Adsorption and Microcalorimetric Measurements on the Interaction of CO and H_2 with Polycrystalline Ru and Ru/TiO_2 Catalyst

V. P. Londhe and N. M. Gupta

Chemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai-400 085, India

A microcalorimeter equipped with gas circulation cells and coupled at outlet to a gas chromatograph was used for the simultaneous measurements of the uptake and the differential heat (q_d) evolved during the adsorption of CO and H_2 pulses over polycrystalline ruthenium metal and a Ru/TiO_2 catalyst in the temperature range 300–475 K and as a function of surface coverage. The initial differential heat for the adsorption of CO and H_2 over polycrystalline ruthenium at 300 K was 120 and 65 kJ mol^{-1}, respectively, the corresponding values in the case of Ru/TiO_2 being around 130 and 57 kJ mol^{-1}. With the rise in sample temperature, the q_d for CO adsorption over Ru metal remained almost constant, while in the case of Ru/TiO_2 it decreased substantially. The fraction of CO or H_2 adsorbed, conversion of CO_{ad} to CO_2, and the corresponding values of heat evolved showed different trends, when these samples were exposed to the successive CO or H_2 pulses at different temperatures. The H_2 adsorption is found to be suppressed on Ru/TiO_2, particularly at the low sample temperatures. Also, the CO adsorption over Ru/TiO_2 at temperatures above 400 K resulted in the partial reduction of the support, and this is facilitated by the heat evolved at the metal/support interfaces during CO chemisorption. On the other hand, the CO dissociation followed by $CO_{(ad)} + O_{(ad)}$ reaction was a predominant step giving rise to CO_2 formation in the case of Ru metal. This study also confirms that, for both the samples, while the CO adsorption remains uninhibited by the preadsorbed H_2, the catalyst surface covered with the CO was completely inaccessible to subsequent H_2 adsorption. © 1997 Academic Press

INTRODUCTION

In the earlier reported studies we used a heat-flow microcalorimeter equipped with the gas circulation cells and coupled at the outlet to a gas chromatograph in order to investigate the CO oxidation reaction over the bulk and the supported forms of noble metal catalysts (1–3). It has been shown that the preponderance of one of the several possible reaction routes depends on the temperature and the chemical nature of the catalyst surface at the time of interaction with the reactants. By simultaneous measurement of the enthalpy changes, gas adsorption, and the reaction products formed, the role played by the lattice oxygen and the localized temperature fluctuations at the metal/support interfaces have been discerned. In continuation, we have now employed similar methodology to study the mechanistic aspects of CO methanation reaction over the bulk and the titania-supported ruthenium catalysts. The choice of Ru was based on its high activity and selectivity for methane formation, particularly at low reaction temperatures.

The hydrogenation of CO continues to draw wide attention, not only because of its industrial importance but also because it serves as a model catalytic hydrogenation reaction where the reactants, products, and transient species at the catalyst surface could be characterized simultaneously. A large volume of work published in this area is reviewed in various articles (4–9). Broadly speaking, two distinct reaction mechanisms have been put forward. According to an earlier school of thought, the CO hydrogenation is governed by the direct participation of CO and H_2 molecules to form oxygenated intermediates. Thus, Storch *et al.* (10) proposed the formation of M–CH_2O species as intermediates which on surface condensation resulted in chain growth. Pichler and Schulz (11) postulated that even though M–CH_2O species are present on the metal surface, chain growth is accomplished by the direct and stepwise insertion of adsorbed CO molecules. Subsequent investigations, however, brought out various flaws in this scheme, such as that it does not explain why alcohols can initiate synthesis but cannot contribute to chain growth by dehydrocondensation. According to another model, which is widely accepted now, while methanol is produced by direct hydrogenation of molecularly adsorbed CO, the synthesis of hydrocarbons is initiated by the dissociation of adsorbed CO to form an active state of carbon species, which transforms directly to hydrocarbons via formation of methyl and methene groups for chain growth. The formation of various forms of carbon during CO dissociation has also been proposed (12, 13). A number of studies supporting "active-carbon" intermediate theory are reviewed in Refs. (4–6).

In the present study we therefore evaluated the heat evolved during exposure of CO, H_2, and $CO + H_2$ (1 : 4) over polycrystalline ruthenium metal and a Ru/TiO_2

catalyst at different temperatures in range 300–470 K. The effect of surface coverage was evaluated by dosing successive pulses of these adsorbates. The fraction of the gases adsorbed and the reaction products formed at different stages were analyzed simultaneously. These data helped us in delineating the role played by the support and the mechanistic routes involved at different stages of CO methanation reaction. While the present paper deals with the adsorption of CO and H_2 the data on the coadsorption of these two gases are included in the following paper.

