Redox Catalysis over Iron Zeolites: Kinetics and Mechanism

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An Fe-Y-zeolite (FeY) and an Fe-mordenite (FeM) were investigated to determine their suitability as catalysts for the oxidation of CO with NO, O_2 , and N_2O . The kinetics and mechanisms of these reactions were investigated using a flow reactor and a Cahn electrobalance working in the flow mode. Both catalysts could be reversibly oxidized and reduced in the temperature range of 350-700°C. Over FeY the oxygen carried by the catalyst was close to 0.5 O/Fe, while over FeM a larger value was recorded when CO was the reducing agent, but not with H₂. The FeM, in spite of its lesser Fe loading, proved to be as active for the CO oxidation as FeY. When O_2 was used as an oxidizing agent, two different rate laws appeared depending upon the external variables and the Arrhenius plot showed a break at 685 K. When NO was used, however, only one pressure dependence and a linear Arrhenius plot were obtained, regardless of redox regime and temperature. Water did not damage the catalyst nor permanently poison it. When the reactions were run in the flow microbalance the catalyst weight properly reflected the oxidation state of the Fe as inferred from the observed pressure dependencies. The data favor a redox-type mechanism.

INTRODUCTION

Base-metal catalysts, could they be used for automotive exhaust cleanup, would provide an important alternative to the precious metals (Pt and Rh) commonly used. Base-metal catalysts are relatively inactive. however, and susceptible to poisoning by H_2O , lead, and sulfur compounds. When base-metal altervalent cations are exchanged into zeolites, these problems may be minimized or circumvented by the special characteristis of the zeolites. The baseexchange cations are held on the lattice by coulombic forces and may be stripped of a coordination sphere of H₂O molecules under relatively mild conditions. Moreover, the molecular sieve properties of the zeolites may be helpful in protecting base-exchange cations from larger molecules such as SO₂ or other sulfur compounds as well as compounds of Pb.

Catalytic properties of several transition metal ion (TMI) zeolites for the oxidation of CO have been reported (1-9). In particular, FeY and FeX have been shown to act as catalysts for the oxidation of CO either with $O_2(1-3, 8)$, NO, or $N_2O(4)$. No data are available for these reactions over TMImordenites except for the results of Paetow and Riekert (10) and L. J. van Damme (9) for the Cu-mordenite system. Garten et al. (11), however, reported that the FeM could be oxidized and reduced reversibly with the H_2/O_2 couple at 400°C. The redox characteristics of the FeY have been reported by investigators using H_2/O_2 (12, 13) or CO/O₂, CO/NO, and CO/N₂O (4). FeY was reported (11) to act as an oxygen carrier with a capacity O/Fe = 0.5. Moreover, it was suggested that this carried oxygen was localized between two Fe cations inside the sodalite unit. This assignment has recently been questioned (14).

Attempts have been made to elucidate the nature and function of the redox sites. Two models have been proposed and there is some support for both points of view.

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The first model is based on the idea that the TMI act as oxygen atom carriers. A site is oxidized when an O atom is deposited by the oxidizing agent, and this oxygen is removed by the reducing agent in a successive step. Kinetic evidence for this type of mechanism has been reported by Fu *et al.* (15), who studied N₂O decomposition on the fully oxidized form of FeY. Further support stems from the fact that stoichiometric oxidation and reduction can be carried out in two steps (11-15) and by the accompanying Mössbauer data.

In the second model, the base-exhanged cation is supposed to act as a template which coordinates the reacting molecules as ligands in its coordination sphere. Seiyama *et al.* (16) have shown that a satisfactory kinetic interpretation can be given in this way for the reaction of NH_3 with NO over CuY.

The present work is a kinetic study of these reactions over FeM and FeY over a wide temperature range and with variation of reactant concentrations from overall oxidizing to reducing conditions. It was aimed at providing further insight into the oxygencarrying capacity and its possible relationship to the catalytic reaction.

