JOURNAL OF CATALYSIS **100**, 533–540 (1986)

Effects of Potassium and Calcination Pretreatment on the Adsorption and Chemical/Physical Properties of Fe/SiO_2

INTRODUCTION

CO and CO_2 adsorptions have been used to estimate surface fractions of metal and potassium oxide promoters in promoted iron catalysts (*2–4*) while both CO (*5–7*) and H_2 (*8–11*) adsorptions have been used in estimating iron metal surface areas in promoted and supported iron catalysts. Previous studies (*1, 2, 8, 11*) indicate that (i) H_2 adsorption on iron at ambient or lower temperatures is slow and activated while CO adsorption rapidly approaches equilibrium even at 77 K and (ii) H_2 adsorbs dissociatively on single crystal or polycrystalline iron at ambient temperatures (*12–14*) while CO adsorbs associatively on single crystal iron (*14–18*) and dissociatively on polycrystalline iron (*19–21*) at ambient temperatures.

Studies of the effects of potassium on CO, CO_2, and hydrogen adsorptions on iron (*14, 16, 17, 22, 23*) indicate that potassium promotion increases heats of adsorption of CO and H_2, enhances the rate of CO dissociation, increases CO saturation coverage, and decreases the CO sticking coefficient.

However, none of the previous studies attempted to correlate adsorption stoichiometries and kinetics of CO, CO_2, and H_2 with the chemical and physical properties of the catalysts such as potassium level, dispersion, metal crystallite size, and extent of reduction or with effects of pretreatment.

The purpose of this work was to investigate the effects of potassium promoter and calcination on the stoichiometries and kinetics of CO, CO_2, and H_2 adsorptions on Fe/SiO_2 and to relate these effects to changes in the physical and chemical properties of the catalyst. The results reveal important differences in behavior for CO and H_2 adsorptions on precalcined Fe/SiO_2 and Fe/K/SiO_2 compared to the adsorptions on single crystal or polycrystalline iron, which may relate to changes in the surface and bulk properties of iron such as potassium coverage and extent of reduction.

EXPERIMENTAL

Fe/SiO_2 catalysts were prepared by impregnation of Cab-O-Sil silica (M-5) with aqueous nitrate solutions, followed by calcination in air at 373 or 473 K for 2 h and reduction at 723 K for 36 h in flowing hydrogen.

H_2, CO, and CO_2 chemisorptions of freshly reduced samples of 1–2 g were measured in a volumetric vacuum apparatus (*24*) after evacuation to 10^{-5} Torr for 45 min at 673 K. Hydrogen was allowed to contact the catalyst during cooling from 673 to 298 K at an equilibration pressure of 400 Torr. CO was contacted with the sample while cooling from 373 to 298 K. CO_2 adsorption uptakes were measured at 298 K. Carbon monoxide and carbon dioxide chemisorption uptakes were determined from the difference between double isotherms, the first measured after evacuation at 673 K, the second after evacuation at 298 K. Temperature-programmed desorptions of H_2, CO, and CO_2 were conducted on catalyst samples weighing 100 to 150 mg using TPD systems and procedures reported previously (*25–26*).

X-Ray powder diffraction (XRD) and

0021-9517/86

TABLE 1

Effects of Potassium Content and Calcination Temperature on H_2, CO, and CO_2 Adsorption Capacities of 15 wt% Fe/SiO_2

Catalyst	Calcination temperature (K)	Total H_2 uptake[a] (μmol/g)	Irreversible H_2 uptake[b] (μmol/g)	Total CO uptake[c] (μmol/g)	Irreversible CO uptake[b]	$\frac{\text{Total CO}^d}{\text{Total H}}$	CO_2 uptake (μmol/g) 298 K	
							Total	Irreversible
15% Fe/SiO_2	373	59, 58[e], 17[f]	—	—	12.1	—	—	—
15% Fe/SiO_2	473	57.0, 12.0[f]	49.6	38.6	22.0	0.34	16.7	4.5
15% Fe/0.2% K/SiO_2	473	54.4	54.1	29.7	17.8	0.27	30.1	15.7
15% Fe/1% K/SiO_2	473	28.7	21.1	7.3	5.1	0.13	71.1	13.9
15% Fe/3% K/SiO_2	473	23.5	16.2	3.4	2.0	0.07	122	24.0
15% Fe/3% K/SiO_2	373	30.9	21.9	9.3	3.6	0.15	118	16.1