EXPERIMENTAL

Catalyst

The Ru/TiO_2 sample used in this study was prepared by coprecipitation method starting with the chlorides of ruthenium and titanium and using a 20% ammonium bicarbonate solution for precipitation at 335 K. The precipitate was separated by centrifugation after 16 h of aging and was washed repeatedly till free from chloride ions. The catalyst was dried in air at 345 K (24 h) and then at 370 K (8 h) followed by sintering at 525 K for 16 h and at 620 K for 8 h under $O_2 + Ar$ (1:1, 60 ml min^{-1}) flow. A 40–80 mesh fraction of this sample having BET surface area of $\sim 90 \, m^2 \, g^{-1}$ was used for all the experiments after 3 h reduction in $H_2 + Ar$ stream (1:1, 60 ml min^{-1}) at 575 K. The samples were cooled and stored under argon atmosphere. The metal content of the sample as evaluated by X-ray fluorescence method was found to be 4.5 wt%. The X-ray diffraction pattern revealed the presence of about 80% anatase and 20% rutile phases of TiO_2, while no XRD signals due to ruthenium were detected indicating its fine dispersion. TEM analysis revealed that the size of the majority of Ru particles ranged between 2 and 4 nm.

A fine powder of ruthenium metal used in this study was prepared by complete reduction of ruthenium trichloride in flowing hydrogen at 575 K. A 40–80 mesh fraction of this sample employed in this study was porous in nature and showed a N_2 adsorption BET surface area of around $6 \pm 2 \, m^2 \, g^{-1}$.

The number of exposed metal sites was evaluated by volumetric hydrogen chemisorption method using the pulse flow technique (Micromeritics, U.S.A., Model-Pulse chemisorb 2700). For this purpose, the samples were pretreated *in situ* at 573 K first in H_2 and then in He. The amount of H_2 chemisorbed at room temperature was found to be 8.6 and 7.8 $\mu mol \, g^{-1}$ for the Ru/TiO_2 and Ru metal samples, respectively. Measurements carried out using temperature-programmed desorption of H_2, however, gave marginally higher values, particularly in the case of the supported metal sample. The two samples may thus be considered comparable in terms of metal surface area even though their BET areas were quite different.

Microcalorimetry

Microcalorimetric measurements of the heats of adsorption were carried out using a Calvet-type heat flow microcalorimeter equipped with stainless-steel gas circulation vessels (C-80 calorimeter, Setaram, France). The procedure is described earlier in detail (1–3). A 100-mg sample was taken in one of the vessels, whereas the reference cell was kept empty. The cells were connected at one end to a common vacuum system or a gas manifold so as to have a provision for evacuation of the vessels or alternatively to maintain a sample under desired gas flow. Fine control needle valves were used to maintain the vessels under identical and steady gas flow conditions. The effluent from the sample cell was analyzed with an assembly of Porapak-P and molecular sieves 5 A colums, both connected in tandem and each followed by a thermal conductivity detector. Both the detectors and the GC columns were thermally insulated and were maintained under ambient conditions. Prior to calorimetric measurements, a sample was treated *in situ* in flowing hydrogen (20 ml min^{-1}) at 475 K for 2 h, followed by evacuating (475 K, 1 h) and heating the sample for 1 h under helium flow at 475 K. While maintaining a sample under helium flow (20 ml min^{-1}) several successive 100 μl (4.1 μmol) pulses of CO or H_2 were dosed over catalyst sample through an injection port at the entry point of the sample cell. The amount of a gas adsorbed over catalyst surface and the corresponding heat evolved were recorded simultaneously using a multipen recorder/integrater. The value of differential or molar heat of adsorption (q_d) was thus obtained by dividing the heat evolved during an individual pulse injection with the amount of gas adsorbed. The values of heat at initial stages of adsorption (q_i) were obtained from the plots of log q_d vs surface coverage by extrapolating them to $\theta = 0$. Each set of experiments was repeated at least two or three times in order to check for the data reproducibility. As mentioned in our earlier publications, the accuracy of q values depended on the accuracy of gas chromatographic data and the variations in the q values were found to be the in range of 5–10%.

Carbon monoxide of 99.9% purity from Airco (U.S.A.) was used after passing through a dry ice trap to remove any carbonyl or moisture impurities. Helium from Airco was also passed through deoxo and molecular sieves traps before its use as a carrier gas. High-purity hydrogen was obtained with an Elhygen H_2-generator.

