

## Methanation Studies over Well-Characterized Silica-Supported Pt-Ru Bimetallic Clusters

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A methanation study over a well-characterized series of silica-supported Pt-Ru bimetallic clusters has been completed. Surface compositions, determined by O<sub>2</sub>-CO titration using a pulse technique, show considerable surface enrichment in Pt. Turnover numbers and activation energies for CH<sub>4</sub> formation were determined for Pt-Ru bimetallic cluster catalysts having the following Pt surface compositions: 17.9, 50, 73, and 99%. The results suggest that Ru ensembles are necessary to catalyze the methanation reaction as Pt-Ru dual sites show a catalytic behavior characteristic of Pt. When the surface composition of Ru is high, the observed turnover number for CH<sub>4</sub> formation is in good agreement with the sum total of the corresponding turnover numbers for methanation on the separate metals. For low surface concentrations of Ru, the reverse is true. A temperature-programmed pulse technique was used to study carbon formation by pulsing CO over each catalyst as the temperature was increased in flowing He. The temperature of incipient carbon formation, as determined by measuring CO<sub>2</sub> formation gas chromatographically, increased as the surface concentration of Pt was increased.

### INTRODUCTION

Methanation studies over well-characterized supported bimetallic clusters have received very little attention in the literature. Methanation studies over supported Ru-Fe (1) and Cu-Ni (2) bimetallic clusters have recently been published. However, surface compositions were not accurately determined.

Ramamoorthy and Gonzalez (3) have had considerable success in measuring the surface composition of silica-supported Pt-Ru bimetallic clusters by a combined infrared and selective chemisorption technique. Advantage was taken of the fact that CO is selectively adsorbed on the Pt component of a Pt-Ru bimetallic cluster while NO is selectively adsorbed on the Ru surface sites. Infrared band intensity measurements of the corresponding CO and NO stretching frequencies were used to estimate surface compositions. The shift in the position of the infrared bands with surface

composition was taken as a positive indication that the resulting bimetallic clusters contained both Pt and Ru atoms. It was concluded as a result of these studies, that there was no miscibility gap and that little or no surface enrichment in either metal occurred. It was also stressed that these results were qualitative and only semiquantitative in nature and that additional characterization techniques such as selective chemisorption were desirable.

A catalytic study of methanation over supported Pt-Ru bimetallic clusters should be especially interesting in view of the very different catalytic properties of the constituent metals for this reaction. Pt adsorbs CO associatively at methanation reaction process temperatures and is, therefore, a poor catalyst for this reaction, whereas Ru adsorbs CO dissociatively and is, therefore, one of the very best methanation catalysts (4). In a previous study, Ramamoorthy and Gonzalez (5) obtained evidence suggesting that CO was dissociatively adsorbed on

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supported Pt-Ru bimetallic clusters at relatively low temperatures. However, dissociative adsorption was only observed over a clean bare surface. When CO was preadsorbed, low-temperature dissociative adsorption did not occur.

These experiments suggested to us the possibility of a synergistic effect for a specific surface concentration of the supported Pt-Ru bimetallic cluster. We, therefore, felt that a careful methanation study over a series of well-characterized supported Pt-Ru bimetallic clusters would be instructive.

#### EXPERIMENTAL

A novel flow system which enables use of the reactor as either a pulse microreactor or a single-pass, differential reactor has been constructed and is shown schematically in Fig. 1. It consists of a 6-port valve, a 4-port valve (Supelco, Inc.), and a 10-port valve (Perkin-Elmer Corp.). Interconnecting lines were assembled using stainless-steel

tubing of standard commercially available sizes; generally, 3.175, 1.587, or 6.35 mm o.d. for connections between gas cylinders and the three-tube mixer (Matheson Corp.). All connections were made using standard-size commercially available stainless-steel swagelock fittings. All valves are shown in the A position. When a valve is switched to the B position, the broken lines become the connecting links.