EXPERIMENTAL

The FeY was the same preparation used in our earlier work (4, 15) where the prepparation method and the unit cell composition were described as Na₁₉Fe(II)₁₃ $(AlO_2)_{58}(SiO)_{134}$ (6.13 × 10²⁰ Fe/g). The FeM was prepared following the procedure used by Delgass et al. (17). The starting materials were synthetic Zeolon obtained from the Norton Company (lot AD22) and highcrystallinity mordenite supplied by Linde (LZM5 lot 8350-5). The ratio zeolite/solution was 10 g/liter of 0.04 M FeSO₄ solution (analytical reagent grade was used). The pH was adjusted to 4.0 using dilute H_2SO_4 . The base exchange was conducted overnight at room temperature in a glove bag purged with pure, dry N₂. A typical unit cell composition of the final catalyst was Na₈

 $Fe(II)(AlO_2)_{11}(SiO)_{40}$ (1.87 × 10²⁰ Fe/g) according to analytical data provided by Galbraith Laboratories. The final preparation was shown to be crystalline by X-ray diffraction examination and by the nitrogen filling factor. At liquid nitrogen temperature, the N₂ uptake values at $p/p_0 \approx 0.5$ were 100 cm³ (NTP)/g for the NaM and 105 cm^3 (NTP)/g for the FeM. The agreement between these values indicates that the internal void volume, and, therefore, the crystallinity of the mordenite, was maintained after the exchange. The gases used were all CP or research grade. The procedures used to further purify them are described elsewhere (4).

Equipment and procedures. Thermal stability and redox chemistry of the FeM were studied using the same Cahn electrobalance (model RG 2000) in a flow mode that was used in the earlier work (4, 18). The same microbalance was used to determine the overall oxidation state of the catalysts under reaction conditions. For this purpose a bypass was added to the microbalance which permitted preparation of the reactant mixtures. The mixtures were made by measuring the flow rate of each gas and the mixture in a soap-bubble flowmeter. To maintain the flow rates constant during the various experiments each gas line was provided with a Moore flow controller and the corresponding needle valve.

Aliquots of the zeolites were dehydrated in flowing dry O_2 as the temperature was slowly increased stepwise during a period of 9 h to 500°C where the temperature was maintained constant until the weight became constant (overnight). This will be called the "standard pretreatment." Weights in ambient gas were plotted continuously on a chart recorder; lined-out weights were taken after a brief flush with He.

Catalytic behavior was studied and kinetic measurements made in a continuousflow single-pass reactor. The detailed experimental conditions and the procedure for the gas chromatographic analysis were the same as those previously described (4, 15).

When the effect of water was studied, it was introduced into the gas stream as vapor at a constant rate using a Sage syringe pump (model 341) filled with H_2O at room temperature to deliver the liquid to the preheater ahead of the catalyst.

The rates of CO oxidation were expressed as the number of molecules of CO transformed into CO₂ per second per gram of catalyst. These were determined under differential reaction conditions as the initial slope of the percentage conversion (α) versus *W*/*F* plot, where *W* was the catalyst weight and *F* the flow rate of CO. Values of *F*/*W* from 200 up to 2000 cm³ (NTP)/g min were used.

The extents of CO conversion were calculated from

$$\alpha = [CO_2]/([CO_2] + [CO]),$$

where the concentrations $[CO_2]$ and [CO] in molecules per cubic centimeter were obtained by integration of the area of the chromatographic peaks from samples of the effluent gas, using a Perkin–Elmer M-1 computing integrator. In all cases the mass balances were verified.

A typical α vs W/F curve is shown in Fig. 1.



FIG. 1. Typical differential reaction rate plot (α vs W/F) for CO with O₂ over FeM at 500°C. The reactant stream contained 1% O₂, 2.0% CO with the remainder to 1 atm He.

To determine the reaction orders, a power rate law was assumed; this could be written for CO with different oxidized agents as

$$r = k p_{\rm CO}^n p_i^m,$$

where

- $p_{\rm CO}$ = partial pressures of carbon monoxide,
 - p_i = partial pressures of oxidized agents (e.g., $i = O_2$, NO, or N₂O),
 - n = reaction order in CO (reducing agent),
 - m = reaction order in O₂, NO, or N₂O (oxidizing agent).

Thus, to determine the reaction order, values of $\ln r$ were plotted vs $\ln p_i$ keeping the concentration of CO in the gas stream constant, and vs $\ln p_{CO}$ while keeping the oxidized agent in the gas stream constant. In all cases the balance to 1 atm was He.

When the steady-state reactions were studied in the microbalance the conditions used in the flow system were reproduced. The samples were purged with He both after being oxidized and reduced, and then they were put in contact with the reactant mixture.