[a] H_2 contact during cooling from 673 to 298 K.
[b] Difference between isotherms measured after evacuation at 673 and 298 K.
[c] CO contact during cooling from 373 to 298 K.
[d] Molecules of total CO adsorbed per total H atom adsorbed.
[e] H_2 uptake after reaction.
[f] H_2 uptake at 298 K.

transmission electron microscopy (TEM) measurements of metal crystallite size on selected samples were performed using equipment previously described (*27*). Mössbauer spectra of fresh and hydrogen-reduced samples were obtained using a system described previously (*28*). Extents of reduction to iron metal were determined by oxygen titration of reduced catalysts at 723 K assuming that iron metal was oxidized to Fe_2O_3. After 45 min evacuation to 10^{-5} Torr, the catalyst sample was exposed to 40 Torr of O_2 (99.99% from Whitmore) for 45 min.

RESULTS

Adsorption Measurements

H_2, CO, and CO_2 uptakes of six Fe/SiO_2 and Fe/K/SiO_2 catalysts are listed in Table 1. Several trends are evident: (i) H_2 and CO uptakes decrease significantly with increasing K content and increasing precalcination temperature, (ii) the percentage decrease in CO adsorption capacity is greater relative to H_2, (iii) CO_2 uptakes increase with increasing K content, and (iv) the iron dispersion or fraction of iron atoms exposed (based on H_2 adsorption) declines with increasing K content (see Table 2).

Figure 1 shows TPD spectra of H_2 desorption from 15% Fe/SiO_2 and 15% Fe/3% K/SiO_2 catalysts (dried at 100°C or calcined at 200°C) following adsorption at different temperatures. The TPD spectra for H_2 desorption from precalcined Fe/SiO_2 (Fig. 1a) are quite complex compared to those observed previously for single crystal iron (Ref. (*14*), Fig. 2), unsupported polycrystalline iron ((*29*), Fig. 1), and Fe/SiO_2 dried at 333–353 K followed by direct reduction in H_2 ((*29*), Fig. 3). At least four different adsorption states (at about 325–350, 450–473, 573–625, and above 723 K) are observed for the precalcined Fe/SiO_2 (Fig. 1) while only two adsorption states (at about 300–350 and 375–400 K) were observed for Fe(100) (*14*), polycrystalline Fe (*29*), and uncalcined Fe/SiO_2 (*29*). It is evident from comparison of the curve areas in Fig. 1a that maximum adsorption of hydrogen does not occur at room temperature, but rather at elevated temperatures. The amount of H_2 adsorbed by cooling from 723 to 298 K is four to five times larger than the amount adsorbed at any given temperature. In other words H_2 adsorption on precalcined Fe/SiO_2 is moderately activated.

Comparison of the TPD spectra in Figs.

TABLE 2

Dispersion and Phase Analysis of K-Promoted Fe/SiO_2 Catalysts

Catalyst	Calcination temperature (K)	% D[a]	Crystallite size				Reduced catalyst Mössbauer spectrum areas			% Reduction	
			H_2 chemisorp[b] d_s (nm)	TEM d_s (nm)	TEM d_v (nm)	XRD d_v (nm)	Fe^{3+}	Fe^{2+}	Fe^0	Mössbauer[c]	O_2 Titration[d]
15% Fe/SiO_2	473	4.7	26	30	36	30	9.7	0	90.3	90.3	89.9
15% Fe/0.2% K/SiO_2	473	4.4	28				10.7	16.3	73.6	79.0	92.6
15% Fe/1% K/SiO_2	473	2.6	47				14.1	25.6	60.3	68.8	81.0
15% Fe/3% K/SiO_2	473	2.7	46			18	25.5	14.7	59.8	64.7	65.2
15% Fe/3% K/SiO_2	373	3.3	37			15	22.6	4.9	72.5	74.2	70.1

[a] Percentage of Fe atoms exposed to surface based on total H_2 uptake.

