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NOTES

An Infrared Spectroscopy Study of the Adsorption of CO on Fe/MgO

Adsorption of carbon monoxide on Fe/MgO catalysts has been studied by infrared spectroscopy. These results were compared to the ir spectra for CO adsorbed on Fe powders. These studies show that the CO stretching frequency can be correlated with the oxidation state of the Fe on the supported catalysts; on Fe^0 the CO stretch is at 1960 cm^{-1}, on Fe^2 the CO stretch is at ca. 2080 cm^{-1}, and on Fe^3 the CO stretch is at ca. 2150 cm^{-1}. *The results support the hypothesis that MgO stabilizes* Fe^{2+} as the most significant iron species.

INTRODUCTION

Catalyst supports are known to play an important role in determining the physical and chemical nature of the metal catalyst. Boudart *et al.* (*1*) found that when Fe was supported on MgO the magnesia interacted with the iron stabilizing the formation of small metallic particles. The Fe particles formed on the magnesia support are much smaller than the Fe particles formed on silica. It was suggested that the Fe particles do not readily sinter on the magnesia support because of strong interactions between the iron and magnesia whereby metallic iron particles are surrounded by an FeO phase. Boudart *et al.* employed Mössbauer spectroscopy and X-ray diffraction to show the existence of a FeO phase in the reduced Fe/MgO catalysts. We have recently employed infrared spectroscopy to characterize CO adsorbed on Fe/MgO catalysts and have found evidence that suggests that this FeO phase is concentrated on the surface of the magnesia. In addition we found that the state of the metal could be correlated with the CO stretching frequency.

EXPERIMENTAL

The experiments were performed on 5% Fe/MgO catalysts prepared from precipitation of magnesium hydroxycarbonate and ferric nitrate as described elsewhere (*1*). The precipitated precursor was dried and ground to a fine powder, then pressed into a wafer on a tungsten mesh screen. Slurried magnesium hydroxycarbonate was also precipitated, dried, ground, and pressed in the same manner. The two wafers were mounted in an aluminum cell fitted with CaF_2 windows, which were mounted in water-cooled flanges. Catalyst pretreatment was done *in situ*. The main body of the cell was heated by nichrome wires wrapped around the cell. A Chromel-Alumel thermocouple mounted in the center of the cell was used to monitor temperature.

Spectra were recorded with a Beckman IR 10 spectrometer operating in the dual-beam differential mode. This compensated for adsorption on the MgO support as well as for interference from the gas phase. Scale expansion of the range 2300–1700 cm^{-1} was done to more accurately determine absorption maxima. The spectrometer was calibrated with a polystyrene standard. Gas-phase CO was found to have aborption maxima at 2175 and 2118 cm^{-1} in agreement with previous investigations (*2*, *3*).

Infrared spectra of CO adsorbed on Fe, FeO, and Fe_2O_3 powders were also obtained to compare with the results for the supported catalyst. Fe, FeO, and Fe_2O_3 powders were obtained from Alfa Chemical. These were ground in Duo Seal pump oil under a nitrogen atmosphere to make a slurry which was placed between two CaF_2 windows and supported in the ir cell. The cell was filled with CO at 1 Pa and room temperature for 12 h and then evacuated for 2 h. After evacuation ir spectra were obtained as described above.

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RESULTS

The initial catalyst treatment was to heat under vacuum. The ir cell was evacuated to 2.2×10^{-2} Pa and heated to 500 K for 6 h and then allowed to cool to 300 K. A spectrum was recorded while the cell was evacuated and indicated nothing in the range 2200–1900 cm^{-1}, as shown in Fig. 1a. Subsequently the cell was filled with CO to a pressure of 1 Pa and a second spectrum was recorded. This spectrum is shown in Fig. 1b. Two absorption peaks were observed, one at 2150 cm^{-1} and the second centered about 2070 cm^{-1}. The catalyst was next reduced in flowing hydrogen at 500 K for 12 h, cooled to 300 K, and then exposed to 1 Pa CO. The spectrum recorded after this reduction is shown in Fig. 1c. The absorption peak at 2150 cm^{-1} was reduced in magnitude and the peak at 2070 cm^{-1} increased in magnitude and its breadth suggested it to be due to more than a single absorption band. Finally the catalyst was reduced at 600 K for 12 h in flowing hydrogen, cooled to 300 K, and then exposed to 1 Pa CO. Spectrum 1d was recorded after this final reduction. The peak at 2070 cm^{-1} decreased in magnitude and the peak at 2150 cm^{-1} essentially vanished. However, there were new peaks with adsorption maxima at 2020 and 1965 cm^{-1}.

