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Strong Oxide–Oxide Interactions in Silica-Supported Magnetite Catalysts

IV. Catalytic Consequences of the Interaction in Water–Gas Shift

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Water–gas shift was studied at 663 K and 0.1 MPa over a series of silica-supported magnetite (Fe_3O_4) catalysts having magnetite particles from ca. 10 to 160 nm in size. The surface sites on these catalysts were titrated using NO adsorption at 273 K and adsorption from a CO_2/CO gas mixture (CO_2 : CO = 85 : 15) at 663 K. For these silica-supported catalysts, the water–gas shift turnover frequency, based on NO adsorption for site titration, decreased with decreasing particle size. In contrast, unsupported magnetite did not show this particle size dependence. For the smallest silica-supported magnetite particles, the turnover frequency was three orders of magnitude lower than over unsupported magnetite. The extent of CO and CO_2 adsorption, per surface site as titrated by NO, was also observed to decrease with decreasing particle size; and, the water–gas shift turnover frequency, based on CO_2/CO adsorption for site titration, is independent of particle size. Thus, while NO adsorption can be used to measure the magnetite surface area of silica-supported samples, the CO_2/CO adsorption uptake is proportional to the number of active sites on the magnetite surface. Compared to unsupported magnetite, the origin of the low catalytic activity of silica-supported magnetite (based on NO adsorption for site titration) is interpreted as being due to the effects of Si^{4+} substitution into the surface of magnetite, which causes the iron cations at the surface to become electron deficient and coordinatively more saturated with oxygen anions.

INTRODUCTION

This is the fourth paper in a series investigating the existence, nature, and effects of a strong oxide–oxide interaction (SOOI) between silica (SiO_2) and magnetite (Fe_3O_4) in silica-supported magnetite catalysts. In the first part of this series (*1*), the existence of this interaction was evidenced through the use of Mössbauer spectroscopy and X-ray diffraction. In particular, while unsupported Fe_3O_4 is oxidized to α-Fe_2O_3 upon treatment in oxygen at 770 K, the interaction between silica and magnetite causes silica-supported Fe_3O_4 to be oxidized to γ-Fe_2O_3 by this same oxygen treatment. Furthermore, the results of Mössbauer spectroscopy suggested that the SOOI arises from the substitution of Si^{4+} into the tetrahedral sites of Fe_3O_4, displacing Fe^{3+} to adjacent octahedral sites. This reaction can be represented by the equation,

$$2\,SiO_2 + 2[Fe^{3+}](Fe^{2+}, Fe^{3+})O_4 \rightarrow [Si_2{}^{4+}, \square](Fe_2{}^{2+}, Fe_4{}^{3+})O_{12} \quad (1)$$

where square brackets represent tetrahedral sites normally filled by Fe^{3+} in Fe_3O_4, parentheses represent octahedral sites normally half filled by Fe^{2+} and half filled by Fe^{3+} in Fe_3O_4, and a square represents a vacancy at a site normally filled by an iron cation in Fe_3O_4.

In the second part of this series (*2*), the substitution of Si^{4+} into Fe_3O_4, as represented by Eq. (1), was shown to occur only in a surface shell, several atomic layers thick. Hence, since a bulk phase did not form, the mixed oxide was identified as the result of a strong oxide–oxide interaction at

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the surface. This was demonstrated by the particle size dependence of the Mössbauer parameters of silica-supported Fe_3O_4. Furthermore, the catalytic activity of silica-supported Fe_3O_4 for water–gas shift was observed to rapidly and irreversibly decrease when the samples were exposed to water vapor at ca. 650 K. This deactivation was attributed to chemical transport of SiO_2 across the surface of the supported Fe_3O_4 crystallites, resulting in a thin shell formed by reaction (1) surrounding a core of unaffected Fe_3O_4. This behavior was observed for a series of catalysts with Fe_3O_4 particle sizes ranging from ca. 10 nm to ca. 160 nm. In the third part of this series (*3*) the chemical transport of SiO_2 by steam, at near-atmospheric pressures and 650 K, was confirmed by direct observation. Specifically, the movement of SiO_2 across an initially clean iron oxide film (prepared by oxidation of a metallic iron foil) was monitored by scanning Auger electron microscopy. (In fact, it was also demonstrated that water-induced mobility of silica is not confined to the Fe_3O_4/SiO_2 system, but that it may be a general phenomenon for silica-supported catalysts.)