RESULTS

Microcalorimetry

CO Adsorption

Ru/TiO_2 catalyst. When a 100-μl ($\sim 4.1 \, \mu mol$) pulse of carbon monoxide was dosed over 100 mg catalyst sample
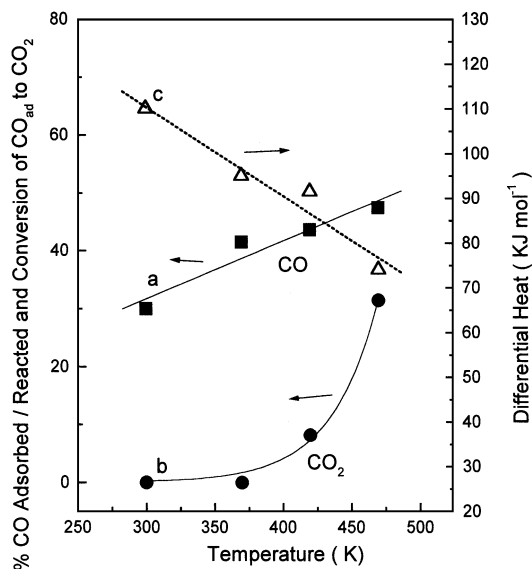
FIG. 1. Percentage of CO adsorbed/reacted (a) and the conversion of $CO_{(ad)}$ to CO_2 (b) when a pulse of 4.1 μmol CO was dosed over a fresh 100 mg Ru/TiO_2 catalyst at different temperatures. Curve c shows the corresponding values of differential heat evolved.

under He flow (20 ml min^{-1}) a part of the CO was adsorbed, a part reacted to form CO_2 while the rest was eluted. The amount of eluted CO or that of the product CO_2 depended upon the catalyst temperature. The amount of CO adsorption from a pulse and its conversion to CO_2 as a function of catalyst temperature are given in Figs. 1a and 1b. Even though the fraction of CO adsorbed increased progressively with the rise in catalyst temperature (Fig. 1a), CO_2 was formed only at the sample temperatures above 370 K (Fig. 1b). Thus, while only ~8% of adsorbed CO was converted to CO_2 at reaction temperature of 425 K, the yield at 470 K was ~32%.

Figure 1c gives the amount of heat evolved (q_d) per mole of adsorbed/reacted CO from the first pulse injection. These data indicate that the q_d decreased progressively with the increase of sample temperature. Thus, compared to a value of $q_d \sim 112$ kJ mol^{-1} for the first pulse CO adsorption at 300 K, the corresponding value for reaction temperature of 475 K was around 75 kJ mol^{-1} (Fig. 1c).

The amount of adsorbed CO was found to reduce progressively when several successive CO pulse (4.1 μmol each) exposures were made at a particular sample temperature, without any in-between pretreatment. The decrease in CO_2 yield during these CO pulse exposure was however only marginal, particularly at a sample temperature of 470 K. These data for different sample temperatures are given in Fig. 2.

Figures 3a–3d summarize the data on the differential heat of CO adsorption as a function of CO adsorbed from the successive 4.1 μmol CO pulses dosed over Ru/TiO_2 at different temperatures. The data in Fig. 3a for the experiment

at 300 K show that the q_d reduced sharply from a value of 112 kJ mol^{-1} for the first pulse injection to a value of ~78 kJ mol^{-1} for the third CO pulse, which was accompanied by the drastic decreases in CO adsorption. A negligibly small heat was evolved for further CO pulse injections. With the rise in sample temperature to 370 K, the adsorption from the first CO pulse increased and the q_d was ~96 kJ mol^{-1}. Smaller amounts of CO continued to adsorb during successive CO pulse injections giving rise to ~70 kJ mol^{-1} heat (Fig. 3b). At a reaction temperature of 470 K, almost constant q_d of ~75–80 kJ mol^{-1} was observed and a large fraction of CO continued to get adsorbed during the successive six pulse exposures over catalyst surface (Fig. 3d).

Ruthenium metal. Almost a similar fraction (~60 ± 2%) adsorbed/reacted when a 100 mg ruthenium metal sample was exposed to the first 4.1 μmol CO pulse at different temperatures in the range 300–470 K. Also, a similar amount of heat (~100 ± 5 kJ mol^{-1}) was evolved during this interaction, irrespective of the catalyst temperature. However, when several successive CO pulses were dosed at a particular temperature, a progressively reduced amount of CO was adsorbed. Figures 4a and 4b show the data obtained for the reaction temperatures of 300 and 370 K. Figures 4c and 4d show the fraction of CO adsorbed/reacted from the successive CO pulses dosed at the sample temperatures of 420 and 470 K, respectively. While no carbon dioxide was produced during CO interaction at the sample temperatures below 400 K, a part of the adsorbed CO gave rise to CO_2 formation at higher temperatures. Figures 4e and 4f give the typical CO_2 yield from the five successive CO pulses
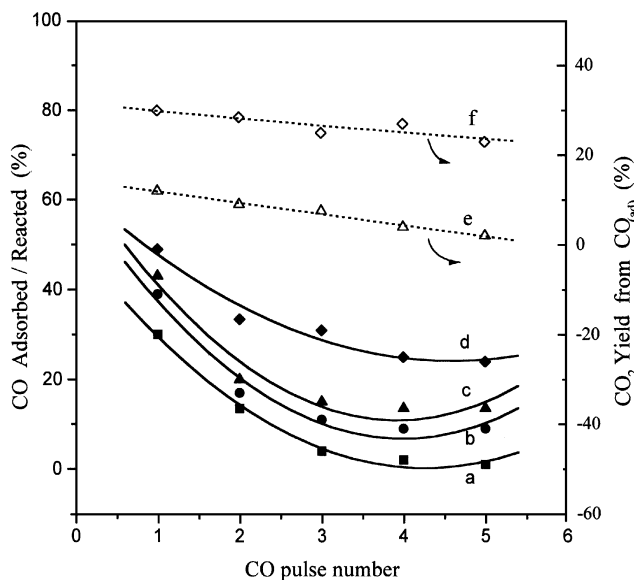

