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Heterogeneous Methanation: *In Situ* Infrared Spectroscopic Study of Ru/Al_2O_3 during the Hydrogenation of CO

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The synthesis of hydrocarbons from CO and H_2 was studied on a high surface area Ru/Al_2O_3 catalyst using transmission infrared spectroscopy. At 523 K in the presence of CO only, a carbonyl stretching band is observed at 2043 cm^{-1} and is attributed to CO adsorbed on Ru. In a flowing gas stream of H_2/CO ratio equal to 3, the carbonyl band appears at 1996 cm^{-1} and is only slightly reduced in intensity compared to CO only. Other infrared bands are attributed to adsorbed hydrocarbons, adsorbed surface formate species and adsorbed water. These latter materials are inactive reaction products as shown by isotope substitution experiments and are apparently adsorbed on the alumina support. At higher temperatures, a deactivation of the catalyst is associated with a decrease in the intensity of the carbonyl band and a shift to lower frequencies. This change is not reversible upon cooling the Ru/Al_2O_3 to 523 K, but can be reversed by a reduction in H_2 at 723 K.

INTRODUCTION

The catalytic hydrogenation of carbon monoxide to methane and other hydrocarbons is currently receiving a great deal of attention. The field has been reviewed (*1*) and a number of mechanisms proposed (*1, 2*). Many of these mechanisms postulate a formyl surface intermediate $(HCOH)_s$, which is subsequently hydrogenated to methane and water. The evidence for this particular structure is mostly indirect, consisting of coadsorption measurements of H_2 and CO alone. The observed adsorption stoichiometry is $H_2:CO = 1:1$, consistent with the species HCOH. However, if the enhanced adsorption is due to the formation of a surface complex HCOH, the presence of significant and observable quantities of this particular surface complex would be expected. This would be true at low temperatures as well as temperatures where reaction begins since similar adsorption results are obtained in both instances. An alternate explanation would consider the CO and H_2 bonded to the metal surface with the enhanced adsorption due to synergistic effects. In this case, the HCOH structure would be a possible reactive intermediate in the hydrogenation of CO with a small surface coverage dependent on the metal, temperature and gas phase composition. Instead of the reaction proceeding through formyl species, a slow step involving the scission of the C=O bond may be operative.

These alternate views should be readily differentiated by experiment since the highly covalent HCOH species would have a characteristic vibrational spectrum. Indeed, infrared results to date show the metal surface to be covered with CO with the C–O double bond nearly intact (*3, 4, 5*). The presence of O–H and C–H infrared bands has been reported on Fe/SiO_2

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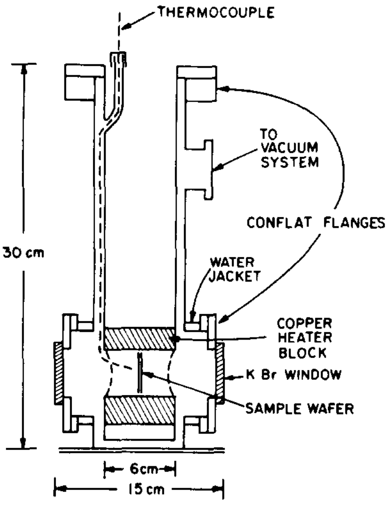

FIG. 1. High temperature *in situ* reaction cell.

catalysts exposed to CO and H_2 (*4*). Since the hydrogenation of CO generates hydrocarbons and water, these infrared bands may arise from product adsorption on the support in which case the surface species would be relatively inert.

In the work presented below a Ru/Al_2O_3 catalyst has been examined in detail by infrared spectroscopy during the hydrogenation of CO. The metal surface is covered mainly with CO but an effort was made to look for other surface species. In addition, infrared spectroscopy is used to follow the changes occurring during long-term catalyst use. In a previous publication from this laboratory it was observed that active methanation catalysts such as Ru and Ni deactivate during steady state operation at high temperature (*6*). This occurred at H_2/CO ratios in which carbon deposition was unlikely. The Ru/Al_2O_3 catalyst was examined under conditions where this deactivation occurs and the character of the surface was found to be significantly altered.

