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Magnetite Surface Area Titration Using Nitric Oxide

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The adsorption of nitric oxide on unsupported Fe_3O_4 has been investigated. Consistent with previous studies, the rate of adsorption follows Elovich kinetics, and the adsorption isotherm obeys the Freundlich equation over the range from 0.133 to 27 kPa at 273 K. However, the time of evacuation of the sample at 650 K prior to NO adsorption is shown to be critical for obtaining reproducible results. Specifically, if the evacuation is carried out for 1 hr, then consistent values of the NO uptake are subsequently obtained. Furthermore, this NO uptake normalized by the nitrogen BET monolayer capacity gives an estimate of the surface cation density that agrees with model calculations based on various low index faces of magnetite. On the other hand, long (ca. 25 hr) evacuation of the sample leads to a reduction of the surface oxidation state resulting in additional NO uptake and reduction of NO to primarily N_2O.

INTRODUCTION

The understanding of catalysis by metals has been significantly advanced by the development of gas chemisorption techniques (e.g., using H_2 or CO) for specific surface area measurement. In this respect, supported metal catalysts have not only served as a means for achieving high dispersions of precious metal atoms, but they have also led to fundamental studies of the effects of metallic particle size and metal–support interaction on the specific catalytic activity of the metal. Yet, an analogous situation does not exist for metal oxide catalysis, and this is attributable to the difficulty of titrating specific surface areas on "supported metal oxide" catalysts. Clearly, one needs a gas that chemisorbs strongly on transition metal oxides, but that interacts only weakly (and preferably reversibly) with typical support materials. Indeed, nitric oxide is a simple molecule that does possess this requisite specificity (*1–8*). In the present paper, we discuss the interaction of NO with magnetite (Fe_3O_4), and the dependence of this interaction on sample pretreatment. Fe_3O_4 was chosen for these studies due to its activity for the water–gas shift reaction and because iron exists in two oxidation states (Fe^{3+} and Fe^{2+}).

There have been several previous investigations of the adsorption of nitric oxide on iron oxides (*1–7*). The interaction of the NO with the iron oxide surface was studied by ir (*2, 4, 5*), ESCA (*7*), isotopic labeling (*3*), and gravimetric adsorption measurements (*1, 2*). However, most studies of NO adsorption on iron oxides have used Fe_2O_3, which is the stable form of iron oxide under highly oxidizing conditions.

Furthermore, there is evidence in the literature that NO is also a suitable titrant for Fe_3O_4 surfaces. For example, metallic

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iron is oxidized to Fe_3O_4 by gaseous NO and not to Fe_2O_3 (*9*), and iron is also known to complex with NO in several forms (*14*). Otto and Shelef (*1*) have looked at NO adsorption on supported Fe_2O_3 and Fe_3O_4 and have reported a one-to-one correspondence between adsorbed NO molecules and exposed iron cations on the surface. They did not examine the effect of catalyst pretreatment, however, which we have found to be of major importance. We have studied unsupported magnetite and have thus been able to examine the stoichiometry of NO adsorption in greater detail. The extension of these results to supported catalysts is then possible since NO has also been shown to adsorb only to a small extent on common support materials such as alumina (*8–12*) and silica (*11, 13*), and most of this adsorption is reversible.

METHODS

Unsupported Fe_3O_4 was precipitated from an aqueous 2:1 molar solution of ferric and ferrous ammonium sulfate salts by the addition of ammonium or sodium hydroxide. The precipitate was thoroughly washed with distilled H_2O. Subsequent XPS studies of the dried precipitate did not show the presence of sulfur, indicating that the rinsing procedure was sufficient to remove sulfate ions from the magnetite slurry. The wet Fe_3O_4 was then either (i) loaded directly into a pyrex adsorption cell and dried at ca. 380 K and 10^{-1} Pa or (ii) dried in an oven under flowing N_2, ground lightly, and loaded into a pyrex cell. The samples were then exposed to a flowing 7:1 molar mixture of CO_2:CO at 650 K for 4 to 5 hr. These conditions favor the formulation of Fe_3O_4 (*15*) and are expected to remove surface oxidation or hydration. Following the gas treatment the samples were cleaned by exposure to vacuum (ca. 10^{-4} Pa). All samples referred to below as having had the "short evacuation" were exposed to the vacuum for 1 hr during which they were allowed to slowly cool from 650 K to room temperature. Samples referred to as having had the "long evacuation" were exposed to the vacuum at 650 K until the cell could be closed and no pressure drop was detectable with an ionization gauge. The condition required from 20 to 30 hr of pumping.