The reactor was constructed from 12-mm Pyrex glass tubing and had a total volume of 20 ml. The catalyst was held in place by means of a porous glass disk and quartz wool. The reactor was externally heated using an oven connected to a variable temperature programmer (Valley Forge model PC-6000). This enabled the selection of any desired heating schedule.

#### Materials

The gases used in this study were subjected to the following purification treatment: CO (New England Oxygen research

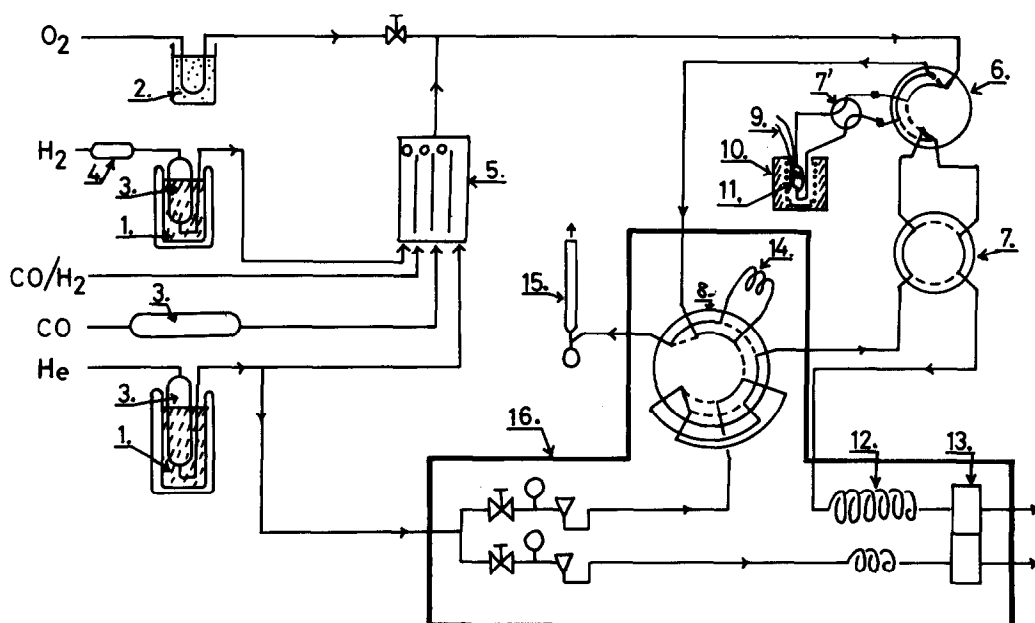


FIG. 1. Flow system. 1, liquid  $N_2$  trap; 2, dry ice trap; 3, molecular sieve; 4, Deoxo unit; 5, flow controller gas mixer; 6, 6-port valve; 7, 7', 4-port valves; 8, 10-port valve; 9, thermocouple; 10, furnace; 11, catalyst bed; 12, Carbosieve S, 1-m column; 13, hot wire detector; 14, sample loop (100 or 550  $\mu$ l); 15, flowmeter; 16, Perkin-Elmer Sigma-3B gas chromatograph.

grade) was purified by passing it through a molecular sieve.  $\text{H}_2$  (New England Oxygen research grade) was purified by first passing it through a Deoxo unit to convert  $\text{O}_2$  impurities to  $\text{H}_2\text{O}$ , which was then removed by a molecular sieve maintained at 77°K by means of a liquid  $\text{N}_2$  trap. He (New England Oxygen high purity) was passed through a molecular sieve maintained at 77°K by means of a liquid  $\text{N}_2$  trap.  $\text{O}_2$  (New England Oxygen research grade) was purified by passing it through a dry ice-acetone bath to remove traces of  $\text{H}_2\text{O}$ . For the measurement of reaction rates, it was found more convenient to use  $\text{H}_2$  and CO (New England Oxygen research grade) premixed in a 3:1 ratio. This mixture was diluted with He to produce a reactant feed stream having a composition of 20% synthesis gas and 80% He.

