JOURNAL OF CATALYSIS 59, 130–137 (1979)

Infrared Evidence for the Low-Temperature Dissociation of CO over Silica-Supported Ru–Pt Bimetallic Clusters

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Received December 17, 1978; revised February 23, 1979

Infrared evidence for the low-temperature decomposition of CO over supported Ru–Pt bimetallic clusters is presented. Both the nominal bulk composition and the surface composition of the clusters were 10 atom% Ru. Other Ru compositions were tried but none was as effective as the 10 atom% Ru catalyst. When small doses of CO were added to a well-reduced sample of this catalyst, a band around 2074 cm^{-1} was observed. The intensity of this band gradually decreased on standing, indicating CO decomposition at room temperature. The band intensity became permanent only after six such additions. The presence of carbon on the surface was confirmed by electron microprobe analysis. The presence of oxygen on the surface following the CO decomposition was verified by adsorbing NO. NO adsorption bands characteristic of a partially oxidized Ru surface were obtained. CO decomposition did not occur when a well-reduced sample of the catalyst was first exposed to excess CO(g). A model is proposed to explain the nature of bonding which is a precursor to CO dissociation.

INTRODUCTION

Recent studies show that the methanation reaction can possibly take place by more than one mechanism depending on whether CO is either associatively or dissociatively adsorbed on the metal. The literature on the subject is quite voluminous (*1–15*); however, there are two schools of thought regarding possible reaction intermediates. The "enol" intermediate has been suggested in order to account for the observed parameters in the kinetic rate expressions (*1, 12*); however, despite numerous efforts, extensive infrared adsorption studies, carried out both *in situ* (*11*) and under reaction conditions (*13*), have failed to produce any evidence of infrared bands characteristic of adsorbed "enol" intermediates. If such an intermediate exists, it must be either very short lived or must occupy a very small fraction of the surface. More recently, there has been a return to the concept of Fischer and Tropsch (*4*) that a carbide intermediate is the precursor to the formation of methane. Rabo *et al.* (*10*) have recently screened several supported metals as to their ability to dissociate CO. They found that metals that were active in promoting CO dissociation were also good methanation catalysts. On the other hand, metals that adsorbed CO associatively were generally poor methanation catalysts but were more active in promoting alcohol formation. Whereas Ni, Ru, Fe, and Rh appear to be good methanation catalysts, Pd, Pt, and Ir have a much lower methanation activity but show a higher activity for alcohol formation under conditions which generally favor the formation of

0021-9517/79/100130-08$02.00/0

alcohols. Recent infrared studies under reaction conditions also suggest rather strongly that methanation proceeds via the hydrogenation of an active surface carbon species (*13*).

These data could be interpreted to mean that in cases where CO is associatively adsorbed, alcohol formation, possibly through an "enol" intermediate, is enhanced and the methanation activity is therefore depressed. On the other hand, a strong prerequisite for high methanation activity is that CO be dissociatively adsorbed. The factors which affect the strength of the CO bond when it is adsorbed on a group VIII metal are therefore important considerations in the understanding of the factors which lead to high methanation activities.

The ease with which the CO bond is cleaved on most group VIII metals is well established; however, there appears to be very little data on the dissociative adsorption of CO on supported bimetallic clusters. One recent study (*14*) of the CO hydrogenation reaction over well-characterized supported Fe–Ru bimetallic clusters show that as the Fe concentration is increased, the turnover number for CH_4 formation generally decreases in agreement with the excellent methanation characteristics of Ru, i.e., there appears to be no synergistic effect due to the presence of the Fe. Methanation studies over supported Cu–Ni alloys (*5*) show that the addition of Cu drastically decreases the methanation activity of these catalysts while high-temperature infrared studies (*6*) show that the dissociative adsorption of CO is inhibited as the concentration of Cu is increased.

In a previous paper (*16*), we have reported on the surface characterization of supported Ru–Pt bimetallic clusters using infrared spectroscopy. We have found that the compositions of both the surface and the bulk are essentially equal over a wide range of bulk compositions. Since Ru and Pt represent extremes in regard to methanation activity, we felt that it might prove fruitful to perform an infrared study of the adsorption of CO as the surface composition of Pt is increased. To our surprise we found that when the surface composition of Ru was 10 atom%, extensive dissociation occurred even at room temperature. We therefore report on the result of this study.

