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Adsorptive and Catalytic Properties of Supported Metal Oxides

III. Water-Gas Shift over Supported Iron and Zinc Oxides

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Supported iron oxide and zinc oxide samples were studied as water-gas shift catalysts at temperatures from 620 to 720 K. The supports studied were SiO_2, Al_2O_3, TiO_2, MgO, ZnO, and Na-mordenite. The catalytic activity of all supported iron samples was significantly lower than that of magnetite (Fe_3O_4). It is suggested that whereas magnetite functions as a catalyst via an oxidation–reduction pathway, all supported iron and zinc oxide samples operate via an associative mechanism for the water-gas shift. The catalytic activities of the supported samples decreased as the acidity of the support or the electronegativity of the support cations increased. It is proposed that carbon monoxide does not readily adsorb or react with acidic catalysts, thereby leading to low water-gas shift activities. On basic oxides, the rate of water-gas shift is inhibited by the adsorption of carbon dioxide.

INTRODUCTION

While supported metal catalysts have been studied extensively, supported metal oxides have not received great attention and as a result, they are not as well understood. In fact, strong interactions of metal oxides with oxidic supports are expected due to the structural similarities between these phases (e.g., see papers in the recent monograph by Grasselli and Brazdil (*1*)). In earlier papers in this series, the interactions between supported iron cations and various oxide supports were investigated using Mössbauer spectroscopy to determine the solid state properties of iron and infrared spectroscopy to study the nature of nitric oxide adsorbed on the iron cations (*2*, *3*). In addition, Iizuka *et al.* (*4*) reported evidence for the interaction of iron cations with oxidic supports in their studies of the oxidation of CO by O_2. The influence of the support on the catalytic properties of iron and zinc cations for the water-gas shift reaction ($CO + H_2O \rightarrow CO_2 + H_2$) is addressed in the present paper.

The supports employed in this study were SiO_2, γ-Al_2O_3, TiO_2, MgO, ZnO, and Na-mordenite. The loading of iron and zinc on these support materials was varied from 1 to 50 cation%. On the low loading samples, the supported cations are highly dispersed on the support materials, and the interaction between the cations and the support is expected to be strong. Higher loading samples were studied to determine if supported, bulk phases of iron oxide and zinc oxide have the catalytic properties of the highly dispersed, lower loading samples or properties of unsupported oxides.

EXPERIMENTAL

Sample preparation. Samples of iron oxide supported on SiO_2, Al_2O_3, TiO_2, ZnO, and MgO were prepared by incipient wetness impregnation, as described elsewhere (*2*). The supported zinc oxide samples were prepared in a similar manner. Briefly, an aqueous solution containing the proper concentration of $Zn(NO_3)_2 \cdot 6H_2O$ (Fisher, certified) was prepared to yield the desired

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loading of zinc cations. The precipitation of zinc hydroxide was avoided by adjusting the pH of the zinc nitrate solution to 1–2 by addition of nitric acid. The support material was impregnated with the solution and allowed to dry in air at 300 K. The amount of solution used per gram of support material and the loadings as determined by Galbraith Laboratories are listed in Table 1. The remaining values in Table 1 will be discussed in more detail below. The sample of iron exchanged into Na-mordenite was provided by the laboratories of W. K. Hall at the University of Wisconsin–Milwaukee, and its properties have been reported elsewhere (*5*).

Prior to water-gas shift kinetics studies, all samples were treated at 420 K for 1 h in a flowing mixture of CO/CO_2 (15/85, premixed from Matheson, 99.8% pure) to decompose the nitrate salts and to evaporate remaining water. The temperature was then increased to 660 K and treatment was continued for at least 4 h. The stable bulk phase of iron under these conditions is Fe_3O_4 (*6*).

Water-gas shift kinetics. Water-gas shift kinetics were measured using the apparatus described by Lund and Dumesic (*7*). Reaction kinetics were measured using a synthesis gas stream prepared by flowing a mixture of CO/CO_2 (89/11, Matheson, 99.5% pure) through a water saturator at 375 K. This yielded a "standard" synthesis gas with the following partial pressures: 32 kPa CO, 4 kPa CO_2, and 64 kPa H_2O. After switching to synthesis gas, catalytic activity was monitored for 24 h to verify that stable activity had been obtained before reaction kinetics studies began. The activation energy was determined by varying the reactor temperature in the range from 630 to 720 K using three or more temperatures. The reactor was operated as a differential reactor with the conversion of CO maintained between 4 and 9%.

