

The Use of CO₂/CO Gas Mixtures to Study Adsorption on Chromia-Promoted Magnetite at Water-Gas Shift Temperatures

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The adsorption of CO and CO₂ on chromia-promoted magnetite was studied volumetrically at temperatures near 650 K using CO₂/CO gas mixtures in which magnetite is the thermodynamically stable form of iron oxide. Specifically, studies were conducted (i) at 637 K using CO₂/CO gas mixtures with partial pressure ratios, $P_{\text{CO}_2}/P_{\text{CO}}$, equal to 5.45, 2.37, and 1.56, and (ii) at 613, 637, and 663 K using a CO₂/CO gas mixture with $P_{\text{CO}_2}/P_{\text{CO}}$ equal to 5.45. By measuring the changes in total pressure and gas composition when a known dose of gas mixture was exposed to the sample, the individual surface coverages by CO and CO₂ were determined. At constant temperature and P_{CO} , the surface coverage by CO was found to decrease with increasing P_{CO_2} ; and, at constant temperature and P_{CO_2} , the surface coverage by CO₂ was found to decrease with increasing P_{CO} . These data could be fit by either a one-site or a two-site model. In the first model, CO and CO₂ compete for a fixed number of adsorption sites; and, in the second model, CO adsorption is associated with surface oxygen vacancies while CO₂ adsorption is associated with surface oxygen species. In both models, the total number of adsorption sites comprises approximately 21% of the BET surface area. While the adsorption data alone cannot distinguish between these models, the two-site model is favored by its ability to provide a quantitative correlation of the CO and CO₂ adsorption data with independent measurements of the oxygen content of the surface.

INTRODUCTION

Adsorption studies in heterogeneous catalysis generally have two objectives: (i) titration and/or poisoning of active sites, and (ii) determination of coverages by surface species under reaction conditions. A necessary condition for carrying out such studies using conventional volumetric techniques is stability of the surface during the course of adsorption measurements. It is for this reason that adsorption isotherms cannot be collected in this manner for gases that are capable of oxidizing or reducing the catalyst at the temperatures of adsorption. These concepts are particularly applicable to the study of CO and CO₂ adsorption at ca. 650 K on magnetite-based (Fe₃O₄) water-gas shift catalysts. On one hand,

knowledge of the equilibrium extent of surface coverage by these gases at reaction temperatures is important in determining the number of adsorption sites on the surface and in assessing the importance of water-gas shift mechanisms that involve reaction between adsorbed reactants to give adsorbed products. However, at typical water-gas shift temperatures (e.g., 650 K), pure CO will reduce Fe₃O₄ to metallic iron and/or iron carbides, while pure CO₂ will oxidize Fe₃O₄ to Fe₂O₃. Adsorption measurements utilizing pure gases at these temperatures are, therefore, complicated by the changes in catalyst structure that take place during this reduction or oxidation of the sample upon exposure to pure CO or CO₂, respectively. Such measurements are further complicated by the consumption of CO and the generation of CO₂ during reduction of the sample, or by the consumption of CO₂ and the generation of CO during oxidation of the sample. This latter behavior was noted, for example, by

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Emmett and Shultz (1) in their study of transformations between metallic cobalt and cobaltous oxide in various CO/CO₂ gas mixtures. Along these lines, previous studies of CO or CO₂ adsorption on Fe₃O₄ have involved either steady-state measurements at conditions far from those at which water-gas shift takes place, or transient measurements during which the surface of magnetite was being oxidized or reduced. For example, measurements of the former type were carried out by Kwan and Fujita (2) in their study of CO₂ adsorption on magnetite at pressures less than 0.15 kPa and temperatures of 273 and 293 K; and, transient measurements of the latter type have been made in the study of CO adsorption at temperatures near 500 K (3, 4), during which reduction of the catalyst took place. Related measurements include the study (5) of CO adsorption at room temperature on iron oxide surfaces that had been previously reduced in H₂, and studies of CO and CO₂ adsorption on Fe₂O₃ at ca. 300–400 K (6–8).