EXPERIMENTAL METHODS

Materials. The gases used in this study were subjected to the following purification treatment: CO (Matheson Research Grade) was purified by passing it through a liquid N_2 trap. NO (Matheson Research Grade) was first purified by a standard vacuum distillation technique in which only the middle cut was retained. Dissolved N_2 was removed by the freeze–thaw technique. In this technique, NO was first frozen at 77 K and evacuated for 5 min. It was then thawed and refrozen several times until a mass spectral analysis showed that the N_2 was reduced to an acceptable level. Commercial H_2 (Cranston Welding) was used in the reduction of the catalyst. It was purified by first passing it through a Deoxo unit to convert O_2 impurities to H_2O which was then removed by a molecular sieve backed up by a liquid N_2 trap.

The silica-supported Ru–Pt bimetallic clusters used in this study were prepared by the coprecipitation of $H_2PtCl_6 \cdot 6H_2O$ (StremChemical) and $RuCl_3 \cdot 3H_2O$ (StremChemical) onto the silica support (Cab-o-Sil, Grade M-5, Cabot Corp.). The procedure used in the preparation of the catalyst is identical to that described in an earlier report (*17*) and will not be repeated here. Total metal loading in each sample was 6% by weight and average particle size as estimated by X-ray line broadening was 60 to 80 Å.

The surface composition of the supported Ru–Pt bimetallic clusters were determined using infrared spectroscopy. In this technique, CO and NO are coadsorbed onto the bimetallic surface at room temperature. Under these conditions, CO is selectively adsorbed on Pt surface sites and NO on Ru surface sites. The relative absorbances of the two bands are a measure of the ratio of surface Pt sites to surface Ru sites. It was found that no surface enrichment occurred over the entire range of surface compositions studied. We are quite confident that the 10 atom% Ru catalyst (based on nominal bulk composition) used also had a surface composition which was 10 atom% Ru.

Apparatus and procedure. A new improved infrared cell was used in this study. The cell was made from a 50-mm O-ring joint without a cooling water jacket. By the use of rectangular tubing, the path length inside the cell was reduced to a minimum and the cell could be easily positioned within the sample compartment of the instrument. Polished NaCl windows were secured in place to the rectangular tubing using glyptal cement. Further details on the design of this cell will be appearing elsewhere (*18*).

Catalyst pretreatment was as follows: heated at 325°C in vacuum for 1 to 2 hr, reduced in flowing H_2 (250 ml/min) for 4 to 5 hr at 325°C, evacuated for 1 hr at 325°C, and cooled slowly to room temperature under vacuum. In one experiment, the surface was purposely oxidized by exposing the sample to 50 Torr of $O_2(g)$ for 30 sec at 325°C. Following the evacuation of O_2 at 325°C for 1 hr, the sample was cooled to room temperature leaving a layer of chemisorbed O_2 at the surface.

Spectra were recorded at room temperature using a Perkin–Elmer Model 521 infrared spectrophotometer using the double-beam technique. Adsorption experiments were performed *in situ* with the infrared cells placed in the sample compartment of the instrument. CO(g) was admitted through a liquid N_2 trap whereas NO(g) was admitted through a dry ice–acetone bath. The adsorption of CO(g) was carried out in several small steps. In each step, a small measured volume of gas was expanded into the infrared cell such that the adsorbed volume of gas was considerably less than a monolayer.

In order to check the carbon deposition, the surface was analyzed using a Jeol JXA-50A Electron Microprobe Analyzer. For carbon (graphite), the characteristic X-ray photon energy is 0.277 keV. A pure carbon standard was used to calibrate the instrument. The number of counts per second of the 0.277-keV photons was monitored and this was taken to be proportional to the number of carbon atoms present on the surface. Detection limits for the Jeol JXA-50 Analyzer (for carbon) was 0.02% (w/w) of any given sample.

