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Hydrogenation of Adsorbed Carbon Monoxide on Supported Platinum Group Metals

KAORU FUJIMOTO,[1] MASATAKA KAMEYAMA,[2] AND TAISEKI KUNUGI

Department of Synthetic Chemistry, Faculty of Engineering, University of Tokyo, Hongo, Bunkyo-ku, Tokyo

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Hydrogenation of adsorbed carbon monoxide on supported platinum group metals was studied by *in situ* ir spectroscopy and reactive temperature-programmed desorption (RTD) methods using hydrogen as a carrier gas. The main product of the hydrogenation was methane. The RTD gave spectra for methane formation which showed peaks between 423 and 650 K depending on the metals. On alumina-supported metals the temperature of maximum methane formation was in the following order: Ru(420 K) $\simeq$ Rh(420 K) $<$ Pd(490 K) $<$ Pt(560 K) $<$ Ir(600 K). It agreed well with the order of catalytic activity for the hydrogenation of carbon monoxide, which had been referenced elsewhere. The ir spectra of the "bridge," "linear," and "twin" types of adsorbed CO were observed on Rh/Al_2O_3 or Ru/Al_2O_3. On both samples the "bridge" CO were hydrogenated at lower temperature than the "linear" CO to form hydrocarbons consisting mainly of methane. The "twin" CO on Rh/Al_2O_3 desorbed without being hydrogenated. Some adsorbed hydrocarbon species were observed on Ru/Al_2O_3 during hydrogenation. Adsorbed CO reacted easily with H_2O in the gas phase to form CO_2.

1. INTRODUCTION

The catalytic hydrogenation of carbon monoxide to methane or higher hydrocarbons has been well known since 1902 (*1*) or 1913 (*2*). The production of oil from synthesis gas was commercially developed during World War II in Germany. Again, CO hydrogenation is being recognized as a potential method of producing clean energy from coal.

It is well known that while CO hydrogenation on Fe, CO, and Ru catalysts gives fairly high molecular weight hydrocarbons (*3*, *4*), the reactions on Ni, Rh, Pd, and Pt catalysts give methane as the predominant product (*5*). In many kinetic works it has been reported that over group VIII metals the reaction orders with respect to CO expressed by a power rate law are close to zero while those of H_2 lie near 1.0 (*6*). These facts suggest that chemisorption of CO on the catalyst under reaction conditions is strong and the coverage ratio is close to unity whereas chemisorption of H_2 is weak and the coverage is very low. Therefore, the hydrogenation of chemisorbed CO is expected to be closely related to the catalytic hydrogenation of CO.

CO has been known to chemisorb in three forms on transition metals. These are the "bridge" type, the "linear" type, and in some cases the "twin" type. The stability of adsorbed species follows the order bridge > linear > twin (*7*, *8*). Dry *et al.* (*9*) proposed a mechanism for the Fischer–Tropsch reaction which consists of the hydrogenation of CO to form adsorbed methyl radical and the insertion of linear CO into the metal–carbon bond. Vannice (*10*) found a volcano-type relationship between the methanation activities and the heat of CO adsorption on group VIII metals, which suggests that there is a particular type of adsorbed CO which is active toward hydrogenation. Eischens (*11*) pointed out that metals on which CO chemisorbs in the

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[1] To whom all correspondence should be addressed.

[2] Present address: Central Research Laboratory, Idemitsu Kosan Co. Ltd.

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bridge form (Ni and Pd) show higher catalytic activity in the methanation of CO than metals on which CO chemisorbs in the linear form (Cu and Pt). These discussions are, however, not based on direct observations but on logic or speculation. Several *in situ* infrared studies of the CO–H_2 reaction have been reported. Heal and his coworkers (*12*) showed that the temperature region of CH_4 formation on Ni/SiO_2 is close to that of the quick decrease in the absorption band of linear CO. They concluded that terminal CO (linear CO) is involved in CH_4 formation. Blyholder and Neff (*13*) studied the reaction on Fe/SiO_2 and reported the presence of O–H and C–H infrared bands suggesting an oxygenated intermediate. Dalla Betta (*14*) reported that the C–O bond of adsorbed CO on Ru/Al_2O_3 is weakened by hydrogen, and he also reported that under real reaction conditions the only active species on Ru is molecular CO and that the observed OH and CH groups are due to water and hydrocarbons adsorbed on the support (*15*). King (*16*) reported adsorbed $-CH_3$, $-CH_2-$, and an unidentified CH_n species, as well as "linear" CO, on Ru supported on silica. He suggested that all adsorbed CO molecules are not equal in reactivity and that more weakly held CO is more highly active toward hydrogenation.

