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Microcalorimetry, Adsorption, and Reaction Studies of CO, O_2, and CO + O_2 over Fe_2O_3, Au/Fe_2O_3, and Polycrystalline Gold Catalysts as a Function of Reduction Treatment

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Thermochemical and volumetric measurements were made for the adsorption and reaction of CO, O_2, and CO + O_2 on catalysts from 300 to 470 K, as a function of H_2 pretreatment. The transformation of Au/Fe_2O_3 to Au/Fe_3O_4 led to inhibited adsorption and oxidation of CO. The exposure of a reduced Au/Fe_2O_3 to CO + O_2 resulted in an $O_{2(ad)}/CO_{(ad)}$ ratio >1 as well as the reoxidation of the support and the progressive restoration of its catalytic activity. The reaction routes involved in the oxidation of CO over polycrystalline gold were different from those over the Au/Fe_2O_3 catalyst. Thus, while the simultaneous adsorption of the reactant molecules was responsible for this reaction on Au metal, the redox mechanism involving the removal and subsequent replenishment of lattice oxygen played a role in both the Au/Fe_2O_3 and Fe_2O_3 catalysts, where the presence of gold promoted these steps. © 1999 Academic Press

Key Words: **CO oxidation; supported gold catalyst; role of lattice oxygen; pretreatment effect.**

INTRODUCTION

In the first part of this study (1), we used microcalorimetry and FTIR methods to demonstrate that the oxidation of CO on the Fe_2O_3 and Au/Fe_2O_3 catalysts involves a common redox mechanism where the removal and replenishment of lattice oxygen plays a prominent role. The increase in the reaction rate in the presence of gold is attributed to the surge in temperature at the Au/Fe_2O_3 interface which in turn is a result of the energy released during CO chemisorption on gold crystallites. To investigate the role of adsorbed and lattice oxygen, similar experiments were performed on Au/Fe_2O_3, Fe_2O_3, and polycrystalline gold samples pretreated in H_2. This enabled us to evaluate the performance of a set of catalysts, containing Au, with similar characteristics but with the support in different oxidation states. H_2 reduction made it easier to work with a gold surface free of adsorbed oxygen. *In situ* x-ray diffraction experiments were performed to monitor the effect of gold on the phase transformations in Fe_2O_3 as a result of a reduction in H_2 at different temperatures.

EXPERIMENTAL

Catalysts

The preparation method and the characteristics of Au (5 at.%)/Fe_2O_3, Fe_2O_3, and polycrystalline gold powder samples are given in Ref. (1). A 40- to 80-mesh fraction (∼150-μm particle size) of these samples was used in all the experiments. The catalyst samples, labeled (r), were reduced in H_2 (e.g., Fe_2O_3(r)). (o) refers to samples treated in O_2.

Microcalorimetry

A Calvet-type heat-flow microcalorimeter (C-80 Cetaram, France), equipped with gas circulation vessels and connected to a GC, was employed in this study as described in our earlier publications (1, 2). A fresh lot of catalyst (200 mg) was placed in the sample holder. To reduce the catalyst, the samples were heated *in situ* in an H_2 flow (20 ml min^{-1}, 475 K, 2 h) followed by evacuation (475 K, 1 h) and heating in He. While keeping the sample in the He flow at a desired temperature, several pulses of 4.1 μmol of CO, O_2, or CO + O_2 (2 : 1) were injected on a sample at intervals of 15–20 min. The heat produced and the amount of gases adsorbed, reacted, or produced in the process were evaluated for each pulse exposure. After 8–10 pulses of CO at a given temperature, a sample was kept in an He flow for about an hour and then exposed to successive O_2 pulses to evaluate the O_2 reactivity of the surface species formed. The cell was flushed with He at the experimental temperature after each O_2 pulse.

Activity

The effect of reducing pretreatment (H_2, 470–570 K) of Au/Fe_2O_3 on its CO oxidation activity was evaluated

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according to the procedure described in (1). Measurements were made in a stream of CO + O_2 + He (2 : 1 : 17, 1200 ml h^{-1} g^{-1}) and at a reaction temperature of 298 K.