The partial pressure dependence of the rate of water-gas shift over the supported samples was determined by the procedure discussed elsewhere (*8*). Briefly, a temperature was selected at which the water-gas shift activity was easily measured (typically 660 K), the concentrations of CO, CO_2, and H_2O were varied, and the data were fit using the power law expression:

$$r = k_{CO} P^{l}_{CO} P^{m}_{H_2O} P^{q}_{CO_2}$$

TABLE 1

Properties of Supported Iron and Zinc Oxide Samples

Sample	Solution volume[a] (cm^3/g)	Loading (cation%)	Surface area (m^2/g)	NO uptake[b] ($\mu mol/g$)	Fe or Zn dispersion
1% Fe/Al_2O_3	0.85	0.95	224	28	0.15
10% Fe/Al_2O_3	0.85	—	175	312	0.17
25% Fe/Al_2O_3	0.85	—	138	468	0.11
1% Zn/Al_2O_3	0.85	0.89	—	—	0.15[c]
1% Fe/TiO_2	0.50	1.23	39	34	0.23
25% Fe/TiO_2	0.50	—	22	150	0.05
1% Fe/SiO_2	2.0	1.27	261	40	0.19
25% Fe/SiO_2	2.0	—	194	56	0.015
50% Fe/SiO_2	2.0	—	130	143	0.019
10% Zn/SiO_2	2.0	—	—	—	0.17[c]
1% Fe/MgO	0.75	0.76	43	48	0.27
1% Fe/ZnO	0.40	1.34	—	—	—

[a] Amount of solution used to impregnate the support.

[b] Corrected for adsorption of support.

[c] By analogy to iron cations.

Studies by others indicate that the reaction is zero order in hydrogen (*6*).

Following reaction kinetics studies, the surface areas of the samples were determined using the BET method. The dispersion of iron on the supports was determined by chemisorption of NO, as described by Kubsh *et al.* (*9*) and Yuen *et al.* (*10*); and the results of these measurements are presented elsewhere (*2, 3, 8*). The apparatus used for chemisorption and BET measurements has been described by Lund *et al.* (*11*).

Turnover frequencies were calculated for the following standard set of conditions: $T = 653$ K, $P_{CO} = 32$ kPa, $P_{CO_2} = 4$ kPa, and $P_{H_2O} = 64$ kPa. These calculations were based on site densities calculated from the NO uptakes, assuming one surface iron cation per adsorbed NO molecule. The dispersions of the supported zinc oxide samples were assumed to be the same as the dispersions of analogous supported iron oxide samples. The water-gas shift activities of the iron and zinc cations supported on Al_2O_3, TiO_2, and SiO_2 were corrected for the low catalytic activities of the supports by subtracting the activities of the supports from the total activities of the supported catalysts. On these samples, the activities of the supports accounted for 5–30% of the overall catalytic activities. For Fe/MgO and Fe/ZnO, however, the activity of the support was, within experimental error, equal to the activities of the supported samples, and the activity of the supported iron cations could not be determined.

Gases. All CO/CO_2 mixtures used in this study were passed through a bed of glass beads at 620 K prior to use. This was done to decompose any metal carbonyl species which may have been present in these gases. Carbon dioxide was obtained from Liquid Carbonic (99.995% pure) and was used without further purification.

RESULTS

The activation energies, power law exponents, and turnover frequencies of the supported samples for water-gas shift are given in Table 2. The temperature ranges over which the activation energies and power law exponents were determined are also indicated. On Fe/Al_2O_3, Fe/TiO_2, and Zn/Al_2O_3 the water-gas shift reaction was approximately first order in CO and about 0.25 order in H_2O. These values are similar to those reported for the bulk oxides Fe_3O_4, ZnO, and MgO (*6, 12*). Over these bulk oxides, CO_2 inhibited the water-gas shift reaction (*12*); however, on the supported samples discussed above, the inhibition by CO_2 is absent, as indicated by the zero order dependence on CO_2. The concentration dependence of the rate was not determined over the other supported samples because of low activity (Fe/SiO_2 and Zn/SiO_2) or interference by the support (Fe/MgO, Fe/ZnO, and Fe-mordenite).