[b] Based on total H_2 uptake.

[c] % Redn. $\sum_i$ [3 − (oxidn. state *i*th phase)][wt% *i*th phase]/3.

[d] Based on formation of Fe_2O_3 at 723 K.

1a and b reveals that addition of K causes a shift in peak maximum to higher temperature at any given adsorption temperature. Indeed, the largest peak for Fe/SiO_2 located at about 450 K (Fig. 1a) is shifted by addition of potassium to 500–525 K (Fig. 1b). Moreover, the area of the spectrum obtained for potassium-promoted iron by cooling from 723 to 298 K is much larger relative to the spectra obtained at other adsorption temperatures. In other words, potassium increases the adsorption activation energy and binding energy for H_2 on Fe/SiO_2.

Calcination of Fe/K/SiO_2 at 473 K causes even more dramatic changes in the TPD spectrum (see Fig. 1c), i.e., it effects a large shift in peak maxima to higher temperatures, e.g., from 350 to 700 K after adsorption at 298 K and from 300 and 500 to 700 K after cooling in H_2 from 723 to 298 K. Thus precalcination effects large increases in the binding energy of hydrogen and the adsorption activation energy for hydrogen on iron.

Figure 2a shows the TPD spectra of carbon monoxide on 15% Fe/SiO_2 corresponding to three different conditions of adsorption. After adsorption at 298 or 373 K a single peak is observed having a maximum at about 350 or 425 K. After cooling in CO from high temperature, an additional strongly bound state of carbon monoxide (peak maximum at about 673 K) is observed which probably corresponds to recombination of C and O (*14*) since a CO_2 peak was also detected at the same temperature during the same experiment. During CO TPD from the catalysts containing potassium there was no evidence of the weakly bound CO species, while the strongly bound high-temperature peak was observed at about the same position. Thus, CO adsorption on unpromoted Fe/SiO_2 is probably associative while that on K-promoted catalysts is dissociative at 298–373 K.

TPD spectra of CO_2 desorption from potassium-promoted Fe/SiO_2 catalyst are shown as a function of potassium level in Fig. 2b. After adsorption at 298 K (solid lines) a low-temperature CO_2 peak having a maximum rate at about 350–373 K was observed the area of which increased significantly with increasing potassium-loading; a high-temperature peak was also observed at about 673 K the area of which was small and independent of potassium content. This high-temperature peak was coincident with a large CO peak (dotted line) observed after cooling in CO_2 from above 673 K. Since its area depends on potassium content, the

