JOURNAL OF CATALYSIS 96, 182–188 (1985)

Redox Catalysis in Zeolites: Investigation of the Behavior of Iron-Exchanged Mordenite toward Carbon Monoxide Reduction

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Received June 19, 1985; revised June 19, 1985

The redox characteristics of different base-metal-exchanged Y- and X-zeolites have been studied by several investigators (*1–14*). Only a few studies have been reported, however, with mordenite (M) as the parent material (*12, 15*). Slinkin *et al.* (*16*) found that copper in CuM and CuNiM could be reduced to Cu^0 crystallites with H_2, but that the reoxidation with O_2 did not result in the formation of a CuO phase; Cu^{2+} returned to the exchange sites within the zeolite structure. Similar results were reported by Herman *et al.* (*10*) with CuY. We have recently shown that by choosing the reductant and carefully selecting the conditions, it is possible to vary the cation valence state from Cu^+ to Cu^0 alternatively at will; only the latter on reoxidation formed a separate CuO phase (*17*).

Garten *et al.* (*15*) found the FeM could be reversibly oxidized and reduced with O_2 and H_2, respectively, at 400°C; they reported an O/Fe ratio of 0.46 for this process. These results led them to conclude that the general behavior of FeM and FeY were similar, but that the chemical states of the exchanged iron ions were dependent upon the nature of the aluminosilicate lattice. These systems lent themselves to interpretation in terms of an Fe^{2+}/Fe^{3+} redox couple (*3*).

Recently, we reported (*18*) that FeM, which has a lower base-exchange capacity and a more constrained pore system than FeY, was about as active for the oxidation of CO as was FeY. The FeM showed a remarkable stability in the oxidation–reduction cycles with various redox couples, viz., CO/O_2, H_2/O_2, CO/NO, and CO/N_2O. Interestingly, two different O/Fe ratios, 0.48 and 0.82, were reported, depending upon whether H_2 or CO, respectively, was used as the reducing gas. The value of 0.82 O/Fe found for CO reduction suggested that some of the iron was reduced to below Fe^{2+}. Thus, either Fe^+ or Fe^0 might have been formed. The present work shows that this is not the explanation. The abnormally high O/Fe ratios observed with CO are due to a second reaction in which CO reacts with structural hydroxyls in a manner similar to the water-gas shift reaction.

MATERIALS AND METHODS

Catalysts

Two FeM preparations were used in this study. Sample No. 1 was the same as used in our earlier work (*18*); its unit cell composition was $Na_8Fe(II)H(AlO_2)_{11}(SiO_2)_{40}$. Sample 2 was prepared by the same procedure and had a unit cell composition of $Na_{3.6}Fe(II)_{1.3}H_{0.4}(AlO_2)_{6.6}(SiO_2)_{40}$ as determined by elemental analyses supplied by the Galbraith laboratories. The H content was taken as that necessary to balance the negative charge on the lattice $(AlO_2)^-$. Samples 1 and 2 contained 1.9×10^{20} and 2.7×10^{20} Fe/g, respectively (dry weight bases).

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0021-9517/85 $3.00

Procedures

Thermal stabilities and redox chemistry were studied using a Cahn microbalance (Model RG 2000) in a flow mode as described previously (*3*) (zeolite weight was ~200 mg). A conventional BET system fitted with a recirculation loop was used for the volumetric measurements. The details of the procedures used to determine the redox capacity are described elsewhere (*3*). Two different reducing gases, CO or H_2, were used and the catalysts (~1 g zeolite) were reoxidized with O_2. In the microbalance experiments, these gases were blended with He. The total flow rate was 250 ml/min, but that of the reactive gas was 25 ml/min. The balance itself was purged with high-purity N_2. In the volumetric studies, pure gases were used to facilitate the measurements. Temperature-programmed reduction (TPR) experiments were made in a conventional flow system (*20*); the consumption of the reducing gases, CO or H_2, was measured by disappearance from the carrying gas stream. Concentration was monitored by a thermal conductivity cell. The gas stream was either 17% CO in He or 17% H_2 in N_2. The total flow rate in these experiments was 60 ml/min. Exact conditions are given in the figure legends for the particular experiment.

Gas Purification

For the volumetric work the O_2 was double distilled between two liquid-nitrogen traps retaining only the center cuts. The pure dry gas was finally distilled into a 5-liter storage bulb. The H_2 and CO were passed through Deoxo units followed by anhydrous magnesium perchlorate columns prior to passing through an activated charcoal trap thermostated at −195°C before storage.

The H_2 and CO used in the TPR and microbalance experiments were purified as described above. The O_2 was passed first through anhydrous magnesium perchlorate and then through a glass-bead trap thermostated at dry-ice temperature. Further procedures are described below.