The activation energies of the supported oxides were lower than those for the corresponding bulk oxides. Activation energies for bulk Fe_3O_4 and ZnO are typically 105–115 kJ/mol (*12*), while a value of 70–80 kJ/mol was observed for Fe/Al_2O_3, Zn/Al_2O_3, Fe/TiO_2, and Zn/SiO_2. The activation energies of some materials were not determined because of low activity (Fe/SiO_2) or support interference (Fe/MgO, Fe/ZnO, and Fe-mordenite).

The following order of decreasing catalytic activity was observed at 653 K: $Fe/Al_2O_3 \approx Zn/Al_2O_3 \approx Fe/TiO_2 > Fe/SiO_2 \approx Zn/SiO_2$. On MgO, ZnO, and mordenite, the activity of the support masked the catalytic activity of the supported iron cations; therefore, it is suggested for these samples that the activity of the supported iron cations is comparable to, or less than that of the support cations.

The turnover frequency for iron or zinc cations on Al_2O_3 and TiO_2 was about 10^{-3} s^{-1}. This is two orders of magnitude lower than the activity observed for magnetite, but it is comparable to the activity of bulk ZnO. The turnover frequency was nearly independent of iron loading, with a factor of 2 decrease in rate as the loading for Fe/

TABLE 2

Kinetic Parameters of Supported Iron and Zinc Oxides for the Water-Gas Shift Reaction

Sample	Activation energy (kJ/mol)	Temperature range (K)	Power law exponents			Temperature (K)	Turnover frequency at 653 K (s^{-1})
			l (CO)	*m* (H_2O)	*q* (CO_2)		
1% Fe/Al_2O_3	83	660–720	0.95	0.30	0.00	695	1×10^{-3}
10% Fe/Al_2O_3	80	660–710	0.80	0.30	−0.05	675	3×10^{-4}
25% Fe/Al_2O_3	86	630–685	0.85	0.15	−0.05	645	3×10^{-4}
1% Zn/Al_2O_3	67	620–695	1.00	0.35	0.00	670	3×10^{-3}
1% Fe/TiO_2	69	645–690	0.90	0.35	0.00	690	1×10^{-3}
25% Fe/TiO_2	—	—	—	—	—	—	4×10^{-4}
25% Fe/SiO_2	—	—	—	—	—	—	4×10^{-5}
50% Fe/SiO_2	—	—	—	—	—	—	4×10^{-5}
10% Zn/SiO_2	70	665–710	—	—	—	—	8×10^{-5}
1% Fe/MgO	—	—	—	—	—	—	—[a]
1% Fe/ZnO	—	—	—	—	—	—	—[a]
Fe-mordenite	—	—	—	—	—	—	—[a]
Fe_3O_4[b]	106	610–675	0.75	0.35	−0.25	625	3×10^{-1}
ZnO[b]	118	655–720	1.0	0.35	−0.25	675	2×10^{-3}

[a] Activity of iron masked by the support.

[b] Data for bulk oxides from Ref. (*12*).

Al_2O_3 was increased from 1 to 10%. Iron and zinc cations on SiO_2 had a turnover frequency of about 10^{-5} s^{-1}. Again, no dependence of the rate on iron loading was observed.

DISCUSSION

The results of these water-gas shift kinetics studies indicate that the catalytic activity of supported iron oxide is significantly lower than that of unsupported Fe_3O_4. In addition, both iron oxide and zinc oxide are two orders of magnitude less active on SiO_2 than on Al_2O_3. In general, the samples can be placed in three groups based on their water-gas shift activities: (i) those which are active (Fe/Al_2O_3, Zn/Al_2O_3, and Fe/TiO_2), (ii) those with low activity (Fe/SiO_2 or Zn/SiO_2), and (iii) those for which the support is as active or more active than the supported iron oxide (Fe/MgO, Fe/ZnO, and Fe-mordenite).

