 formation through reaction (2): N_2 vs partial pressure of H_2 , P_{H_2} . $T = 102^\circ C$; cyclopropane partial pressure = 0.03 atm. \square , R100; \circ , R089; Δ , R064; \bullet , R010.

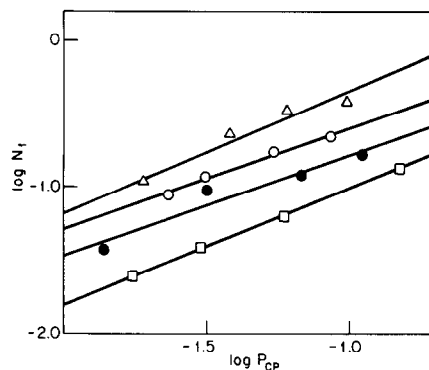


FIG. 3. Rate of C_3H_8 formation through reaction (1): N_1 vs partial pressure of cyclopropane, P_{cp} . $T = 100^\circ C$; H_2 partial pressure = 0.20 atm. \square , R100; \circ , R089; Δ , R064; \bullet , R010.

ity, S , was observed by changing the hydrocarbon concentration. Exponent, m , for reaction (1) was zero or slightly positive with the exception of Ru powder on which a value of $m = -0.12$ was measured. Values of m for reaction (2) were always lower than those measured for reaction (1), giving an increase in selectivity, S , with H_2 partial pressure.

The influence of temperature on the reaction rates was investigated in the range 29–170°C and typical results obtained on R100 are reported in Fig. 5. At $T < 110^\circ C$ rates of cyclopropane conversion to CH_4 and C_2H_6 were approximately identical indica-

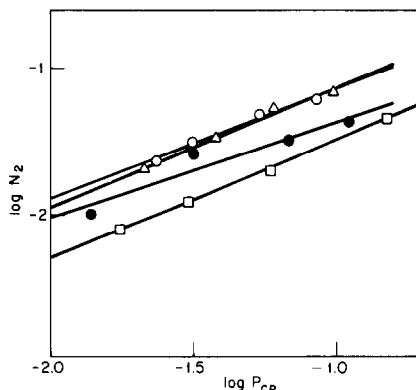


FIG. 4. Rate of C_2H_6 formation through reaction (2): N_2 vs partial pressure of cyclopropane, P_{cp} . $T = 100^\circ C$; H_2 partial pressure = 0.20 atm. \square , R100; \circ , R089; Δ , R064; \bullet , R010.

TABLE 2

Pressure Dependence Exponents and Activation Energy for the Reaction of Cyclopropane and H₂

Catalyst	Reaction	Reaction order in H ₂ <i>m</i> (±0.1)	Reaction order in cyclopropane <i>n</i> (±0.1)	Activation energy (Kcal mole ⁻¹)	Temperature range (°C)
R100	(1)	0.12	0.80	8.0	29–101
	(2)	-0.24	0.84	10.5	
R089	(1)	0.00	0.69	8.1	64–101
	(2)	-0.34	0.76	8.7	
R069	(1)	0.26	0.84	9.5	66–98
	(2)	-0.35	0.83	10.4	
R010	(1)	0.16	0.68	6.8	89–125
	(2)	0.07	0.66	9.3	
0.6% Ru/SiO ₂	(1)	0.12	0.66	11.6	76–100
	(2)	0.14	0.60	12.3	
Ru (Sponge)	(1)	-0.12	0.76	13.4	71–100
	(2)	-0.50	0.80	17.9	

ting the absence of reaction (3). However, at higher temperatures an increase of the ratio CH₄/C₂H₆ was found, and the rate of propane formation reached a maximum at about 160°C. The Arrhenius plot for the total reaction (Fig. 5) shows an increase in the apparent activation energy at tempera-

tures higher than 125°C. All but two samples, namely, R010 and 0.6% Ru/SiO₂, gave results similar to those shown in Fig. 5.

On R010 and 0.6% Ru/SiO₂, reaction (3) was not detected even at temperatures as high as 170°C. The plot of log *N* versus 1/*T* gave a straight line over the range of temperatures investigated and the ratio CH₄/C₂H₆ remained constant and equal to 1. Typical results obtained on R010 are shown in Fig. 6.