Initial Catalyst Activation

The Fe^{2+} ions were introduced into the zeolite by base exchange under anaerobic conditions as described previously (*1–3*). This process was carried out in a glove bag flushed with purified N_2 to prevent oxidative precipitation in the pore system. The filtered catalyst was loaded into the calcination vessel under this N_2 atmosphere. It was first dried by flushing at successively higher temperature (50°C increments) with He (or alternatively under vacuum) to 400°C. Upon cooling to ambient temperature, it was exposed to flowing dry O_2 and the temperature was increased stepwise to 500°C where it was calcined overnight. After cooling, the zeolite was stored in a vial with a screw-top lid, inside a desiccator.

RESULTS

Microbalance redox studies showing the apparent difference in reducibility of FeM by CO or by H_2 are summarized in Fig. 1. Whereas the weight in the oxidized state remained constant, two different weights were obtained when the catalyst was re-

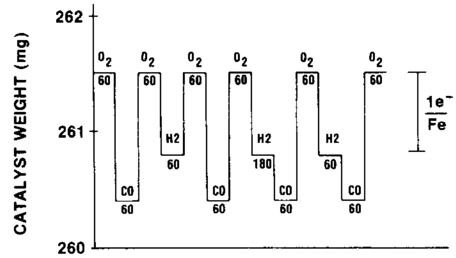

FIG. 1. Summary of microbalance studies of FeM (Sample 1) in oxidation–reduction cycles at 500°C. The gas flowing over the catalyst is identified above the "lined-out" weights (in He) shown as horizontal lines. Values for treatment times (in minutes) are given below. The preparation was oxidized with O_2 and reduced with CO and H_2 in one or two steps. The weight as oxygen atoms equivalent to a one-electron reduction or oxidation is shown as the vertical arrow on the right. Initially, the catalyst had been oxidized completely to Fe^{3+}.

duced alternatively in H_2 or in CO. As shown by the vertical arrow at the right, the former corresponded to the oxygen equivalent of the one-electron reduction from Fe^{3+} to Fe^{2+}; the latter approximated e/Fe = 1.6 as previously reported (*18*). The two different catalyst weights for the two reducing agents could be reached from the same starting point (oxidized state) or in two steps as shown in the fourth cycle of Fig. 1 where the catalyst was first reduced in H_2 and then, after sweeping out this gas with He, further reduced in CO. The difference in weight must be attributed to the additional oxygen removed from the catalyst in CO. Except for the final weights in CO, the data are similar to those reported for FeY (*18*).

Temperature-programmed reduction was carried out to further explore the differences in the CO and H_2 reductions. These results are summarized in Fig. 2. The samples were pretreated in flowing dry He at successively higher temperatures to 500°C prior to a preliminary oxidation at this temperature. The samples were then flushed in dry N_2 and cooled to ambient temperature before starting the TPR experiments. When reduced in H_2, only one peak appeared (with a maximum at about 287°C); no peak appeared above 300°C (Fig. 2A). The results from a duplicate experiment using CO as the reducing gas (Fig. 2B) produced two peaks (at 275°C and about 500°C). Moreover, the integrated peak areas showed that the lower temperature peak near 280°C corresponded to about 1 e/Fe in both experiments.

In another experiment the sample was first reduced in H_2 (Fig. 2A) and cooled to 100°C in dry N_2 where the TPR program for reduction in CO was initiated, the TPR spectra shown in Fig. 2C was generated. This time only the peak near 500°C was produced. (This peak temperature is artificial because the program was stopped and the temperature held constant once 500°C was reached.) From these data, it is evident that two separate processes are occurring: a low-temperature reduction of Fe^{3+} to Fe^{2+}

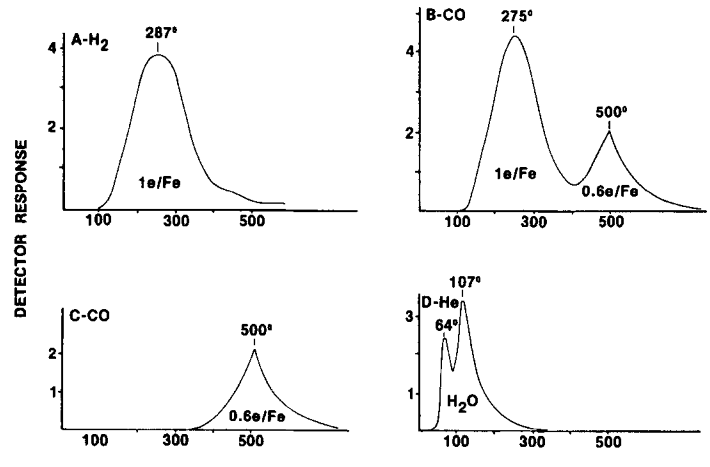

FIG. 2. Temperature-programmed reduction of FeM (1.3 g of Sample 1). TPR spectra were recorded with a programmed rate of temperature increase of 5°C per minute using a thermal conductivity detector. (A) Sample was heated in a mixture of N_2 (50 cm³/min) and H_2 (6 cm³/min). (B) Sample was heated in a mixture of He and CO with flow rates of 30 and 5.5 cm³/min, respectively. (C) Sample was treated as in (A), then cooled in flowing N_2 to 100°C. The gas mixture was switched to pure He and flushed for 1 h. After flushing, 5.5 cm³/min of CO was added to the flowing stream to duplicate conditions in (B). After an additional 15 min the sample heating schedule was started. (D) Sample heated under dry, oxygen-free He flowing at 12 cm³/min.