In the present paper, the catalysts prepared and characterized in previous parts of this series are evaluated as water–gas shift catalysts and compared to unsupported Fe_3O_4. A chemisorption technique developed by Kubsh *et al.* (*4*) is then shown to successfully titrate the active sites for the reaction, thereby providing information about the nature of these sites on magnetite.

EXPERIMENTAL

The catalysts used in this investigation have all been described and characterized previously (*1, 2, 5*). Briefly, a silica-supported catalyst with magnetite crystallites 10 nm in size was prepared by incipient wetness impregnation of silica gel, using a ferric nitrate solution, followed by treatment in a CO_2/CO gas mixture ($CO_2 : CO = 85 : 15$) at 660 K (*1*). Larger magnetite crystallites supported on silica were prepared by adding SiO_2 to liquid $Fe(NO_3)_3$, mixing, heating to decompose the nitrate, and treating in the CO_2/CO gas mixture at 660 K. (It should be noted that for convenience these samples are described as magnetite supported on silica, even though some of these samples contained as little as 3% SiO_2, and as such the silica cannot be rigorously called a support.) Large particles of unsupported magnetite were also prepared in the above manner by neglecting to add SiO_2 to the $Fe(NO_3)_3$ melt (*2*). Small particles of unsupported Fe_3O_4 were prepared by precipitation from a 2 : 1 molar solution of ferric and ferrous ammonium sulfates using ammonium hydroxide (*5*). In addition, an industrial, chromia-promoted magnetite catalyst (SK-12, Haldor Topsøe A/S) was used in powdered form for comparison with the unpromoted Fe_3O_4/SiO_2 catalysts. The magnetite surface area of all catalysts, except SK-12, was determined by NO chemisorption at 273 K, as described elsewhere (*5–7*). The surface area of SK-12 was determined from a BET isotherm measured using N_2 at 77 K. Since it has been shown elsewhere that the NO uptake of Fe_3O_4/SiO_2 is essentially the same before and after exposure of the catalyst to water–gas shift reaction conditions (*2*), all NO surface areas were measured following treatment in CO_2/CO at 660 K, but prior to kinetic studies. Table 1 lists for all samples the magnetite loading in weight percent, the magnetite surface area in m^2 (g catalyst)$^{-1}$, and the average magnetite particle size (calculated from the magnetite surface area, assuming the particles to be spherical and to have the density of bulk Fe_3O_4). Sample sizes between 0.5 and 2.0 g were used in all adsorption studies.

The water–gas shift activities of all catalysts were evaluated in a Pyrex reactor system using a differential reactor and gas chromatographic analysis of both reactants and products. The reactor system was described previously (*2*), and a more thorough discussion of the apparatus and data collec-

TABLE 1

Chemisorptive Characterization of Water–Gas Shift Catalysts

Weight percent Fe_3O_4	Surface area $[m^2(g_{catalyst})^{-1}]$	Equivalent spherical particle diameter (nm)
20	20.9	10.8
59	32.9	20.6
91	15.9	66.4
97	7.0	159.6
100[a]	5.9	196.0
100[b]	28.0	41.0
SK-12	40.1	29.0

[a] Prepared by nitrate decomposition (see text).

[b] Prepared by precipitation (see text).

tion procedures is available elsewhere (*6*). Carbon monoxide/carbon dioxide gas mixtures were obtained from Matheson (C. P. grade) and before use were passed through a Pyrex tube at 473 K to decompose any metal carbonyls present. Water was twice distilled before use. All catalytic activities reported are steady-state values, determined at 663 K and 0.1 MPa in a reactant mixture containing 50% H_2O, 45% CO, and 5% CO_2. For SiO_2-supported catalysts, steady state was reached after ca. 1.5×10^5 s (4.2 h), following the previously noted catalyst deactivation upon initial exposure of the sample to water–gas shift reaction conditions (*2*). The apparent turnover frequency (i.e., based upon the NO adsorption uptake of the fresh catalyst) was then determined from the average of several kinetic measurements. Small deviations in measured catalytic activity, due to fluctuations in temperature and partial pressures from the above standard conditions, were corrected using Bohlbro's (*8*) rate expression for the water–gas shift:

$$N = k\, P_{CO}{}^{0.9} P_{H_2O}^{0.25} P_{CO_2}^{-0.6} \left\{1 - \frac{P_{CO_2} P_{H_2}}{K_{eq} P_{CO} P_{H_2O}}\right\} \quad (2)$$

where k is a rate constant, K_{eq} is the water–gas shift equilibrium constant, and P_i are partial pressures. (The correction to N resulting from Eq. (2) never exceeded 11% and was typically less than 6%. The activation energy employed, 112.5 kJ/mol, was the value measured on SK12 (*6*).) This expression has been shown to describe water–gas shift kinetics over magnetite at temperatures from 600 to 770 K.