XRD Study

For phase characterization after H_2 reduction at different temperatures, XRD patterns of Au/Fe_2O_3 and Fe_2O_3 samples were recorded using a MRC model X-86-N3 high-temperature attachment, mounted to a Philips wide-angle goniometer. A small amount of powdered sample was placed on a platinum–40% rhodium plate, which also served as a heater. The sample was treated *in situ* in a stream of H_2 + He (1 : 1) flow (120 ml min^{-1}) at a temperature between 300 and 773 K for about 30 min, after which the XRD pattern was recorded. The high-temperature attachment was calibrated and aligned using a Si standard and the reflection of the Pt–40% Rh heater as an internal standard. A Philips x-ray diffraction unit and Cu$K\alpha$ radiation were used in this study.

RESULTS

Au/Fe_2O_3 and Fe_2O_3 Catalysts

CO adsorption. Figure 1 shows the average fraction of CO adsorbed (curves a and b) and the yield of CO_2 (curve c), when Au/Fe_2O_3(r) and Fe_2O_3(r) samples were exposed at different temperatures to five successive pulses of 4.1 μmol of carbon monoxide. The changes in enthalpy during the process are given in Figs. 1d and 1e. On one hand, a greater amount of CO was adsorbed over Au/Fe_2O_3 (curve a), compared to Fe_2O_3 (curve b). On the other hand, a smaller amount of CO was held over the Au/Fe_2O_3(r) and Fe_2O_3(r) samples at all exposure temperatures, compared to the corresponding samples pretreated in oxygen. Thus, compared to 40–60% adsorption of CO over the Au/Fe_2O_3(o) sample (1), the fraction adsorbed/reacted was only 10–30%, depending on the temperature of the sample, when a pulse of CO was injected over a reduced sample (Fig. 1a). In contrast to the temperature-dependent CO → CO_2 conversion of 2–60% over Au/Fe_2O_3(o) (1), no CO_2 was formed during the interaction of CO with Au/Fe_2O_3(r), irrespective of the sample temperature (Fig. 1c). Accordingly, only a small amount of heat was produced, the ΔH being ~50–60 kJ mol^{-1} for CO exposure below 350 K and increasing to ~100 kJ mol^{-1} at higher temperatures (Fig. 1d). A higher q value (~110 kJ mol^{-1}) was found for the CO interaction on Au/Fe_2O_3(o) samples (1). As in the case of Au/Fe_2O_3(r), no CO_2 formed during the adsorption of CO on Fe_2O_3(r) samples also at all temperatures. The q value was about 110 kJ mol^{-1} of CO adsorbed, irrespective of the adsorption temperature (Fig. 1e), compared to q values of 125–175 kJ mol^{-1} found for the Fe_2O_3(o) sample (1).

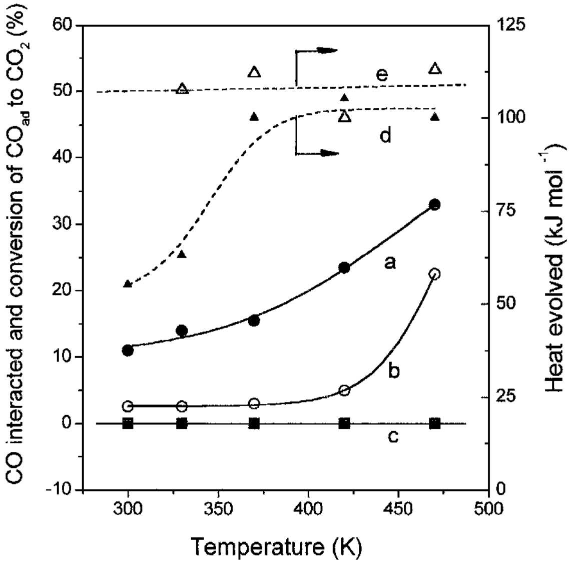

FIG. 1. Average fraction of CO adsorbed/reacted (a, b), conversion $CO_{ad} \rightarrow CO_2$ (c), and the heat produced in the process (d, e) when a 4.1-μmol pulse of CO was injected over Au/Fe_2O_3(r) and Fe_2O_3(r) catalysts. (a, c, d) Au/Fe_2O_3(r); (b, c, e) Fe_2O_3(r).