and a second higher temperature process in which oxygen is removed from the catalyst as CO_2 (collected in a −195°C trap ahead of the detector).

In both experiments, the high-temperature peak area corresponded to about 0.6 *e*/Fe in good agreement with the microbalance data. Note that the latter measures the weight loss due to oxygen removed from the catalyst whereas in the TPR experiments, the reducing agent consumed is measured by its disappearance from the gas stream.

Volumetric Studies

Redox cycles were made to further elucidate the chemistry. The recirculation system and techniques have been described previously (*3*). The condensable products (H_2O or CO_2) were collected continuously in a trap thermostated at −195°C. They could be recovered and measured by backfilling into the BET portion of the system following the experiment. The disappearance of reactant was determined quantitatively from the pressure decrease caused by the reaction. Any residual noncondensable gas left at the end of the reaction was analyzed by GLC (quantitatively) and by mass spectrometry (qualitatively).

Data collected in a series of experiments carried out at 500°C over FeM are given in Table 1. In the first step the H_2 consumed was, within experimental error, equivalent to reduction of all the Fe from Fe^{3+} to Fe^{2+}. The consumption of O_2 in the second step confirmed this stoichiometry. The H_2O recovered from these two steps fell far short of that required to balance the H_2 consumption. Separate IR experiments showed the lost hydrogen to be held not as H_2O, but as structural hydroxyl groups introduced into the zeolite lattice. In this respect, the data differ from those reported earlier (*3*) for FeY.

An interesting paradox appeared in the third step. Whereas the apparent consumption of CO (Column 2) agreed well with that expected from the preceeding H_2 reduction, the CO_2 produced, and hence the actual re-

TABLE 1

Volumetric Redox Cycles of Fe Mordenite[a] at 500°C

Reactant	Volume (cm^3 (NTP)/g)				O/Fe	*e*/Fe
	Apparent reactant consumed	Hydrogen product formed	Actual reactant consumed	Condensed product[b]		
H_2	4.72	0	4.72	1.80	0.49	0.98
O_2	2.38	0	2.38	0.27	0.48	0.96
CO	4.76	0.41	5.17	5.19		
O_2	2.31	0	2.31	0	0.46	0.92
H_2	4.71	0	4.71	1.96	0.49	0.98
CO	−0.04[c]	0.81	0.77	0.84		
CO	0.00	0.66	0.66	0.75		
CO	−0.06	0.72	0.66	0.74		
CO	0.00	0.36	0.36	0.38		
O_2	2.39	0	2.39	0	0.49	0.98

[a] Sample No. 2 contains 2.7 × 10^{20} Fe/g. A reaction time of 2 h was allowed for each step. The recirculation was 50 ml/min.

[b] Either CO_2 or H_2O, depending on whether CO or H_2 was the reducing agent, respectively.

[c] Negative value indicates the volume of reducing gas increased over the course of the reaction.

actant consumed (Column 4), was significantly greater, yet on reoxidation (Step 4) the O_2 consumption was in good agreement with the apparent CO consumption of the previous step. When the noncondensable gas phase from Step 3 was analyzed, an amount of H_2 equivalent to the difference between the *apparent* and the *actual* CO consumptions was found. This H_2 was quantified by passing a measured sample of the noncondensable gas in a flowing stream of ultrapure He (0.03 ppm impurity) through a silica gel trap and then a subsequent trap filled with 5A molecular sieves. Both these traps were thermostated at −195°C; the first removed CO while the second adsorbed the H_2. The individual gases were released on warming to room temperature and quantified by passing through a thermal conductivity detector as described by Burwell and Brenner (*19*).