The silica-supported samples used in this study were prepared by impregnation or co-impregnation. Initially, the appropriate weight of  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  (Strem Chemical) or  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  (Strem Chemical) was dissolved in an amount of deionized water sufficient to ensure the complete wetting of the silica support. The solutions were mixed with Cab-O-Sil, grade M-5 (Cabot Corp., Boston, Mass.), until a slurry having the consistency of a thin paste was formed. The slurry was dried in a vacuum desiccator at room temperature for 1 or 2 days and stirred regularly during the drying process to retain uniformity. The dried catalyst was then ground into a fine powder before use. In the case of the supported bimetallic clusters, the identical procedure was followed except that the impregnating solution contained both salts mixed in the appropriate proportions.

#### *Procedure*

A fresh catalyst was treated as follows: evacuated at 400°K for 1 hr, temperature increased in flowing  $\text{H}_2$  from 400 to 600°K at about 10°C/min, reduced in flowing  $\text{H}_2$  (25 ml/min) at 600°K for 2 hr, followed by evacuation at 720°K for 30 min. The pur-

pose of evacuating the catalyst at a higher temperature than that used in the reduction, was to ensure the dehydroxylation of the support at the highest temperature of the run. The microreactor containing about 300 mg of the catalyst was then isolated from the pretreatment vacuum system by means of two four-way stopcocks and transferred to the reaction flow system.

The pretreatment used in the methanation studies was as follows: evacuated at 400°K for 1 hr, temperature increased in flowing  $\text{H}_2$  from 400 to 600°K at about 10°C/min, and reduced in flowing  $\text{H}_2$  (25 ml/min) at 600°K for 2 hr. The microreactor containing the catalyst was then isolated from the pretreatment vacuum system as in the previous case and transferred to the reaction flow system. The catalyst was then rereduced in flowing  $\text{H}_2$  for 1 hr (25 ml/min) at the highest reaction temperature of the run (680°K in the case of supported Pt and Pt-rich bimetallic clusters).

The CO titration measurements were performed as follows: measured  $\text{O}_2$  pulses (100  $\mu\text{l}$ ) were pulsed over the catalyst until several successive peaks observed on the gas chromatograph (Perkin-Elmer, model Sigma 3b) had identical peak heights. The surface of the catalyst which was now saturated with  $\text{O}_2$  was titrated using CO pulses (100  $\mu\text{l}$ ). The  $\text{CO}_2$  evolved was separated from CO by means of a 1-m stainless-steel column, 3.175 mm in diameter, packed with Carbosieve S and maintained at 140°C. The titration was considered complete when no further  $\text{CO}_2$  was evolved from the catalyst and when successive CO gas chromatographic peak responses were of equal height. The volume of  $\text{O}_2$  adsorbed, CO uptake, and  $\text{CO}_2$  evolved could be accurately measured for each catalyst. Dispersion measurements for each catalyst were made using  $\text{O}_2$  and CO chemisorption.

In order to determine the temperature of incipient carbon formation arising from the disproportionation of CO for each of the catalysts studied, CO was pulsed over the catalyst as the temperature was increased

in flowing He (25 ml/min) at a rate of 10°C/min. The volume of CO added in each pulse was 550  $\mu$ l, which was equivalent to about two or three monolayers of CO. The volume was measured by replacing the 100- $\mu$ l sample used in the titration experiments by a second loop having a volume of 550  $\mu$ l. Carbon deposition could be followed by measuring the evolution of CO<sub>2</sub> as a function of temperature.

In order to determine turnover numbers for the rate of methane formation on the various supported bimetallic catalysts, a 20% synthetic gas mixture in He, having a H<sub>2</sub>-CO ratio of 3:1, was reacted over each catalyst. Prior to making a rate measurement, the catalyst was contacted with the reaction mixture until the reaction stabilized, usually about 30–60 min. Flow rates were kept at 60 ml/min. Temperatures were bracketed in order to minimize effects due to changes occurring on the catalyst as a result of the reaction.