EXPERIMENTAL METHODS

Apparatus

The infrared cell was similar to that described by Hughes and White (*7*) but was constructed entirely of stainless steel and is shown in Fig. 1. The catalyst wafer was contained in a 2.7 cm diameter tube welded to the 6.5 cm diameter central Dewar portion of the cell. This sample chamber was surrounded by a copper block heated by six high temperature cartridge heaters. A thermocouple was also imbedded in the copper block for temperature control. A second stainless steel sheathed thermocouple passed through a vacuum tight feedthrough and was positioned near the sample wafer. Potassium bromide windows made a vacuum tight seal to conflat flanges (Varian Ass.) using Glyptal insulating varnish. The catalyst sample was changed by removing the central Dewar from the cell body. The cell was mounted in the spectrometer sample compartment and was attached to a stainless steel vacuum system comprised of an 80 liters s^{-1} Vacion pump (Varian Ass.), a molecular sieve sorption pump, ionization, thermocouple and pressure transducer gages and a gas handling and flow system.

The gas flow system was similar to that described earlier (*6*) and permitted continuous flow of He, H_2 and CO mixtures. The standard gas mixture used in this work was 0.025 mol fraction CO, 0.075 mol fraction H_2 and 0.90 mol fraction He at atmospheric pressure and a total flow of 200 ml min^{-1}. The low CO partial pressure gave only a weak gas phase spectrum and permitted operation without a compensation cell in the reference beam. The gas flow entered the cell through the evacuation port, flowed across the sample and exited at the bottom of the cell. The catalyst sample was in the form of a self-supporting wafer prepared by pressing 80–200 mg of catalyst powder in a 2.86 cm diameter metallurgical die under a force of 2×10^5 Newtons.

Spectra were recorded with a Perkin-Elmer Model 180 filter grating spectrophotometer operated with a variable slit to maintain constant reference beam energy. The spectrometer was continuously purged with dry nitrogen. Spectral resolution was approximately 8 cm^{-1} in the region 3700–2600 cm^{-1} and 3 cm^{-1} in the region 2400–1200 cm^{-1}. Since this spectrometer chops the beam before the sample, infrared spectra can be recorded at high temperature without interference from sample emission.

Adsorption isotherms were measured in a Pyrex constant volume adsorption system as described previously; and the linear portion of the isotherm was extrapolated to zero pressure to calculate surface areas (*8*).

Initial rates were measured in a batch recycle differential reactor and steady state rates in single pass continuous flow reactor operated differentially. Both systems have been described and CO hydrogenation rates measured on a number of catalyst systems have been reported previously (*6*, *9*).

Materials

The 5% Ru/Al_2O_3 was prepared by impregnation of Dispal M alumina (Continental Oil Co.) with ruthenium trichloride using sufficient aqueous solution to just wet the support. This material was dried at 80°C and reduced in flowing hydrogen at 450°C for 2 hr. Hydrogen adsorption on this sample gave a Ru metal surface area of 165 $\mu mol/g^{-1}$ of surface Ru. Cylinder gases were purified as described previously (*6*, *8*, *9*). Both deuterium, 99.5 atom% pure, and 1-butene, 99% pure, were obtained from Matheson and used as received.

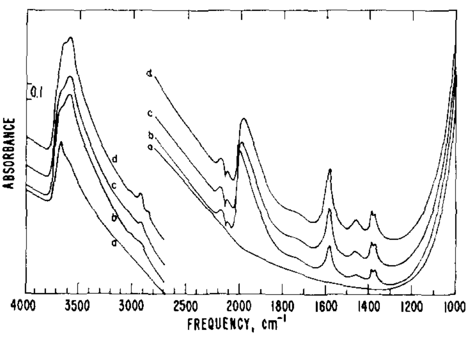

FIG. 2. Reaction of H_2 + CO on 5% Ru/Al_2O_3 at 523 K: (a) background after reduction; after reaction for (b) 1 hr, (c) 6 hr, (d) 18 hr.

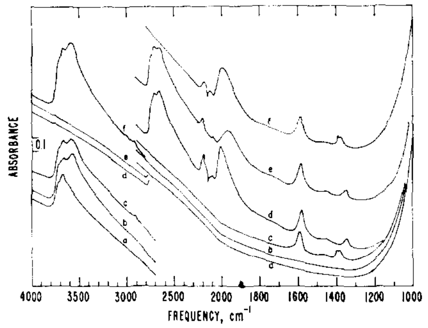

FIG. 3. 5% Ru/Al_2O_3 at 523 K: (a) background, (b) adsorption of H_2O, (c) adsorption of formic acid, (d) reaction of D_2 + CO for 6 hr, (e) purge of (d) with He, (f) reaction of H_2 + CO for 2 hr.