This study was conducted to study the reactivities and other characteristics of three types of chemisorbed CO on supported platinum group metals and the effects of carriers on the reactivity of chemisorbed CO by combining ir adsorption measurements and reactive thermal desorption (RTD).

2. EXPERIMENTAL

Catalysts. The supported metals were prepared by making a slurry of an aqueous solution of metal chloride ($RhCl_3$, $RuCl_3$, H_2PtCl_6, $IrCl_3$) with Aerosil (obtainable from Deutsche Gold-und-Silber Scheideanstalt, Frankfurt) or Alon-G (obtainable from Godrey L. Cabot, Inc., Boston, Mass.) so that the final composition was 5 wt% metal and 95 wt% support. The slurry was dried on a water bath and degassed at 423 K for 3 h. The metal chloride–support mixture was calcined in air at 700 K for 2 h and then powdered. About 50 mg of the powder was pressed into a disk 20 mm in diameter and used for ir measurement. For RTD measurement the powder was used as it was.

Reactive thermal desorption. About 500 mg of the powder was placed in a flow-through cell (made from 4-mm-i.d. Pyrex glass tube) connected to a typical glass vacuum system and reduced by flowing hydrogen (50 ml/min) at 673 K for 3 h. Then the cell was evacuated at the same temperature for 1 h. After evacuation the flow-through cell containing the sample was cooled to room temperature and about 2.67×10^4 Pa of CO was introduced to contact the sample for 30 min and to measure the gas adsorption. The cell was then evacuated at room temperature for 30 min to remove gaseous and physisorbed CO and again 2.67×10^4 Pa of CO was introduced to measure the amount of physisorbed CO. Again, gaseous and physisorbed CO was removed by evacuation. Deoxygenated dry hydrogen was passed through the cell (20 ml/min) and the cell was heated at a constant rate (400 K/h) up to 670 K. The effluent gas was analyzed with a FID gas chromatograph using an active charcoal column and hydrogen carrier gas, every 2 min. A Ru (0.5 wt%)/γ-alumina column (60 cm long) held at 673 K was placed between the active charcoal column and the FID detector to methanate CO and CO_2. The efficiency of methanation proved to be more than 98% using a mixed gas (CO, CO_2, CH_4, and He) of known concentration.

Infrared spectral measurement. A conventional flow-through cell which was similar to that reported by Noto *et al.* (*17*) was used in connection with a glass vacuum system with a circulation pump. The cell body was made of Pyrex glass with CaF_2 windows sealed in place with an epoxy resin. The experimental techniques were similar to those described in the literature (*18*). All spectra were recorded in the temperature range 297 to 623 K on a JASCO Model IRA-2 infrared spectrometer using the double-beam method.

The sample in the cell was pretreated by evacuation at 673 K for 3 h, reduced and evacuated for 2 h at 673 K, and then cooled down to room temperature under vacuum. Then the chemisorbed CO was formed by the same procedure as that of RTD. The catalyst which held CO on it was heated in the circulating hydrogen gas (1 atm) and the temperature was raised stepwise (100 K steps) at the rate of 400 K per hour. The ir spectrum was recorded at room temperature and 373, 423, 473, and 573 K.

3. RESULTS AND DISCUSSION

3.1. Reactivity of Adsorbed Carbon Monoxide

Figures 1 and 2 show the desorption spectra of methane formed from CO adsorbed on nobel metals which are supported on alumina and silica. If we follow the theory of thermal desorption (*19*) the temperature of desorption represents the strengths of adsorption, that is, the species which desorbs at lower temperature is bound more weakly on the catalyst. In the case of hydrogenation of adsorbed CO the temperature of methane formation represents the reactivity of adsorbed CO. The adsorption of methane is so weak that it desorbs immediately after being formed. Table 1 shows the lowest temperature of methane formation (T_l) and the temperature at which the rate of methane formation is maximum (T_M). Generally, T_M shifted to higher temperature with increase in the heating rate. However, this problem is not