RESULTS AND DISCUSSION

The spectra of increasing doses of CO adsorbed on a 10 atom% Ru, supported Ru–Pt bimetallic cluster sample were recorded as shown in Fig. 1. Following the first addition, a small broad band centered at 2052 cm^{-1} was observed (Fig. 1b). This band disappeared after a 5-min period. Subsequent small additions of CO did not show absorption bands in the 2000 to 2100 cm^{-1} region. The spectrum was traced 5 min after each dose was added. Each dose, when expanded into the infrared cell, yielded a pressure approximately equal to 1×10^{-5} Torr and was estimated to be about 15% of a CO monolayer. Following the addition of six such doses, a substantial absorption band was observed at 2072 cm^{-1} (Fig. 1c). This absorption band decreased in intensity after 15 min and the frequency was shifted to 2078 cm^{-1} (Fig. 1d). At this point, the sample was exposed to 20 Torr of CO(g). A strong absorption band centered at 2074 cm^{-1} which was slightly asymmetric to the low-frequency side was observed. Furthermore, this band was stable and

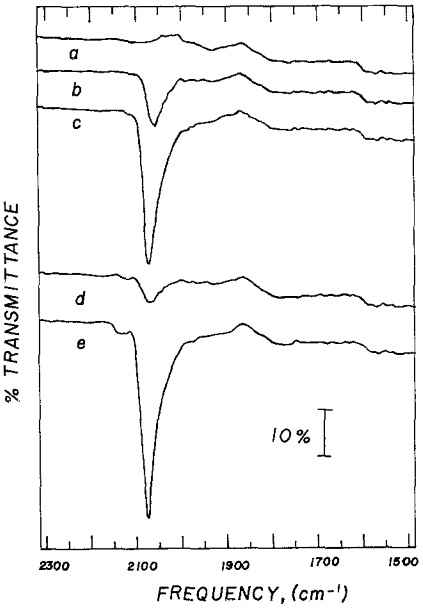

FIG. 1. Infrared spectra of increasing small doses of CO adsorbed on a 10 atom% Ru, Pt-Ru bimetallic sample at 25°C: (a) background; (b) first dose of CO added; (c) six doses of CO added; (d) 1c after standing for 15 min; (e) 20 Torr of CO(g) added.

showed no further decrease in intensity on standing (Fig. 1e). In addition to the strong band at 2074 cm^{-1}, a weak broad band centered at 2135 cm^{-1} was also observed. From these experiments, and the fact that the CO band did not reach its maximum intensity until six doses of CO had been added, we conclude that total carbon deposition corresponded to about a monolayer of C. Furthermore, this monolayer of carbon had very little effect on the total volume of CO adsorbed.

These bands have previously been assigned as follows (*19*): The strong band at 2074 cm^{-1} is assigned to CO linearly adsorbed on a Pt surface site, Pt-CO. The asymmetry which appears on the low-frequency side of this band has been assigned to CO linearly adsorbed on a Ru surface site, Ru-CO (*20*). The weak, high-frequency band centered at 2135 cm^{-1} has been assigned to CO linearly adsorbed on an oxygen-perturbed Ru surface site.

This result is strongly suggestive of the dissociative adsorption of CO on the supported Ru-Pt bimetallic clusters. The possibility does exist, however, that rather than dissociating, the CO molecules have reverted to a different adsorbed state, i.e., one in which the CO has a different orientation with respect to the surface. Such an adsorbed state which is infrared inactive, has recently been suggested by Roberts (*7*) as a precursor to dissociation.

In order to distinguish between these two possibilities, NO(g) was added in a stepwise manner to a sample on which CO was presumed to have dissociated as in Fig. 1e, following the evacuation of CO(g) for 5 min. These spectra are shown in Fig. 2. Following the addition of the first dose of NO(g), a weak broad band centered at 1798 cm^{-1} was observed in addition to another very weak broad band at 1580 cm^{-1} (Fig. 2b). When excess

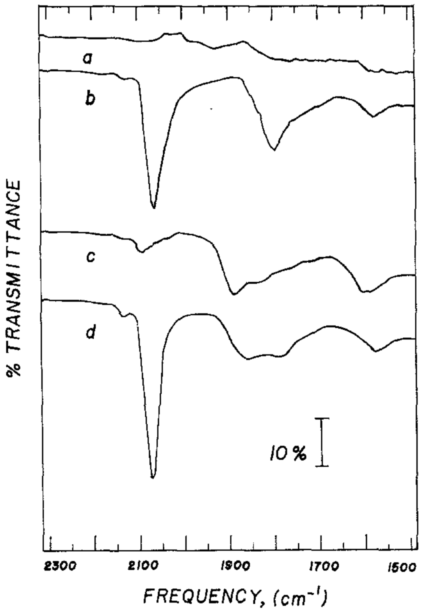

FIG. 2. Infrared spectra showing the effect of adding NO to a 10 atom% Ru bimetallic sample exposed to increasing small doses of CO: (a) background; (b) one small dose of NO added; (c) excess NO(g) added; (d) infrared cell evacuated and exposed to 20 Torr of CO(g).