RESULTS AND DISCUSSION

Reaction of H_2 and CO at 250°C

A reduced sample of 5% Ru/Al_2O_3 was placed in the infrared cell and after evacuation, reduced in flowing hydrogen at 723 K for at least 2 hr. Spectrum a in Fig. 2 was recorded in flowing hydrogen after cooling the sample to 523 K. The $H_2/CO/He$ reaction mixture (0.075:0.025:0.900 mol fraction) was then passed through the cell at 200 ml min^{-1} and spectra b, c, and d were recorded after 1, 6, and 18 hr, respectively. The major spectral feature, the C–O stretching band for adsorbed CO shifts from 2006 cm^{-1} in b to 1996 and 1988 cm^{-1} in c and d. The other spectral features include: (a) a broad increase in absorbance from 3700 to 3300 cm^{-1} peaking at 3600 cm^{-1}; (b) several weak bands at 2850, 2928, and 2960 cm^{-1}; (c) the *P* and *R* branches of gas phase CO with absorption maxima at 2120 and 2180 cm^{-1}; (d) an intense and a weak band at 1585 and 1460 cm^{-1}; and (e) a doublet with peak positions of 1378 and 1392 cm^{-1}. Comparison of spectra 2b, c and d show that the surface has changed very little after 6 hr and that the steady state form of the surface (Fig. 2d) is very similar to the

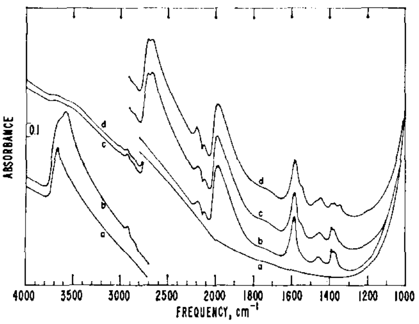

FIG. 4. Isotope substitution during reaction, 5% Ru/Al_2O_3 at 523 K: (a) background, (b) $H_2 + CO$ for 6 hr, (c) substitute D_2 for H_2 for 1 hr, (d) after 6 hr.

clean, H_2 covered surface, shortly after exposure to the reaction mixture.

Identification of Infrared Bands

To identify the surface species giving rise to the observed infrared bands, a number of experiments were performed. Addition of water vapor to a reduced clean 5% Ru/Al_2O_3 catalyst sample at 523 K followed by a short purge with H_2 at 523 K gave spectrum b in Fig. 3. The large increase in adsorption in the 3600 cm^{-1} region is due to the OH stretching vibrations of water adsorbed on the alumina support. The infrared spectrum is very similar in the OH region to that presented in Fig. 3 f and the new band maximum at 3580 cm^{-1} is identical to that observed during reaction. The sample wafer was slightly thinner than that used in Fig. 2 giving less intense bands.

After again cleaning the sample in H_2 at 723 K including a short purge with D_2, deuterium and CO were passed over the catalyst under identical conditions and spectrum d in Fig. 3 recorded after 6 hr. The surface hydroxyl groups, exchanged to OD, and the product deuterium oxide appear at 2710 and 2650 cm^{-1}. The weak bands at 2928 and 2850 cm^{-1} in Fig. 2, most likely due to C–H stretching vibrations, now appear under the gas phase CO absorption bands. Upon removing the gaseous CO from the cell by purging with helium at 523 K, spectrum 3c reveals C–D stretching vibrations at 2200 and 2095 cm^{-1}. The ratio of band positions (CH/CD) are 1.33 and 1.36, respectively, consistent with the shift expected upon substitution of hydrogen by deuterium in saturated hydrocarbons (*10*). Nearly identical bands were observed by Lucchesi and co-workers (*11*) for ethylene adsorbed on η-alumina and were assigned to a σ-diadsorbed ethylene, $S{-}CH_2{-}CH_2{-}S$.