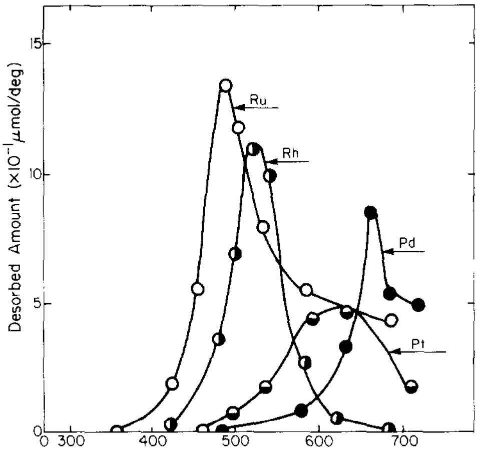

FIG. 2. Desorption spectra of methane of silica-supported metals: 5 wt% metal on SiO_2; programmed rate, 400 K/h; H_2, 20 ml/min.

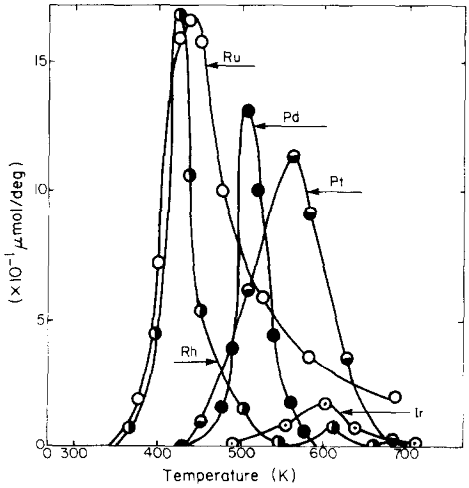

FIG. 1. Desorption spectra of methane on alumina-supported metals: 5 wt% metal/Al_2O_3; programmed rate, 400 K/h; H_2, 20 ml/min.

TABLE 1

T_l and T_M of RTD Spectrum on supported Platinum Group Metals

Catalyst	T_l[a] °K	T_M[b] °K
Ru-Al_2O_3	350	420
Rh-Al_2O_3	350	420
Pd-Al_2O_3	430	490
Pt-Al_2O_3	425	555
Ir-Al_2O_3	475	600
Ru-SiO_2	355	470
Rh-SiO_2	370	495
Pt-SiO_2	455	605
Pd-SiO_2	470	650

[a] The lowest temperature of CH_4 formation.

[b] The temperature where the rate of CH_4 formation is maximum.

discussed in this paper. On alumina-supported metals T_I and T_M lie within the ranges 350 to 420 K and 420 to 670 K, respectively. The order of T_M is Ru ≃ Rh(423 K) < Pd(493 K) < Pt(653 K) < Ir(603 K). Since it can be thought that the adsorbed CO which reacts with H_2 to form methane at lower temperature has higher reactivity, the above-mentioned order should express the order of the reactivity. This order agrees well with the order for catalytic activity of alumina-supported noble metals determined by using the turnover number (*5*, *6*). Thus, the reactivity of adsorbed CO toward H_2 can be said to have a close relationship with catalytic activity.

As is apparent from the data shown in Figs. 1 and 2, T_M on alumina-supported metals are always lower than those on silica-supported metals. In particular, the silica-supported palladium, which is reported to be a much less active catalyst compared to Pd/Al_2O_3 (*5*, *10*), exhibits high T_M (670 K) compared to the alumina-supported sample (T_M = 500 K). Why the reactivity of adsorbed CO is affected by the carrier material is not clear yet.