A set of experiments in which the catalyst was first reduced in H_2 and then given four successive reductions with CO (without intermediate reoxidations) are shown in Rows 5 through 9 of Table 1. Results from the H_2 reduction were in good agreement with those reported in Row 1 above. In the subsequent CO reduction steps, within experimental error, there was no apparent gas consumption, but both CO_2 and H_2 were produced in nearly stoichiometric amounts. These data are listed in Columns 5 and 3, respectively, and the actual consumption of CO (Column 4) was calculated from the data of Column 2 by correcting for the hydrogen produced (Column 3). Interestingly, the H_2 left on the catalyst in Step 5 ($4.71 - 1.96 = 2.75$ cm^3 (NTP)/g) is fairly well accounted for by the total H_2 released into the gas phase in the four subsequent CO reduction steps (2.55 cm^3 (NTP)/g) and by the total CO_2 produced in these steps (2.71 cm^3 (NTP)/g). Finally, the consumption of oxygen required to reoxidize the catalyst in the last step was just that needed to reoxidize the Fe^{2+} to Fe^{+3} and no further condensable products were formed. These data demonstrate unequivocally that the high-temperature TPR peaks of Figs. 2B and C correspond to CO consumed in a process analogous to the water-gas shift reaction and not to reduction of the Fe^{3+} base-exchange cations to valence states lower than Fe^{2+}, as suggested earlier (*18*).

Blank experiments in which NaM and HM were contacted with CO at 500°C and higher failed to detect any shift reaction. Similarly, none was observed with FeY. Thus, the presence of Fe^{2+}/Fe^{3+} (or perhaps another transition metal cation) appears to be an essential, but insufficient condition for this process.

In another ancillary experiment, CO was introduced into an infrared cell containing a platelet of Sample 2, which had previously been reduced in flowing H_2. The platelet was heated for various times to 500°C in the static CO gas, then cooled to room temperature, and the spectra recorded. The zeolite thus served to trap the CO_2 produced. Both the OH region decreased in intensity and the carboxylate region grew as the time of treatment was extended. The latter could be removed simply by evacuation at 500°C.

At first sight, the microbalance data of Fig. 1 appear to be in excellent agreement with those of Table 1. Upon closer examination, however, a significant difference is apparent. In the microbalance experiments, an amount of H_2O was released corresponding to 1 *e*/Fe, whereas this is not the case in the volumetric recirculation system where a sizable portion of the H_2 consumed remained with the zeolite. The TPR experiments behaved like those obtained in the volumetric system. This may be understood since both measurements are for the disappearance of reactant from the gas phase. The puzzling feature was that the H_2 released (weight loss) in the microbalance was found to be complete. Evidently, removal of H_2O is much more efficient from the smaller sample size (200 mg) and the much higher flow rates of the H_2/He mixture used in the microbalance than from the larger samples (~1 g) and much lower flow rates used in the volumetric and TPR experiments. If this is so, why then do the microbalance experiments yield the same excess CO consumption as in the other two experiments? Equally puzzling is why the weight of the sample in the oxidized state in the microbalance experiments was the same regardless of whether H_2 or CO was used in the previous reduction step. Stated another way, if the zeolite is dehydroxylated nonreductively in the high-temperature reaction process with CO, how is this water replaced so as to regain the same initial weight on reoxidation? These questions led us to wonder whether the hydroxyls were somehow replaced during the reoxidation process. Therefore, the microbalance experiment was repeated with rigorous attention given to removal of trace amounts of H_2O from the oxygen stream. To the glass-bead trap thermostated at the temperature of dry ice was added a silica gel trap thermostated at the temperature of liquid nitrogen. Sufficient He was mixed with the O_2 to maintain the vapor pressure of the latter below that corresponding to the thermostat temperature. When this was done the behavior changed to that reminiscent of the volumetric experiments. In repeated cycles of reduction in CO followed by reoxidation, the weight of the zeolite in the oxidized state decreased from step to step as more and more "water" was removed from the catalyst. However, when H_2 was substituted for CO at this point, and H_2O was released during the reduction, the catalyst returned to its initial weight on reoxidation. These observations explain some of the second-order effects which we have reported earlier (*18*).

The contribution of the shift reaction to the total CO consumed (or the weight lost by the catalyst) will depend upon the amount of zeolitic OH available for reaction, on the temperature and activation energy of the process, upon the pretreatment given the zeolite, and even its preparation and final composition. For example, the ratio of the apparent extent of reduction with CO vs H was 1.6 for Sample 1, but only 1.3 for Sample 2 with otherwise duplicate conditions. Most important, the present work illustrates once again the hazards accompanying the use of weight loss in measurements of the extent of reduction. Our first conclusion (*18*) was that FeM, unlike FeY, was reduced more deeply by CO than by H_2, and this has proved erroneous. This may stand as a warning to others. On the positive side, the interesting new chemistry uncovered suggests the possibility of building into the mordenite system a water-gas shift catalyst function.

ACKNOWLEDGMENTS

The authors are grateful to the National Science Foundation for continued support of this project under Grant CHE 8207077. W.S.M. owes thanks to the Union Oil Foundation for financial assistance in carrying out part of this program. Also, one of us (J.L.) thanks the Foreign Department of France for the award of a fellowship for study at University of Wisconsin–Milwaukee.

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