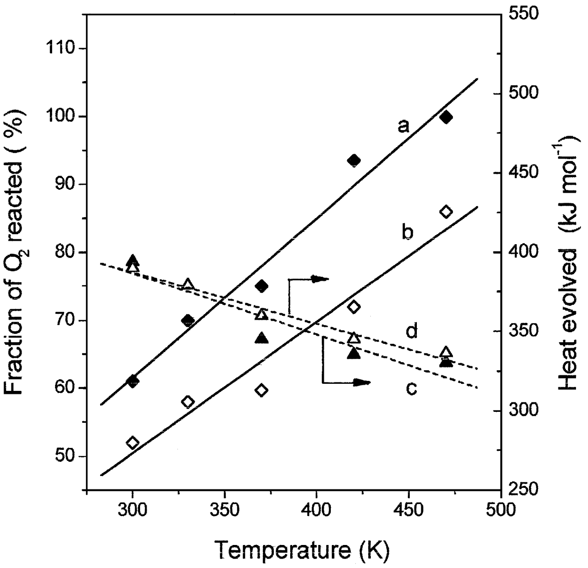

FIG. 2. Fraction of O_2 adsorbed (a, b) and the heat produced (c, d) at different temperatures when Au/Fe_2O_3(r) and Fe_2O_3(r) catalysts were exposed to a 4.1-μmol pulse of O_2 subsequent to the injection of 10 pulses of CO followed by flushing under helium. (a, c) Au/Fe_2O_3(r); (b, d) Fe_2O_3(r).

O_2 adsorption. A greater amount of oxygen reacted with the Au/Fe_2O_3(r) (Fig. 2a) as compared to that with Fe_2O_3(r) (Fig. 2b), when the samples were exposed to a pulse of 4.1 μmol of oxygen following exposure to 10 successive pulses of CO and flushing with He at different catalyst temperatures. On one hand, successive pulses of O_2

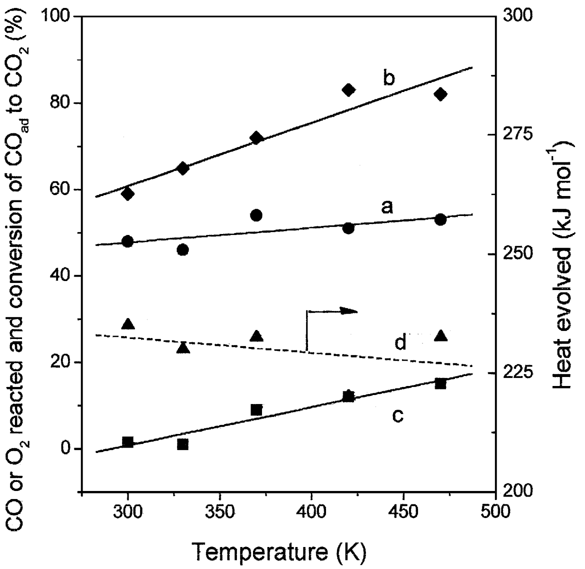

FIG. 3. Fraction of CO (a) and O_2 (b) reacted and the conversion of CO_{ad} to CO_2 (c) when an Au/Fe_2O_3(r) catalyst was exposed to a pulse of 4.1 μmol of $CO + O_2$ (2 : 1) at different temperatures. (d) Enthalpy change.