RESULTS

Prior to kinetic measurements, each catalyst was reduced overnight (ca. 15 h) at 663 K and 0.1 MPa in a flowing CO_2/CO gas mixture (CO_2 : CO = 85 : 15). The activity of each catalyst was then determined as discussed above. Figure 1 shows the steady-state, apparent turnover frequencies of the catalysts as a function of the magnetite crystallite size as determined from NO chemisorption at 273 K. In this figure the solid circles are for silica-supported catalysts, the open circles are for unsupported catalysts, and the open square represents SK-12.

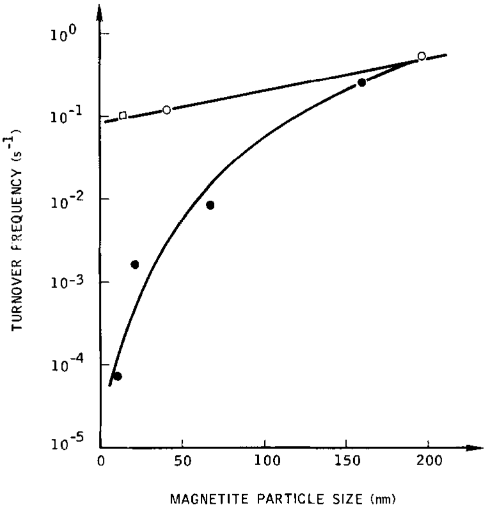

FIG. 1. The Fe_3O_4 particle size dependence of the water–gas shift activity of magnetite. Open circles represent unsupported Fe_3O_4, solid circles represent silica-supported catalysts, and the open square represents SK-12. Surface site titration for calculation of turnover frequencies employed nitric oxide adsorption for all samples except SK-12, for which the nitrogen BET monolayer capacity was used.

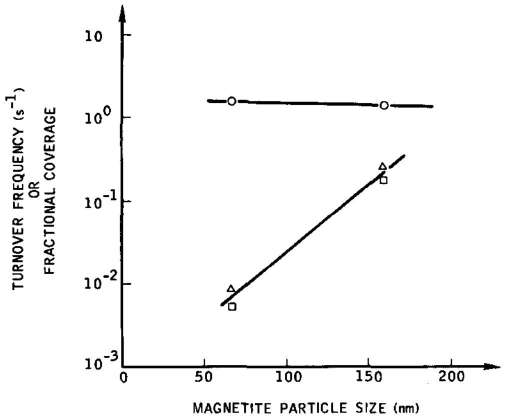

FIG. 2. Comparison of the Fe_3O_4 particle size dependence of the CO_2/CO adsorption uptake with the water–gas shift turnover frequencies based on NO adsorption or CO_2/CO adsorption for titration of surface sites on two silica-supported catalysts. Squares represent the CO_2/CO saturation coverages, expressed as fractions of the NO adsorption uptakes. Triangles represent turnover frequencies based on NO adsorption for surface site titration (from Fig. 1), and circles represent turnover frequencies based on CO_2/CO adsorption for surface site titration.

In addition to the NO adsorption uptake of the catalysts, the total adsorption uptake from an 85% CO_2, 15% CO gas mixture was measured at 663 K. Specifically, following kinetic measurements, each catalyst was treated in this CO_2/CO gas mixture at 663 K and 0.1 MPa for 1.8×10^4 s (5 h), and subsequently evacuated at ca. 0.13 Pa and 663 K for 3600 s (1 h). A total gas adsorption isotherm at 663 K was then measured on each catalyst using the same CO_2/CO gas mixture. This measurement utilizes the method developed by Kubsh *et al.* (*4*) whereby the high temperature adsorptive properties of magnetite are probed using gas mixtures in which magnetite is the thermodynamically stable phase of iron. The monolayer coverages by adsorbed CO_2 and CO, determined by fitting the data as Langmuir isotherms, were subsequently determined. Figure 2 shows the CO_2/CO monolayer coverage (expressed as a fraction of the NO uptake) plotted as a function of the magnetite particle size. The turnover frequency based on NO uptake, and the turnover frequency based on the total CO_2/CO uptake, are also shown in this figure. An attempt was made to also measure the CO_2/CO uptake of the 20% Fe_3O_4/SiO_2 catalyst; however, the uptake was too small to be measured on the quantity of catalyst available (ca. 2.0 g).