The influence of temperature on selectivity, *S*, is reported in Fig. 7. On all catalysts, selectivity, *S*, decreases with increasing temperatures from about 88% at 30°C to about 77% at 100°C. The selectivity was determined at H₂ and cyclopropane partial pressures of 0.20 and 0.03 atm, respectively, and at conversion levels between 0.5 and 6%. At temperatures higher than 125°C R010 and 0.6% Ru/SiO₂ showed higher selectivity toward reaction (1) than the other samples.

To investigate the influence of ruthenium particle size, sample 0.6% Ru/SiO₂ was fired at 700°C in air for 4 hr and reaction rates were measured at 164°C. Selectivity, *S*, dropped from about 70 to 45% and the

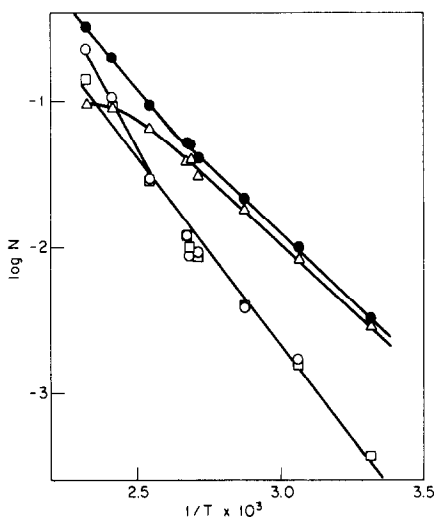


FIG. 5. Effect of temperature on the reaction rates. Catalyst R100; $P_{H_2} = 0.20$ atm; $P_{C_3H_6} = 0.03$ atm. ○, CH₄ formation ($N_2 + N_3$); □, C₂H₆ formation (N_2); △, C₃H₈ formation (N_1); ●, disappearance of cyclopropane ($N_1 + N_2 + N_3$).

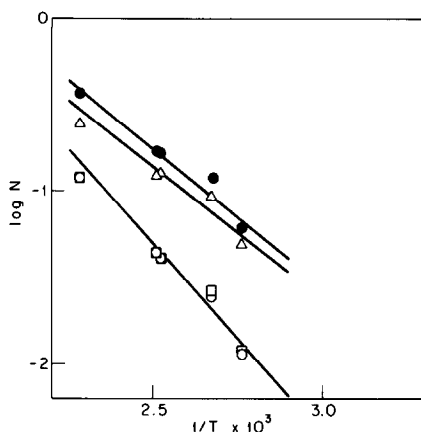


FIG. 6. Effect of temperature on the reaction rates. Catalyst R010, $P_{H_2} = 0.20$ atm, $P_{C_3H_6} = 0.03$ atm. \circ , CH_4 formation ($N_2 + N_3$); \square , C_2H_6 formation (N_2); \triangle , C_3H_8 formation (N_1); \bullet , disappearance of cyclopropane ($N_1 + N_2 + N_3$).

ratio CH_4/C_2H_6 was found to be 1.8, indicating the occurrence of reaction (3).

The reaction rates, measured at $100^\circ C$ and at H_2 and cyclopropane partial pressures of 0.23 and 0.03 atm, respectively, are reported in Table 3.

DISCUSSION

The data reported in the previous section show that the reaction between cyclopropane and hydrogen produces methane and ethane in addition to propane. This agrees with the findings of Dalla Betta and co-workers (13) and Wallace and Hayes (14). On a 10% Ru/SiO₂ catalyst, using conditions of H_2 and cyclopropane partial pressures similar to those employed in this present study Dalla Betta (13) found that equimolar quantities of methane and ethane were formed in the temperature range $0-80^\circ C$. He concludes that the fragmentation of cyclopropane occurred only via reaction (2). Wallace and Hayes (14) studied the cyclopropane hydrogenation on Ru sponge in the temperature range $20-220^\circ C$. At temperatures up to approximately $120^\circ C$ the methane to ethane ratio was close to unity, while at higher temperatures the methane production increased significantly. A comparative study of propane cracking demon-

strated that the formation of CH_4 cannot be explained completely by the consecutive reaction of readsorbed product propane.