The present paper introduces an experimental method, based on simple thermodynamic concepts, that allows equilibrium adsorption studies to be conducted for gases that are capable, when present as pure components, of oxidizing or reducing the catalyst at the temperature of adsorption. The specific system that will be studied is the adsorption of CO and CO₂ on magnetite at temperatures from 610 to 660 K. In short, the method of measurement used in this study employs CO₂/CO gas mixtures to collect the individual isotherms for adsorbed CO₂ and CO. In this way, the thermodynamic oxygen partial pressure required for stability of magnetite during studies at 650 K (ca. 10⁻²⁵ Pa) is maintained by proper choice of the partial pressure ratio, $P_{\text{CO}_2}/P_{\text{CO}}$. A similar strategy was used by Kul'kova *et al.* (9) to study adsorption on magnetite from a H₂O/H₂ gas mixture; however, their study was initiated by contacting the catalyst with pure H₂ and allowing H₂O to be produced by reduction of the

catalyst (instead of using a H₂O/H₂ gas mixture at the outset), and no attempt was made to analyze the data in terms of the individual H₂O and H₂ isotherms. In contrast, the $P_{\text{CO}_2}/P_{\text{CO}}$ ratio is carefully controlled in the present study, since it has been shown that the oxygen content of the magnetite surface is dependent on the $P_{\text{CO}_2}/P_{\text{CO}}$ ratio (10). This is despite the fact that magnetite is thermodynamically stable over a wide range of $P_{\text{CO}_2}/P_{\text{CO}}$ ratios (11). Moreover, by carrying out adsorption measurements using different $P_{\text{CO}_2}/P_{\text{CO}}$ ratios, it is possible to study how the adsorption of CO and CO₂ may be affected by the oxygen content of the surface. Indeed, such studies may provide information about the number of adsorption sites and the surface coverages by CO and CO₂ under water-gas shift reaction conditions.

EXPERIMENTAL

The sample used for the volumetric adsorption measurements of the present study was ca. 1.4 g of a magnetite water-gas shift catalyst (Haldor Topsøe A/S) structurally promoted by ca. 7 wt% Cr₂O₃. The details of the all-glass apparatus used for the volumetric adsorption studies may be found elsewhere (12). In short, the sample is placed in a Pyrex cell (i), through which gases can be flowed during sample treatment, (ii) which can be evacuated to ca. 10⁻⁴ Pa prior to adsorption studies, and (iii) into which known amounts of gases can be introduced during adsorption measurements.

Adsorption isotherms were collected at 637 K using CO₂/CO mixtures with $P_{\text{CO}_2}/P_{\text{CO}}$ ratios equal to 5.45, 2.37, and 1.56. Isotherms were also determined at temperatures of 613 and 663 K, for $P_{\text{CO}_2}/P_{\text{CO}}$ equal to 5.45. Before each isotherm was collected, the sample was reduced for approximately 12 h in a flowing CO₂/CO gas mixture with the same composition as that used during the adsorption measurements. For adsorption studies at

613 or 637 K, a reduction temperature of 653 K was used, while a reduction temperature of 693 K was used prior to adsorption studies at 663 K. Following reduction, the sample was evacuated to ca. 10^{-3} Pa for 1 h at 653 K. This "standard evacuation" has been found to be appropriate for preparing magnetite surfaces for adsorption studies (12). The sample temperature was then adjusted to the isotherm temperature, and an initial dose of the corresponding CO_2/CO gas mixture was introduced into the Pyrex cell containing the sample. A precision pressure gauge (Texas Instruments) was used to measure the decrease in total pressure when this dose of gas was expanded into the adsorption cell. After appropriate corrections (12), this decrease in pressure is used to calculate the total amount of gas adsorbed on the surface.

After the dose of CO_2/CO reached equilibrium with the catalyst (as indicated by reaching a constant total pressure), the gas phase composition was determined by selectively freezing CO_2 out of the gas phase. This was accomplished using a glass appendage attached to the manifold connecting the adsorption cell and the precision pressure gauge. Specifically, the cell was first isolated from the manifold by closing a stopcock attached to the cell, and the CO_2 in the remainder of the system (manifold plus pressure gauge) was frozen into the appendage by immersing the latter in liquid nitrogen. By comparing the pressures before and after immersion of the appendage in liquid nitrogen (gas phase containing CO_2/CO and CO , respectively), the gas composition prior to freezing the CO_2 can be determined, after corrections are made for the decrease in CO pressure due to changing the temperature of the gaseous CO in the appendage. It should be noted that by isolating the adsorption cell from the manifold prior to freezing the CO_2 , the equilibrium over the sample is not disturbed during the determination of gas phase composition. Following the compositional determination, the manifold was

evacuated to ca. 1 Pa and refilled with the CO_2/CO gas mixture. This gas mixture was then dosed into the adsorption cell by opening the stopcock which separated the cell from the manifold, and the above procedures were repeated. With each successive dose, the pressure in the cell is increased, and the adsorption isotherm is thereby determined. Following completion of each isotherm, the BET monolayer capacity of the sample was determined using N_2 adsorption at liquid nitrogen temperature.