The bands at 1585 and 1378 cm^{-1}, shifted only slightly in the presence of D_2 to 1583 and 1345 cm^{-1}, are assigned to the asymmetric and symmetric OCO stretching vibrations of adsorbed formate ion. The band at 1392 cm^{-1}, which disappears in the presence of D_2, is assigned to the C–H deformation mode of the surface formate. This band should appear at about 1050 cm^{-1} but the steep background may obscure its presence. To confirm the latter assignments, formic acid vapor was added to a clean 5% Ru/Al_2O_3 sample at 523 K and the cell was purged with H_2. The spectrum, presented in Fig. 3c, gives bands at 1585, 1392 and 1378 cm^{-1}. The weak band at 1460 cm^{-1} is assigned to a carbonate structure as discussed in the high temperature experiments to follow. A very weak band may be present at 2905 cm^{-1}. These band positions are identical to those found during reaction of H_2 and CO and agree well with a number of reports in which formic acid is adsorbed on metal surfaces (*12, 13*) or where formate ion is produced on alumina by methanol decomposition (*14*). Identical spectra are obtained when formic acid is adsorbed on alumina alone or when formaldehyde is adsorbed on Ru/Al_2O_3 or alumina.

The data presented above identify a number of surface structures on a Ru/Al_2O_3 catalyst during the reaction of CO and H_2 at 523 K. The OH stretching bands are due mainly to surface hydroxyl groups and possibly to some strongly bound water on the high surface area alumina. The CO is adsorbed on the Ru metal surface since no similar infrared band is observed on alumina alone. The hydrocarbon C–H stretching bands and the formate bands are the most interesting surface structures observed, however, the data indicate they are reaction products or by-products adsorbed on the alumina. The observation that the infrared bands are formed slowly and continue to grow in intensity even after the reaction has reached steady state (Fig. 2) indicate that these surface species are not reaction intermediates. To ascertain if the observed hydrocarbons and formates are "active," that is, involved in the reaction of CO and H_2 to produce methane, an isotope substitution experiment was performed by forming the surface structures from CO and H_2 then switching to a reaction mixture of CO and D_2. These data are presented in Fig. 4. After reducing the catalyst sample in H_2 as described previously, H_2 and CO was reacted over the catalyst at 523 K for 6 hr and spectrum 4b was recorded. Then D_2 was substituted for H_2 in the reactant stream and after 1 hr spectrum 4c was recorded. The C–H bands at 2925 and 2855 cm^{-1} as well as the formate C–H deformation band at 1392 cm^{-1} did not decrease in intensity. The support hydroxyl bands have, however, exchanged almost totally with the gas phase D_2 to OD. Since the activity of Ru, corrected to the reactant partial pressures used here, is 4×10^{-3} s^{-1} (expressed as a turnover number) (*9*), any surface species involved in the reaction should have shown significant deuterium content in less than 1 hr. Even after 6 hr, Fig. 4d, no decrease in the preformed hydrogen containing species is apparent. *These structures must be regarded as inactive reaction products or by-products adsorbed, most likely, on the alumina support.*

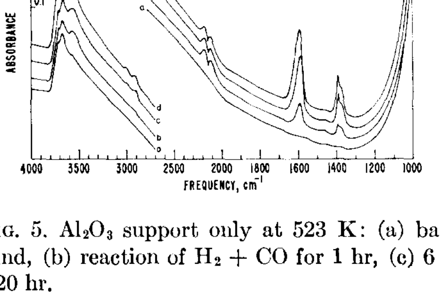

FIG. 5. Al_2O_3 support only at 523 K: (a) background, (b) reaction of H_2 + CO for 1 hr, (c) 6 hr, (d) 20 hr.

It is well known that Ru forms substantial amounts of higher hydrocarbons during methanation, so the appearance of hydrocarbons especially CH_2 structures, on the alumina support is reasonable. The origin of the surface formate is less obvious. Its inertness, as mentioned previously, would argue against its location on the metal surface. Partial hydrogenation on the metal then transfer to the support is a possible pathway. However, a blank experiment in which H_2 and CO are reacted over the alumina support alone shows the formation of intense formate bands. Figure 5a is the background spectrum of the reduced alumina wafer and 5b is after 1 hr in a flow of H_2, CO and He (0.075, 0.025 and 0.900 mol fraction, respectively). The bands continue to grow and after 16 hr (Fig. 5d) the formate bands are much more intense than those observed on the 5% Ru/Al_2O_3 (Fig. 2a). Even stringent cleaning of the reactant gases using freshly activated high area charcoal and activated 4A molecular sieve does not diminish the formate bands. However, the bands are not formed when 0.025 mol fraction CO in helium was passed over alumina at 523 K. In this latter case, addition of a small amount of water (<100 ppm) to the reactant stream leads to rapid appearance of the formate bands. This latter result is consistent with the observed formation of surface formate during the water-gas shift reaction on oxides such as ZnO and MgO (*15*). The formate bands, therefore, are formed directly on the alumina from the reaction of H_2 and CO and do not require metallic Ru.