Two mechanisms are thought to be important for the water-gas shift reaction: a regenerate mechanism and an associative mechanism (*13*). In the regenerative mechanism, H_2O oxidizes the surface with the formation of H_2, and in a subsequent reaction CO reduces the surface with the formation of CO_2, thereby "regenerating" the surface. This is depicted below:

$$H_2O + * \rightleftarrows H_2 + O^* \qquad (1a)$$

$$CO + O^* \rightleftarrows CO_2 + * \qquad (1b)$$

where * and O* are vacant and oxygen-containing surface sites, respectively. In the associative mechanism, adsorbed reactant species interact to form an adsorbed intermediate, generally thought to be a formate, which decomposes to water-gas shift products as follows:

$$CO + * \rightleftarrows CO^* \qquad (2a)$$

$$H_2O + 2^* \rightleftarrows OH^* + H^* \qquad (2b)$$

$$CO^* + OH^* \rightleftarrows {}^*COOH^* \qquad (2c)$$

$$*COOH* \rightleftarrows CO_2^* + H^* \qquad (2d)$$

$$CO_2^* \rightleftarrows CO_2 + * \qquad (2e)$$

$$2H^* \rightleftarrows H_2 + 2^* \qquad (2f)$$

The regenerative mechanism for water-gas shift is thought to dominate over magnetite (*12, 13*) while the associative mechanism is thought to be dominant over ZnO (*12, 14*). Surface cations which can change their oxidation state are required for the regenerative mechanism. The rapid electron hopping between the Fe^{2+} and Fe^{3+} cations in the octahedral sites of magnetite is thought to facilitate the regenerative mechanism (*13, 15*). Mössbauer spectroscopy results (*2*) indicate that iron cations are stabilized as Fe^{2+} in a variety of CO/CO_2 gas mixtures over Al_2O_3, TiO_2, and SiO_2. The formation of a surface phase containing iron cations and cations from the support could account for this stability of Fe^{2+}. In fact, surface spinels (MAl_2O_4, where M is a divalent metal cation) have been postulated to exist for iron (*16, 17*) and zinc (*18*) cations supported on Al_2O_3; and, Lund and Dumesic (*7, 15, 19, 20*) have reported that a surface phase containing iron cations and silicon cations was responsible for the low water-gas shift activity of Fe_3O_4/SiO_2 samples. Since the iron cations do not readily undergo changes in oxidation state, the regenerative mechanism does not take place; therefore, the associative mechanism is proposed to be the dominant reaction mechanism for the supported iron and zinc oxides examined in this study.

In a study of the water-gas shift activity of bulk oxides, the electronegativity scale of Zhang (*21*) was shown to correlate catalytic activity (*12*). The results of the present study for the supported iron oxide and zinc oxide samples can also be interpreted in this manner. The electronegativities of cations included in this study increase in the order $Fe^{2+} \approx Zn^{2+} < Fe^{3+} \approx Mg^{2+} < Al^{3+} \approx Ti^{4+} < Si^{4+}$ (see Table 3). Supporting an oxide on a support which is more acidic (i.e., has a higher electronegativity) than that oxide may be expected to increase the acidity of the supported oxide. Both zinc and iron cations are less acidic than SiO_2, Al_2O_3, and TiO_2. Since more acidic oxides were shown to be less active for the water-gas shift reaction (*12*), the supported oxides should decrease in activity as the support becomes more acidic.

TABLE 3

Zhang Electronegativities and Metal–Oxygen Bond Strengths for Oxides Included in This Study

Cation	Z[a]	Oxides	M–O strength[b] (kJ/mol O)
Fe^{2+}	0.39	FeO	650
Zn^{2+}	0.66	ZnO	1000
Fe^{3+}	1.31	Fe_2O_3	1200
Na^+	1.38	—	—
Mg^{2+}	1.40	MgO	640
Al^{3+}	3.04	Al_2O_3	1300
Ti^{4+}	3.06	TiO_2	2000
Si^{4+}	8.10	SiO_2	3300

[a] Zhang electronegativities (*21*).

[b] Metal–oxygen bond strength as calculated elsewhere (*12*).