Carbon monoxide (CP grade, 99.5% pure, minimum) and CO_2 (bone dry grade, 99.8% pure, minimum) were obtained from Matheson. The CO was purified by passage over copper turnings at 600 K followed by activated 13X Davison molecular sieves at 195 K. Carbon dioxide was taken directly from the cylinder and mixed with the purified CO to form the flowing CO_2/CO gas mixture used for reduction of the catalyst. For the static volumetric adsorption measurements, however, the CO_2 was purified by freezing the cylinder gas at 77 K and then evacuating the gas phase above the solid to ca. 10^{-2} Pa. This purified CO_2 was combined with purified CO , and the resulting CO_2/CO gas mixture was stored in a glass manifold which had been previously evacuated to ca. 10^{-3} Pa. The composition of the gas mixture was checked using the freezing technique described previously.

RESULTS

Figure 1 presents the total adsorption isotherms obtained at 613, 637, and 663 K using a $P_{\text{CO}_2}/P_{\text{CO}}$ ratio of 5.45; and, Fig. 2 shows total adsorption isotherms obtained at 637 K using $P_{\text{CO}_2}/P_{\text{CO}}$ ratios of 5.45, 2.37, and 1.56. In both figures, the data have been plotted as P_T/θ_T versus P_T , as prescribed by the Langmuir isotherm,

$$\frac{P_T}{\theta_T} = \frac{1}{K_T \theta_T^{\text{sat}}} + \frac{P_T}{\theta_T^{\text{sat}}}, \quad (1)$$

where P_T is the total pressure, K_T is the adsorption equilibrium constant, θ_T is the

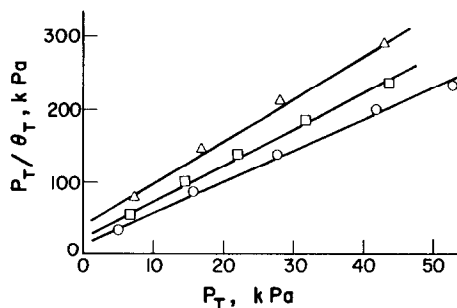


FIG. 1. Langmuir isotherms for total CO₂/CO adsorption on chromia-promoted magnetite as a function of temperature for $P_{CO_2}/P_{CO} = 5.45$: \circ , \square , \triangle represent data collected at 613, 637, and 663 K, respectively.

total surface coverage, and θ_T^{sat} is the saturation value of θ_T attained at high total pressures. All surface coverages reported in this paper are expressed as moles adsorbed per mole of N₂ in the BET monolayer. Each point on these plots was obtained after waiting ca. 20 h for the gas to equilibrate with the catalyst and for the gas to become well mixed in the manifold after adsorption. The BET surface area remained constant at 34.2 m²/g (351.2 μ mol N₂/g) during the course of this study.

While the P_{CO_2}/P_{CO} ratios are nominally equal to 5.45, 2.37, and 1.56 for the isotherms of Figs. 1 and 2, small but systematic departures of the P_{CO_2}/P_{CO} ratio from that value characteristic of the dosing gas

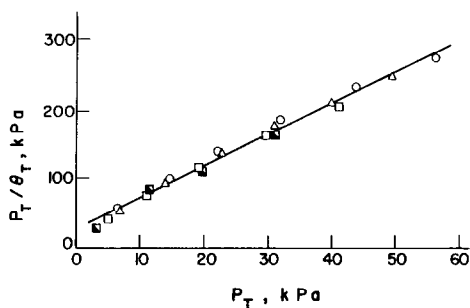


FIG. 2. Langmuir isotherms for total CO₂/CO adsorption on chromia-promoted magnetite at 637 K as a function of P_{CO_2}/P_{CO} ratio: \circ , \triangle , \square represent data for $P_{CO_2}/P_{CO} = 5.45, 2.37,$ and 1.56 , respectively. \blacksquare are for a second isotherm collected at $P_{CO_2}/P_{CO} = 1.56$ following successive expansion into vacuum of the gas phase for isotherm \square .