3.2. Reactions of Adsorbed CO on Supported Ruthenium and Rhodium

The RTD spectra are shown in Figures 3 to 7. The material balances of the RTD which are determined from the amount of adsorbed CO and the amount of products obtained by integrating the spectra are shown in Table 2. On all samples tested the major product was methane and minor products were CO, CO_2, and C_2 and C_3 hydrocarbons. The amount of desorbed CO was small; especially on Ru/Al_2O_3 little CO desorbs. As can be seen in Table 2 the yield of total products is higher than 80% on each sample, which is satisfactory considering the inaccuracy of the integration. Thus the amount of products, if any, other than the above mentioned must be small. In Figs. 3 and 4 (a) the RTD spectra of CO are shown on Ru/SiO_2 and Ru/Al_2O_3. On Ru/SiO_2 methane formation begins at about 370 K and after reaching a maximum at 430 K the rate decreases with a rise in temperature. Methane formation still continues at 670 K or higher. Small amounts of C_2 and C_3 hydrocarbons are formed on the Ru/Al_2O_3 and Ru/SiO_2 (not shown in the figure) in the temperature range between 370 and 470 K. The desorption spectrum of CO is similar to that of methane except that the amount was far less than that of methane. The formation of CO_2 begins at 373 K, reaches a maximum of 453 K, and finishes at 573 K. The characteristic features of the RTD spectrum on Ru/Al_2O_3 are that the CH_4 and CO_2 spectra shift to lower temperature (428 K for CH_4 and 393 K for CO_2) and that little CO desorbs at any temperature tested. This indicates that CO binding is stronger on

TABLE 2

Material Balances of the Hydrogenation of Adsorbed CO

Sample	CO_{ad} (μmol/g)	Dispersion (%)	Product (%/CO_{ad})			
			CO	CO_2	CH_4	Total
$Rh-Al_2O_3$	170.2	35.0	9.6	1.9	71.2	82.7
$Rh-SiO_2$	89.0	18.1	12.6	3.3	82.0	97.9
$Ru-Al_2O_3$	130.7	26.4	0.0	3.0	90.4	93.4
$Ru-SiO_2$	125.0	25.3	2.5	4.6	81.6	88.7

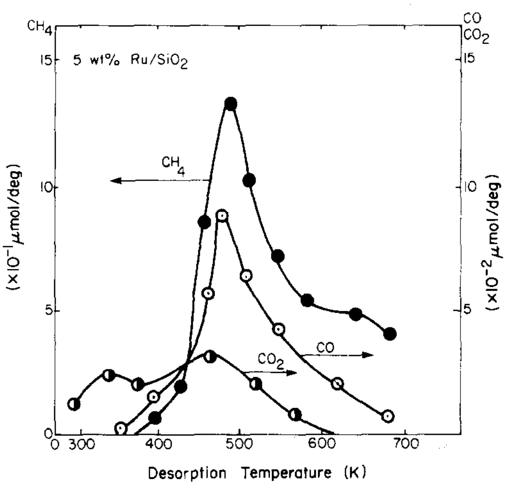

FIG. 3. Desorption spectra of CO, CO_2, and methane on 5 wt% Ru/SiO_2: programmed rate, 400 K/h; H_2, 20 ml/min.

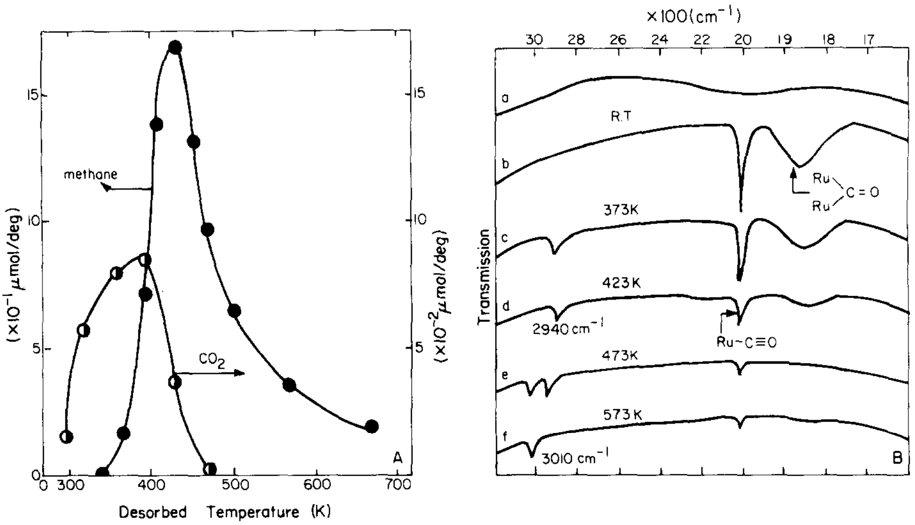

FIG. 4. RTD and ir spectra of adsorbed CO on 5 wt% Ru/Al_2O_3. (A) RTD spectrum; (B) ir spectra: (a) Background, (b)–(f) correspond to spectra of adsorbed CO taken at 297, 373, 423, 473, and 573 K in H_2.