FIG. 2. Percentage of CO adsorbed/reacted and conversion of CO_{ad} to CO_2 when five successive CO pulses (4.1 μmol each) were dosed over Ru/TiO_2 at different temperatures: (a) 300 K, (b) 370 K, (c) 420 K, (d) 470 K, (e) 420 K, and (f) 470 K.
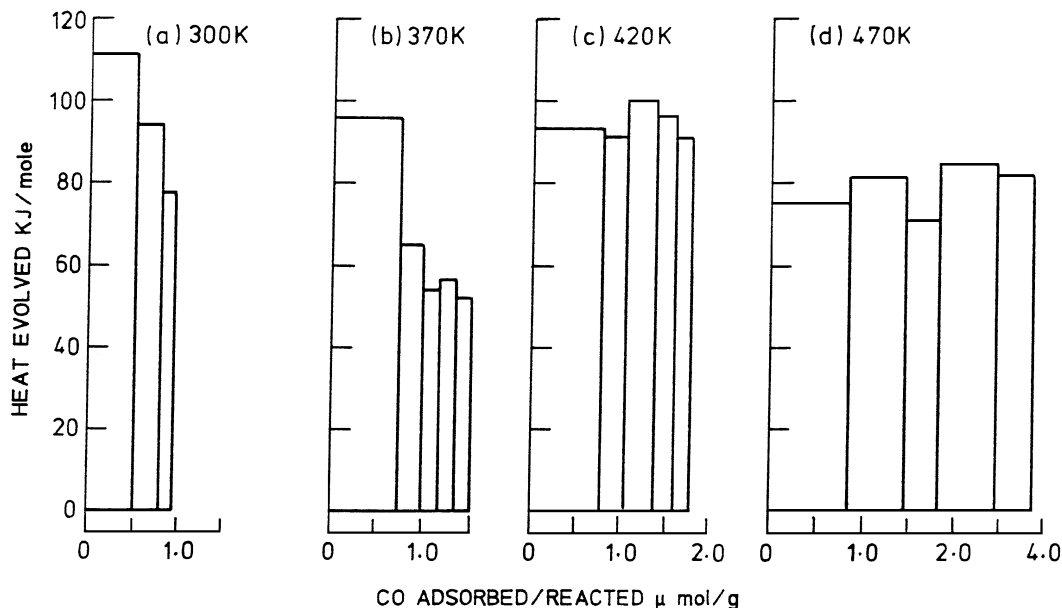
FIG. 3. Differential heat evolved as a function of surface coverage when a 100 mg Ru/TiO$_2$ catalyst was exposed to successive 4.1 μmol CO pulses at different temperatures.

at the reaction temperatures of 420 and 470 K, respectively. It is of interest to note that no CO$_2$ formed from the first CO pulse injection; an increasing amount of CO$_2$ was produced during the next two pulse injections, the yield being higher at higher reaction temperatures (Figs. 4e and 4f). Furthermore, no CO$_2$ was produced during the fourth and the fifth CO pulse exposures.

Figure 5 presents the microcalorimetry data for the successive CO pulse adsorption on the ruthenium metal sample. In each experiment the heat of adsorption from the first pulse was ~110 ± 5 kJ mol^{-1}. However, the q_d decreased progressively with the increasing surface coverage, particularly at lower exposure temperatures. Thus, for a catalyst temperature of 300 K, the value of q_d decreased to ~60 kJ mol^{-1} for the fifth pulse injection (Fig. 5a). On the other hand, it remained almost constant at 110 kJ mol^{-1} for all the dosed CO pulses at a sample temperature of 470 K (Fig. 5c).
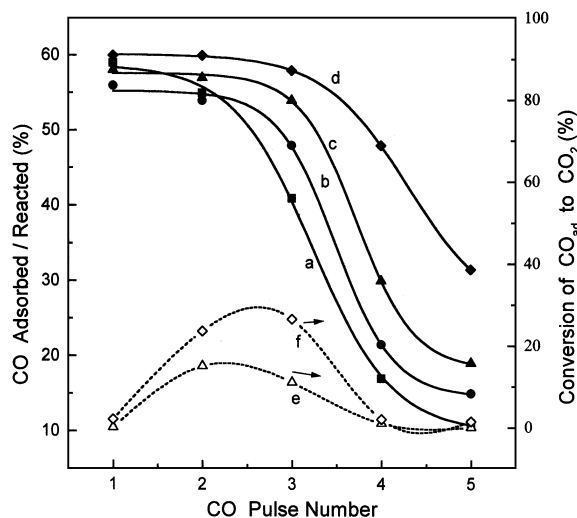