mixture were observed for each point on a given isotherm. These deviations in P_{CO_2}/P_{CO} ratio are of the order of 20%, and as such this ratio can be considered to be essentially constant in comparing the various total adsorption isotherms of Figs. 1 and 2. However, from these changes in P_{CO_2}/P_{CO} ratio upon dosing a given CO₂/CO gas mixture into the adsorption cell, the relative surface coverages by CO and CO₂ can be determined. For example, a decrease in the measured P_{CO_2}/P_{CO} ratio suggests that CO₂ is preferentially adsorbed on the surface, compared to the adsorption of CO. This information, coupled with the total adsorption isotherms, allows the individual adsorption isotherms for CO and CO₂ to be determined. Accordingly, Figs. 3 and 4 depict the individual CO and CO₂ adsorption isotherms at 613, 637, and 663 K for P_{CO_2}/P_{CO} equal to 5.45; and, Figs. 5 and 6 show these isotherms at 637 K for P_{CO_2}/P_{CO} ratios of 5.45, 2.37, and 1.56. All isotherms have been plotted as P_i/θ_i versus P_i , in accordance with the Langmuir isotherms,

$$\frac{P_i}{\theta_i} = \frac{1}{K_i \theta_i^{sat}} + \frac{P_i}{\theta_i^{sat}}, \quad (2)$$

where P_i, K_i, θ_i and θ_i^{sat} have meanings analogous to those symbols of Eq. (1).

It is important to note that the above separation of the total adsorption isotherm into individual CO and CO₂ isotherms is

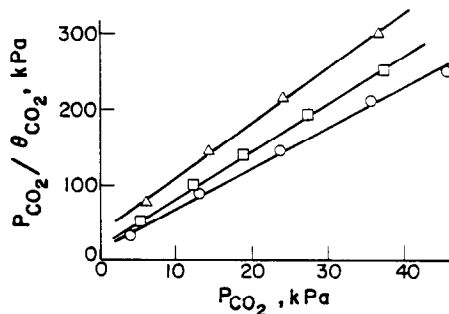


FIG. 3. Langmuir isotherms for the CO₂ adsorption on chromia-promoted magnetite as a function of temperature for $P_{CO_2}/P_{CO} = 5.45$: \circ , \square , \triangle represent data collected at 613, 637, and 663 K, respectively.

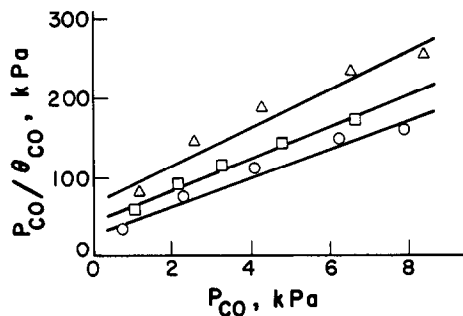


FIG. 4. Langmuir isotherms for CO adsorption on chromia-promoted magnetite as a function of temperature for $P_{\text{CO}_2}/P_{\text{CO}} = 5.45$: \circ , \square , \triangle represent data collected at 613, 637, and 663 K, respectively.

based on two assumptions. The first assumption is that there is no net change in the oxygen content of the surface (excluding the oxygen in CO and CO_2) during collection of a given isotherm. That is, the thermodynamic oxygen pressure and hence the oxygen content of the surface in a CO_2/CO gas mixture are dependent on $P_{\text{CO}_2}/P_{\text{CO}}$ and independent of total pressure. The validity of this assumption will be discussed later. The second assumption is that the oxygen content of the surface is unchanged by the "standard evacuation" (i.e. 1 h at 653 K). That is, this evacuation prior to adsorption measurements serves

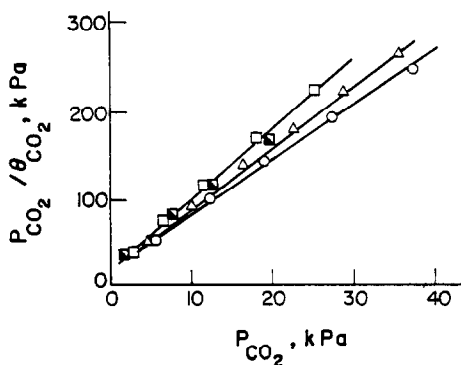


FIG. 5. Langmuir isotherms for CO_2 adsorption on chromia-promoted magnetite at 637 K as a function of $P_{\text{CO}_2}/P_{\text{CO}}$ ratio: \circ , \triangle , \square represent data for $P_{\text{CO}_2}/P_{\text{CO}} = 5.45$, 2.37, and 1.56, respectively. \blacksquare are for a second isotherm collected at $P_{\text{CO}_2}/P_{\text{CO}} = 1.56$ following successive expansion into vacuum of the gas phase for isotherm \square .