## RESULTS AND DISCUSSION

### *Chemisorption Stoichiometry*

The adsorption of CO and O<sub>2</sub> on both Pt and Ru was measured in order to determine the stoichiometry of adsorption. On Pt, the observed CO:O<sub>2</sub> adsorption ratio of 2:1 was in good agreement with results reported in the literature (6, 7). If it is assumed that each adsorbed CO molecule counts one Pt surface site, it follows that the O/Pt ratio must also be unity. This result is consistent with that of Wilson and Hall (7), who also reported an O/Pt ratio of 1. These authors did find, however, that O/Pt ratios were somewhat dependent on dispersion. For the metal loadings and dispersions used in this study it appears that the O/Pt ratio is very close to unity.

On Ru, the adsorption stoichiometry is more complex. An experimental CO/O<sub>2</sub> ratio of 1.2 was obtained. On the assumption that each Ru surface site adsorbs one CO molecule, the O<sub>2</sub>/Ru stoichiometry is close to 1. Several workers (6, 8, 9) have also

reported an O<sub>2</sub>/Ru stoichiometric ratio very close to 1, implying that quite possibly a small number of surface Ru sites are coordinated to more than one CO molecule. On the basis of infrared evidence, Brown and Gonzalez (10) have observed that at moderate Ru dispersions, only linearly adsorbed CO is present. However, they also pointed out that even following extensive reduction in H<sub>2</sub>, some unreduced Ru capable of adsorbing more than one CO molecule remains on the surface. The CO/Ru stoichiometric ratio has also been shown to be somewhat dispersion dependent (11, 12), giving support to our contention that the CO/Ru is more likely to be slightly greater than 1 than the O<sub>2</sub>/Ru ratio.

### *CO-O<sub>2</sub> Titration*

When a monolayer of O<sub>2</sub> adsorbed on Pt is titrated with CO, it is found that the volume of CO required is approximately 4 times the volume of O<sub>2</sub> adsorbed. At the endpoint in the titration the volume of CO<sub>2</sub> evolved is found to be twice that of the O<sub>2</sub> adsorbed. When a monolayer of O<sub>2</sub> adsorbed on Ru is titrated with CO, it is found that the volume of CO required is approximately equal to that of the O<sub>2</sub> adsorbed. At the endpoint in the titration, the volume of CO evolved is found to be only 0.3 times the volume of O<sub>2</sub> adsorbed. These strikingly different titration stoichiometries enabled us to make reasonable estimates of the surface composition of a series of silica-supported Pt-Ru bimetallic clusters.

On the basis of the above stoichiometries, one may write,

$$S_{O_2} = \frac{1}{2}(Pt)_s + (Ru)_s, \quad (1)$$

$$S_{CO} = 2(Pt)_s + (Ru)_s, \quad (2)$$

$$S_{CO_2} = (Pt)_s + 0.3(Ru)_s, \quad (3)$$

where  $S_{O_2}$  represents the volume of chemisorbed O<sub>2</sub>,  $S_{CO}$  is the volume of CO required to titrate an adsorbed monolayer of O<sub>2</sub>, and  $S_{CO_2}$  is the volume of CO<sub>2</sub> evolved at the endpoint in the titration.