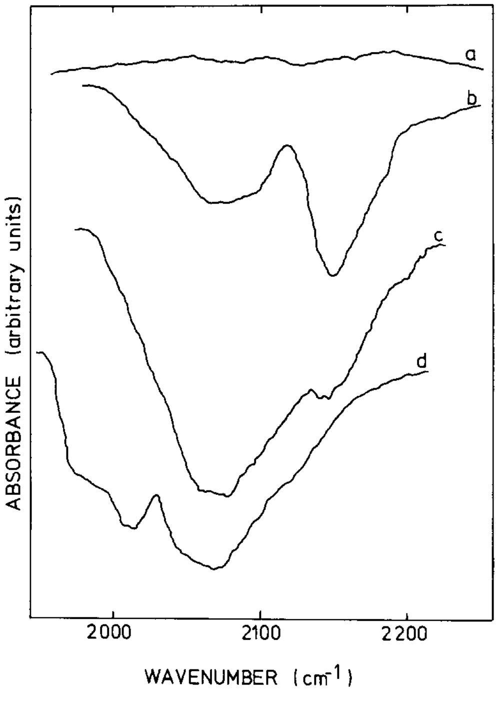

Fig. 1. Infrared absorption spectra for CO adsorption on Fe/MgO catalyst: (a) background spectrum of evacuated cell; (b) adsorption on unreduced catalyst; (c) after 12 h reduction in H_2 at 500 K; (d) after 12 h reduction in H_2 at 600 K.

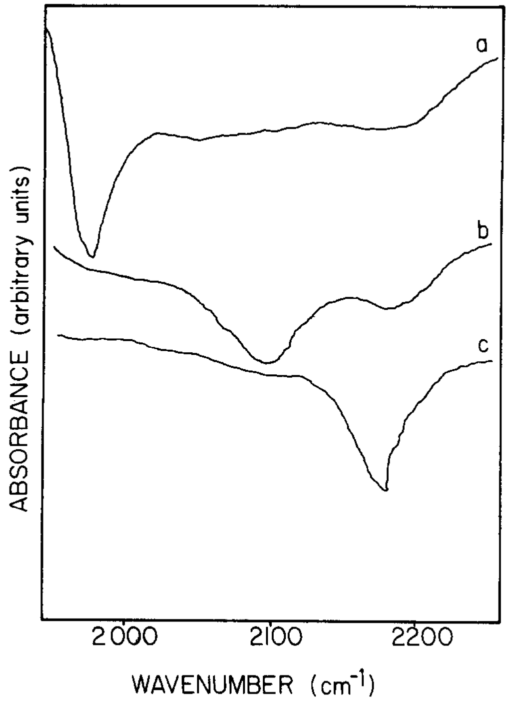

Fig. 2. Infrared absorption spectra for CO adsorption on iron powders: (a) Fe; (b) FeO; (c) Fe_2O_3.

These spectra show three distinct absorption bands. With no reduction of the Fe/MgO catalyst there was a strong band at 2150 cm^{-1} and a weaker band at 2070 cm^{-1}. It seems likely that these bands correspond to CO adsorption on Fe^{3+} (Fe_2O_3) and Fe^{2+} (FeO), respectively. Partial reduction of the iron catalyst reversed the magnitudes of these two peaks indicating Fe^{+} to be the dominant form of the iron. Further reduction resulted in the complete reduction of Fe^{3+} and the appearance of metallic iron as evidenced by CO absorption bands around 2000 cm^{-1}. This reduction scheme was completely reversible. It was found that the catalyst could be exposed to air at 500 K for 1 h, and after exposure to CO the ir spectrum was identical to that shown in Fig. 1b.