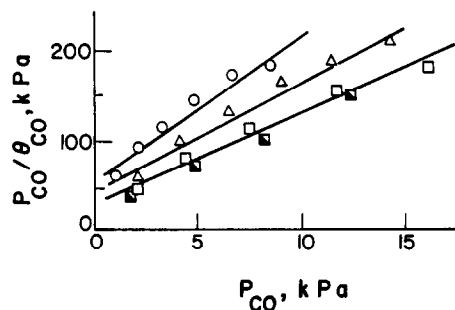


FIG. 6. Langmuir isotherms for CO adsorption on chromia-promoted magnetite at 637 K as a function of $P_{\text{CO}_2}/P_{\text{CO}}$ ratio: \circ , \triangle , \square represent data for $P_{\text{CO}_2}/P_{\text{CO}} = 5.45$, 2.37, and 1.56, respectively. \blacksquare are for a second isotherm collected at $P_{\text{CO}_2}/P_{\text{CO}} = 1.56$ following successive expansion into vacuum of the gas phase for isotherm \square .

only to remove adsorbed CO and CO_2 . To test the validity of this assumption, the following experiments were conducted at 637 K using a $P_{\text{CO}_2}/P_{\text{CO}}$ ratio of 1.56. A first isotherm was collected in the manner described above, using the "standard evacuation" prior to commencing the adsorption measurements. Upon completion of this isotherm, the gas pressure over the sample was reduced by successive expansions of the gas phase into the previously evacuated manifold. This process was continued until the pressure in the adsorption cell was decreased to ca. 1 Pa. Using this procedure it is possible to remove adsorbed CO and CO_2 by reducing P_{CO} and P_{CO_2} , and at the same time to maintain essentially the same oxygen content of the surface by keeping $P_{\text{CO}_2}/P_{\text{CO}}$ approximately constant. Following this procedure, a second adsorption isotherm was collected. This total isotherm and the separate CO_2 and CO isotherms are shown in Figs. 2, 5, and 6 (denoted by \blacksquare). Only small differences can be detected between the first and second isotherms for total adsorption (Fig. 2), CO_2 adsorption (Fig. 5), and CO adsorption (Fig. 6). Thus, while the "standard evacuation" may lead to small changes in the oxygen content of the surface, these changes do not significantly change the general features of

the total, CO₂, and CO adsorption isotherms.

The observation that the first and second adsorption isotherms at 637 K are similar indicates that CO and CO₂ adsorption on magnetite are essentially reversible at this temperature. This allows the isotherms of Figs. 3 and 4 to be used to estimate heats of adsorption, Δ*H*_{ads} (by comparing the pressures required to reach a certain surface coverage at different temperatures). For CO₂ adsorption, Δ*H*_{ads} is thereby estimated to be 190., 164., and 140. kJ/mol for θ_{CO₂} equal to 0.09, 0.11, and 0.13, respectively; and for CO adsorption Δ*H*_{ads} is estimated to be 126., 84., and 45. kJ/mol for θ_{CO} equal to 0.02, 0.03, and 0.04, respectively. However, while the three values of Δ*H*_{ads} for CO₂ adsorption vary by less than 20%, the three corresponding values for CO adsorption vary by 50%. This is reflected in the poorer fit of the CO adsorption data to a Langmuir isotherm when compared to the CO₂ adsorption data.

DISCUSSION

Several general observations can be made from the various adsorption isotherms on chromia-promoted magnetite at 637 K: (i) the total adsorption coverage, θ_T, for the conditions investigated reaches only about 21% of the BET monolayer capacity, as indicated by the slope in Fig. 2 (see Eq. (1)), (ii) at constant CO pressure, the coverage by carbon monoxide, θ_{CO}, decreases as the CO₂ pressure is increased (see Fig. 5), and (iii) at constant CO₂ pressure, the coverage by carbon dioxide, θ_{CO₂}, decreases as the CO pressure is increased (see Fig. 6). The first observation simply indicates that only a fraction of the total surface area is capable of adsorbing CO and CO₂ at the conditions studied. This statement is independent of the assumption made in separating the total adsorption isotherm into individual CO and CO₂ isotherms. The second and third observations indicate that the surface coverages by CO and CO₂ are not

independent. Two models will be discussed below to quantitatively fit these data.