RESULTS

The stability of the FeM in the oxidation-reduction cycles was verified using different oxidation-reduction couples, viz., CO/O_2 , H_2/O_2 , CO/NO, and CO/N_2O . The experiments were made at different temperatures in the range 350-700°C. Typical results are summarized in Fig. 2. The catalyst was stable and could be reversibly oxidized and reduced through many cycles. With the CO/O_2 couple, the weight change indicated that the amount of oxygen removed or added was higher than O/Fe =0.5. This is in contrast with the results for FeY (4). Except for the first cycle at 400° C. where it was 0.7, the ratio was 0.82 ± 0.02 and was almost independent of the temper-



FIG. 2. Flow microbalance studies of the Fe-mordenite in oxidation-reduction cycles. The gas flowing over the catalyst (O₂ or CO) is identified above the lines which correspond to the lined-out weights; values for treatment time (in minutes) are given below (OV = overnight). Note how the weight in O₂ varies with temperature.

ature. This unusually high value was checked repeatedly with preparations made from the two mordenite sources. Interestingly, we obtained O/Fe = 0.48 when the H_2/O_2 couple was studied, in fair agreement with Garten *et al.* (13). Note also the apparent inverse change in weight in the fully oxidized or reduced states with temperature.

The oxidation and reduction processes appeared to have two well-defined steps. The first step was fast; 70% of the total weight change occurred in the first 4 min. A much longer time was needed to reach the lined-out condition (second step). Comparable results were obtained when the couples NO/CO and N₂O/CO were used.

Catalytic Behavior

The FeY might reasonably be expected to be more active than the FeM. It had about 3 times the base-exchange capacity, 3.3 times more Fe, and a more accessible pore system. The FeM preparations were, however, about as active for the oxidation of CO as FeY when O_2 , NO, or N_2O was used as the oxidizing agent. NaM was tested under the same conditions and found to be inactive for these reactions.

The relative effectiveness of the three oxidizing agents over FeY and FeM is depicted in Figs. 3A and B, respectively. These experiments were carried out under overall oxidizing conditions, but the same relationships between the different oxidizing agents were obtained when the ratio of the gases was reversed. The mordenite data look normal. Presently we do not have an explanation for the apparent low reactivity of N₂O over FeY.

A comparison of the rate constant (k) at several temperatures for these two catalysts is given in Table 1. The values are expressed in terms of molecules per second per Torr per Fe, where Fe is the total number of Fe atoms per gram of catalyst (6.13×10^{20} and 1.87×10^{20} Fe/g for the FeY and FeM, respectively). Interestingly, FeM was at least as active as FeY for these reactions with the possible exception of the CO/O₂ couple at high temperatures (above 400°C) and the mordenite catalyst was much more active than the Y-zeolite when N₂O was the oxidizing agent. As with FeY (4), the CO/



FIG. 3. Comparison of Fe–Y zeolite (solid symbols, A) with Fe–mordenite (open symbols, B) for the reactions of CO with different oxidizing agents: 2% O₂; 4%NO and N₂O. In all experiments 2% CO was used, with the balance to 1 atm He. The total flow rate was 200 cm³ (NTP)/g min.

NO reaction over FeM formed only N_2 . This could be expected in view of the much greater oxidizing activity of N_2O than that of NO (Fig. 3, Table 1).

When increasing amounts of CO were added into a flowing stream of He containing fixed percentages of O_2 and NO at 520°C, the conversion of CO was complete until its concentration exceeded that required to remove completely both of the oxidizing agents. The former was the preferred reactant as shown in the selectivity plot of Fig. 4; thus, these zeolites, like most known catalysts, are not very selective for removing NO from exhaust gases.

The effect of water on the activity of the FeY and FeM was investigated. The results in the oxidation of CO with NO and O_2 are collected in Table 2. The presence of water in the feed stream caused a decrease in the conversion of the CO of about 50% with FeY, and about 35% with FeM, regardless of the oxidizing agent. The water did not permanently poison the catalyst, however; when removed from the stream, the initial conversions were recovered in approximately 45 min.