Carbon monoxide (CP grade, 99.5% pure, minimum), CO_2 (bone dry grade, 99.8% pure, min), N_2O (CP grade, 99.0% pure, min), and NO (CP grade, 99.2% pure, min) were obtained from Matheson. CO, CO_2, and N_2O were used without further purification. NO was purified by the method of Turnham (*11*). The gas from the cylinder was precooled to 195 K and passed slowly through a trap of 12 to 28 mesh silica gel (Davison, grade 408, activated under vacuum for more than 2 hours at 710 K and outgassed to less than 4×10^{-2} Pa at room temperature) at the same temperature and gradually dosed into a storage flask that had been evacuated overnight to ca. 10^{-4} Pa. The purified gas was then frozen at 77 K and removed of nitrogen by evacuation. The solid was white. An infrared analysis of the gas 46 days after this purification showed no peaks that were not identifiable as NO. N_2 (prepurified) and He (laboratory grade) were obtained from the University of Wisconsin Stores and were further purified by passage over copper turnings at 700 K followed by activated 13X Davison molecular sieves at 195 K.

The vacuum/adsorption apparatus was an all-glass high vacuum system capable of pressures down to less than 10^{-4} Pa. Adsorption experiments were conducted volumetrically in a well-calibrated portion of the system where pressure was measured by a precision, quartz coil differential Bourdon capsule. The apparatus included a number of 5-liter reservoirs in which purified gases could be stored. Helium was used to determine volumes during adsorption experiments by successive expansions from a known volume into each of the unknown volumes.

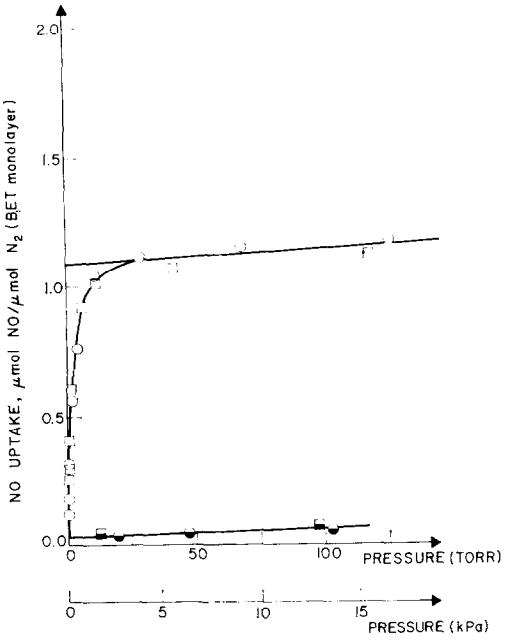

FIG. 1. The NO uptake at 273 K of two unsupported Fe_3O_4 samples which had received the short evacuation. □ and ○ are the first isotherms, ■ and ● are the second isotherms. (Note: 1 Torr = 133.3 N m^{-2}.)

RESULTS

Figure 1 shows the adsorption isotherms of two different samples of unsupported Fe_3O_4 recorded at 273 K immediately after the short evacuation described above. Adsorption is reported as the ratio of micromoles of NO adsorbed to the micromoles of N_2 taken up in the BET monolayer vs NO pressure in Pascals. A BET monolayer uptake was determined using N_2 adsorption at liquid nitrogen temperature.

Two NO isotherms were recorded on each sample with a 0.5-hr evacuation at 273 K and ca. 10^{-4} Pa between the first and second isotherms. The first isotherm consists of both irreversible and reversible adsorption while the second consists of only reversible adsorption. By extrapolation of the linear, high pressure portion of each isotherm back to the axis and subtraction of the reversible portion as shown in the figure, the amount of irreversible adsorption was determined to be 1.05 μmol NO/μmol N_2 (BET monolayer).

The isotherms were calculated assuming that none of the NO had been reduced to N_2O or N_2. The first isotherms required between 36 and 96 hr to complete, while the second isotherms required between 3.4 and 5.6 hr. Adsorption was assumed complete when the change in pressure (or amount adsorbed) during 1 hr was less than 0.2% of the total change for that point. The samples had a specific BET uptake of ca. 309 μmol/g or 30 m^2/g. It should also be noted that the NO adsorption data were observed to fit the Freundlich isotherm and the rate of adsorption followed Elovich kinetics; this behavior is in agreement with the results of Otto and Shelef (*1*).