A simple model that can be used to describe the interdependence of the CO and CO₂ adsorption isotherms is that of competitive adsorption on a fixed number of surface sites (occupying ca. 21% of the total surface area). In such a model, the surface coverages by CO and CO₂ are given by:

$$\theta_{CO} = \frac{K_{CO}P_{CO}\theta_T^{sat}}{1 + K_{CO}P_{CO} + K_{CO_2}P_{CO_2}}, \quad (3)$$

$$\theta_{CO_2} = \frac{K_{CO_2}P_{CO_2}\theta_T^{sat}}{1 + K_{CO}P_{CO} + K_{CO_2}P_{CO_2}}, \quad (4)$$

where *K*_{CO} and *K*_{CO₂} are the equilibrium constants for adsorption of CO and CO₂, and θ_T^{sat} is the fraction of the total surface that is capable of adsorbing CO and CO₂ (see Eq. (1)). For the case in which *K*_{CO} approximately equals *K*_{CO₂} (i.e., *K*_{CO} ≅ *K*_{CO₂} = *K*_T), Eqs. (3) and (4) can be simplified, rearranged, and compared to Eq. (1):

$$\frac{P_{CO}}{\theta_{CO}} = \frac{P_{CO_2}}{\theta_{CO_2}} = \frac{1}{K_T\theta_T^{sat}} + \frac{P_T}{\theta_T^{sat}} \quad (5)$$

Figure 7 shows the 637 K adsorption data plotted in this fashion. It can be seen that the CO and CO₂ isotherms collected for the three different *P*_{CO₂}/*P*_{CO} ratios superimpose

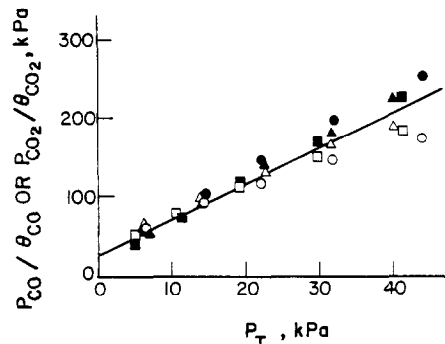


FIG. 7. Langmuir isotherms for competitive adsorption (Eq. 5) of CO and CO₂ on chromia-promoted magnetite at 637 K: ○, △, □ represent data for *P*_{CO₂}/*P*_{CO} = 5.45, 2.37, and 1.56. Open symbols refer to CO adsorption while filled symbols refer to CO₂ adsorption.

quite well, as predicted by Eq. (5). This model of competitive adsorption also predicts that the three total adsorption isotherms collected at different $P_{\text{CO}_2}/P_{\text{CO}}$ ratios (but at constant temperature) should collapse to a single line when plotted as P_T/θ_T versus P_T . Figure 2 shows that this behavior is followed at 637 K. In short, the CO and CO₂ adsorption isotherms at 637 K appear to be adequately fit by a model involving competitive adsorption, with K_T equal to 0.173 kPa⁻¹, on a fraction of the total surface area, with $\theta_{\text{O}^*}^{\text{sat}}$ equal to 0.217.

While the competitive adsorption model offers a convenient description of the experimental data, it is not necessarily true that this model properly explains why θ_{CO} and θ_{CO_2} are interrelated in CO₂/CO gas mixtures. In fact, there is good reason to believe that this model presents an overly simplified description of the magnetite surface. For example, it has been shown elsewhere (10) that in a CO₂/CO gas mixture, the equilibrium surface oxygen content of chromia-promoted magnetite (on the same sample used in the present study) depends on the $P_{\text{CO}_2}/P_{\text{CO}}$ ratio. These data were described by the following reaction:



where O* and * are oxygen-containing and oxygen-vacant surface sites, respectively. Furthermore, by changing the $P_{\text{CO}_2}/P_{\text{CO}}$ ratio, the fractions of the total surface consisting of oxygen-containing sites and vacant sites, θ_{O^*} and θ_* , were varied, and the following relationship was found to apply:

$$\theta_{\text{O}^*} + \theta_* = \theta_{\text{O}^*}^{\text{sat}}, \quad (7)$$

where $\theta_{\text{O}^*}^{\text{sat}}$ is the saturation coverage of the surface by oxygen, equal to 9% of the BET monolayer. Figure 8 summarizes these results as a plot of θ_* versus $P_{\text{CO}_2}/P_{\text{CO}}$ at 637 K. Numerous examples can be found in the literature of CO₂ and CO adsorption on metal oxides being associated with surface oxygen species (8, 13, 15, 16) and unsaturated metal cations (13, 16, 17), respectively. It thus seems reasonable to attempt