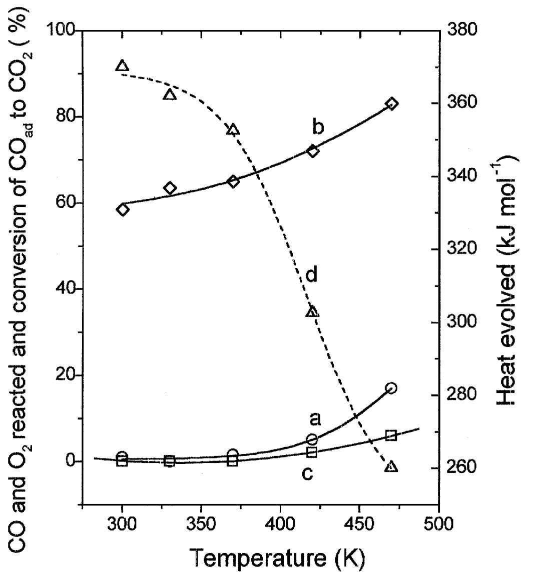

FIG. 4. Fraction of reacted CO (a) and O_2 (b) and the conversion of CO_{ad} to CO_2 (c) when a Fe_2O_3(r) catalyst was exposed to a pulse of 4.1 μmol of $CO + O_2$ (2 : 1) at different temperatures. (d) Enthalpy change.

gave rise to a decreasing fraction of adsorbed O_2, the effect being more pronounced at higher reaction temperatures. On the other hand, a similar amount of heat was produced with the Au/Fe_2O_3 and Fe_2O_3 samples upon adsorption of O_2, the q value decreasing progressively from 400 kJ mol^{-1} at 300 K to ~325 kJ mol^{-1} at 470 K (Figs. 2c and 2d).

$CO + O_2$ adsorption. Average values of the fraction of CO or O_2 adsorbed/reacted, conversion of CO_{ad} to CO_2, and the corresponding values of changes in enthalpy during the injection of a 4.1-μmol $CO + O_2$ pulse on Au/Fe_2O_3(r) and Fe_2O_3(r) samples are given in Figs. 3 and 4, respectively. Only a small amount of CO_2 (~12% in Au/Fe_2O_3 and 5% in Fe_2O_3) was observed during the interaction of CO and O_2 over reduced samples at 470 K; the yields decreased further at lower reaction temperatures (Figs. 3 and 4 (curve c)). The trend of CO and O_2 adsorption on the two reduced samples was, however, quite different. Thus, while the maximum adsorption of CO on Fe_2O_3(r) was about 10%, depending on the catalyst temperature (Fig. 4a), on one hand, about 50% of the dosed CO was adsorbed from a $CO + O_2$ pulse over Au/Fe_2O_3(r), irrespective of the temperature (Fig. 3a). On the other hand, about 60–80% of O_2 was adsorbed/reacted from a $CO + O_2$ pulse over both Au/Fe_2O_3(r) and Fe_2O_3(r) catalysts, the amounts being slightly higher over samples containing gold (Figs. 3 and 4 (curve b)).

The amount of heat produced on $CO + O_2$ pulse exposures over two samples also showed a different trend. Thus, while the average q value for Fe_2O_3(r) decreased progressively from ~370 to 260 kJ mol^{-1} with an increasing sample temperature (300–470 K) (Fig. 4d), the value was constant at 232 ± 2 kJ mol^{-1} for the Au/Fe_2O_3(r) sample (Fig. 3d).

Au Catalyst

CO adsorption. In contrast to the negligible adsorption on Au(o) (1), about 5% of CO was adsorbed on the Au(r) sample when a 4.1-μmol pulse was injected at 300 K; this amount decreased as the catalyst temperature increased (Fig. 5a). No CO_2 was formed, however, and a small amount