All catalysts used in the present study produced ethane and methane even at temperatures as low as $30^\circ C$. The methane to ethane ratio remained close to unity up to $110^\circ C$. The selectivity S , calculated by expression (5), decreased with increasing temperature from 88% at $30^\circ C$ to 77% at $110^\circ C$. Using Dalla Betta's (13) data a selectivity value of 84% could be estimated on Ru/SiO₂ in the temperature range $0-80^\circ C$. The apparent activation energy for both the hydrogenation reaction and the fragmentation reaction was reported to be 12 kcal/mole. This agrees well with our experimental results on 0.6% Ru/SiO₂ where values of 11.6 and 12.3 kcal/mole were found for reactions (1) and (2), respectively. On the MgO-supported samples, a range of 6.8 to 10.5 kcal/mole has been determined. The activation energies on Ru sponge were 13.4 kcal/mole for reaction (1) and 17.9 kcal/mole for reaction (2) (Table 2).

On Ru/MgO and on Ru sponge, reaction (3) becomes a significant pathway at temperatures higher than $120^\circ C$. This can be detected easily by the increase in the ratio

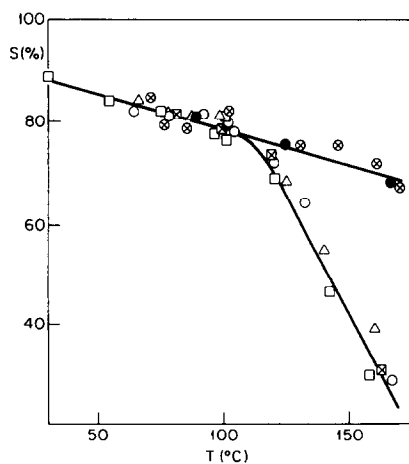


FIG. 7. Influence of temperature on selectivity, S ; $P_{H_2} = 0.20$ atm; $P_{C_3H_6} = 0.03$ atm. \square , R100; \circ , R089; \triangle , R064; \bullet , R010; \otimes , 0.6% Ru/SiO₂; \square , Ru sponge.

TABLE 3
Influence of Au Composition upon Activity^a

Catalyst	Au (atom%)	$N_1 \times 10^2$	$N_2 \times 10^2$
		$\left[\frac{\text{molecules}}{\text{sec} \times \text{Ru(s)}} \right]$	$\left[\frac{\text{molecules}}{\text{sec} \times \text{Ru(s)}} \right]$
R100	0	3.7	1.2
R089	11	10.0	2.8
R064	36	16.6	3.0
R010	90	7.8	2.1
R000	100	—	—
0.6% Ru/SiO ₂	0	<80.46	<16.4
Ru (Sponge)	0	2.54	0.78

^a $T = 100^\circ\text{C}$; $P_{\text{H}_2} = 0.23 \text{ atm}$; $P_{\text{C}_3\text{H}_6} = 0.03 \text{ atm}$.

N_1 = rate of C₃H₈ formation

N_2 = rate of C₂H₆ formation

of methane to ethane. However, on 0.6% Ru/SiO₂, the complete cleavage of the cyclopropane molecule through reaction (3) does not take place up to a temperature as high as 170°C, where the ratio CH₄/C₂H₆ is still close to unity. In view of these facts it can be concluded that the active sites for reactions (1) and (2) are present in all Ru samples regardless of the support and particle size, whereas reaction (3) requires specific surface sites that are not available on our 0.6% Ru/SiO₂.

Which properties can account for this different behavior of Ru sponge, Ru/MgO on one side and Ru/SiO₂ on the other?

(a) From a macroscopic point of view there is a difference in the support material and indeed, the nature of the support has been known to influence the activity of supported metals.

(b) Table 1 shows that the Ru/SiO₂ sample has a significant smaller particle size (<30 Å compared to 129 Å for Ru/MgO and 1000 Å for Ru sponge) which lies in the so-called "mitoedrical" region where a change in the diameter of the metal crystallites can cause a change in the catalytic activity (17).

In the latter case, an increase in the particle size of the Ru/SiO₂ sample should result in a selectivity, toward reaction (1), similar to that found on Ru/MgO and Ru

sponge. After firing 0.6% Ru/SiO₂ at 700°C in air for a period of 4 hr, reaction (3) was detected and the selectivity *S* at 164°C dropped to a value of 45% which is very close to the selectivity found on Ru/MgO and Ru sponge at the same temperature (Fig. 7). Transmission electron microscopy showed that the firing procedure resulted in an increase in particle size from <30 Å up to a final value of about 200 Å.