In another set of experiments, after the catalyst reached stable reaction conditions at 350°C in a flowing gas mixture (CO + NO + H_2O or CO + O_2 + H_2O) in He (total flow rate of 200 cm³ (NTP)/g min), the temperature was increased until the sample recovered its initial conversion (before adding H_2O). The data are given in the last column

TABLE 1

Comparison of Catalytic Activities in Terms of the Rate Constant^a and TON for Redox Reactions^b

	$CO + \frac{1}{2}O_2$				CO + NO				$CO + N_2O$			
	FeY		FeM		FeY		FeM		FeY		FeM	
(°C)	(1) ^c	(2) ^d	(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)
350	11	165	13	195	1.0	39.3	6	167.6	40	120	3,400	44,587
400	121	1815	150	2250	4.0	157.3	14	391.1	17	510	18,600	243,917
500	516	7740	317	4760	59.0	2242.0	63	1760.0	210	6300	_	

Note. GM (standard oxidizing catalyst) gave at 400°C, $r_{CO+102} = 6.0 \times 10^{20}$ molecules g^{-1} sec⁻¹, and $r_{CO+NO} = 1.44 \times 10^{20}$ molecules g^{-1} sec⁻¹. For comparison with FeY and FeM, the TON must be multiplied by 6.13×10^{20} and 1.87×10^{20} , respectively.

" $k = r/P_{CO} P_j^m$, where n + m = 1 (j is an index for O₂, NO, or N₂O).

 b Gas composition: 2% of O₂, 4% of NO and N₂O; 2% CO was used in all experiments with the balance to 1 atm He.

^c (1) $k \times 10^5$ molecules Fe⁻¹ sec⁻¹ Torr⁻¹.

^d (2) TON \times 10⁵ molecules of CO reacted Fe⁻¹ sec⁻¹.



FIG. 4. Selectivity of Fe-mordenite at 520°C for reaction of CO with O_2 rather than NO. Feed composition was 0.75% NO and 2.7% O_2 with varying amounts of CO (up to 10%) with the balance to 1 atm He. Total flow rate was 250 cm³ (NTP)/g min. Dashed line is hypothetical curve for equal reactivity.

of Table 2, where,

$$\Delta T = T_{\rm f} - T_{\rm a},$$

where T_a is the temperature used in a waterfree system and T_f is the temperature required to reach the same conversion in the presence of water. When, after the treatment described above, the water was removed from the stream and the temperature was lowered to the initial value, the activity for the oxidation of CO with O₂ or NO over FeM returned to its initial value. This shows the good steam stability of this catalyst. Neither FeY nor the FeM showed any activity for the water-gas shift reaction for the conditions studied (500°C, 300 cm³ (NTP)/g min, 15% CO, 12% H₂O).

Kinetic Studies

Pressure dependencies were determined for FeY and FeM in two different temperature ranges, i.e., above 400°C (high temperatures) and below 400°C (low temperatures). They were also studied in two different redox regimes, viz., under overall oxidizing conditions and overall reducing conditions. In all cases the results could be conveniently expressed as power rate laws. Some results are shown in Fig. 5 where data for the oxidation of CO over FeM are presented for the different oxidizing agents at high temperatures under overall oxidizing conditions. Similar results were obtained under the other conditions studied with both FeM and FeY. The results are summarized for both catalysts in Table 3. The effect of the partial pressure of the product CO₂ was tested under all conditions with the three oxidizing agents. Even when present in excess, it had no effect on the reaction rate.

Activation energies were deduced from the Arrhenius plots shown in Figs. 6 and 7.

TABLE 2

Catalyst	In	ilet gas o (vo	composit I%)ª	ion	Percentage CO	Time needed to recover initial	ΔT to recover the initial	
	со	NO	O_2	H ₂ O	conversion	(min)	(°C)	
$\overline{\text{FeY}}$ (6.1 × 10 ²⁰ Fe/g)	2.0	3.0	_	_	30.0			
	2.0	3.0	—	7.0	17.5	45	100	
	2.0	_	2.8	_	100.0	_		
	2.0		2.8	7.0	58.5	45	110	
FeM $(1.9 \times 10^{20} \text{ Fe/g})$	2.6	4.0	_		100.0		—	
	2.6	4.0	_	8.1	77.0	45	68	
	2.6	_	2.65	_	100.0	_	—	
	2.6	—	2.65	8.1	65.0	45	65	

The Effect of H₂O on the Oxidation of CO with NO and O₂

^a With the balance to 1 atm He.



FIG. 5. Power rate law plots for FeM under overall oxidizing condition. The gas composition was in the range of $0.5 \sim 10.0\%$ for all the gases. Open symbols are for variation of the oxidizing agents and the solid symbols are for varying reducing-agent concentrations: $(\blacksquare, \square) CO + O_2, (\bullet, \bigcirc) CO + NO, (\blacktriangle, \triangle) CO + N_2O, r in molecules g^{-1} sec^{-1}$.