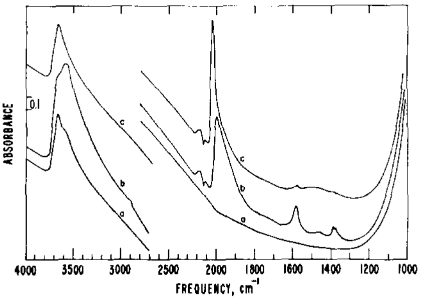

FIG. 6. Comparison of CO adsorption with $CO + H_2$ reaction on 5% Ru/Al_2O_3: (a) background, (b) reaction of $H_2 + CO$ for 1 hr at 523 K, (c) CO adsorption at 523 K after 1 hr on a surface reduced and evacuated at 723 K.

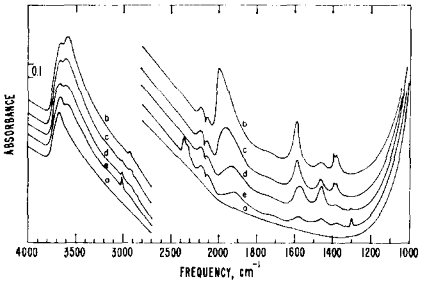

FIG. 7. Reaction of $H_2 + CO$ on 5% Ru/Al_2O_3 at 523 to 673 K: (a) background, (b) 523 K for 2 hr, (c) 573 K for 2 hr, (d) 623 K for 2 hr, (e) 673 K for 2 hr.

The above results are in essential agreement with previous infrared studies of CO hydrogenation on metallic catalysts. An Fe/SiO_2 catalyst, after reaction at 453 K, showed C–H bands at 3020 and 2940 cm^{-1} (*4*). The first band is due to gas phase methane and the 2940 cm^{-1} band corresponds to the more intense 2928 cm^{-1} band observed in this work. Inert bands were also observed at 1563 and 1436 cm^{-1} and since these are due to formate and carbonate species on the SiO_2 support surface, a shift from the bands on Ru/Al_2O_3 is expected. No surface species other than CO were observed on $Ni/Si\text{–}O_2$ (*5*). Work in this laboratory reveals that Ni/Al_2O_3 and Ni/ZrO_2 at 523 K behaves similarly to Ru/Al_2O_3 in that inert surface formate and hydrocarbon species are also observed (*16*). Calculations by extended Hückel theory indicate that enol type complexes may be more stable on Fe than on Co or Ni, the preferred species on Ni being a surface methylene radical (*17*).

It should be noted that efforts were made to search for other surface species at temperatures as low as 353 K. No new bands were observed, but the bands at 2928 and 2850 cm^{-1} became much more intense while the 1585, 1392 and 1378 cm^{-1} bands were less intense compared to data taken at 523 K.

Comparison with a Hydrogen Free System

The one band attributed to adsorption on the metal surface, the broad CO stretching band at 2000 cm^{-1}, deserves a more detailed examination. To obtain a characteristic spectrum of a metal surface covered by CO only, a sample of the 5% Ru/Al_2O_3 catalyst was evacuated to remove H_2 before exposure to CO. The spectra in in Fig. 6a is the catalyst background after reduction and 6b is after reaction of H_2 and CO for one hour at 523 K. After cleaning the catalyst at 723 K in H_2, the catalyst was evacuated at 723 K for 2 hr. A final pressure of 1×10^{-5} Pa was obtained. The background spectrum of the evacuated sample at 523 K is identical to that in Fig. 6a. Carbon monoxide at 0.025 mol fraction in helium was passed over the sample and after 1 hr, the spectrum in 6c was recorded. This spectrum remained stable for several hours. After cleaning the sample again at 723 K in H_2, reaction of H_2 and CO (0.075 and 0.025 mol fraction, respectively) for 1 hr reproduced spectrum 6b. On a hydrogen free surface the CO stretching band is centered at 2043 cm^{-1} while in the presence of H_2 the position is 1996 cm^{-1} and the band is much broader. Comparison of the integrated band areas for the sequence $CO + H_2$, CO only, $CO + H_2$ shows that the CO stretching band is smaller by 12% during the reaction of H_2 and CO.