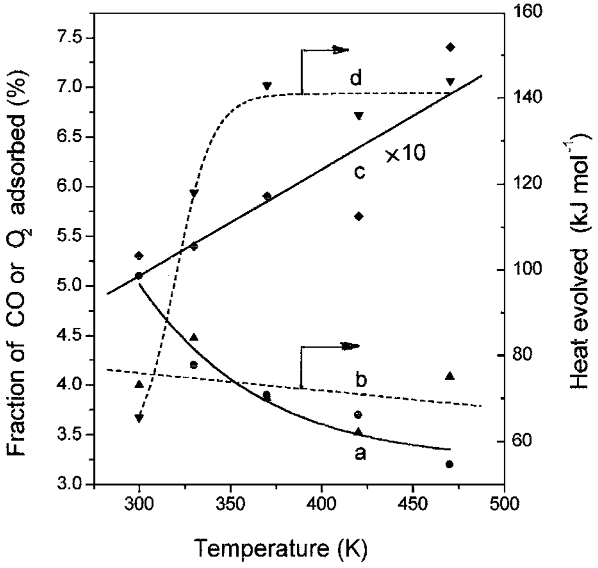

FIG. 5. Fraction of CO adsorbed (a) and the amount of heat produced (b) during exposure of a 4.1-μmol pulse of CO over a polycrystalline gold sample pretreated in H_2. Curve c shows the amounts of O_2 adsorbed and curve d the heat produced when an Au(r) catalyst was exposed to a pulse of 4.1 μmol of O_2 following exposure to 10 successive pulses of CO and flushing in He. Curve c must be multiplied by a factor of 10.

of heat (~75 kJ mol^{-1}) was produced (Fig. 5b). The amount of CO_{ad} decreased with successive CO pulse injections; the data in Fig. 5 refer to the first pulse.

O_2 adsorption. Curves c and d in Fig. 5 give data on adsorption and the q value for Au(r), when following CO pulse exposures as mentioned above the sample was flushed in He and then exposed to a pulse of 4.1-μmol O_2. About 50% of oxygen was adsorbed at 300 K; this value increased to about 70% with an increasing sample temperature, up to 470 K (Fig. 5c). At the same time, the q value increased from ~60 to 145 kJ mol^{-1} (Fig. 5d).

The amount of O_2 adsorbed and the q value decreased sharply when successive pulses of O_2 were injected over a catalyst, the effect being more pronounced at higher temperatures.

$CO + O_2$ adsorption. Larger fractions of CO and O_2 were adsorbed/reacted over Au(r) as compared to those over Au(o), when exposed to a pulse of $CO + O_2$ under similar conditions; the ratio O_2(ad)/CO(ad) was about 1.3 at all the reaction temperatures (Figs. 6a and 6b). Almost complete conversion of CO_{ad} to CO_2 was found, irrespective of the reaction temperature (Fig. 6c). The value of q increased from 155 to 175 kJ mol^{-1} with an increasing temperature (300–470 K) (Fig. 6d).

Effect of gold on the reduction of Fe_2O_3. Reduction of Fe_2O_3 in flowing H_2 ($H_2 + He \sim 1:1$) gave rise to the formation of Fe_3O_4 above 450 K, reaching a maximum concentration at about 570 K. Above 600 K, the intensity of the XRD lines due to Fe_3O_4 decreased, while new reflections, corresponding to α-Fe, were observed. Almost complete reduction of α-Fe_2O_3 to α-Fe was observed above 700 K. FeO was not detected at any stage under the present reduction conditions.

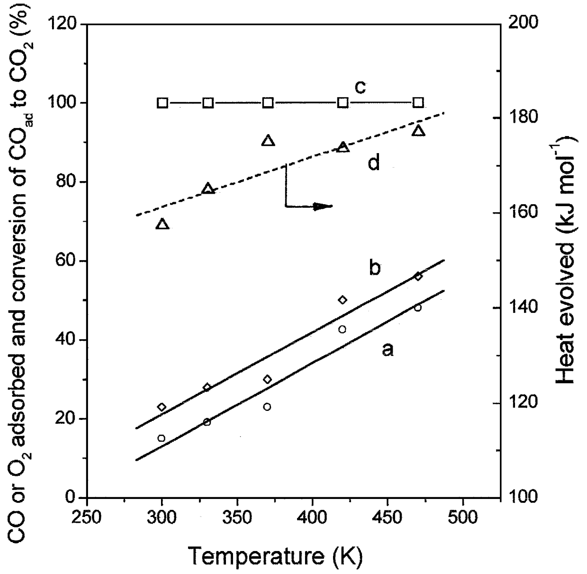

FIG. 6. Average percentage of CO (a) and O_2 (b) adsorbed/reacted and conversion of CO_{ad} to CO_2 (curve c) when a polycrystalline Au(r) sample was exposed to a 4.1-μmol pulse of $CO + O_2$ (2 : 1) at different temperatures. Curve d shows the heat produced.