Ru/Al_2O_3 and higher in reactivity with hydrogen than on Ru/SiO_2. It suggests that the adsorbed CO which has a strong metal–carbon bond and thus a weak carbon–oxygen bond (*20*) is easily hydrogenated.

The infrared spectra of CO adsorbed on Ru/Al_2O_3 as a function of temperature in an H_2 atmosphere are shown in Fig. 4(b). Two major bands are observed. One is a sharp band at 2020 cm^{-1} which has been assigned to "linear" CO (*21*). The combination of spectra shown in Fig. 4(a) and Fig. 4(b) makes the following discussion possible. While the band of bridge-type CO decrease markedly in intensity between 373 and 423 K the change in the band of linear CO is small. Since the main desorption products in this temperature region are methane and hydrocarbons of low molecular weight, bridge CO on Ru/Al_2O_3 is considered to be hydrogenated to hydrocarbons more easily than linear CO. In the temperature range 373 to 473 K a new band at 2940 cm^{-1} appeared. This could, most probably, be assigned to the asymmetric stretching vibration of the adsorbed CH_3– or –CH_2– complex (*18, 22*); however, the lack of a band at about 2850 cm^{-1} makes the final assignment difficult. The band is possibly attributed to the surface hydrocarbon adsorbed on the metal (*16*) or the support (*15*). Although we have no evidence, here, we assume that it is adsorbed on the metal. If correct, this species may be an intermediate complex adsorbed CO to hydrocarbon and it suggests that half hydrogenated species are more stable on Ru than on Rh where no such band is observed. The high stability of the intermediate on the catalyst means that there is a better chance of its polymerization to form a high molecular weight product. This idea is consistent with the facts that the Fischer–Tropsch synthesis on Ru catalysts gives high molecular weight products (*23–25*) and that, on Ru/Al_2O_3, C_2 and C_3 hydrocarbons are formed within the same temperature range in which the band appeared. The absorption band at about 3010 cm^{-1} appeared above 470 K and could be attributed to the C–H vibration of gaseous CH_4, because CH_4 was always detected in the gas phase at temperatures where the band was observed on both Ru/alumina and Rh/alumina. The band of linear CO, on the other hand, decreases in intensity between 423 and 573 K, but is still observed at 573 K. Since neither CO nor CO_2 is de-

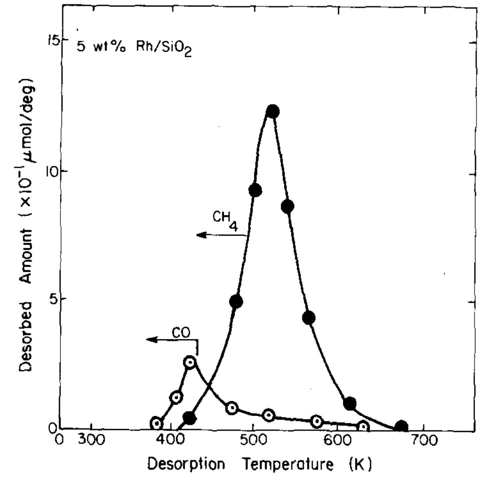

FIG. 5. Desorption spectra of adsorbed CO on 5 wt% Rh/SiO_2: programmed rate, 400 K/h; H_2, 20 ml/min.

tected in the gas phase in this temperature range, linear CO is also hydrogenated to CH_4. However, whether it is hydrogenated directly or after shifting to the bridge form is not clear. Above 573 K methane was formed on both catalysts although no absorption band was observed. This suggests that dissociated CO or carbonaceous material exists on the sample to be hydrogenated.