TABLE 1  
Summary of Surface Composition Measurements

Catalyst <sup>a</sup>	Weight (g)	O <sub>2</sub> -Co titration (ml)			Surface composition <sup>b</sup> (%Pt)	Surface composition (%Pt)	Dispersion (%)	Calculated <sup>c</sup> volume of CO <sub>2</sub> (ml)
		O <sub>2</sub>	CO	CO <sub>2</sub>				
Pt/SiO <sub>2</sub>	0.2780	0.243	0.933	0.460	100	—	$D_{O_2} = 30.2$ $D_{CO} = 29.2$	--
Ru/SiO <sub>2</sub>	0.2804	0.241	0.229	0.075	0	—	$D_{O_2} = 13.2$ $D_{CO} = 12.5$	--
Pt-Ru (75-25)	0.2863	0.100	0.395	0.204	99.0	—	10.9	0.198
Pt-Ru (50-50)	0.2163	0.278	0.764	0.388	73.6	80.0 <sup>d</sup>	31.6	0.359
Pt-Ru (25-75)	0.2990	0.151	0.300	0.116	50.0	62.5 <sup>e</sup>	10.4	0.129
Pt-Ru (10-90)	0.2992	0.300	0.388	0.168	17.9	17.0 <sup>f</sup>	17.0	0.140

<sup>a</sup> Metal loading: 0.3 mmole/g support.

<sup>b</sup> Calculated from Eqs. (1) and (2) in text.

<sup>c</sup> Calculated from Eq. (3).

<sup>d</sup> Obtained from Ref. (15).

<sup>e</sup> Obtained from CO/O<sub>2</sub> chemisorption.

<sup>f</sup> Obtained from Ref. (14).

From a knowledge of the volume of O<sub>2</sub> adsorbed and the volume of CO required in each titration, Eqs. (1) and (2) are solved for the surface concentrations of Pt and Ru. The volume of CO<sub>2</sub> evolved during the titration can be calculated through the use of Eq. (3) and compared to the measured volume. The results, which are summarized in Table 1, clearly show that there is significant enrichment in Pt. The volume of CO<sub>2</sub> evolved is also in very good agreement with that calculated using Eq. (3).

A second estimate of the surface composition can be obtained provided the assumption is made that the CO/O<sub>2</sub> chemisorption ratio on the separate metals is independent of the surface composition. This estimate was made for the catalyst having a nominal Pt-Ru composition of 1:3. For this catalyst, the measured CO/O<sub>2</sub> chemisorption ratio was 1.7. Extrapolation of this CO/O<sub>2</sub> ratio between the CO/O<sub>2</sub> ratios obtained for Pt and Ru gave a surface composition of 62% Pt which was in fair agreement with the value of 50% Pt ob-

tained by the CO-O<sub>2</sub> titration method. In Fig. 2, a plot of surface composition vs bulk composition over the range of catalyst compositions studied, shows the extent of Pt surface enrichment actually observed.

The surface composition data presented in this study are in some disagreement with

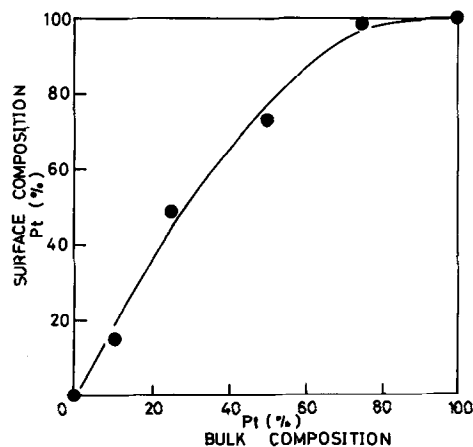


FIG. 2. Surface composition vs bulk composition.

an earlier study by Ramamoorthy and Gonzalez (3) who concluded that no substantial surface enrichment occurred over a wide range of supported Pt-Ru bimetallic compositions studied (3). Surface compositions were measured using a combined selective chemisorption and infrared technique. It is well established that a mixture of CO and NO adsorbs on a silica-supported Pt-Ru bimetallic catalyst in such a way that CO is selectively adsorbed on Pt surface sites and NO is selectively adsorbed on Ru surface sites (3, 13). By measuring the relative absorbances of the infrared bands assigned to the CO and NO stretching frequencies, it was concluded that surface enrichment in either metal was not extensive. The discrepancy between these two studies is most likely due to surface reconstruction attributable to the very strong NO-Ru chemisorption bond. It appears likely that segregation of Ru atoms to the surface is induced by the adsorption of NO on Ru sites.