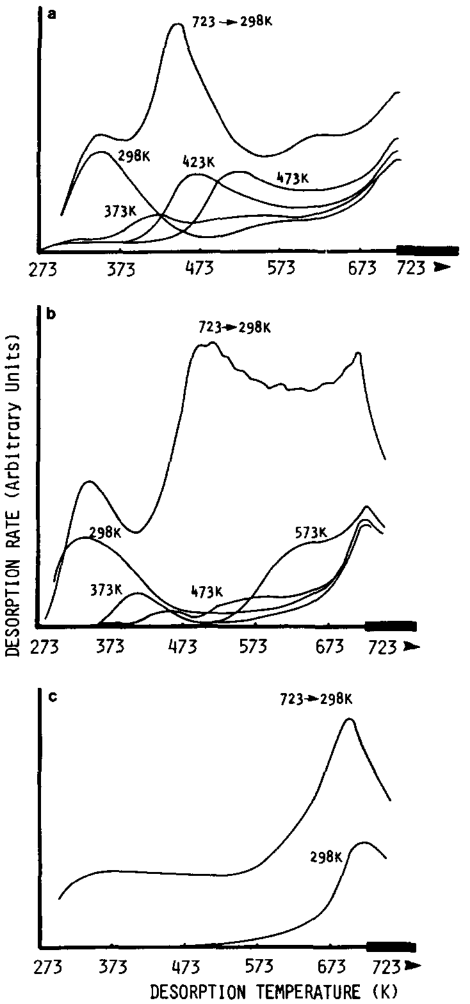

FIG. 1. (a) Temperature-programmed desorption spectra of H_2 from 15% Fe/SiO_2 as a function of adsorption temperature (catalyst was calcined at 473 K). (b, c) Temperature-programmed desorption spectra of H_2 from 15% Fe/3% K/SiO_2 as a function of adsorption temperature. (b) Calcined 373 K; (c) calcined 473 K.

low-temperature peak probably corresponds mainly to CO_2 adsorbed on potassium oxide (only a small amount of CO_2 desorbed at this temperature from unpromoted Fe/SiO_2). The high-temperature peak most likely corresponds to recombination of CO and O on Fe metal or in other words is a measure of CO_2 adsorbed on the metal.

Mössbauer Spectroscopy and X-Ray Diffraction

Mössbauer spectra of reduced Fe/SiO_2 and $Fe/K/SiO_2$ catalysts are shown in Fig. 3. The spectrum for the unpromoted catalyst consists predominantly of the characteristic six-line spectrum for α-Fe but also contains a small central doublet assignable to superparamagnetic Fe(III) oxide. As potassium level is increased the central doublet becomes more prominant and a new peak appears at about +2 mm/sec assignable to small particles of Fe(II) oxide. Areas

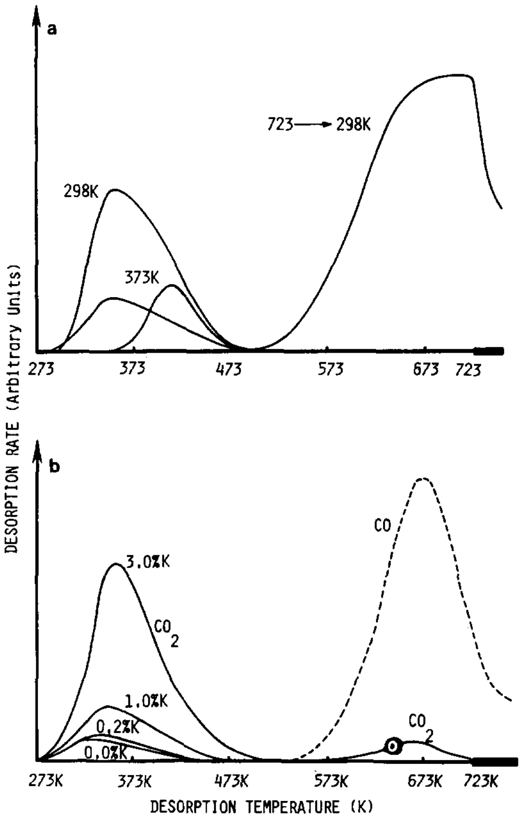

FIG. 2. (a) Temperature-programmed desorption spectra of CO from 15% Fe/SiO_2 as a function of adsorption temperature (catalyst was calcined at 473 K). (b) Temperature-programmed desorption spectra of CO_2 from potassium-promoted Fe/SiO_2. The solid lines correspond to experiments after adsorption at 298 K. The dotted line corresponds to a spectrum observed after cooling in CO_2 from 723 to 298 K, the area of which was independent of K content.

under the central and six-line peaks determined by Mössbauer are listed in Table 2 together with calculated percentage reductions of iron to the zero-valent state determined from O_2 titration. Extents of reduction determined from oxygen titration of the reduced samples are generally in good agreement with those derived from Mössbauer. It is evident that extent of reduction decreases with increasing potassium content and with increasing temperature of precalcination.