A number of authors have presented data to show that in the presence of H_2 and CO Ru adsorbs nearly a monolayer of CO and more than a monolayer of H_2 simultaneously (*18, 19*). The presence of hydrogen bonded to the metal surface may increase the availability of electrons for back-bonding from the metal to the adsorbed CO. This would lead to a decrease in the C–O stretching frequency as observed here [see discussion in Refs. (*20* and *21*)]. This should also cause an increase in the strength of CO binding as observed by Kraemer and Menzel (*22*). Nickel does not show an increased heat of adsorption (*19*). It should also be noted that increased back-bonding to the CO may result in an increase in extinction coefficient for the C–O stretching band (*21, 23*). The high CO coverage and effect of H_2 adsorption on CO bonding is consistent with the observed kinetics, negative order in CO and positive order in H_2 (*6*).

The above discussion serves mainly to show that the active Ru metal surface is covered with nearly a monolayer of adsorbed CO ($\pm 10\%$) and probably hydrogen during reaction at 523 K. It has been shown previously that during steady state operation at 523 K, the activity of Ru/Al_2O_3 catalysts are very near the initial activity of clean well-reduced catalyst samples (*9*). For such samples, the concentration of intermediates or surface species other than CO (albeit with a weakened C–O bond) is small and must be restricted to less than 10% and possibly even 5% of the surface. These data may lend support to a mechanism in which scission of the C–O bond is the slow step, a process consistent with the lack of a kinetic isotope effect when D_2 is substituted for H_2 (*16*).

Reaction of H_2 and CO at Temperatures above 523 K

In a similar manner, spectra were obtained of the Ru/Al_2O_3 catalyst during reaction at temperatures above 523 K. Spectrum a in Fig. 7 is the background spectrum after reduction and 7b is the spectrum after reaction of H_2 and CO (0.075 and 0.025 mol fraction in helium) at 523 K for 2 hr. Spectrum 7c was recorded after 2 hr at 573 K, 7d after 2 hr at 623 K and 7e after 2 hr at 673 K. With increased reaction temperature the CO stretching band shifts markedly to lower frequency, appears to broaden and, at the highest temperature, exhibits a significantly rereduced integrated intensity. The C–O stretching band positions are 1998 cm^{-1} at 523 K, 1962 cm^{-1} at 573 K, 1936 cm^{-1} at 623 K, and 1925 cm^{-1} at 673 K. Continued operation at 673 K overnight causes little change in the infrared spectrum. The weak CO band at 673 K is not due to simple desorption of the CO at high temperature since cooling the sample to 523 K in the reaction mixture results in very little change; the observed CO stretching region is similar to that at 673 K.

Other differences in the infrared spectra include the appearance of gas phase methane bands (*Q* branch) at 3017 and 1305 cm^{-1} and gaseous CO_2 at 2340 cm^{-1} when the reaction rate is sufficiently fast to permit observation of the reaction products. Also, the formate bands at 1585, 1392, and 1378 cm^{-1} decrease in intensity and are replaced by bands at 1570 and 1460 cm^{-1}. These later bands are due to a surface carbonate formed either from the decomposition of the formate species or by reaction of the CO_2 with the alumina support (*24*).