The surface composition results reported here are in good agreement with surface composition measurements that we have made using different analytical techniques. From the measurement of extinction coefficients (14), a surface composition of 83% Pt was obtained for the supported Pt-Ru catalyst having a nominal composition of 90% Ru. This is in excellent agreement with the 82% Pt obtained in the present study. It should also be mentioned that the extinction coefficient measurements were performed using a synthesis gas mixture in order to duplicate the conditions encountered under actual methanation conditions as closely as possible. In a related study (15) using temperature-programmed desorption, a surface composition of 80% Pt was obtained for the supported Pt-Ru bimetallic catalyst having a nominal composition of 50% Pt. This is also in good agreement with the 74% Pt obtained in the present study. Gómez *et al.* (6) have recently measured the surface composition of a series of alumina-supported Pt-Ru bimetallic clusters using a combined  $H_2-O_2$  ti-

tration and CO chemisorption technique. Their results are also in qualitative agreement with those reported in this study. We therefore feel quite confident that considerable surface enrichment in Pt has occurred for the series of silica-supported Pt-Ru bimetallic clusters studied. This is what one would expect in view of the lower heat of sublimation observed for Pt. It is important to point out, however, that surface compositions are influenced by the adsorbed phase. It is apparent that NO, for example, concentrates Ru atoms at the surface.

#### *Methane Formation*

Turnover numbers for methane formation were obtained for catalysts having the following surface concentration of Pt atoms: 100, 99, 73, 50, 18, and 0%. The results, which are summarized in Table 2, show a decrease in the turnover number as the surface concentration of Pt is increased. In addition to the observed turnover number, we have also included the turnover number calculated from the surface composition on the assumption that each surface metal atom contributes to the total rate in a measure which is independent of its next nearest neighbor in the bimetallic cluster. Since the calculated turnover numbers are much greater than those actually observed, it must be concluded that a Pt-Ru dual site is not as effective in catalyzing methane formation as a Ru-Ru dual site. Catalytically speaking this implies that there is a greater similarity between a Pt-Ru site and a Pt-Pt site than between a Pt-Ru dual site and a Ru-Ru dual site. as the surface concentration of Ru is increased, the difference between observed and calculated turnover numbers decreases. This strongly suggests that the methanation reaction over supported Pt-Ru bimetallic clusters is structure sensitive requiring ensembles of Ru surface sites. Turnover numbers for methane formation over Pt obtained in this study are in reasonable agreement with results reported by Vannice (16). However, turnover numbers over Ru are somewhat

TABLE 2

Summary of Kinetic Data for Methane Formation over Silica-Supported Pt-Ru Bimetallic Clusters

Catalyst Pt-Ru	Surface composition (%Pt)	Initial dispersion (%)	Turnover number at 500°K (molec. site <sup>-1</sup> sec <sup>-1</sup> × 10 <sup>3</sup> )	E (kcal/mole)	ln A	Turnover number at 500°K calculated from surface composition (molec. site <sup>-1</sup> sec <sup>-1</sup> × 10 <sup>3</sup> )
100-0	100	29	0.154	15.2	6.5	0.154
75-25	99.0	10.9	0.174	16.8	8.2	0.84
50-50	73.6	31.6	0.443	20.0	12.4	18.20
25-75	50.0	10.4	5.82	20.3	15.2	34.70
10-90	17.9	17.0	60.3	28.3	25.6	56.50
0-100	0	12.5	68.8	25.7	23.1	68.8

higher. This discrepancy is in part due to the dependence of methanation rates on Ru dispersion (12). As expected, methanation rates are faster over large particles due to the larger number of Ru atoms in the catalytically active ensembles.