NO(g) was added to this sample, a broad band of medium intensity centered at 1882 cm^{-1} appeared and the low-frequency band at 1580 cm^{-1} intensified and broadened. The strong, sharp band centered at 2074 cm^{-1} nearly disappeared in the presence of excess NO(g) (Fig. 2c). The infrared cell was then evacuated for 5 min and excess CO(g) was added. The strong, sharp Pt–CO band centered at 2074 cm^{-1} reappeared and the high-frequency band assigned to CO adsorbed on an oxygen-perturbed Ru surface site intensified slightly (Fig. 2d). The band at 1074 cm^{-1} was now completely symmetrical suggesting that under these conditions, CO was selectively adsorbed on Pt surface sites and NO on Ru surface sites. All bands were stable to 20 Torr of CO(g).

These data are entirely consistent with previously published results on the adsorption of NO on supported Ru *(21)* and supported Ru–Pt clusters *(17)*. When NO is adsorbed on a well-reduced silica-supported Ru sample, initial adsorption gives rise to a strong band a 1810 cm^{-1}, (Ru–NO). Further adsorption of NO(g) occurs dissociatively resulting in a partial oxidation of the Ru surface. Adsorption of NO(g) on these oxidized Ru surface sites gives rise to an absorption band at 1860 cm^{-1} *(21)*. When NO(g) is adsorbed on silica-supported Ru–Pt bimetallic clusters, the dissociation of NO is strongly inhibited and the only bands observed are the Ru–NO bands at around 1810 and 1580 cm^{-1} *(16, 17)*. It has also been determined that NO(g) reacts with CO adsorbed on Pt to give N_2O(g) and CO_2(g) and that NO adsorbed on Ru is stable to excess CO(g) *(19)*. These conclusions were reached by analyzing the gas phase mass spectrometrically. In the case of excess NO(g) in contact with CO adsorbed on Pt, N_2O(g), and CO_2(g) were observed, whereas in the case of excess CO(g) in contact with NO adsorbed on Ru, only CO was observed in the gas phase.

With this background in mind, our results can be interpreted as follows: Initial CO adsorption occurs on both Pt and Ru surface sites. As each successive dose of CO is added, the CO adsorption band at 2074 cm^{-1} is observed but rapidly disappears because the adsorbed CO dissociates. After several such additions, CO apparently stops dissociating and the CO absorption band at 2074 cm^{-1} reaches its maximum intensity. The simultaneous appearance of the high-frequency band centered at 2135 cm^{-1} strongly suggests that additional CO adsorption takes place on the oxygen-perturbed Ru surface sites. We interpret this to mean that a Ru–Pt dual site is probably involved in the dissociation of CO. As dissociation proceeds, a layer of chemisorbed oxygen accumulates on the Ru surface sites. Adsorption of CO(g) on these oxygen-perturbed Ru surface sites gives rise to the 2135 cm^{-1} band. When these dual Pt–Ru surface sites become saturated with oxygen, CO dissociation apparently stops. Any further CO adsorption occurs on either a Pt surface site or a Ru surface site.

When NO is added to a bimetallic cluster surface treated in this way, it initially displaces CO from oxygen-free Ru surface sites giving rise to the band at 1798 cm^{-1}. This absorption band as can be recalled, is due to NO linearly adsorbed on a well-reduced Ru surface site (Ru–NO). As these surface sites become saturated with NO, further NO adsorption on oxygen-perturbed Ru surface sites gives rise to the absorption band at 1882 cm^{-1}. When the cell is evacuated and excess CO(g) is added, the intensity of the 2135 cm^{-1} band increased thereby suggesting that further oxidation of the surface has occurred due to the addition of NO(g).

In order to confirm the presence of carbon deposition on a supported Ru–Pt bimetallic sample on which CO had decomposed, an electron microprobe analysis of the surface was made using a Jeol JXA-50A Electron Microprobe Analyzer. A pure carbon standard was used to calibrate the instrument for the 0.277-keV yield in counts per second. The results are shown in Table 1.

These results although qualitative rather than quantitative, clearly show that carbon decomposition occurred on Sample B in agreement with the infrared observation.