FIG. 4. Percentage of CO adsorbed/reacted and conversion of CO$_{ad}$ to CO$_2$ when five successive CO pulses (4.1 μmol each) were dosed over 100 mg polycrystalline Ru at different temperatures. (a) 300 K, (b) 370 K, (c) 420 K, (d) 470 K, (e) 420 K, and (f) 470 K.
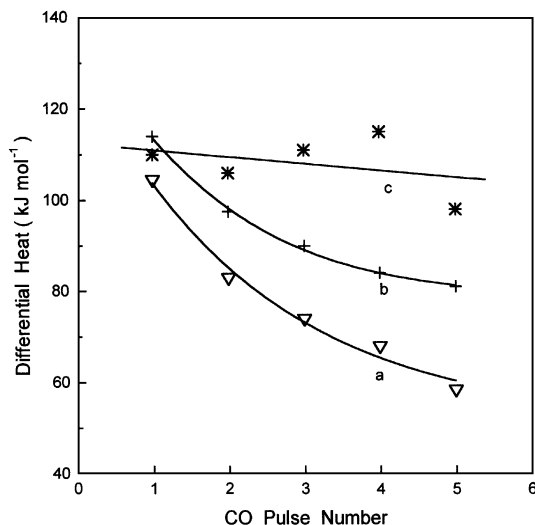
FIG. 5. Differential heat evolved during exposure of a 100-mg polycrystalline Ru sample to five successive 4.1-μmol CO pulses at different temperatures: (a) 300 K, (b) 420 K, and (c) 470 K.

Hydrogen Adsorption

Ru/TiO₂ catalyst. An almost similar amount was adsorbed at a particular temperature when five to six successive H₂ pulses (4.1 μmol each) were dosed over a 100 mg sample of Ru/TiO₂. However, the amount of adsorbed H₂ increased progressively with the rise in catalyst temperature. Thus, about 12, 28, and 40% of the dosed H₂ was adsorbed from an individual pulse when the sample temperature was 300, 370, and 470 K, respectively. Figures 6a–6c present these data.

Figures 6d and 6e give the values of q_d when the Ru/TiO₂ sample was exposed to five successive H₂ pulses as mentioned above. As seen in Fig. 6d, about 48 kJ heat was evolved per mole of H₂ adsorbed from the first pulse dosed at a sample temperature of 300 K, while the subsequent H₂ pulse exposures gave rise to a smaller amount of heat ($\sim$30 kJ mol^{-1}). For the exposure temperature in the 370–470 K range, an almost similar $q_d \sim 37$ kJ mol^{-1} was observed for the first H₂ injection, the value being $\sim$30 kJ mol^{-1} for the subsequent H₂ pulse exposures (Fig. 6e).

Ru metal. The catalyst temperature had only a marginal effect on the hydrogen adsorption from the first pulse injection. Thus, while around 70% of the injected H₂ was adsorbed at 300 and 370 K, the amount adsorbed was $\sim$60% for the sample temperature of 470 K. Furthermore, a progressively smaller fraction of H₂ was adsorbed from the successive pulses dosed at a particular temperature. These data are plotted in Fig. 7.

Figure 8 gives the q_d values for the first five H₂ pulses dosed over Ru metal at different temperatures. The first H₂ pulse gave rise to $\sim$45 $\pm$ 3 kJ mol^{-1} heat, irrespective of the

FIG. 7. Percentage of H₂ adsorbed over 100 mg polycrystalline Ru during exposure to successive 4.1-μmol H₂ pulses at different temperatures.

exposure temperature. The q_d was lower for the successive pulse injections made at the sample temperatures of 300 and 370 K (Figs. 8a and 8b). The heat value at higher sample temperatures was, however, found to be almost constant for all the injected H₂ pulses (Fig. 8c).
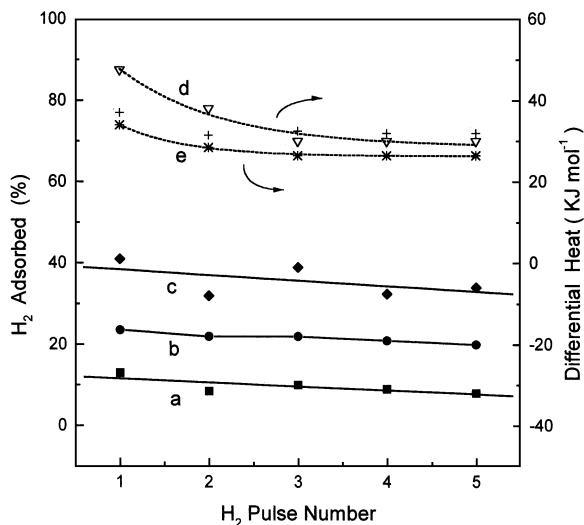