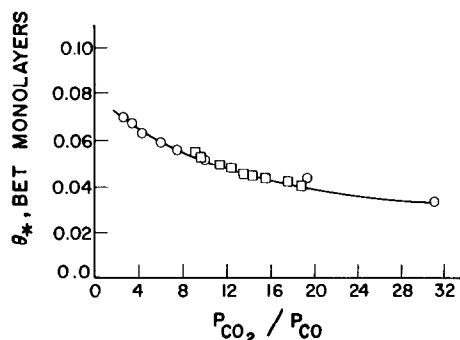


FIG. 8. Surface concentration of oxygen vacancies, θ_* , versus $P_{\text{CO}_2}/P_{\text{CO}}$ for chromia-promoted magnetite at 637 K. \circ and \square represent gravimetric data from Ref. (10), obtained by pulsing CO and CO₂, respectively, into CO₂/CO gas mixtures.

to correlate θ_{CO_2} with θ_{O^*} and to correlate θ_{CO} with θ_* in the present study.

The slopes in Figs. 5 and 6 can be used to determine, at different $P_{\text{CO}_2}/P_{\text{CO}}$ ratios, the saturation surface coverages by carbon monoxide and carbon dioxide, $\theta_{\text{CO}}^{\text{sat}}$ and $\theta_{\text{CO}_2}^{\text{sat}}$ (see Eq. (2)). Table 1 provides a summary of these values, as well as the values of θ_{O^*} and θ_* for the three corresponding $P_{\text{CO}_2}/P_{\text{CO}}$ ratios as determined from Fig. 8 and Eq. (7) with $\theta_{\text{O}^*}^{\text{sat}} = 0.087$. It can be seen therein that $\theta_{\text{CO}}^{\text{sat}}$ is approximately equal to θ_* for all $P_{\text{CO}_2}/P_{\text{CO}}$ ratios. Furthermore, the change in $\theta_{\text{CO}_2}^{\text{sat}}$ ($\Delta\theta_{\text{CO}_2}^{\text{sat}}$) is nearly equal to the change in θ_{O^*} ($\Delta\theta_{\text{O}^*}$) as the $P_{\text{CO}_2}/P_{\text{CO}}$ ratio is varied. This suggests a two-site adsorption model in which CO is associated with surface oxygen vacancies and CO₂ is associated with surface oxygen species, as described by the following two equations:

$$\frac{\theta_{\text{CO}}}{\theta_*} = \frac{K_{\text{CO}}P_{\text{CO}}}{1 + K_{\text{CO}}P_{\text{CO}}}, \quad (8)$$

$$\frac{\theta_{\text{CO}_2}}{\theta_{\text{O}^*} + \phi_0} = \frac{K_{\text{CO}_2}P_{\text{CO}_2}}{1 + K_{\text{CO}_2}P_{\text{CO}_2}}, \quad (9)$$

where ϕ_0 is a constant. The inclusion of the parameter ϕ_0 is necessary in this two-site adsorption model since the saturation value of θ_{O^*} is ca. 9% of the BET monolayer while values of θ_{CO_2} as high as 15% of the BET monolayer were measured. In short, while

TABLE 1

 Summary of Adsorption Site Densities on Chromia-Promoted Magnetite in CO₂/CO Gas Mixtures at 637 K

$P_{\text{CO}_2}/P_{\text{CO}}$	θ_*	θ_{CO} at saturation	$\frac{\theta_{\text{CO}}^{\text{sat}}}{\theta_*}$	θ_{O^*}	θ_{CO_2} at saturation	$\frac{\Delta\theta_{\text{CO}_2}^{\text{sat}}}{\Delta\theta_{\text{O}^*}}$
5.45	0.060	0.061	1.02	0.027	0.156	1.31
2.37	0.073	0.080	1.10	0.014	0.139	1.38
1.56	0.086	0.095	1.10	0.001	0.121	—

certain surface oxygen species may not be capable of participating in reaction (6) under the conditions of the present study, these oxygen species may still be capable of adsorbing CO₂. Thus, ϕ_0 represents the fraction of the surface which does not participate in reaction (6) but on which CO₂ may still be adsorbed. From the above two equations and the isotherms of Figs. 5 and 6, it is found that at 637 K, K_{CO} equals 0.33 kPa⁻¹, K_{CO_2} equals 0.43 kPa⁻¹, and ϕ_0 equals 12.5% of the BET monolayer.