CO desorbs first during the RTD of adsorbed CO on Rh/SiO_2 and Rh/Al_2O_3. On Rh/SiO_2 the desorption of CO begins at 390 K, reaches a maximum at 420 K, and finishes at 623 K, whereas the formation of CH_4 begins at 423 K, reaches a maximum at 523 K, and finishes at 673 K. Little CO_2 is formed on Rh/SiO_2. The RTD spectrum on Rh/Al_2O_3 is similar to that on Rh/SiO_2 except that the desorption of CO finishes at 390 K, and the desorption spectra of CO and CH_4 shift to a lower temperature by about 50 and 100 K, respectively. CH_4 is the only hydrocarbon product, and a small amount of CO_2 is formed between 353 and 453 K. There are four major bands observed in the ir spectra of adsorbed CO on Rh/Al_2O_3 (Fig. 6(B)). Bands at 2120 and 2060 cm^{-1} have been assigned to symmetric and asymmetric stretching vibrations on two molecules of CO adsorbed to one Rh atom ("twin" type) (*7*). A sharp band at 2080 cm^{-1} and a broad band at 1850 cm^{-1} can be attributed to linear CO and bridge CO, respectively (*7*). The band of twin CO disappears in flowing H_2, between room temperature and 373 K, in which temperature region the desorption of CO occurs as is apparent from the spectrum in Fig. 6(A), indicating that twin CO desorbs without being hydrogenated. The band of bridge CO decreases markedly in intensity between 373 and 423

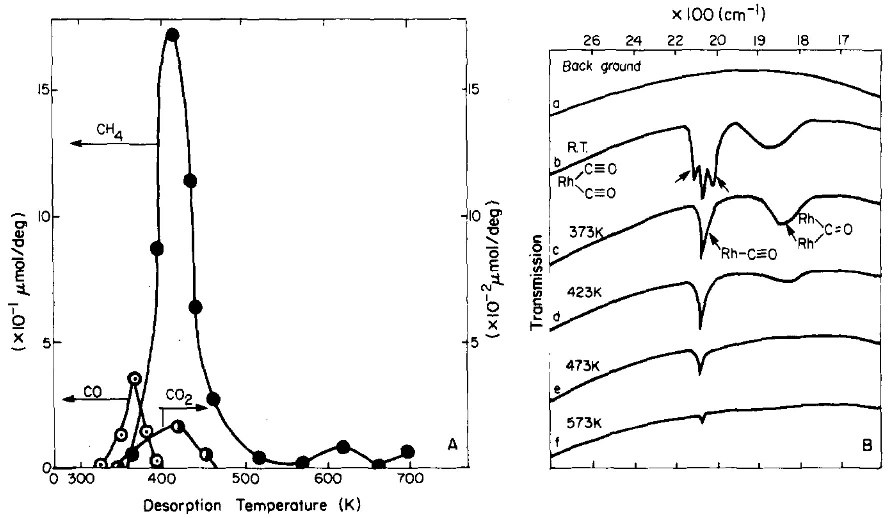

FIG. 6. RTD and ir spectra of adsorbed CO on 5 wt% Rh/Al_2O_3: (A) RTD spectrum; (B) ir spectra: (a) Background, (b)–(f) correspond to spectra taken at 297, 373, 423, 473, and 573 K in H_2.

K, whereas the band of linear CO remains almost unchanged. Since the RTD spectrum shows CH_4 as the only product in this region, the bridge CO on the Rh/Al_2O_3 is concluded to be more active toward hydrogen than linear CO as is the case on Ru/Al_2O_3. It is reasonable that bridge CO which has a weak carbon–oxygen bond is more easily hydrogenated if the slow step of CO hydrogenation is the scission of the carbon–oxygen bond as Dalla Betta suggested (*15*). Linear CO is also hydrogenated slowly to CH_4 above 423 K without desorbing into the gas phase. Neither the band at about 2940 cm^{-1} nor high molecular weight hydrocarbons are detected, suggesting the lower stability of the intermediate hydrogenated species. This fact is consistent with the lower selectivity of high molecular weight hydrocarbons during CO–H_2 reaction on a Rh catalyst than on a Ru catalyst (*10*).