FIG. 6. Percentage of H₂ adsorbed and corresponding differential heat evolved when a 100-mg Ru/TiO₂ catalyst sample was exposed to five successive 4.1-μmol H₂ pulses at different temperatures. (a) 300 K, (b) 370 K, (c) 470 K, (d) 300 K, and (e) 370 and 470 K.
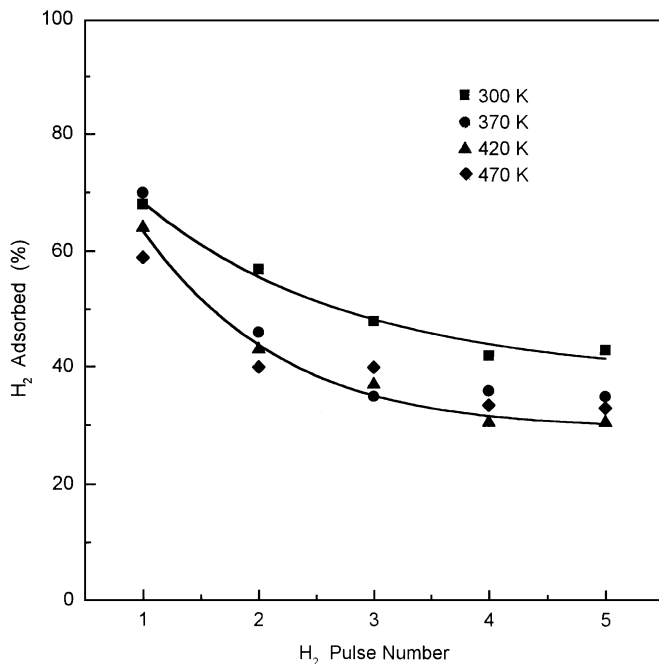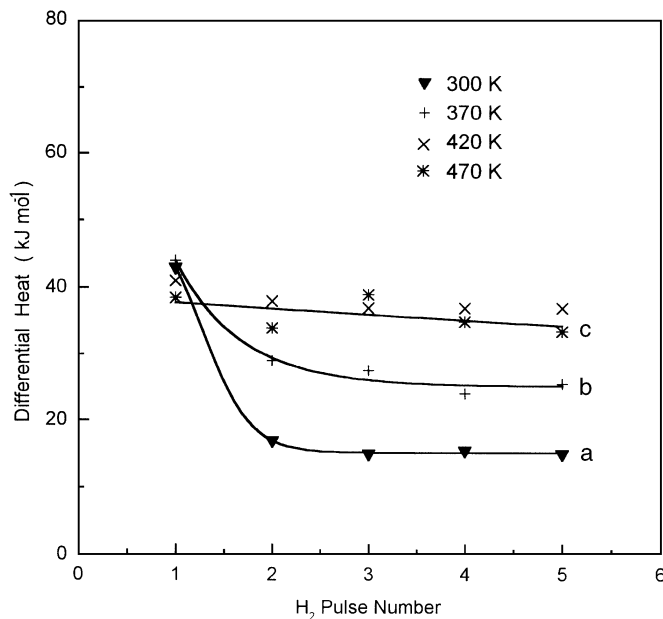

FIG. 8. Differential heat evolved during exposure of a polycrystalline Ru metal sample to successive 4.1-μmol H₂ pulses at different temperatures.

Effect of Preadsorbed Gases

The tests performed on Ru/TiO$_2$ showed that the catalyst surface covered with carbon monoxide at room temperature was not accessible to hydrogen molecules. Thus, no hydrogen was adsorbed over catalyst sample exposed to 10 successive CO pulse doses under He flow (20 ml min^{-1}) at 300 K followed by flushing for 30 min under He. Correspondingly, no heat was evolved during these H$_2$ pulse injections. On the other hand, when a sample exposed similarly to 10 successive pulses of 4.1 μmol H$_2$ and flushed with He (30 min) was dosed thereafter with CO pulses at 300 K, the amount of gas adsorbed was only marginally lower than that shown in Fig. 1. Thus, about 28% of CO was adsorbed over Ru/TiO$_2$ from the first pulse, compared to a value of 30% in the case of a fresh sample. The amount adsorbed from the three successive pulses was 13, 5, and 2% respectively (cf. Fig. 1a). The heat evolved during this process was around 92 ± 3 kJ mol^{-1} compared to a value of 110 kJ mol^{-1} in Fig. 3a.

Similar results were obtained using a ruthenium metal sample.