In the above two-site model it is assumed that the total number of oxygen-vacant sites (θ_* , with and without adsorbed CO) and the total number of oxygen-containing sites (θ_{O^*} , with and without adsorbed CO₂) are dependent on the $P_{\text{CO}_2}/P_{\text{CO}}$ ratio and independent of the absolute values of P_{CO_2} and P_{CO} . That is, adsorbed CO and CO₂ do not change the reactivities of * and O* in reaction (6). Indirect support for this assumption comes from work published elsewhere (10). If, for example, the above assumption is taken to be correct, then it was found that the forward and reverse rates of reaction (6) varied linearly with θ_{O^*} and θ_* , respectively. This is despite the fact that these measurements were made over a range of total pressures for which the fraction of the O*-sites associated with CO₂ and the fraction of the *-sites associated with CO were not constant. In addition, using the above assumption the calculated values of θ_* and θ_{O^*} (from gravimetric measurements in CO₂/CO gas mixtures) were found to be independent of total pressure at a given $P_{\text{CO}_2}/P_{\text{CO}}$ ratio. Thus, with the data available at present, more complicated as-

sumptions, involving effects of adsorbed CO and CO₂ on the reactivities of * and O* sites, do not seem to be warranted.

While the magnetite sample used in the present study was promoted with chromia (to stabilize the surface area), the presence of this textural promoter does not alter the above conclusions. In particular, the same chromia-promoted sample was used to generate the equilibrium surface oxygen-content data of Fig. 8 as was used to collect the adsorption data of the present study; therefore, the correlations of the two-site model remain valid. The presence of chromia, however, does make it impossible to describe unambiguously, from the results of this study alone, the adsorption sites on chromia-promoted magnetite in terms of crystallographically identifiable surface sites. Chromia and magnetite form a homogeneous solid solution for the chromia-content of the present study (ca. 7 wt% Cr₂O₃), and the adsorption data do not reflect adsorption on distinct phases of Cr₂O₃ and Fe₃O₄. Preliminary ESCA studies of the chromia-promoted magnetite sample used in this study indicate, however, that the surface of this homogeneous solid solution is enriched in chromium, compared to the bulk composition. Furthermore, it is probable that the reactivity (for reaction (6)) and adsorption characteristics of a given surface oxygen species on chromia-promoted magnetite may be related to the number of chromium and iron cations to which it is coordinated. This may explain the small value of $\theta_{\text{O}^*}^{\text{sat}}$ and the need to introduce ϕ_0 into the two-site adsorption model. These possible effects of chromium

substitution into magnetite are currently under investigation in our laboratory.

CONCLUSIONS

Two different models can be used to describe the adsorption of CO and CO₂ on chromia-promoted magnetite in CO₂/CO gas mixtures at temperatures near 650 K. The first is a one-site model involving competitive adsorption of CO and CO₂ on a fixed number of sites; and, the second is a two-site model in which adsorption of CO is associated with oxygen-vacant sites (i.e., unsaturated metal cations) and adsorption of CO₂ is associated with surface oxygen species. In both models, the total number of adsorption sites corresponds to approximately 21% of the BET surface area. In the second model, however, the relative number of CO adsorption sites and CO₂ adsorption sites depends on the $P_{\text{CO}_2}/P_{\text{CO}}$ ratio. Although the present data cannot distinguish between these two models, other considerations favor the two-site model. Specifically, this model provides a quantitative correlation of the CO and CO₂ adsorption data with independent measurements of the oxygen-content of the surface at various $P_{\text{CO}_2}/P_{\text{CO}}$ ratios. Furthermore, the two-site model is consistent with the acid-base properties of CO and CO₂: the Lewis basicity of CO favoring adsorption on acidic sites (such as unsaturated metal cations), and the Lewis acidity of CO₂ favoring adsorption on basic sites (such as surface oxygen species).

In general terms, the present study illustrates the utility of conducting adsorption measurements with gas mixtures (e.g., CO₂/CO). In this way it is possible to determine the adsorption isotherms for species which, when present as pure components, are capable of oxidizing or reducing the catalyst at the temperatures of adsorption. In short, by controlling the composition of the gas mixture, it is possible to

control the oxidation state of the catalyst. Accordingly, adsorption can be studied on oxides with intermediate oxidation states (e.g., Fe₃O₄) and as a function of the oxygen content of the surface.

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