Thus, it seems reasonable to correlate the different selectivity to a particle size effect, without completely excluding that the growth of Ru particles resulted in a decrease of the Ru-support interaction. Furthermore, a change in particle size affects reactions (1) and (2) to a much smaller extent than reaction (3). Consequently, according to Boudart's classification (18), reactions (1) and (2) can be described as structure-insensitive reactions, in agreement with previous findings on Pt where the hydrogenation of cyclopropane (reaction (1)) was found to be essentially independent of the form of the catalyst, the nature of the carrier, and the state of dispersion (19). Reaction (3), on the other hand, seems to be a structure-sensitive reaction.

Generally, structure-sensitive reactions are slowed down by "alloying" the active metal component with an inert one. Struc-

ture-insensitive reactions, on the contrary, are practically not influenced. This led to the hypothesis that a single metal atom is the active site for a structure-insensitive reaction, while an "ensemble" of two or more atoms with a specific geometry is required for structure sensitivity.

The results of the previous section show that the addition of Au (up to 36%) does not modify the catalytic behavior of Ru. The kinetic parameters (Table 2) measured on the bimetallic samples were very similar to those obtained on Ru/MgO. However, when the amount of Au reached 90%, a significantly higher selectivity was found in the temperature range 110 to 160°C where reaction (3) was not detected. The data for samples R089 and R064 seem to contradict the hypothesis that structure-sensitive reactions can be suppressed by the addition of an inactive metal component.

The discrepancy can be explained by a comparison with previous results (1, 2). An infrared investigation of CO chemisorption on the same MgO-supported catalysts gave no evidence for the existence of Au on the surface of R089 and R064, while on R010 the presence of both Ru and Au absorption sites were detected (1). This was confirmed by a more detailed study of the same samples using transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), extended X-ray absorption fine structure (EXAFS), small-angle X-ray scattering (SAXS), wide-angle X-ray scattering (WAXS), H₂ chemisorption, diffuse reflectance spectroscopy, and isotopic exchange between CO and CO₂ (2). On the basis of these results it is now clear why the "alloying" effect did not appear for R089 and R064 where the surface was found to be made of Ru atoms only.

On Ni and Ni-Cu alloy powders, Beelen and co-workers (15) found that the hydrogenation of cyclopropane proceeds via two parallel routes, namely, reactions (1) and (2). Alloying of Ni with copper influenced both reactions in a different way. A promotion effect was found in the case of reaction

(1), while reaction (2) was dramatically suppressed. This resulted in an increase in selectivity toward reaction (1) from about 85% on pure Ni to about 96% when 5% Cu was added to Ni. This was taken as evidence for the existence of two different intermediates for the hydrogenation (reaction (1)) and hydrocracking (reaction (2)) of cyclopropane. This conclusion is not supported by the results of the present work. It seems, in fact, that on the Ru samples, reactions (1) and (2) either have the same intermediate or they require a surface site having the same geometry. Neither a change in particle size nor an addition of Au to the surface produced a change in the ratio between reactions (1) and (2).

In a subsequent theoretical study (16) the results of Beelen *et al.* (15) were explained by assuming that at least two Ni nearest neighbors are necessary for the cracking reaction and only one or none of the Ni nearest neighbors are required for the hydrogenation reaction. Furthermore, it was suggested that if the breaking of C-C bonds is related to an electron charge transfer and to a filling of the Ni *d*-holes, then chemisorption and breaking of C-C bonds on Ni require several Ni atoms, due to their almost filled *d*-band. According to this explanation, metal atoms having a lower *d*-band occupancy than Ni (as, e.g., Ru) should be able to break C-C bonds on a smaller ensemble of metal atoms. A direct consequence will be a lower effect of particle size and addition of an inert metal on reaction (2), as found in the experiments with ruthenium. The apparent difference between Ni and Ru could also be caused by the ability of Ru to form adsorption complexes involving more than one metal-carbon bond on one single Ru surface site.

In summary, the use of the reaction between cyclopropane and hydrogen as a test reaction cannot be unrestrictedly recommended. In fact, the results obtained at temperatures up to 110°C could lead to the erroneous conclusion that there are no interactions between Au and Ru. Reaction

(2), which was found to be structure sensitive in the case of Cu-Ni and was suppressed by Cu addition (15), is, in the case of Ru, a structure-insensitive one. Only at higher temperatures does the existing interaction between Au and Ru become visible by the influence on reaction (3).