Initial Heat of Adsorption

The heat values corresponding to initial stages of adsorption, as calculated from the coverage dependent microcalorimetry data in Figs. 3, 5, 6, and 8 are given in Table 1.

Adsorption over Titania

Only a negligible (1–2%) fraction of CO was absorbed over the metal-free titania sample, prepared and pretreated under conditions similar to those used for Ru/TiO$_2$, when dosed with successive 4.1-μmol pulses at the sample temperatures in the range 300–470 K. Also, no CO$_2$ was formed and no heat was evolved in this process. Similarly, no H$_2$ was found to adsorb over titania under the experimental conditions of this study.

DISCUSSION

Only a few calorimetric studies have so far been reported on the adsorption of H$_2$ and CO over ruthenium

TABLE 1

Differential Heat at Initial Stage of Adsorption (q_i) of CO and H$_2$ over Polycrystalline Ru Metal and Ru/TiO$_2$ Catalyst at Different Temperatures

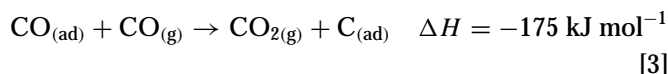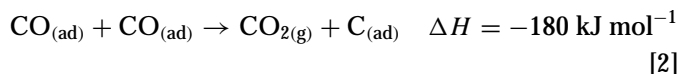| Catalyst temperature (K)	Ru metal (kJ mol^{-1})		Ru/TiO$_2$ catalyst (kJ mol^{-1})	
	CO	H$_2$	CO	H$_2$
300	120	65	130	57
370	121	60	120	40
420	120	42	94	—
470	110	37	75	32

metal, particularly in its supported form. Also, to the best of our knowledge no such study has so far been carried out on this catalyst system under the actual reaction conditions. This becomes apparent from the recent reviews by Cardona-Martinez and Dumesic (14) and Toyoshima and Somorjai (15) which include most of the earlier studies on calorimetric measurements of CO and H$_2$ adsorption over noble metals. The initial heat (q_i) values obtained in our study for CO and H$_2$ adsorption at room temperature (Table 1) are quite in agreement with the reported values. Thus the $q_i \sim 120$ kJ mol^{-1} for CO adsorption over polycrystalline Ru (Table 1) matches the value reported in Ref. (15). Guerrero-Ruiz (16) reported an initial enthalpy of ~ 138 kJ mol^{-1} for the adsorption of carbon monoxide over ruthenium graphitized carbon black catalysts, which is consistent with the q_i observed in our study over Ru/TiO$_2$ at 300 K (Table 1).

A comparison of the data in Figs. 3 and 5 shows a large difference in the CO chemisorption behavior of Ru metal and Ru/TiO$_2$, particularly at the higher exposure temperatures. Thus while an almost constant $q_d \sim 110$ kJ mol^{-1} was evolved during the first pulse injection over ruthenium metal at different temperatures (Fig. 5), a progressively decreasing q_d was observed with the rise in temperature using Ru/TiO$_2$. Also, the data in Fig. 1a show that the amount of CO adsorbed from the first pulse increased with the rise in sample temperature, contrary to the data of Fig. 4. IR spectroscopy studies have shown that the interaction of CO with a Ru/TiO$_2$ catalyst gave rise to the vibrational bands at around 1223, 1360, 1428, 1529, and 1590 cm^{-1} which are identified with the oxygenate species such as bridged carbonates and bicarbonates (17–20). In addition, bands were observed due to chemisorbed CO (1900–2150 cm^{-1}), physisorbed CO (2185 cm^{-1}) and the adsorbed CO$_2$. No such species were, however, formed when a metal-free TiO$_2$ sample was exposed to CO. We can thus conclude that the heat evolved during chemisorption of CO over Ru/TiO$_2$ promotes the formation of carbonate type surface species at metal/support interfaces which dissociate at elevated temperatures to form CO$_2$ (Fig. 1b). The over all process thus amounts to reduction of TiO$_2$, for example,

$$2\text{TiO}_2 + \text{CO} \rightarrow \text{Ti}_2\text{O}_3 + \text{CO}_2\uparrow, \quad \Delta H = +80 \text{ kJ mol}^{-1}.$$
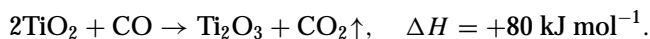
The increasing contribution of this endothermic step, in addition to the exothermic adsorption of CO at Ru sites, explains the observed decrease in q_d values with the rise in temperature (Fig. 1c). The data on CO adsorption and its conversion to CO$_2$ may thus be correlated with the availability of reducible sites at the metal/support interfaces. A similar decrease in the differential heat with the increase in CO coverage was observed by Sharma et al. (21) over various supported Pt catalysts at 403 K and has been attributed to the decrease in adsorption strength due to presence of lateral repulsive interactions between adsorbed species.