The temperature was varied in a random manner and data could be accurately reproduced on returning to a previously tested



FIG. 6. Arrhenius plot for the oxidation of CO with different oxidizing agents over FeM. Oxidizing regimes: $2\% O_2$, 4% NO or N_2O ; 2% of CO in all the cases (solid symbols). Reducing regimes: $1\% O_2$ and 2% NO or N_2O ; 3% of CO in all the cases (open symbols). The balance to I Atm was He. (\blacksquare, \bigcirc) CO + O_2 , $(\blacktriangle, \triangle)$ CO + NO; (\bullet) CO + N_2O .

temperature. When O_2 was used as the oxidizing agent under overall oxidizing conditions one rate law and one Arrhenius plot described the data accurately over the en-

	Temperature		FeM ^a	FeY ^a		
	(°C)	Rate law	Apparent activation energy ^b	Rate law	Apparent activation energy ^b	
		(A)	$CO + O_2$			
Ratio ^c CO/O ₂						
<2	200-500	$kP_{\rm CO}P_{\rm O}^{0.1}$	13	kP_{CO}	21	
>2	200-412	$kP_{\rm CO}P_{\rm O_2}^{0.1}$	13	$kP_{\rm CO}$	21	
>2	412-520	$kP_{\rm CO}^{0.1}P_{\rm O_2}$	25	kP_{O_2}	13	
		(B)	CO + NO			
Ratio ^c CO/NO						
<1	200-530	$k P_{\rm CO}^{0.1} P_{\rm NO}^{0.9}$	14	$k P_{\rm CO}^{0.1} P_{\rm NO}$	26	
>1	200-530	$k P_{\rm CO}^{0.1} P_{\rm NO}^{0.9}$	14	kP&d PNB	26	
		(C)	$CO + N_2O$			
Ratio ^c CO/N ₂ O						
<1	200-400	kP&3P%20	13	$k P_{\rm N2O}^{0.9}$	27	
>1	350-400	kP&&PN20	18	kP_{N_20}	27	

TABLE 3

Summary of Kinetic Information

^a Addition of CO₂ had no effect on the rate.

^b Expressed in kilocalories per mole.

^c Reducing/oxidizing agent.



FIG. 7. Arrhenius plot for the oxidation of CO with different oxidizing agents over FeY. Oxidizing regimes: 2% O₂, 4% NO or N₂O; 2% of CO in all the cases (solid symbols). Reducing regimes: 1% O₂, 2% NO or N₂O; 3% of CO in all the cases (open symbols). The balance to 1 atm was He. (\bullet ,O) CO + O₂; (\blacksquare ,□) CO + N₂O; (\blacktriangle ,△) CO + NO.

tire temperature range for both catalysts (Table 3, Figs. 6 and 7). Moreover, the rate law did not differ when overall reducing conditions were used when the temperature was below 412°C. Above this temperature, however, both pressure dependencies and activation energy changed under reducing conditions. The rate approached first order in O_2 and was nearly independent of P_{CO} ; however, with FeM, E_a increased while with FeY it decreased (Figs. 6 and 7).

A different behavior was found when NO was used as the oxidizing agent. Regardless of the ratio, CO/NO, only one pressure dependency and one Arrhenius plot described the experimental data accurately over the entire temperature range. These results were identical for FeM and FeY (Fig. 6 and Table 3B). With N₂O markedly contrasting results were obtained. As with NO, one pressure dependence (first order in N₂O, zero order in CO) and one Arrhenius plot were obtained with the FeY system (Fig. 7, Table 3C), whereas with the FeM the results were similar to those when O₂ was used. The main difference was that under overall reducing conditions the change in pressure dependence and activation energy occurred at lower temperatures (350° instead of 412°C). See Table 3C. Interestingly, the activation energy under overall oxidizing conditions was the same with both oxidizing agents.

It is perhaps significant that the rate laws summarized in Table 3 were close to first order in the oxidizing or reducing agents, depending on the conditions under which the reactions were studied (oxidizing agent, temperature, oxidizing or reducing regime). This suggested that reaction rates (CO/NO, CO/O₂, CO/N₂O) may be controlled by the rate of oxidation or rate of reduction, i.e., one or the other of the two steps of a redoxtype mechanism. Thus, the catalyst would operate near its fully oxidized state when reduction is rate limiting and near its completely reduced state when oxidation is rate limiting.