Within this context, the structure sensitivity of reaction (3) has to be related to a more complex reaction intermediate and/or surface geometry. It should be noted that reaction (3) as written describes only the overall stoichiometry. The production of methane can arise from a decomposition of the product propane and/or as a primary product from the complete hydrogenolysis of cyclopropane. Figure 5 shows that the excess methane production is accompanied by a leveling off of propane production and, at the same time, an increase in the overall cyclopropane consumption. This could suggest that reaction (3) is the result of the superimposition of both a consecutive and a parallel reaction.

The results of reaction orders can be explained qualitatively on the basis of a Langmuir-Hinshelwood scheme in which both reactants are chemisorbed. Assuming that the rate-determining step involves the addition of chemisorbed hydrogen to adsorbed cyclopropane, then the rate of reaction will be

$$V = \frac{kb_{cp}P_{cp}(b_H P_H)^{1/2}}{(1 + b_{cp}P_{cp} + (b_H P_H)^{1/2})^2}.$$

Under the limiting condition of $(b_H P_H)^{1/2} \gg (1 + b_{cp}P_{cp})$ the rate of reaction V will be proportional to $P_{cp}P_H^{-0.5}$. Experimentally, orders of reaction of 0.6 to 0.8 with respect to cyclopropane and of -0.5 to 0.1 with respect to hydrogen were found (Table 2).

ACKNOWLEDGMENTS

We express thanks to Ms. L. Flagg for help in the experimental work. S.G. expresses his appreciation to

Montedison S.p.A. for financial support. The authors acknowledge with thanks the support of the National Science Foundation through Grants ENG 75-14193 and CHE 76-11255.

REFERENCES

1. Schwank, J., Ph.D. thesis, University of Innsbruck, Austria (1977); Schwank, J., Parravano, G., and Gruber, H. L., *J. Catal.*, in press.
2. Bassi, I. W., Garbassi, F., Vlaic, G., Marzi, A., Tauszik, G. R., Gocco, G., Galvagno, S., Parravano, G., submitted.
3. Hansen, M., and Anderko, K., "Constitution of Binary Alloys," 2nd ed., p. 230. McGraw-Hill, New York, 1958; Rudnitskii, A. A. and Novikova, O. A., *Russ. J. Inorg. Chem.* **4**, 722 (1959).
4. Sinfelt, J. H., *J. Catal.* **29**, 308 (1973).
5. Sinfelt, J. H., Lam, L. Y., Cusumano, J. A., and Barnett, A. E., *J. Catal.* **42**, 227 (1976).
6. Sachtler, W. M. H., *Catal. Rev. Sci. Eng.* **14**(2), 193 (1976).
7. Sachtler, W. M. H., and Dorgelo, G. J. H., *J. Catal.* **4**, 654 (1965).
8. Sachtler, W. M. H., and Jongepier, R., *J. Catal.* **4**, 665 (1965).
9. Bouwman, R., and Sachtler, W. M. H., *J. Catal.* **19**, 127 (1970).
10. Stephan, J. J., Ponec, V., and Sachtler, W. M. H., *Surface Sci.* **47**, 403 (1975).
11. Bouwman, R. G., Lippits, J. M., and Sachtler, W. M. H., *J. Catal.* **25**, 350 (1972).
12. Chevreau, T., and Gault, F. G., *J. Catal.* **50**, 124 (1977).
13. Dalla Betta, R. A., Cusumano, J. A., and Sinfelt, J. H., *J. Catal.* **19**, 343 (1970).
14. Wallace, H. F., and Hayes, K. E., *J. Catal.* **29**, 83 (1973).
15. Beelen, J. M., Ponec, V., and Sachtler, W. M. H., *J. Catal.* **28**, 376 (1973).
16. Moran-Lopez, J. L., Bennemann, K. H., *Surface Sci.* **75**, 167 (1978).
17. Poltorak, O. M., Boronin, V. S., and Mitrofanova, A. N., in "Proceedings, 4th International Congress on Catalysis, Moscow, 1968," p. 1235, Paper No. 68.
18. Boudart, M., in "Advances in Catalysis" (D. D. Eley, H. Pines, and P. B. Weisz, Eds.), Vol. 20, p. 153. Academic Press, New York, 1969.
19. Boudart, M., Aldag, A., Benson, J. E., Dougharty, N. A., and Harkins, C. G., *J. Catal.* **6**, 92 (1966).