Consistent with the above arguments, the activities of the supported iron oxide and zinc oxide samples decreased in the order: $Zn/Al_2O_3 \approx Fe/Al_2O_3 \approx Fe/TiO_2 > Zn/SiO_2 \approx Fe/SiO_2$. Cations on the more acidic support (SiO_2) were less active than those on amphoprotic supports (TiO_2 and Al_2O_3); and, the supported iron samples were comparable in activity to the supported zinc samples. It is important to note that the low catalytic activities of iron oxide supported on SiO_2, Al_2O_3 and TiO_2 (compared to Fe_3O_4) were observed at all iron loadings investigated in this study. This is despite the fact that in addition to Fe^{2+}, Fe_3O_4 particles were detected by Mössbauer spectroscopy on SiO_2 and Al_2O_3 at the higher loadings (*2*). The turnover frequencies of the three samples for water-gas shift should be comparable to Fe_3O_4; however, they were found to be two orders of magnitude less active than magnetite. This suggests that the Fe_3O_4 particles on the support were covered by a surface phase. It is interesting to note that an $FeAl_2O_4$ surface phase has been proposed to stabilize the dispersion of bulk Fe_3O_4 promoted with Al_2O_3 (*22*). This is also in agreement with the conclusion of Lund and Dumesic (*7, 15, 19, 20*) in their study of the effects of silica on the water-gas shift activity of magnetite.

As mentioned earlier, the water-gas shift activity of iron cations on ZnO, MgO, and mordenite was masked by the activity of the support material. Since the Zhang electronegativities of Fe^{2+} and Fe^{3+} cations are similar to those for Zn^{2+} and Mg^{2+}, the activities of these materials for the water-gas shift reactions should, in fact, be similar.

Both Al^{3+} and Si^{4+} have higher electronegativities than Fe^{2+} or Fe^{3+} cations, and the catalytic activity of iron oxide supported on alumina and silica was higher than that of either support alone. This suggests that the water-gas shift activity of iron might be measurable in mordenite, which is a silica–alumina structure. This was not the case. The observation that the activity of Fe-mordenite was similar to that of Na-mordenite can be explained by several factors. For example, the Na^+ cation has a similar Zhang electronegativity to Fe^{3+} and may have a similar water-gas shift activity. Indeed, Amenomiya and Pleizier (*23*) observed enhancement of the water-gas shift activity of Al_2O_3 by promotion with Na^+.

Iwamoto *et al.* (*24*) studied the activity of a series of metal-ion exchanged zeolites for the water-gas shift reaction, and they found that the activity increased as the electronegativity of the exchanged cation decreased. The lower water-gas shift activity of the acidic cations was explained by these authors in terms of acid/base properties. Carbon monoxide is a soft base and interacts more strongly with soft acid sites. The adsorption of CO is generally considered to be a rate-controlling step in the water-gas shift reaction (e.g. (*13*)). Cations of lower acidity are generally softer acids and as such may adsorb CO more readily, thereby increasing the water-gas shift activity. This model is modified and applied to a potential associative pathway for the water-gas shift reaction in Fig. 1. In this pathway, H_2O adsorbs on an anion vacancy and a surface oxygen (step a). Carbon monoxide adsorbs on a coordinatively unsaturated cation to form a carbonyl species which then reacts with a hydroxyl group to generate a formate intermediate (steps b and c). In steps d and e, the formate species reacts further with surface oxygen (hydroxyl groups) to form a carbonate (bicarbonate) which decomposes to give gaseous CO_2 and a surface oxygen (hydroxyl group). Finally, two hydrogen atoms combine to form H_2, returning the surface to its initial state (step f). We suggest that the adsorption of CO is fast and reversible (*25*) and that a slow step is the reaction of the carbonyl with a surface hydroxyl (i.e., activation of CO) to generate a formate (step b). The rate of this reaction may be related to the metal–oxy-

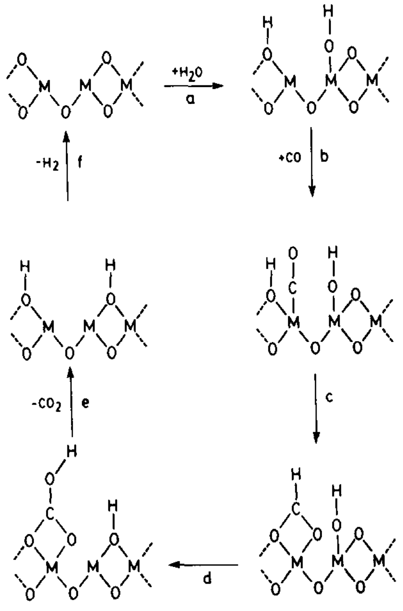

FIG. 1. Pathway for the water-gas shift reaction. (a) H_2O adsorbs on an anion vacancy and a surface oxygen, (b) CO adsorbs on an anion vacancy, (c) adsorbed CO reacts with an hydroxyl to form a formate, (d) formate reacts to form bicarbonate, (e) CO_2 desorbs, (f) H_2 desorbs.