To substantiate these ideas, the catalytic reactions were carried out in the flow microbalance. The results for FeM in the CO/ O₂ and CO/NO reactions are presented in Figs. 8A and B. The gases in contact with the zeolite are indicated above the lines corresponding to the steady-state weights and the duration of the experiment (in minutes) are given below. The two reactant gas ratios used in these experiments are indicated by r_1 and r_2 , respectively, where the former designated overall reducing, and the latter overall oxidizing, conditions. The experimental temperatures, indicated at the top, were selected to test the two regimes defined in Fig. 6. In a general way the results obtained matched expectations. The weights of the oxidized and the reduced states, obtained when O2 or CO was the sole gas in the stream, were determined as bench marks. When these two gases were present together (diluted in He), the weight of the catalyst was intermediate, but close to the reduced state in the high-temperature regime when the feed stream was overall reducing (Fig. 8A), indicating that reduction was faster than oxidation. Otherwise,



FIG. 8. Flow microbalance studies of the reactions of CO with O_2 (A) and of CO with NO (B) over FeM under overall reducing conditions (r_1) and under overall oxidizing conditions (r_2) . The gases flowing over the catalyst are identified above the lines, values for the duration of the experiments (in minutes), below. Feed composition was 8.0 and 2.0% of O_2 , 12.0 or 3% of NO; 8% of CO was used in all experiments with the balance to 1 atm He. When used singly, the CO, O_2 , and NO were at 1 atm.

in agreement with the rate laws of Table 3A, the catalyst operated in its nearly completely oxidized state. The rate of oxidation was now faster than that of reduction. The same steady-state weight was obtained when the reaction was initiated either from the oxidized state or the reduced state.

Related results were obtained when NO was used as the oxidizing agent instead of O_2 . However, now the catalyst worked near its completely reduced weight regardless of the temperature or the CO/NO ratios (Fig. 8B). This was again in agreement with the pressure dependence data (Table 3B) and the Arrhenius plot of Fig. 6. In all cases the oxidation step was slower than the reduction.

When the same experiments were made using the FeY catalyst the results again obtained matched the pressure dependences when either O_2 or NO was used as an oxidizing agent. The only exception appeared in the CO/O₂ reaction under overall reducing conditions at high temperatures. Now the weight of the catalyst was 40% higher than the weight in the reduced state. This could be interpreted as indicating that under reaction conditions not all of Fe³⁺ could be reduced, i.e., that not all the Fe participated as active sites in the reaction.

When N_2O was used as an oxidizing agent with the FeM catalyst the mirobalance results did not match the pressure dependence data quite so well. With FeY the rate was approximately first order in P_{N_2O} And independent of the P_{N_2O}/P_{CO} ratio over the regime studied, suggesting that the catalyst should be operating near its reduced state as it did when NO was the oxidizing gas. Instead, regardless of the redox ratio, the catalyst weight was constant and roughly halfway between the oxidized and reduced states (Fig. 9B). Similarly, with FeM, the pressure dependence data of Table 3 suggested that the rates of oxidation and reduction were comparable, but with oxidation a bit faster when $P_{\rm CO}/P_{\rm N_{2}O} < 1$ and reduction a bit faster when $P_{\rm CO}/P_{\rm N_{2}O} > 1$



FIG. 9. Flow microbalance studies of the reaction of CO with N₂O over (A) FeM and (B) FeY, under overall reducing conditions, r_1 , and overall oxidizing conditions, r_2 . The gases flowing over the catalyst are identified above the line; values for the duration of the experiments (in minutes), below. Feed composition was 12 and 4% of N₂O; 8% of CO was used in all the experiments with the balance to 1 atm He. When used singly, the O₂, CO, and N₂O were at 1 atm.

1. In the former case (r_2) the catalyst should operate near the oxidized state and in the latter (r_1) near the reduced state as shown in Fig. 9A. Thus, the picture fitted much better with FeM than with FeY, and it was the latter which behaved in an unexpected way when the rates were compared (Fig. 3 and Table 3).