To study the conditions under which decomposition occurred, an experiment was carefully performed by exposing the sample directly to 20 Torr of CO(g). These spectra are shown in Fig. 3. A single intense band centered at 2074 cm^{-1}, which was asymmetric to the low-frequency side was observed (Fig. 3b). The band was stable to 20 Torr of CO(g) and did not decrease when the gas phase was evacuated. When NO(g) was added to this sample with full CO surface coverage, the CO band at 2074 cm^{-1} became sharp and symmetric and only one additional band centered at 1804 cm^{-1} was observed (Fig. 3c). The sample was then evacuated and 20 Torr of CO(g) was added to the infrared cell. Only two sharp symmetric bands were observed. Under these conditions, CO was selectively adsorbed on Pt surface sites (2074 cm^{-1}) and NO was selectively adsorbed on Ru surface sites (1804 cm^{-1}) (Fig. 3d). There were no infrared absorption bands at 2135 or 1882 cm^{-1} due to CO or NO adsorbed on oxygen-perturbed Ru surface sites. It is clear that under these conditions there was no dissociative adsorption of CO.

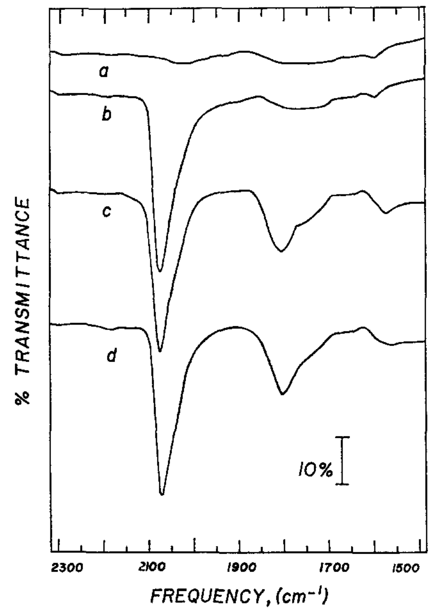

FIG. 3. Infrared spectra showing the effects of adding excess CO and NO to a 10 atom% Ru, Pt–Ru bimetallic sample: (a) background; (b) 20 Torr of CO(g) added; (c) 20 Torr of NO(g) added; (d) infrared cell evacuated and 20 Torr of CO(g) added.

TABLE 1

Electron Microprobe Analysis of Supported Pt–Ru Bimetallic Cluster Surfaces

	cps	Carbon as a percentage of the total surface[a] (%)
Pure carbon standard	1000	100
Sample A[b]	<5	0.5
Sample B	20	2.0

[a] Includes metal and support.

[b] Sample A had been treated according to the normal pretreatment procedure but it had not been subjected to a decomposition experiment.

It was found by repeating the above experiments several times, that in order for dissociative adsorption to occur, it was necessary to add small doses of CO to a bare surface of the catalyst. After a monolayer of CO was adsorbed, no further dissociation occurred. This observation is in agreement with our dual bimetallic site model described earlier in the text. Initial adsorption takes place on a Pt surface site corresponding to a Ru–Pt dual surface site. As dissociation proceeds, oxygen is chemisorbed on Ru surface sites. Further addition of CO can cause a partial reduction of these oxidized sites by reacting to

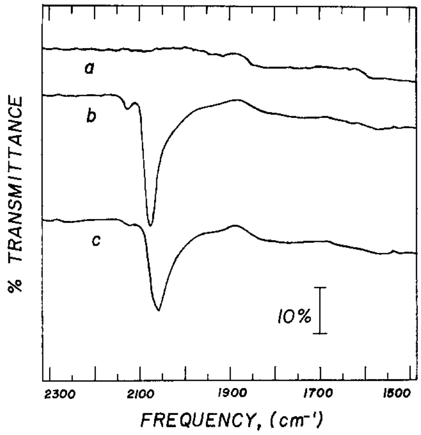

FIG. 4. Infrared spectra showing the effects of adding small doses of CO to a 10 atom% Ru, Pt–Ru bimetallic sample exposed to O_2: (a) background; (b) several small doses of CO added; (c) 4b after evacuation and standing for 80 min.

form $CO_2(g)$. This reduced Ru surface site can therefore participate in the decomposition of another CO molecule. As the CO monolayer is approached, these dual sites appear to be poisoned for CO decomposition.