Metal crystallite diameters calculated from XRD line broadening, TEM, and H_2 uptakes assuming H/Fe = 1 are also listed in Table 2. The values determined for the unpromoted catalyst are in good agreement. Although discrepancies in the crystallite diameters of the promoted catalysts estimated from XRD and chemisorption result from suppression of H_2 adsorption by K decoration of Fe, the data indicate that the average iron crystallite size did not change substantially and based on the XRD data certainly did not increase as a result of potassium addition.

DISCUSSION

The comparison of adsorption, XRD, and TEM data of this study (Table 2) provides evidence that hydrogen adsorbs on Fe/silica with a stoichiometry of one hydrogen atom per surface iron atom, if the total uptake is measured while cooling in hydrogen from 673 K to avoid kinetic limitations due to highly activated adsorption. The adsorption data (Table 1) also indicate that less than 0.5 of a monolayer of carbon monoxide adsorbs on Fe/silica at 300–373 K (CO/H = 0.34) probably because bridged species predominate.

The data of this study also provide evidence for significant changes in the kinetics and stoichiometries of CO, CO_2, and H_2 adsorptions on Fe/silica and for changes in the bulk and surface chemistry of iron due to addition of potassium. Some of these effects of potassium addition (e.g., decreases in CO and H_2 adsorptions, an increase in CO_2 adsorption and an increase in CO dissociation rate) are the same as reported earlier for single crystal and polycrystalline iron surfaces (*14, 16, 17*); others are different or were not previously reported (e.g., the increase in adsorption activation energy for hydrogen on iron and the decrease in extent of reduction with increasing potassium content).

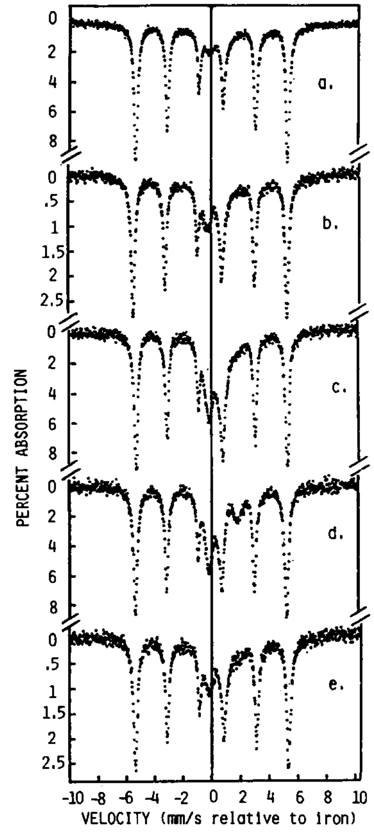

FIG. 3. Room-temperature Mössbauer spectra of reduced Fe/SiO_2 and $Fe/K/SiO_2$ catalysts: (a) 15% Fe/SiO_2 precalcined at 473 K, (b) 15% Fe/0.2% K/SiO_2 precalcined at 473 K, (c) 15% Fe/1% K/SiO_2 precalcined at 473 K, (d) 15% Fe/3% K/SiO_2 precalcined at 473 K, (e) 15% Fe/3% K/SiO_2 precalcined at 373 K.

The data in Table 1 indicating that CO and H_2 uptakes are decreased by the addition of potassium to Fe/silica provide evidence that potassium oxide or silicate is present on the iron surface and effectively blocks adsorption sites. This conclusion is consistent with the observations of Emmett

TABLE 3

Percent K Surface Coverage of K-Promoted Fe/SiO_2 Catalysts

Catalyst	Calcination temperature (K)	From total CO_2 chemisorption[a] (298 K)	From irreversible CO_2 chemisorption[a] (298 K)	From XRD[b]	From total H_2 chemisorption[c]
15% Fe/0.2% K/SiO_2	473	18	15		5
15% Fe/1% K/SiO_2	473	72	12		50
15% Fe/3% K/SiO_2	473	139	25	60	59
15% Fe/3% K/SiO_2	373	118	16	60	46

[a] % K coverage = 100 [CO_2 uptake (K-promoted) − CO_2 uptake (unpromoted)] × 1.5/[H_2 uptake unpromoted × 2].