DISCUSSION

As outlined above, the kinetic results suggested that an oxygen transfer (redox) mechanism might be used to explain the observations. In a simplified way the chemistry may be written:

Catalyst Reduction—

$$\operatorname{CO} + \operatorname{O-}(\operatorname{S}) \xrightarrow{\kappa_1} \operatorname{CO}_2 + \Box,$$
 (1)

$$N_2O + O(S) \xrightarrow{\kappa_2} N_2 + O_2 + \Box,$$
 (2)

or

$$20-(S) \xrightarrow{k_3} O_2 + 2\square.$$
⁽³⁾

The catalyst may be reoxidized according to:

$$\mathbf{N}_{2}\mathbf{O} + \square \xrightarrow{k_{4}} \mathbf{N}_{2} + \mathbf{O} \cdot (\mathbf{S}), \qquad (4)$$

$$NO + \Box \xrightarrow{\kappa_5} \frac{1}{2}N_2 + O(S), \qquad (5)$$

or

$$\frac{1}{2}O_2 + \square \xrightarrow{k_6} O_{-}(S), \tag{6}$$

where O-(S) represents an oxidized site (we will later elaborate on this) and \Box denotes a vacancy caused by the removal of an oxygen from the site.

Assuming that the steady-state approximation may be applied to [] and to [O-S] and neglecting the contribution of Eq. (3), it is possible to write in a general way

$$d[\square]/dt = k_{\rm r} P_{\rm r}[{\rm O-S}] - k_{\rm ox} P_{\rm ox}[\square] = 0, \quad (7)$$

where P_{ox} and P_r are the partial pressures of oxidizing and reducing agents, respectively.

Reasoning as in the N_2O decomposition over FeY (14) that these sites are in constant supply,

$$C = [\Box] + [O-S]. \tag{8}$$

From (7) and (8) the overall reaction rate deduced for either the catalyst reduction or oxidation is

$$Rate = Ck_{ox}k_r P_{ox}P_r / (k_{ox}P_{ox} + k_r P_r).$$
(9)

This expression, which is of the same type as the one develped by Mars and van Krevelen (19), may be used to describe our experimental results. The limiting (first order) cases are obvious. Additionally, the microbalance data are consistent with these predictions. The decomposition of NO was not observed over FeM at temperatures up to 600°C, confirming the report by Fu *et al.* (15) with FeY. Thus, reduction via Eq. (3) does not make an appreciable contribution and was neglected in this derivation.

From the pressure dependence data of Table 3A it follows that when O₂ was reacted with CO, the reaction rate was limited by step (1), i.e., $k_6 \ge k_1$. This holds under both overall oxidizing conditions (for the whole temperature range) and overall reducing conditions (at low temperatures). The microbalance results (Fig. 8A) confirmed this idea. Under reducing conditions at high temperatures, however, the rate became controlled by Eq. (6), i.e., $k_1 \gg k_6$. Again, the kinetic data (Table 3A, Fig. 6) and the microbalance data (Fig. 8) were in agreement with this deduction. Note, however, that the activation energy may be either higher or lower than that for reduction when reoxidation becomes rate controlling. The reason for this is not apparent.

When NO was used as the oxidizing agent, $k_1 \ge k_5$, regardless of the temperature range or redox regime tested (Table 3B, Figs. 6-8). The rate accordingly became close to first order in NO and zero order in CO because the rate of reaction was now limited by the rate of reoxidation of the catalyst.

Additional support for a redox mechanism was again supplied by the microbalance data. The catalyst weight remained close to that for the reduced state. Invariably, the weight during reaction accurately reflected the rate-limiting step as interpreted from the kinetics.

With FeM, N₂O was the best oxidizing agent (Fig. 3, Table 3) and fair agreement was obtained between the pressure dependence and the microbalance results. Thus, the main reaction pathways in the CO oxidation appeared to be via Eqs. (1) and (4) with insignificant contribution from Eq. (2) or (3). As noted above, the data for FeY do not fit harmoniously into this picture. The rates approximate those for NO. It is suspected that the rate of catalyst oxidation is limited in this case by some processes other than reaction of N₂O with an oxidizable site (\Box), i.e., Fe²⁺ ions. These results offer an interesting avenue for further research.