To verify the correctness of this model, an experiment was performed in which the sample was purposely exposed to O_2 for 30 sec at 325°C to ensure a monolayer of chemisorbed O_2. The sample was then slowly cooled to room temperature and small doses of CO were adsorbed on the oxidized surface. The spectra of the CO adsorption are shown in Fig. 4. At monolayer coverage, there is a strong absorption band centered at 2074 cm^{-1} and a weak band at 2135 cm^{-1} (Fig. 4b). The infrared cell was evacuated and allowed to stand for 80 min at room temperature and another spectrum was obtained. The intensity of the CO absorption band at 2074 cm^{-1} was reduced and its frequency was shifted to 2058 cm^{-1}; however the reduction was not nearly as large as that observed on a bare Ru–Pt bimetallic surface.

Other supported Ru–Pt bimetallic cluster samples having different surface Ru concentrations were studied; none was found to dissociate CO as effectively as the 10 atom% Ru sample. We are not sure why this is so but the coordination of the Ru surface atoms with respect to the Pt surface atoms appears to be rather critical.

It is interesting to speculate as to the nature of the adsorbed CO species which is a precursor to dissociation. One possibility is that of a "π-complex" with π electron donation from the CO molecule to the two surface metal atoms followed by back donation between the "d" orbitals of the metal and the π^* antibonding orbitals of CO. This concerted back donation of electrons could weaken the CO bond to the extent where dissociation would occur. A possible bonding model for CO adsorbed in this configuration is shown in Fig. 5. In this model, initial electron donation is from a bonding π orbital of CO to the d_{Z^2} orbitals of the metal (Fig. 5a), followed by back donation from the d_{xy}, d_{yz}, and d_{xz} orbitals of the metal atoms to the π^* orbitals of CO (Fig. 5b).

It is always tempting to suggest that geometric effects such as covalent radii might have some bearing on the distortion of the adsorbed intermediate, however there do not appear to be any correlations between the covalent radii and the ease with which group VIII metals appear to dissociate CO.

We have not explored the nature of the carbon monolayer, however, it is clear that it does not inhibit CO adsorption. Recently, Dwyer *et al.* (*22*) have observed that carbon formed in the decomposition of CO over rhodium and iron loses its methanation activity on heating to 800 K. Using Auger spectroscopy, these authors find that rapid graphitization occurs at these temperatures and conclude that the carbon which is active in the methanation reaction is not graphitic but is probably bound to the metal by carbene-like metal–carbon bonds. This picture is consistent

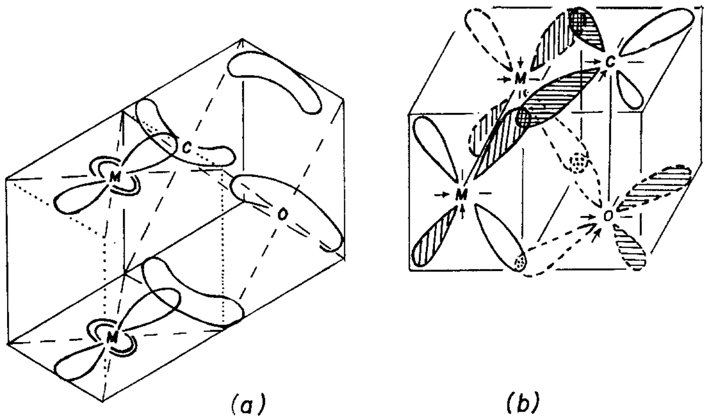

FIG. 5. Bonding model for a possible precursor leading to the dissociation of CO.

with our observations that CO adsorption is not inhibited by carbon deposition, however, this is not a guarantee that this particular catalyst will be active in the methanation reaction. As several monolayers of carbon are deposited on the metal surface, one would expect that CO adsorption should be inhibited.

CONCLUSIONS

We have shown that CO will readily dissociate on a supported Ru–Pt bimetallic cluster catalyst at room temperature. The optimum concentration for dissociation to occur appears to be about 10 atom% Ru; however dissociation occurs only on a surface not fully covered by CO. A methanation study using supported bimetallic Ru–Pt clusters is planned.

ACKNOWLEDGMENTS

We wish to acknowledge both the Petroleum Research Fund of the American Chemical Society and the Department of Chemistry at the University of Rhode Island, from which funds for both a Research Associate and research support were obtained. We also wish to acknowledge helpful discussions with Mr. Charles Grill regarding the nature of the adsorbed intermediate.

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