The reduced intensity at high temperature of the band due to adsorbed CO is the result of a change in the ruthenium surface. The steady state rate of CO hydrogenation on Ru/Al_2O_3 at 523 K was shown previously to be very near the initial rate observed on clean, well-reduced Ru surfaces (*6*). This is consistent with the infrared results at 523 K where the metal surface is initially covered with adsorbed CO and does not change with continued reaction. However, as the catalyst temperature is raised, the catalyst is found to deactivate so that at 673 K the observed steady state rate is only slightly higher than the rate at 523 K and 25 times lower than the rate expected from an extrapolation of the initial rate data to 673 K. In the cited work we also showed that this deactivation was not reversible by simply lowering the temperature but is not due to an irreversible deterioration of the catalyst. Reduction and oxidation treatments, used to clean the metal of carbonaceous materials, restored the original high activity. The infrared results at 673 K show a surface with a greatly reduced coverage by adsorbed CO as expected for a surface contaminated with carbonaceous deposits. However, if only the access to the surface was restricted by the contaminant, as might occur for an amorphous carbon overlayer, the CO adsorbed on the remaining surface would be expected to exhibit a stretching band similar to that observed at lower temperatures and not shifted to low frequencies as observed in this work. This implies an interaction of the carbonaceous material with the metal surface, an interaction such that the C–O bond strength is decreased.

The structure responsible for the low activity may be a surface carbide. This is supported by experiments in which a clean reduced Ru/Al_2O_3 sample was exposed to 40 kPa of 1-butene at 523 K for 30 min. Such a treatment should carbide the surface without the presence of oxygen or the need for high temperatures. After evacuation, H_2 and CO were passed over the catalyst at 523 K and subsequent infrared spectra showed the surface to be identical to a sample that has been heated to 673 K (Fig. 7c).

A bulk ruthenium carbide apparently does not exist but a surface carbide or a strong interaction of carbon at the Ru surface may occur at the conditions employed. The species RuC and RuC_2 have been reported in the gas phase with dissociation energies of 157 and 131 kcal mol^{-1} (*25, 26*). Nickel is found to behave in a similar manner both with respect to high temperature deactivation (*6*) and surface structures observed by infrared spectroscopy during reaction (*16*). Nickel forms a stable carbide and its properties, which have been extensively studied, may clarify the behavior of Ru described above. Nickel reacts with a number of carbon containing compounds in the temperature range 440–520 K to form bulk nickel carbide (*27*). However, at temperatures above 573 K bulk nickle carbide decomposes to nickel and carbon. In the presence of both CO and H_2, the reaction of Ni with CO to form the carbide competes with the reaction of the carbide with H_2 to give CH_4 and Ni. Both reactions

$$3Ni + CO \rightarrow Ni_3C + CO_2, \qquad (1)$$

$$Ni_3C + 2H_2 \rightarrow 3Ni + CH_4, \qquad (2)$$

have been studied and at 563 K the rates of reaction (1) and (2) are nearly equal (*28, 29*). However, reaction (1) has an activation energy of 35 kcal mol^{-1} while that for (2) was found to be 4.5 kcal mol^{-1}. Thus, at temperatures above 573 K, reaction (1) may produce a carbide even though the bulk carbide is unstable. The formation of such a carbide-like structure at the surface would explain the deactivation of Ni and Ru catalysts at high temperature and the observed infrared results. For example, recent data indicate that addition of carbon to a metal to form a carbide alters the electronic structure at the metal surface. By apparently contributing electrons to the metal, the carbon causes an increase in the density of *d*-electron states at the Fermi level (*30, 31*). This could account for the infrared band shift (*20*) while a carbon overlayer reduced the apparent CO coverage. The above results were obtained in relatively water free systems and at atmospheric pressure. The presence of steam is expected to inhibit carbon deposition and possibly surface carbide formation. However, recent results (*32*) indicate that addition of more than 10 mol% water did not significantly decrease the high temperature deactivation.

SUMMARY

The ruthenium surface of a Ru/Al_2O_3 catalyst is covered almost entirely by adsorbed CO during the hydrogenation of CO at temperatures from 353 to 523 K. The adsorbed CO retains its double band character although this is weakened somewhat in the presence of H_2. Other surface species observed during reaction are best ascribed to reaction products adsorbed on the support surface. These substances, which include adsorbed hydrocarbons and formates, are inert and apparently do not participate in the catalytic reaction. Reaction intermediates occupying less than 5% of the surface probably would not have been observed.

At higher temperatures the metal surface is altered, possibly by the incorporation of carbon, to form a surface with the adsorbed CO exhibiting a much lower stretching frequency and a greatly reduced intensity. Such changes in the metal surface can be correlated with an observed decrease in catalytic activity and may be due to a number of effects including reduced CO coverage, a change in the strength of CO binding or an inhibition of hydrogen adsorption.

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