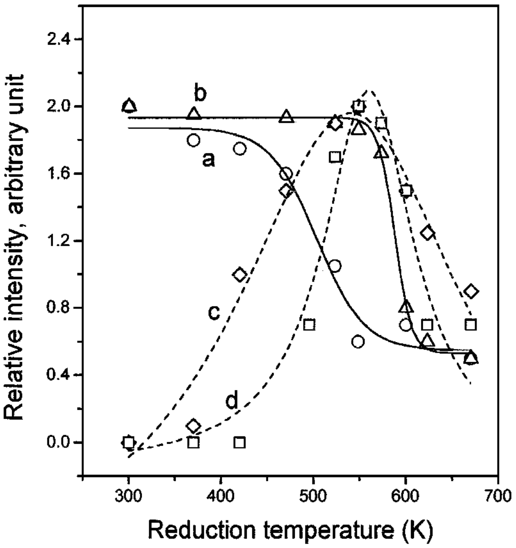

FIG. 7. XRD data showing the effect of gold upon the reduction of Fe_2O_3 in a flow of H_2 at different temperatures. Curves a and b show the relative intensity of Fe_2O_3 signals, while c and d show the reflections due to Fe_3O_4. (a, c) Au/Fe_2O_3; (b, d) Fe_2O_3.

The presence of gold resulted in the reduction of α-Fe_2O_3 at much lower temperatures and the beginning of Fe_3O_4 formation in Au/Fe_2O_3 was observed at temperatures as low as 370 K. Similarly, the formation of α-Fe began in this case at about 500 K compared to 600 K in the case of pure Fe_2O_3. Figure 7 presents the relative intensity of the reflections due to Fe_3O_4 ($2\theta = 35.45°$) and Fe_2O_3 ($2\theta = 33.17°$), showing the comparative reduction of the two samples.

Effect of reduction on catalytic activity. The CO oxidation activity decreased considerably when an Au/Fe_2O_3 catalyst was pretreated in hydrogen; the extent of activity loss depended on the reduction temperature. The activity, however, reached its original level when the catalyst was kept in a stream of $CO + O_2$ for a prolonged period. Figure 8 gives the time-dependent catalytic activity at 298 K of an Au/Fe_2O_3 sample prereduced in H_2 at three different temperatures from 473 to 573 K. The catalytic activity reached 100% within about 100 min, irrespective of the reduction temperature.

DISCUSSION

The salient features of this study are the following:

1. The loss of catalytic activity on the transformation of Fe_2O_3 to Fe_3O_4 under hydrogen reduction conditions of this study and its restoration during prolonged contact with

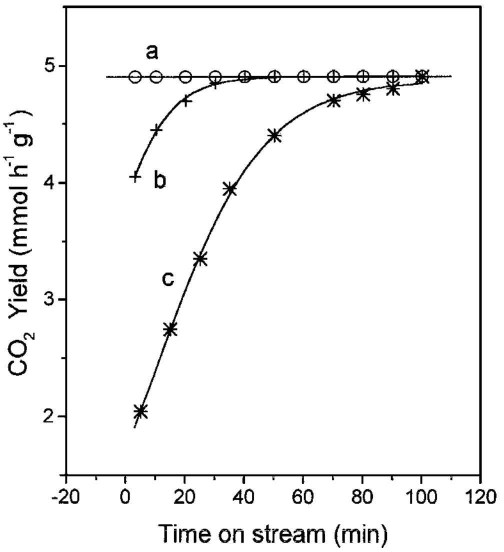

FIG. 8. The effect of H_2 reduction on the CO oxidation activity of an Au/Fe_2O_3 catalyst measured at 298 K as a function of time on stream. Reduction temperature: (a) 473 K, (b) 523 K, and (c) 573 K.

$CO + O_2$ (Figs. 7 and 8) confirm the crucial role of oxygen in the support in CO_2 formation.