DISCUSSION

It can be seen in Figure 1 that the water–gas shift on silica-supported magnetite appears to be a structure-sensitive reaction. Yet, it must be remembered that silica is mobile in the presence of steam at water–gas shift temperatures, resulting in the substitution of Si^{4+} into the surface of magnetite (*3*). In fact, the figure shows that magnetite particles as large as 50 nm still show significant deviations from bulk catalytic activity when these particles are supported on silica. In contrast, unsupported magnetite does not show this apparent dependence of rate on particle size for magnetite particles of similar size. Thus, the apparent structure sensitivity of silica-supported magnetite is due to effects of Si^{4+} substitution into the surface of magnetite, rather than an intrinsic variation of catalytic activity with particle size.

If the transport of silica over the magnetite surface led to the encapsulation of the magnetite particles by a thick shell of SiO_2, then all silica-supported magnetite catalysts would show a common (low) turnover frequency characteristic of pure SiO_2. Figure 1 illustrates that this is not the case. In addition, this encapsulation of magnetite by silica would cause the NO adsorption uptake of the silica-supported catalysts to decrease markedly after exposure of the samples to water–gas shift reaction conditions (since NO adsorbs only on iron cations and exposure to water–gas shift reaction conditions leads to water-induced migration of silica). As noted earlier, the NO adsorption uptake does not decrease in this manner. Instead, the number of iron cations accessible to NO is not significantly decreased by the incorporation of Si^{4+} into the magnetite surface. Finally, the results of Fig. 1 cannot be explained by a partial encapsulation of magnetite by SiO_2, resulting in thick patches (or islands) of SiO_2 on the magnetite surface. This follows because the rates of water–gas shift are expressed per surface iron cation as titrated by NO (i.e., turnover frequencies are reported). One must therefore conclude that water-induced migration of silica leads to the formation of a Si^{4+}-containing surface of magnetite that is capable of adsorbing NO but that shows a low catalytic activity for water–gas shift and a low CO_2/CO adsorption uptake relative to silica-free catalysts. Furthermore, the nature of this surface depends on the magnetite particle size.

It may be suggested that the presence of the Si^{4+} at the surface of magnetite alters the chemical properties of the iron cations and associated oxygen anions at the surface. It was noted above that Mössbauer spectroscopy studies of silica-supported magnetite suggested that Si^{4+} substitutes into the tetrahedral sites near the surface of Fe_3O_4 with the displacement of Fe^{3+} to the octahedral sites (*1*, *2*). This leads to an electron deficiency on the octahedral sites of silica-supported magnetite, relative to pure magnetite. Electron hopping between the octahedral Fe^{2+} and Fe^{3+} cations would tend to delocalize this electron deficiency over the entire particle of magnetite, while the requirement of local charge neutrality would tend to localize this electron deficiency near the surface (where reaction (1) takes place). Another effect of silica incorporation into the surface of magnetite can be seen by comparing the ionization potentials of silicon and iron. The third and fourth ionization potentials of silicon are 33.49 and 45.13 eV, respectively, while the second and third ionization potentials of iron are 16.18 and 30.64 eV, respectively (*9*). Hence, electron transfer from Fe^{2+} to Si^{4+} is energetically favorable. Since the 3s and 3p valence levels of Si are involved in bonding with neighboring oxygen anions, this electron transfer can be accomplished by making these bonds more covalent. Correspondingly, the bonding between oxygen and the octahedral iron cations would become more ionic. Moreover, the substitution of the smaller Si^{4+} for the larger Fe^{3+} in the tetrahedral sites of magnetite would cause the oxygen parameter to decrease (i.e., the tetrahedral sites contract and the octahedral sites expand), also increasing the covalency of the bonding in the tetrahedral sites while increasing the ionicity of the bonding in the octahedral sites. In summary, all of the above arguments suggest that the substitution of Si^{4+} into a surface shell around magnetite creates an electron deficiency at the octahedral iron cations near the surface; however, due to electron hopping in the octahedral sublattice, this effect is moderated by the core of pure magnetite within the particle. Thus larger particles, where the volume of the unsubstituted core of Fe_3O_4 is great, may supply electrons more effectively to the surface shell (through the electron hopping process) than small particles which have a smaller unsubstituted core volume. This latter effect may be partially responsible for the observed particle-size dependence of the catalytic activity for water–gas shift over silica-supported magnetite. The proposed electron deficiency of the octahedral iron cations of silica-supported magnetite, with respect to pure magnetite, is consistent with the low catalytic activity of these samples for water–gas shift. For example, Topsøe and Boudart (*10*) found that the introduction of Pb^{4+} into the tetrahedral sites of chromia-promoted Fe_3O_4 led to an expansion of the tetrahedral sites, a contraction of the octahedral sites, and an increase in catalytic activity for water–gas shift. Thus, these authors showed that an increase in covalency of oxygen bonding to the octahedral iron cations increased catalytic activity, and the present study suggests that decreased covalency of this bonding leads to decreased catalytic activity.