A sample of unsupported Fe_3O_4 was prepared and given a long evacuation. Two

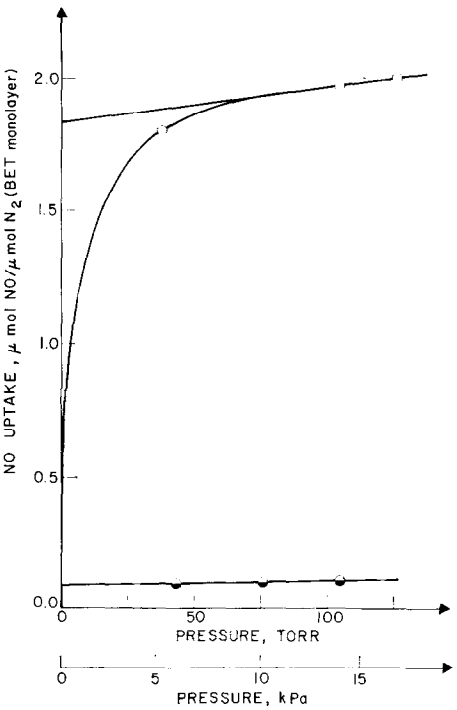

FIG. 2. The NO uptake at 273 K of an unsupported Fe_3O_4 sample which had received the long evacuation. ○ and ● are the first and second isotherms, respectively.

successive NO isotherms were run and are shown in Fig. 2. The BET surface area was then determined. Using the same procedure as with all samples, the irreversible NO uptake was determined to be 1.75 μmol/μmol N_2 (BET monolayer).

The same sample was then subjected to a second CO_2/CO treatment at 650 K for 7 hr and was then evacuated for 1 hr at 650 K (short evacuation). After only 1 hr of pumping there was almost no change in pressure upon closing off the cell (as measured with an ionization gauge) and the NO uptake per BET monolayer was found to be 1.55 μmol/μmol N_2 (BET monolayer).

While the NO uptake did indeed decrease from the amount of uptake in Fig. 2, it did not drop to the value of approximately 1 which was observed with the short-evacuation samples of Fig. 1. However, the fact that the pressure hardly changed when the cell was closed (which is the determining criterion of our "long evacuation") indicates that the sample was in a state more like those having had a long evacuation than like those having had a short evacuation.

Figure 3 shows NO adsorption isotherms recorded at 273 K on three other samples which had received the long evacuation. BET surface areas were subsequently determined for each sample. These isotherms further confirm the observations of Fig. 2 and also show that samples which are subjected to the long evacuation are not consistent from sample to sample. While the samples having received the short evacuation always approached an uptake of ca. 1 NO/N_2 (BET) (as in Fig. 1 and other data not shown), Fig. 3 demonstrates that samples having received the long evacuation do not approach any single value of the uptake (but all values are significantly greater than unity). The shapes of the isotherms are also quite different. For each of these samples only one isotherm was collected, consisting of both irreversible and reversible adsorption,

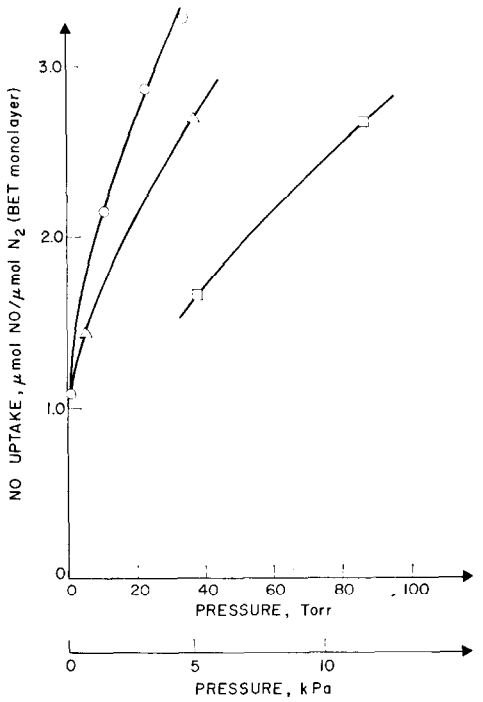

FIG. 3. The NO uptake at 273 K of three unsupported Fe_3O_4 samples which had received the long evacuation.

however, the results above (Fig. 2) indicate that the reversible adsorption is less than 10% of the total.