[b] % K coverage (XRD) = 100 [1 − (d_x/d_H)] where d_x = XRD diameter; d_H = H_2 diameter.

[c] % K coverage (H_2 ads.) = 100 [H_2 uptake (unpromoted) − H_2 uptake (K-promoted)]/H_2 uptake (unpromoted).

and Brunauer (*1*) and Dry (*30*), who reported that the CO adsorption capacity of unsupported iron decreased with addition of potassium due to the presence on the surface of K_2O (in precipitated iron) or $K_2O(SiO_2)_2$ (in fused iron). Dry (*30*) observed that K_2O does not go into solid solution with iron but is present at the interface between iron particles.

The observations in this study that potassium promotion increases the binding energy of hydrogen with iron and the activation energy for hydrogen adsorption on iron while increasing the rate of CO dissociation provide further evidence that potassium was present on the iron surface and indicate, in addition, that a chemical/electronic interaction between potassium oxide or (potassium silicate) and iron affects the chemical properties of metallic iron sites not covered by potassium.

The data in Table 1 showing a greater decrease in CO adsorption capacity relative to that of hydrogen with increasing addition of potassium have significant implications. Since both H_2 and CO adsorptions were dissociative under these conditions and since metal crystallite sizes were not significantly different in the catalysts of different potassium content, they suggest that dissociative CO adsorption involves an ensemble containing a larger number of metal atoms than for H_2 adsorption. These results also suggest the possibility that the potassium species are uniformly distributed on the iron surface; otherwise the decrease in the number of CO molecules adsorbed relative to the decrease in metal atoms available for adsorption (measured by H_2 adsorption) would have been less dramatic.

The H_2, CO, and CO_2 adsorption data provide a basis for estimating potassium coverages in the promoted catalysts; estimates from CO_2 adsorption are based on the assumption that all of the potassium is located on iron metal or metal oxide rather than the support. The fairly poor agreement among the potassium coverages calculated from either irreversible or total CO_2 uptakes relative to those determined from decreases in H_2 adsorption (Table 3) suggests that at least part of the reversibly held CO_2 adsorbs on K-covered support while irreversibly held CO_2 underestimates potassium coverage on the metal. Thus, CO_2 adsorption does not appear to be a reliable quantitative method for estimating K coverage on supported Fe; nevertheless, a combination of H_2 adsorption with XRD or TEM may be quantitatively reliable. Since 40–55% of the metal surface is available for H_2 adsorption in the catalysts containing 1 and 3% potassium, the potassium oxide phase is either present in the form of crystallites or largely present on the support, as 0.2% K is sufficient for monolayer coverage of the iron surface.

The observation from this study of decreasing extent of reduction to metallic iron with increasing potassium content is a new, significant result (see Table 2). This effect is possibly a result of a strong interaction between potassium oxide or potassium silicate and unreduced iron oxide. Such a strong potassium oxide–iron oxide interaction could prevent the reduction of the iron underlying or adjacent to the promoter (*31*).

The results of this study indicate that precalcination of Fe/K/silica lowers its adsorption capacities for H_2 and CO, increases greatly its binding energy for H_2 and its activation energy for hydrogen adsorption, and significantly lowers its extent of reduction to iron metal, but does not affect its CO_2 adsorption capacity, metal particle size, or potassium coverage. In a companion study (*32*) of the same catalysts in CO hydrogenation it was determined that the precalcination of Fe/K/silica causes a 10-fold decrease in activity and a dramatic shift in selectivity to light olefins. The simultaneous lowering of activity and adsorption capacities for H_2 and CO at constant potassium coverage suggests that the calcination caused contamination of the surface with a species in addition to potassium, e.g., potassium silicate or silica. The strong interaction of magnetite with silica to produce a silica-covered iron surface at reasonably low temperature has been reported by Lund and Dumesic (*33*).

ACKNOWLEDGMENTS

The authors gratefully acknowledge the technical assistance of Gordon Weatherbee and Glenn Witt and financial assistance from DOE (Contract DE-AC01-79ET14809).

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Received January 29, 1985