Compared with the presently observed effect of Si^{4+} substitution into magnetite, it has been found that the catalytic activity of ferrites, MFe_2O_4, for CO oxidation varies by less than one order of magnitude as M is changed from Fe^{2+} to Mn^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}, and Mg^{2+} (*11–13*). Similar results were found for the oxidation of hydrogen (*14*), the oxidation of methane (*15*), the oxidation of propylene (*16*), and hydrogen peroxide decomposition (*13*) over ferrites. The water–gas shift over chromites, MCr_2O_4, has also been found to vary little as M is changed between Mg^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, and Zn^{2+} (*17*). In all of the above cases, the different cations used to vary M had the same charge and similar sizes and ionization potentials. Furthermore, the substitution of these cations is uniform throughout the oxide volume.

In contrast, the charge, size, and ionization potentials of Si^{4+} are significantly different from those values for the above cations, and the substitution of Si^{4+} occurs only near the surface of magnetite. These differences may be responsible for the marked decrease in water–gas shift activity when Si^{4+} is incorporated into the magnetite surface, compared to the smaller effects of the above divalent cations in oxidation reactions. Due to the tetravalent state of Si^{4+} it may be suggested that this cation would tend to remain coordinatively saturated, and hence prefer to be located *beneath* the surface. The cation vacancies of reaction (1) would accordingly be located *in* the surface. The oxygen anions associated with these surface cation vacancies would be attracted to the positive charge of the iron cations in the surface. As a result, the extent of coordinative unsaturation of these iron cations would be decreased, thereby decreasing the number of active sites for water–gas shift. In fact, this effect would be enhanced by the electron deficiency on the octahedral iron cations which is induced by the neighboring Si^{4+} (as discussed above). It must be proposed, however, that while Si^{4+} substitution into magnetite leads to a decrease in the coordinative unsaturation of the surface iron cations, the ability of these cations to chemisorb NO is not significantly altered. This is consistent with the known propensity of NO to reconstruct oxide surfaces (e.g., *18*), leading to NO adsorption on cations which are inaccessible to more weakly chemisorbed gases such as CO and CO_2.

Insight into the nature of the active sites for water–gas shift over magnetite and the effects of Si^{4+} substitution into the surface is obtained with reference to Figs. 1 and 2. The change in water–gas shift turnover frequency shown in Fig. 1, based on nitric oxide titration of surface iron cations, is paralleled in Fig. 2 by a decrease in the CO_2/CO adsorption uptake, expressed as a fraction of the corresponding NO uptake. Accordingly, if a water–gas shift turnover frequency is calculated using the CO_2/CO uptake as a measure of the number of surface sites, then this frequency is independent of particle size for the two samples shown in Fig. 2. This is to be contrasted with the order of magnitude change in water–gas shift turnover frequency based on NO adsorption for these same two samples. Furthermore, this correlation between catalytic activity and CO_2/CO uptake is also reflected in the observation that the 20% Fe_3O_4/SiO_2 catalyst (with 11 nm particles of Fe_3O_4) showed a very low catalytic activity (Fig. 1) and a CO_2/CO uptake that was too small to measure with the present apparatus. In short, while NO adsorption at 273 K can be used to determine the magnetite surface area on silica-supported magnetite, CO_2/CO adsorption from a CO_2/CO gas mixture ($CO_2 : CO = 85 : 15$) at 663 K effectively titrates those surface sites that are active for water–gas shift.

That the adsorption of CO_2/CO can be used to titrate the surface sites on magnetite which are active for water–gas shift is consistent with the results of Kubsh *et al.* (*4*, *19*) who studied chromia-promoted magnetite. These authors found that the saturation surface coverage by CO_2/CO was related to the number of surface sites that could readily participate in reversible, oxidation–reduction at 650 K (*4*); and, according to the regenerative mechanism for water-gas shift (*20*), one pathway for water-gas shift involves reduction of the surface by CO coupled with oxidation of the surface by H_2O. Since Kubsh and Dumesic (*19*) have shown that this regenerative mechanism is a primary pathway for water-gas shift over magnetite, the number of sites capable of undergoing reversible oxidation/reduction should be related to the catalytic activity. A correlation between catalytic activity and CO_2/CO adsorption thereby results, as observed experimentally in the present paper.