Since CO_2 had no effect on the reaction rate the desorption of CO₂ was evidently fast and the formation or decomposition of a carbonate intermediate species (if any) was not a rate-limiting step. Moreover, the facts that both NaY and NaM were inactive for the oxidation of CO under the conditions studied, but became active after the exchange with Fe clearly indicated an association between activity and the presence of Fe (or other TMI). How the cations participate is not directly clear and various possibilities may be suggested. The TMI may act directly as sites to bind and carry oxygen as suggested earlier (11-15), or indirectly as a supply depot for electrons with the oxygen being carried somehow on the lattice. During the process of oxidation, molecular bond rupture of O_2 (or NO or N_2O) must be accompanied by electron transfer and reduction to form the oxidation products will result in electron transfer in the opposite direction. This overall process, as suggested by the above discussion, proceeds stepwise by consecutive reactions (20).

According to the ideas of Garten *et al.* (13), in FeY the oxygen is carried as a bridge between two Fe cations inside the sodalite cages. This model leaves unanswered some critical questions. How did the O atom get there in the first place?

When O_2 acts as the oxidizing agent, how is it dissociated and what happens to the other half? Similarly, if NO is the oxidizing agent, what happens to the N atom and how does it combine with another to form N_2 and is N_2O an intermediate? Should not the catalytic rates be strongly diffusion limited by the necessity to transport the reactants inside the sodalite cages of FeY?

Pearce *et al.* (25), using X-ray diffraction, found no evidence for the bridge oxide complex. An alternative possibility was suggested by Segawa *et al.* (14). Because of the mobility of the Fe in the zeolite structure and the ability of a strongly chemisorbed species to trap cations at sites of high accessibility, the Fe³⁺ could be held by an O in the supercages at sites III' where the complex could readily participate in the redox reactions. Support for this idea was found in the results of their ir and Mössbauer studies of NO chemisorbed on FeY.

A similar iron-oxygen-iron bridge reportedly forms in the main channel of FeM (11). Mössbauer data supported this idea as did the ratio O/Fe = 0.45 (H₂/O₂ redox cycles at 400°C). When CO was used as the reducing agent, however, the ratio O/Fe was found to be higher (0.82). This requires some reconsideration. Reduction and reoxidation occurred in two well-defined steps. An O/Fe ratio of 0.5 would correspond to a reduction from Fe³⁺ to Fe²⁺ as found for the H₂O₂ couple. The higher ratio found with CO suggested a deeper reduction, possibly to Fe⁺. Another possibility, however, is that some molecular form of oxygen is bonded to the zeolite even under vacuum at 500°C, e.g., a superoxo (O_2^-) compound of type (22)



The location of the Fe would be along the main channel of the mordenite, where the redox-type reaction is likely to occur. We hope to distinguish between these possibilities by future Mössbauer experiments.

If the more general picture is applicable where the cations assume the role of a depot to furnish or store electrons as the catalyst is oxidized and reduced rather than act as a specific oxygen trap, then presumably lattice oxygen functions in the reaction. Thus, the "site" becomes delocalized.

The FeM had a lower loading of Fe, a more accessible pore system, and a lower base exchange capacity than the FeY zeolite. Nevertheless, it had a comparable catalytic activity in the redox-type reactions (even higher when N₂O was used). This is indeed interesting because it is generally recognized (24) that higher Si/Al ratios lead to higher steam stability. This could become vital if TMI zeolites were to be used as catalysts for automotive exhaust gas emission control. Moreover, the smaller port size conceivably could be helpful in excluding large poison molecules such as PbCl₄.

There are many differences between FeY and FeM which may contribute to the higher activity of the latter. Two of them are worthy of attention: (a) Accessibility of the Fe to reactant gases. (If the cations of the FeY must diffuse to sites in the supercage, where the reaction occurs, only a fraction of the ions would be accessible in the steady state. This problem does not exist in the FeM where the Fe are located along the main channels.) (b) The chemical environment of the Fe may be very important in the redox-type reaction due to the effect of the ligand field in altering the energy required for detaching electrons from the cations; this would modify the oxygen carrying capacity and even the lability of the O that participate in the reaction. Interestingly, the catalyst with higher O/Fe ratio showed a higher catalytic activity.

Finally, it is important to point out that the effect of H₂O as a poison in the FeY and FeM in the redox-type reactions was not severe. The values of ΔT reported in Table 2 were, in all cases, much lower than the ones reported by Kobylinsky and Taylor (23) in a study of the reduction of NO over iron oxide supported on alumina and over chromium oxide ($\Delta T \sim 200^{\circ}$ C). This clearly indicated that the TMI zeolites are much less susceptible to poisoning by H₂O than are the alumina-supported base-metal oxides.

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