3.3. CO_2 Formation

There are two possible routes through which CO_2 is formed during RTD. One is the reaction of adsorbed CO with H_2O (shift reaction) and another is the disproportionation of CO (Boudouard reaction). Two temperature-programmed desorption (TPD) spectra of adsorbed CO on Ru/Al_2O_3 are shown in Figs. 7 and 8 using deoxygenated dry He (deoxygenated and dried by passage through a column of reduced copper catalyst at 523 K and a column of Molecular Sieve 5A at 190 K in series) and wet He (moisture is added by making He pass through water at 293 K) as the carrier gas. In dry He, CO desorbs over a wide range of temperature and CO_2 desorbs above 570 K. However, the total amount of desorbed CO and CO_2 is far less than that of chemisorbed CO. In wet He, on the other hand, while only a small amount of CO desorbs between 320 and 420 K a large amount of CO_2 is formed in the temperature range 370 to 670 K, giving two peaks in its TPD spectrum, at 430 and 620 K, respectively. As can be easily understood CO_2 formation between 373 and 473 K is attributed to a shift reaction, while CO_2 formation above 570 K should be attributed mainly to disproportionation. Since most of CO_2 in the RTD of adsorbed CO desorbs between 373 and 473 K it is concluded that the main path of CO_2 formation is the reaction between adsorbed CO and the H_2O which formed by the hydrogenation of other adsorbed CO. It seems peculiar that the formation of CO_2 starts at a lower temperature than methane, which is the coproduct of the hydrogenation with

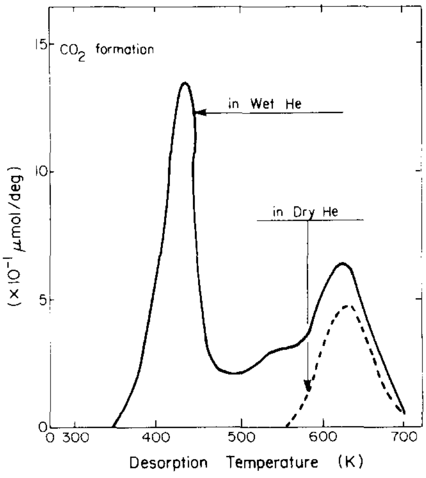

FIG. 7. CO_2 formation from adsorbed CO on 5 wt% Ru/Al_2O_3 in wet and dry He: programmed rate, 400 K/h; He, 20 ml/min; P_{H_2O}, 400 Pa.

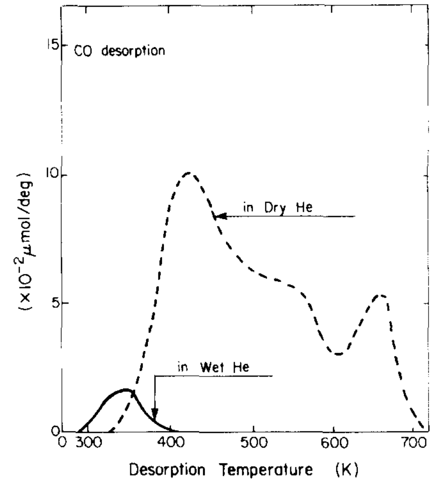

FIG. 8. Desorption spectra of adsorbed CO on 5 wt% Ru/Al_2O_3 catalyst in wet and dry He: programmed rate, 400 K/h; He, 20 ml/min; P_{H_2O}, 400 Pa.

H_2O (Figs. 3 and 4). The phenomenon is, at present, interpreted as: the first step of the hydrogenation of adsorbed CO is reaction (1a) or (1b) and (1c) (*26*) which are followed by reactions (2) and (3).

$$CO_{ad} + 2H_{ad} \longrightarrow C_{ad} + H_2O, \quad (1a)$$

$$CO_{ad} \longrightarrow C_{ad} + O_{ad}, \quad (1b)$$

$$O_{ad} + 2H_{ad} \longrightarrow H_2O, \quad (1c)$$

$$C_{ad} + 4H_{ad} \longrightarrow CH_4, \quad (2)$$

$$CO_{ad} + H_2O \longrightarrow CO_2 + 2H_{ad}. \quad (3)$$

On a catalyst on which reaction (3) proceeds more easily than reaction (2), CO_2 may be formed at a lower temperature than methane.

4. CONCLUSIONS

1. It is found that the reactivities of chemisorbed CO on supported platinum group metals correlate closely with their catalytic activities for the CO–H_2 reaction.

2. On alumina-supported Ru and Rh catalysts, bridge-type CO is more active toward H_2 than linear-type CO which suggests the bridge CO as an active intermediate in the CO–H_2 reaction.

3. CO_2 formation in the temperature range 373 to 473 K is mainly attributed to the reaction between adsorbed CO and H_2O.

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