In order to test the hypothesis that the different absorption bands are due to different oxidation states of the metal we examined the ir spectra of CO adsorbed on iron powders of different oxidation states. The spectra in Fig. 2 are for CO adsorbed on Fe, FeO, and Fe_2O_3 powders. Metallic iron (Fe^0) was found to show a single strong absorption maximum at 1960 cm^{-1}. Spectrum 2a also shows absorption from 2000 to 2200 cm^{-1}; this may be attributed to oxidation of some of the iron powder. The CO absorption maximum for absorption on Fe^{2+} was found to occur at 2100 cm^{-1} (see Fig. 2b). A second absorption maximum at 2175 cm^{-1} appears to be due to adsorption on Fe^{3+} as the spectrum for CO adsorbed on Fe^{3+} showed a single maximum at 2175 cm^{-1} (Fig. 2c). The results for the iron powders show the same trends as observed on two supported catalysts for the variation in CO stretching frequency with reduction of the iron.

DISCUSSION

The absorption bands for CO adsorbed on the reduced catalyst agree well with results on other iron-supported catalysts. Blyholder and Neff (*4*) found bands at 1980 and 2020 cm^{-1} for CO adsorbed on Fe/SiO_2. Results reported here for CO adsorbed on Fe/MgO indicate the reduced catalyst gives absorption maxima at 1965 and 2020 cm^{-1}. Eischens and Pliskin (*5*) found CO adsorbed on Fe/SiO_2 gave absorption maxima at 1960 and 2020 cm^{-1}. Bianchi *et al.* (*8*) reported the same absorption maxima for CO adsorbed on Fe/Al_2O_3. These results show a remarkable consistency for the absorption maxima, which show little sensitivity to the support material. This is remarkable as the spectrum for CO adsorbed on Fe^0 powders, reported here and by Blyholder (*6*), showed a single adsorption maximum at 1960 cm^{-1}. The absence of the absorption band at 2020 cm^{-1} on iron powders suggests that this must be due to a unique feature of the supported metal, such as a particle size effect of metal–support interactions. The lack of sensitivity of the 2020-cm^{-1} maximum to support material suggests that the 2020-cm^{-1} band may well be a particle size effect. It may be noted that iron carbonyls show a strong adsorption at ca. 2020 cm^{-1} (*9*), suggesting that this band may be due to CO adsorption on very small iron clusters resembling iron carbonyls.

The oxidations of Fe/MgO and Fe/SiO_2 show a significant difference. Eischens and Pliskin found that exposing their Fe/SiO_2 catalyst to air and subsequently adsorbing CO resulted in an ir absorption peak at 2128 cm^{-1}. There were no other absorption maxima observed. Heal *et al.* also studied CO adsorption on Fe/SiO_2 catalysts using ir (*7*). They observed an absorption maximum at 2169 cm^{-1} which was attributed to adsorption on oxide impurities. The work reported here suggests that these peaks are due to absorption on Fe^{3+} which gave rise to the 2150-cm^{-1} peaks on Fe/MgO catalyst and the peak at 2175 cm^{-1} on Fe_2O_3 powders. The unique feature found on Fe/MgO catalysts was the ir absorption peak at 2070 cm^{-1}. This falls intermediate to the maxima corresponding to CO adsorbed on metallic iron and Fe_2O_3. The results for CO adsorbed on FeO powder suggest that the absorption maximum at 2070 cm^{-1} is probably due to CO adsorption on Fe^{2+} species. Results for CO adsorption on Fe/SiO_2 do not show a significant adsorption maximum in the 2080-cm^{-1} regime, indicating that Fe/MgO is unique in its ability to stabilize Fe^{2+} species.

In their study of the preparation of Fe/MgO catalysts Boudart *et al.* found that more than 50% of the iron on the reduced catalysts was in the Fe^{2+} state. The structural model proposed was that of a metallic iron island surrounded by a reef of FeO in a sea of MgO. The results presented here conform to that model. The ratio of the absorption peaks at 2000 and 2070 cm^{-1} for the reduced Fe/MgO catalyst is 1 : 3, which is about twice the value that Boudart *et al.* found for the metallic iron-to-Fe^{2+} ratio. The factor of 2 difference in these ratios is probably due to a lower degree of reduction of the iron in the experiments reported here, resulting from a lower reduction temperature. However, the ir results presented here show that adsorption of CO on Fe^{2+} is a major contributor to the total chemisorption and suggest that a substantial portion of the FeO must be situated on the surface of the catalyst support. It should be noted that the ir absorption spectra of CO adsorbed on Fe/SiO_2 catalysts gave no evidence for an Fe^{2+} phase (*4, 5, 7*), which is further evidence of the support–metal interaction in the Fe/MgO catalyst system.

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