In order to determine whether the surface composition was changed as a consequence of the reaction, surface compositions were remeasured following reaction. In the case of Pt-rich bimetallic clusters, only small changes in surface composition were observed, with perhaps a slight surface enrichment in Pt occurring. As the surface composition of Ru was increased, however, a larger surface enrichment in Pt was observed. A careful consideration of this apparent surface enrichment in Pt proved to be artificial. Apparently, traces of carbon deposited on the support during the reaction could not be completely removed following reduction with H<sub>2</sub>. This deposited carbon was sufficient to alter the chemisorption stoichiometry of adsorbed O<sub>2</sub>. For this reason, in reporting the data initial surface compositions and initial dispersions were used in calculating turnover numbers. Dispersions, as measured by CO chemisorption, were only slightly changed as a consequence of the chemical reaction. We conclude from these results that silica-supported Pt-Ru bimetallic clusters are

reasonably stable under reaction conditions, unlike silica-supported Pt-Pd bimetallic clusters (17).

Activation energies were obtained for all surface concentrations studied. The corresponding Arrhenius plots, shown in Fig. 3, are linear and the activation energies show an increase from 15.7 kcal/mole on supported Pt to 25.7 kcal/mole on supported Ru. Activation energies on Pt and Ru are in excellent agreement with results published in the literature for these two metals (16).

The mechanism for the methanation reaction can be presumed to occur through the following sequence of steps (2):

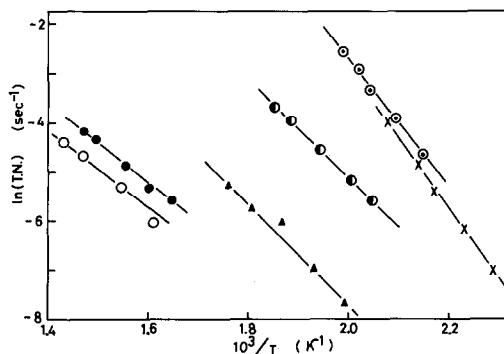
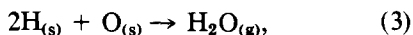
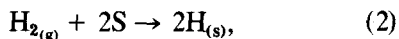
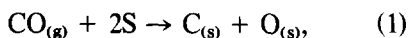


FIG. 3. Arrhenius plots,  $\ln TN$  vs  $10^3/T$ .  $\circ$ , Pt;  $\bullet$ , Pt-Ru (75-25);  $\odot$ , Ru;  $\ominus$ , Pt-Ru (25-75);  $\blacktriangle$ , Pt-Ru (50-50). Compositions are bulk compositions.



In addition to the above reactions,  $\text{CO}_2$ , formed as a result of the water gas shift reaction must also be considered.

It is instructive to consider both  $\text{H}_2\text{O}$  and  $\text{CO}_2$  formation in the light of the results obtained in this study. On supported Pt at 700°K, the  $\text{CO}_2$  yield corresponding to a 10.6% conversion based on methane formation was 1.6%, and was somewhat less than the  $\text{H}_2\text{O}$  yield which was only qualitatively determined. For the bimetallic catalyst having a surface composition of 99% Pt, the  $\text{CO}_2$  yield increased to 4.9% based on a 9.6% conversion to methane with only a trace of  $\text{H}_2\text{O}$  being observed. The temperature of this run was 680°K. The data for the bimetallic catalyst having a surface composition of 73% Pt were particularly revealing. At 623°K the  $\text{CO}_2$  yield was much greater than that of  $\text{H}_2\text{O}$ . However, at 573°K the situation was reversed. For studies on the bimetallic catalysts having a surface concentration of Pt lower than 73%, no  $\text{CO}_2$  was detected in the products. The reaction on these catalysts was studied at lower temperatures. In view of these results, it is reasonable to attribute the formation of  $\text{CO}_2$  to the water gas shift reaction rather than reaction (4). On thermodynamic grounds (18), the water gas shift reaction is still highly favorable at 700°K. Turnover numbers and activation energies were also determined for  $\text{CO}_2$  formation in the  $\text{CO-H}_2$  reaction on a 6% Pt– $\text{SiO}_2$  catalyst. The turnover number for  $\text{CO}_2$  formation at 623°K was  $0.51 \times 10^{-3}$  molec. site<sup>-1</sup> sec<sup>-1</sup> and the activation energy was 22 kcal/mole in excellent agreement with recent results obtained by Grenoble *et al.* (19) for the water gas shift reaction. Because of these results, we conclude that

$\text{CO}_2$  formation, particularly at higher temperatures, is produced as a result of a secondary reaction, i.e., the water gas shift reaction, rather than reaction (4).