gen bond strength on the surface as discussed by Rethwisch and Dumesic (*12*), with weaker metal–oxygen bonds favoring this process. The Zhang electronegativities and the metal–oxygen bond strengths of the oxides investigated in this study are given in Table 3. In general, the metal–oxygen bond strength of an acidic oxide is greater than that of a basic oxide; therefore, hydroxyl groups on basic oxides are expected to react more readily with carbonyl species than those on acidic oxides. On an acidic catalyst such as SiO_2, the metal–oxygen bond is too strong and formate species cannot form under water-gas shift conditions. On amphoprotic species (Al_2O_3 or TiO_2) the surface oxygen is more labile and CO may react with hydroxyl groups; however, the metal–oxygen bond is too strong for subsequent reaction to form carbonates or bicarbonates. Over basic oxides (MgO, ZnO, and FeO_x), formates are formed and react further with surface oxygen to give carbonate species. This general behavior has been verified by infrared spectroscopy studies of bulk oxides in CO/CO_2 gas mixtures or under water-gas shift reaction conditions (*26*).

Ross and Delgass (*27*) studied the reverse water-gas shift reaction over unsupported Eu_2O_3 and over Eu_2O_3 supported on Al_2O_3 and SiO_2. These authors observed that CO_2 inhibited the reaction over unsupported Eu_2O_3, while it did not inhibit the reaction over supported Eu_2O_3. In addition, the activation energy decreased when Eu_2O_3 was supported. Unlike the supported iron and zinc oxide samples of the present study, no decrease in activity was observed when europium was supported on Al_2O_3 or SiO_2. Mössbauer spectroscopy of the europium indicated the presence of both Eu^{2+} and Eu^{3+}; therefore, it was proposed that the regenerative mechanism was active over both supported and unsupported Eu_2O_3. The decreased inhibition by CO_2 and the reduction in activation energy when the europium was supported were explained by the assumption that the supported Eu_2O_3 does not adsorb CO_2 as strongly.

The decrease in the inhibition by CO_2 and the decrease in activation energy for water-gas shift over supported iron and zinc oxides, compared to the corresponding unsupported oxides, can be described by the aforementioned model of Ross and Delgass. The decrease in the inhibition of the reaction by CO_2 suggests that carbonate species are destabilized on the supported materials. This destabilization is accompanied by a decrease in the desorption energy of CO_2, thereby causing a reduction in the activation energy for the water-gas shift. These results can be explained by an increase in the metal–oxygen bond strength for the supported samples which makes it more difficult to form carbonate species from CO and surface oxygen. In acid/base terms, Al_2O_3 and TiO_2 are more acidic than FeO_x and ZnO, and the iron and zinc cations become more acidic when supported on these oxides. Since CO_2 is an acid, it is less strongly adsorbed on an acidic oxide.

Finally, the presence of both Fe^{2+} and Fe^{3+} was observed in Mössbauer spectroscopy studies of Fe/MgO (*2*). This suggests that the presence of both of these cations is not sufficient to achieve the high reactivity of the regenerative mechanism for water-gas shift over magnetite (since Fe/MgO is much less active than Fe_3O_4). The dominance of this reaction pathway over magnetite suggests that the electron hopping which takes place in the octahedral sites facilitates the oxidation/reduction cycles necessary for the regenerative mechanism.

CONCLUSIONS

The water-gas shift activities of supported iron oxide and zinc oxide were found to be dependent on the nature of the support. The low activity of supported iron oxide relative to magnetite is explained by a change in the dominant reaction pathway from the regenerative mechanism over magnetite to the associative mechanism over the supported samples. The catalytic activities of the supported samples were related to the acid/base properties of the support, with more acidic surfaces having lower activity. The acid/base properties of the support are thought to affect the water-gas shift activity of iron and zinc oxides by altering the metal–oxygen bond strength. Acidic supports have strong metal–oxygen bonds, and CO does not readily adsorb and react to give reaction intermediates such as formate species. In contrast, CO adsorbs and reacts readily on basic oxides. Carbon dioxide also adsorbs strongly on basic oxides, thereby inhibiting the water-gas shift reaction.

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