A comparison of CO_2 yields in Figs. 2e and 2f and Fig. 4 for successive pulse exposures shows that while the CO_2 formation commenced from first CO pulse injection in case of Ru/TiO₂ and the CO_2 yield was almost constant during successive CO pulse injections, the formation of CO_2 on Ru metal was observed only for the second and the third pulse exposures. Also, no CO_2 was formed from the subsequent pulse exposures. These data thus suggest that a different mechanism was responsible for the CO_2 formation over Ru metal. The possible reaction routes in this case may be identified as

$$CO_{ad} \rightarrow C_{(ad)} + O_{(ad)} \quad \Delta H = -8 \text{ kJ mol}^{-1} \quad [1]$$

$$CO_{(ad)} + CO_{(ad)} \rightarrow CO_{2(g)} + C_{(ad)} \quad \Delta H = -180 \text{ kJ mol}^{-1} \quad [2]$$

$$CO_{(ad)} + CO_{(g)} \rightarrow CO_{2(g)} + C_{(ad)} \quad \Delta H = -175 \text{ kJ mol}^{-1} \quad [3]$$

$$CO_{(g)} + O_{(ad)} \rightarrow CO_{2(g)} \quad \Delta H = -143 \text{ kJ mol}^{-1} \quad [4]$$

$$CO_{(ad)} + O_{(ad)} \rightarrow CO_{2(g)} \quad \Delta H = -140 \text{ kJ mol}^{-1} \quad [5]$$

The heat values given above indicate the order of the magnitude and are either quoted from the literature (14, 15, 22) or evaluated from the heats of adsorption and formation of different molecules over platinum group metals (23).

An almost similar amount of CO adsorption during the first CO pulse exposure (Fig. 4) suggests that the mode of CO adsorption over bulk Ru was independent of the catalyst temperature. The CO_2 yields from the successive CO pulse injections suggest the involvement of the Eley–Rideal-type reaction mechanism, i.e., steps [1], [3], and [4]. The low exothermicity of step 1 may explain why the observed q_d values were lower than the q_d values expected for steps [3] or [4]. Also, the carbon deposition during this step may account for the progressive blockage of the adsorption sites, leading to the reduced CO_2 yield and the lower heat of adsorption from the successive CO pulse doses (Figs. 4 and 5). The estimation of the quantitative contribution of the above-mentioned individual steps is, however, not feasible now.

The data in Figs. 6 and 7 show that the hydrogen adsorption also depends strongly on the dispersion state of Ru. Thus only a small (~10%) fraction of hydrogen was adsorbed on Ru/TiO₂ at 300 K and it increased progressively with the rise in catalyst temperature, the adsorbed fraction being ~40% at a catalyst temperature of 470 K. The heat value per mole of H₂ adsorbed, however, remained the same indicating similar mode of hydrogen adsorption. The near consistency in the amount of hydrogen adsorbed from successive pulses indicates a weak hydrogen bonding which is also reflected in a lower q_d value (Fig. 6). The initial heat of hydrogen adsorption on Ru/TiO₂ at 57 kJ mol⁻¹ is similar to a value observed for the H₂ adsorption over supported palladium and platinum catalysts (14, 24). Chou and Vannice (24) have demonstrated that the heat of hydrogen adsorption was independent of the support used but it increased sharply with the decrease in average particle size. The lowering of q_d to ~30 kJ mol⁻¹ with the increase in surface coverage, irrespective of the catalyst temperature, reflects on the weakening of hydrogen bonding presumably due to multilayer adsorption (Fig. 6). A similar observation has been reported by Sharma *et al.* (21).

The q_i for the hydrogen adsorption over bulk ruthenium (~65 kJ mol⁻¹) is of similar magnitude to that reported for the bulk Pd (14, 24). The lowering of q_d values during successive pulse injections (Fig. 8) may be attributed to the multilayer adsorption of H₂ as discussed above.

In conclusion, we may thus state that the chemisorption behavior of Ru is changed considerably on dispersion over a reducible oxide support, such as titania. The H₂ adsorption was found to be suppressed considerably over Ru/TiO₂, particularly at the low reaction temperatures. The CO adsorption, on the other hand, resulted in the reduction of the titania support to a lower oxidation state, the extent of which depended on the catalyst temperature. The heat evolved at Ru–TiO₂ interfaces during CO chemisorption at metal sites may facilitate this process since no reduction of titania was observed in the absence of Ru. This is in agreement with the conclusions reached in our earlier study on the tin oxide-supported platinum (1). In the case of bulk Ru metal, the dissociation of CO and the subsequent reaction of the surface-adsorbed species give rise to CO_2 formation. The experiments performed with the preadsorption of one of the gases have unequivocally shown that, for both Ru metal and Ru/TiO₂, the CO adsorption remains uninhibited by the preadsorbed H₂, but the catalyst surface covered with the CO was completely inaccessible to subsequent H₂ adsorption.

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