In all the adsorption calculations it was assumed that none of the NO had been converted to N_2 or N_2O. A thermodynamic analysis of the NO/Fe_3O_4 system shows that the oxidation of the Fe_3O_4 to Fe_2O_3 is favored with production of N_2 or N_2O. The reactions are

$$2Fe_3O_4 + NO \rightarrow 3Fe_2O_3 + \tfrac{1}{2}N_2, \quad (1)$$

$$2Fe_3O_4 + 2NO \rightarrow 3Fe_2O_3 + N_2O. \quad (2)$$

In an effort to see if these reactions would affect the results of the long-evacuation samples and account for the discrepancy between the NO and BET, the gas phase over one sample of Fig. 3 ($\triangle$) was analyzed.

Eight hundred and thirty-five micromoles of NO had been admitted to the sample which then was held at 273 K for 60 hr and

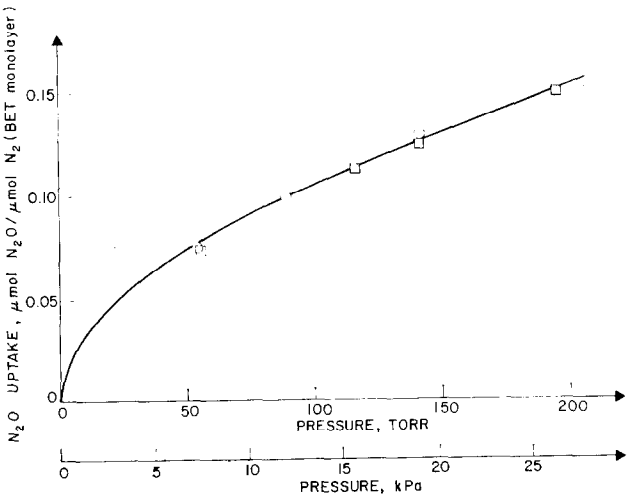

FIG. 4. The N_2O uptake at 273 K of an unsupported Fe_3O_4 sample which had received an evacuation intermediate between the long and short evacuations. ○ and □ are the first and second isotherms, respectively.

at room temperature for an additional 60 hr. After this period the gas phase was analyzed gas chromatographically using a Porapak QS column and showed 70% NO, 22% N_2O, and 8% N_2. At the end there were 294 μmol of gas (total) in the gas phase, and using reactions (1) and (2) this means that 85 μmol of O/g Fe_3O_4 had been incorporated into the lattice and that an additional 345 μmol NO/g was adsorbed on the (initially) 1.31 g sample. The BET monolayer was 157 μmol N_2/g; therefore, half a monolayer of O was added. Even considering the uncertainty of the gas analysis and that reversible adsorption was not taken into account, the NO uptake is still approximately 1.5 to 2.0 times the BET monolayer uptake. The chromatographic results were checked in a separate experiment where the gas phase was analyzed by freezing out the various components and yielded similar results. Another unsupported Fe_3O_4 sample was prepared with an evacuation midway between the long and short methods. After NO adsorption at 273 K, the gas phase was analyzed by mass spectroscopy to verify that only N_2, N_2O, and NO, and no other nitrogen-oxygen species were present.

Another unsupported Fe_3O_4 sample was prepared and evacuated for 14 hr at 650 K. This sample pretreatment was intermediate between the long and short ones discussed above. Subsequently an N_2O isotherm at 273 K was obtained. As Fig. 4 shows, the N_2O adsorption is almost completely reversible and the amount taken up is less than 20% of the measured BET monolayer capacity. Together with the gas chromatography measurements, these results indicate that the increased uptake after the long evacuation is indeed due to the adsorption of more NO, and not due solely to increased reaction of $2NO \rightarrow N_2O + O$ with N_2O remaining as the adsorbed species and O becoming part of the lattice.

DISCUSSION

Upon examination of the results of the NO adsorption on unsupported Fe_3O_4 with the short evacuation (Fig. 1) it is not obvious that the μmol uptake should be similar for NO and N_2 (BET), i.e., that the limiting ratio should approach unity. The NO is expected to be selective and to adsorb only on the iron cations whereas the N_2 should not be so. For this reason, model

TABLE 1

Calculated Site Densities and NO/BET Ratios

Crystallographic face	(i) Cation density		(ii) Unsaturated cation sites		(iii) Unsaturated cation sites (reduced surface)	
	cm^{-2}	NO/N_2 (BET)	cm^{-2}	NO/N_2 (BET)	cm^{-2}	NO/N_2 (BET)
(100)	7.10×10^{14}	1.15	8.52×10^{14}	1.38	9.94×10^{14}	1.61
(110)	6.03×10^{14}	0.98	6.03×10^{14}	0.98	8.04×10^{13}	1.3
(111)	4.9×10^{14}	0.80	9.84×10^{14}	1.59	11.1×10^{14}	1.79
(111)	4.9×10^{14}	0.80	8.20×10^{14}	1.33	9.8×10^{14}	1.59