2. Even though ~10–30% of carbon monoxide was adsorbed from a CO pulse injected over an Au/Fe_2O_3(r) catalyst (Fig. 1a), no CO_2 was produced from 300 to 470 K (Fig. 1c), indicating that there will not be a disproportion of CO (i.e., $2CO \rightarrow C + CO_2$) at the gold sites under these reaction conditions. Similar conclusions may be drawn from the data for a pure gold sample.

3. The q values of ~70–100 kJ mol^{-1} (Fig. 1d) are attributed to the adsorption of CO at Au^0 sites at low temperatures and at both the metal and support sites at higher reaction temperatures (Table 1, steps I and IV) (1). Enthalpy values in Fig. 1e correspond to the adsorption of CO over Fe_2O_3 (Table 1, step IV) (1).

4. Heat values given in Figs. 2c and 2d (400–350 kJ mol^{-1}) clearly indicate the predominent role played by the reoxidation of Fe_3O_4 formed during the reduction of iron oxide, i.e., $4Fe_3O_4 + O_2 \rightarrow 6Fe_2O_3$ ($\Delta H = -460$ kJ mol^{-1}), over the Au/Fe_2O_3(r) and Fe_2O_3(r) samples (Table 1, step IX) (1). Data in Figs. 2a and 2b clearly demonstrate that the presence of gold promoted the above-mentioned step.

5. Data in Fig. 3 show that although considerable fractions of CO and O_2 were adsorbed from a $CO + O_2$ pulse over the Au/Fe_2O_3(r) catalyst (curves a and b), the yield of CO_2 from CO_{ad} was very low (Fig. 3c) compared to that in similar experiments with Au/Fe_2O_3(o) (1). This clearly indicates that the direct reaction of CO_{ad} and O_{ad} at gold sites may also play a negligible role in the oxidation of CO, particularly at reaction temperatures below 400 K. This finds support in the data of Fig. 8, showing the loss of catalytic activity of Au/Fe_2O_3 on reduction, while the characteristics of gold remained unchanged.

6. The heat values for Fe_2O_3(r) (Fig. 4d) are again commensurate with the enthalpy changes associated with steps VIII and IX in Table 1 (Ref. (1)), i.e., the removal of lattice oxygen ($\Delta H = -50$ kJ mol^{-1}) and its subsequent replenishment ($\Delta H = -460$ kJ mol^{-1}). The individual contribution of these steps will depend upon the reaction temperature, the role of step VIII increasing with an increasing catalyst temperature, thus explaining the temperature-dependent variation in q values (Fig. 4d). In the case of Au/Fe_2O_3(r), the q values are also influenced by the chemisorption of CO at Au sites, as discussed above, thereby leading to a lower q value of ~230 kJ mol^{-1} (Fig. 3d). The thermochemical data of this study thus reveal that a similar reaction mechanism prevails during the oxidation of CO over Au/Fe_2O_3 in different temperature ranges.

7. On one hand, in the case of pure gold, CO or O_2 gases are adsorbed in molecular form when dosed individually, as is evident from the q values given in Fig. 5; these values correspond to the heat values of steps I and II in Table 1 (1). On the other hand, the increasing amounts of CO and O_2 were adsorbed on polycrystalline gold from a pulse of $CO + O_2$ with an increasing catalyst temperature (Figs. 6a and 6b); almost complete conversion of CO_{ad} to CO_2 occurred, irrespective of the temperature (Fig. 6c). The q value of $\sim 170 \pm 10$ kJ mol^{-1} (Fig. 6d) agrees with the simultaneous adsorption and reaction of CO and O_2 at the gold sites (Table 1, step VII) (1).

From the points listed above, it is clear that the catalytic behavior of pure gold is different from that of the gold dispersed over Fe_2O_3. While in the case of polycrystalline gold the reaction occurred via a Langmuir–Hinshelwood-type mechanism, i.e., simultaneous adsorption and reaction of CO and O at gold sites, the redox mechanism involving the removal and the replenishment of lattice oxygen played a dominant role in the CO oxidation over Fe_2O_3-based catalysts. The presence of highly dispersed gold promoted the adsorption of both CO and O_2, as concluded in (1). In this respect, the behavior of Au is comparable to that of group VIII metals such as Pt and Pd (2, 3).

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