#### Carbon Formation

The temperature required for incipient carbon formation was investigated over each catalyst studied in order to explore the effect of surface composition on the decomposition of CO. In a previous study, Ramamoorthy and Gonzalez (5) found infrared evidence for the low-temperature dissociative adsorption of CO over silica-supported Pt–Ru bimetallic clusters. However, the low-temperature dissociation of CO occurred only when the surface was bare. If the surface was covered with adsorbed CO, the dissociation of CO was suppressed.

In this study, pulses of CO (550  $\mu\text{l}$ ) were reacted over each catalyst as the temperature was increased at a rate of 10°C/min in flowing He (25 ml/min). Carbon formation could be monitored by measuring the volume of  $\text{CO}_2$  evolved. In general, the volume of each CO pulse was equivalent to about two or three monolayers of CO. This means that following the addition of the first pulse of CO, the catalyst surface was completely saturated with CO. The results of this study are shown in Fig. 4. Over supported Pt, carbon formation was not observed at temperatures below 673°K, while over supported Ru carbon formation started at about 573°K. This is in line with the activity of Pt and Ru in the methanation reaction. It is important to emphasize that in these experiments the surface was saturated with CO. When CO was pulsed over a bare surface, carbon formation was observed to occur at about 423°K. It appears, therefore, that a monolayer of CO has an inhibiting effect on the decomposition of CO. It also seems reasonable to conclude from this observation that the decomposition of CO is favored by an ensemble of Ru surface sites. This conclusion is reinforced by recent observations that methanation rates over supported Ru catalysts are structure sensitive



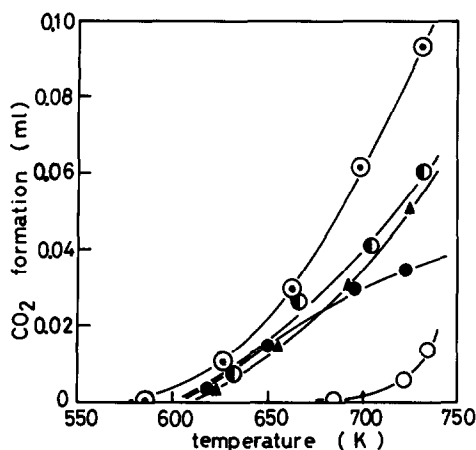


FIG. 4. CO<sub>2</sub> formation as a function of temperature. ○, Pt; ●, Pt-Ru (75-25); ⊙, Ru; ⊖, Pt-Ru (25-75); ▲, Pt-Ru (50-50). Compositions are bulk compositions.

(12). Turnover numbers for methane formation increase with decreasing metal dispersion.

Over the supported bimetallic clusters, carbon formation was observed to occur above 598°K for all surface compositions studied. However, the rate of carbon formation increased more rapidly for the catalysts having a larger concentration of surface Ru atoms.

#### CONCLUSIONS

The following conclusions may be derived from this study:

(1) When silica-supported Pt-Ru bimetallic clusters are prepared by impregnation, there appears to be a considerable surface enrichment in Pt.

(2) Turnover numbers for methane formation over well-characterized silica-supported Pt-Ru bimetallic clusters suggest that this reaction is catalyzed by Ru ensembles and is, therefore, structure sensitive.

(3) The rate of carbon formation, as observed by the evolution of CO<sub>2</sub>, is proportional to the surface concentration of Ru atoms.

(4) CO<sub>2</sub> is formed as a result of the water gas shift reaction.

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