calculations were made for the following Fe_3O_4 surfaces: (100), (110), and two different (111) faces obtained by cutting at different locations (*16*, *17*). A unit cell built up on any of these four faces will be lamellar with successive "sheets" of ions alternating between net positive and net negative charge. When the surface is formed, it is more likely that the uppermost layer will only be half filled rather than fully populated, as discussed by Kummer and Yao (18). Calculations were made for each of these four faces to determine (i) the density of cations, (ii) the density of unsaturated cation sites (i.e., an octahedral Fe with only four surrounding oxygens would count as two sites), (iii) the density of unsaturated cation sites if enough oxygen were removed from the surface to reduce all surface Fe^{3+} to Fe^{2+} and (iv) the NO/BET ratio expected for each of these cases assuming N_2 occupies 0.162 nm^2. These results are shown in Table 1. A value of $a = 0.839$ nm (*19*) was used. The values are seen to vary from 0.8 NO/BET to 1.79 NO/BET. Thus the experimentally observed value of ca. 1 for the short evacuation samples can be seen to be well within these limits, and suggests that column (i) or column (ii) of Table 1 more closely describes the sample than does column (iii). Based on the results of NO uptake combined with gas phase analysis for a sample given the long evacuation, it appears that as the length of evacuation at high temperature is increased oxygen is removed from the surface (i.e., the magnetite surface approaches that represented in column (iii)) and more sites for NO adsorption are created. Indeed, the reduction of Fe^{3+} to Fe^{2+} upon high-temperature vacuum treatment has been seen by Mössbauer spectroscopy (*20*). As the evacuation is continued, the magnetite surface can be further reduced with the removal of as much as a monolayer of oxygen; yet, when the sample is subsequently exposed to NO, the oxygen-deficient surface is replenished by reactions (3) and (4),

$$\square + 2NO \rightarrow \circledcirc + N_2O, \qquad (3)$$

$$\square + NO \rightarrow \circledcirc + \tfrac{1}{2}N_2, \qquad (4)$$

where $\square$ and $\circledcirc$ are vacant and filled oxygen sites, respectively. When a state like that in column (iii) is achieved, the remaining cation sites are filled by NO. This uptake is still more than that of a surface having had the short evacuation.

In the case of the short evacuation it has been shown (*1*) that reactions (1) and (2) are not important and can therefore be ignored in the calculations. In addition, the agreement of the NO and BET uptakes indicates that the effect of reactions (1) and (2) is negligible. Reactions (3) and (4) would, however, be more likely on surfaces which had received the long evacuation and

were consequently oxygen deficient. Furthermore, chromatographic analyses showed that reaction (3) takes place to a greater extent than does reaction (4) over the oxygen deficient surfaces at 273 K. Indeed, the stoichiometry of reaction (3) is such that for each oxygen atom incorporated into the surface, the total number of gas phase molecules is decreased by one molecule. Thus, reaction (3) and the adsorption of NO on magnetite are similar in that both reactions show a one-to-one correspondence between change in gas phase number of molecules and the interaction with surface iron ions (oxidation of or adsorption on iron, respectively). For this reason, total pressure measurements can still be used in the NO titration of magnetite surfaces that have had the long evacuation, although the shape of the measured isotherm must reflect the combination of surface adsorption and reaction.

CONCLUSIONS

While evidence in the literature indicates that NO adsorption is suitable for magnetite surface area titration, we have found that the magnetite pretreatment has a significant effect on the subsequent NO interaction. Specifically, long high-temperature evacuation has been shown to produce a surface which has a variable degree of reduction and which consequently takes up a variable quantity of NO (as measured in a static adsorption apparatus which can not distinguish between nitric oxide oxidation of the surface or adsorption on the surface). In this case, the titration of the magnetite surface can still be carried out by combining a means of gas phase analysis with the static adsorption measurements. Yet, the best procedure for magnetite surface area titration is to use the short evacuation subsequent to CO_2/CO pretreatment. Indeed, our results show that exposure of the sample to flowing 7:1 molar CO_2/CO for 5 hr at 650 K followed by evacuation at 10^{-4} Pa and 650 K for 1 hr will produce clean Fe_3O_4 surfaces with consistent NO/BET uptake at 273 K. Extension of the procedure to supported samples is a straightforward matter, however, the possibility of a support–oxide interaction exists which could affect the reducibility of the oxide and hence results obtained even with a short evacuation.

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