The magnetite particle size dependence of the CO_2/CO adsorption uptake and the water-gas shift activity (per magnetite surface area, as titrated by NO adsorption) is not fully understood at present. As noted previously, the core of unsupported magnetite beneath the Si-substituted shell at the surface of the magnetite particles may modify the catalytic properties of the surface iron cations, due to fast electron hopping in the octahedral sublattice of magnetite. In addition, it is also possible that the extent of Si^{4+} substitution into magnetite may increase with decreasing magnetite particle size. Accordingly, the number of tetrahedral cation vacancies and thus the coordinative unsaturation of the surface octahedral iron cations would decrease with decreasing particle size as postulated previously.

Implicit in all the above discussions is a relationship between the octahedral cations of magnetite and the catalytic activity of this material. This is not without precedent, as Topsøe and Boudart (*10*) and Schwab *et al.* (*13*) have interpreted the catalytic properties of ferrites for water-gas shift and CO-oxidation, respectively, in terms of the octahedral cations. Moreover, it was noted earlier that the substitution of Si^{4+} into the surface of magnetite takes place at the tetrahedral sites, with the displacement of the originally tetrahedrally coordinated Fe^{3+} cations to octahedral sites. Hence, the surface of all the silica-supported catalysts is essentially void of tetrahedral iron cations. If the tetrahedral iron cations were the primary active sites, all catalysts should exhibit a common low activity, contrary to experimental observation.

Two types of mechanisms for water-gas shift have been proposed in the literature: the regenerative and adsorption mechanisms. Both of these can also be argued to involve octahedrally coordinated iron cations. The regenerative mechanism involves reduction of the surface by CO or H_2 coupled with oxidation of the surface by H_2O or CO_2 (e.g., see (20)). Due to electron hopping in the octahedral sublattice of magnetite, the average oxidation state of each octahedral iron cation is 2.5, and this would allow these cations to readily undergo reversible oxidation/reduction reactions. Furthermore, each oxygen anion in Fe_3O_4 is coordinated to three octahedral cations and one tetrahedral cation, suggesting also that the removal of oxygen from the surface (reduction) and addition of oxygen to the surface (oxidation) are associated primarily with octahedrally coordinated cations. In the adsorption mechanism (e.g., see (*21*, *22*)), the surface of magnetite does not undergo oxidation-reduction, but instead the water-gas shift proceeds via adsorption of reactants (CO, H_2O), formation of intermediates (e.g., formates), and desorption of products (CO_2, H_2). One of the slow steps in this process is believed to be the adsorption of CO (*21*, *22*), which involves the interaction of CO with a coordinatively unsaturated metal cation followed by the formation of carbonate or bicarbonate species (*23*–*27*). Because CO is a soft base (*28*), it interacts more strongly with soft acids than with hard acids. Accordingly, since Fe^{2+} is a softer acid than is Fe^{3+}, it may be anticipated that CO will interact more strongly with Fe^{2+} than with Fe^{3+}. The octahedrally coordinated iron cations (i.e., $Fe^{2.5+}$) are thereby favored over the tetrahedrally coordinated iron cations (i.e., Fe^{3+}) with respect to interaction with CO.

CONCLUSIONS

It has been observed that a strong oxide–oxide interaction between Fe_3O_4 and SiO_2 causes the water–gas shift turnover frequency, based on NO chemisorptive titration of surface sites, to decrease with decreasing magnetite particle size. The extent of CO_2/CO adsorption at 663 K, measured using a CO_2/CO gas mixture as described by Kubsh *et al.* (*4*), shows a similar dependence on magnetite particle size. The adsorption of CO_2/CO can, therefore, be used to titrate the surface sites that are active for water–gas shift on magnetite. The decreased water–gas shift activity of silica-supported magnetite, compared to unsupported magnetite, is due to the substitution of Si^{4+} into the tetrahedral cation sites near the surface of magnetite. This causes the iron cations at the surface to become electron deficient and coordinatively more saturated with oxygen anions. The dependence of catalytic properties on magnetite particle size is suggested to result from a greater extent of Si^{4+} substitution into the magnetite surface with decreasing particle size or to fast electron hopping between the octahedrally coordinated iron cations at the surface and in the bulk.

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