# Problems in preparation of FeZSM-5 catalysts

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FeZSM-5 catalysts for SCR of NO to $N_2$ can be made in a highly durable form that may be useful for automotive exhaust cleanup, but not presently reproducible. Herein we outline the properties and characteristics of good versus poor catalysts and provide results of experiments that effect the properties of the final preparation. It is shown how Mössbauer characterization will be useful in understanding the changes that occur as the catalysts age. The problem has not yet been resolved. This letter is meant to challenge research by others.

**Keywords:** zeolite chemistry, stability factors, Mössbauer and reaction studies, characterization of good versus poor preparations

The extraordinary hydrothermal stability, high loadings and resistance to poisoning by 20% $H_2O$ achieved in our previously published work [1,2] were made from a single sample of NaZSM-5 having a Na/Al ratio of about 1.2. This material was a gift from Air Products and Chemical Company. It had been made by the template-free method. To avoid oxidation of $Fe^{2+}$ to $Fe^{3+}$ and the precipitation of FeOOH and/or $Fe(OH)_3$, great care was used to exclude $O_2$ during base-exchange [1]. The $Fe^{2+}$ concentration was kept constant by using solid $FeC_2O_4$ in equilibrium with that in the saturated solution at about $10^{-3}$ M. The pH was maintained in the range $5.5 < \mathrm{pH} < 7.0$ by addition of $10^{-3}$ M NaOH as required. As shown previously [1], the principal ion in solution in this range was $[FeOH]^+$, so that exchange of one $[FeOH]^+$ for one $Na^+$ should result. Hence by the conventional arithmetic, equating one $Fe^{2+} = 2Na^+$, overexchange up to 200% could be achieved. Interestingly, preparations previously reported seldom exceeded $\sim$70%, whereas by our method values between 180 and 199% were readily obtained. Moreover, the sum of the Fe and the residual Na after base-exchange ratioed to Al was unity within experimental error ($\sim$5%) showing that $Fe(OH)^+$ replaced $Na^+$ on the base-exchange centers [1].

It was postulated that hydrothermal breakdown could be minimized by eliminating the bridged Brønsted hydroxyl groups from the lattice. These are thought to be the centers attacked by steam [3]. Thus, excess $Na^+$ may be essential; $NH_4^+$ ions must be avoided and template-free preparations of NaZSM-5 may be necessary to achieve this end and for the long term stability demonstrated in [2].

A problem of reproducibility appeared when we attempted to scale up the batch size from 2–3 g to 15–20 g. We had insufficient Air Products zeolite for this purpose, so we substituted another NaZSM-5 (a templated preparation) that was available in large quantities and had properties that we thought would be superior to the earlier preparation. Concomitantly, we increased the vessel volume and the rate at which the system was flushed by corresponding amounts. These preparations when tested yielded disappointing results. Whereas the early preparations were invariably "good" catalysts, the new scale-up preparations varied from poor to those approaching, but never achieving, the quality of our early ones. For convenience, these inferior catalysts will be lumped together and called "poor" catalysts. Initially, we supposed that they resulted from the scale-up and might be due to incomplete exclusion of $O_2$. After repeated preparations including several of the original 2–3 g size, it was found that it was easy to make a "poor" catalyst and extremely difficult with the new zeolite to make one approaching the quality of our original "good" catalysts. Therefore, a systematic investigation was initiated with a view to understanding the origin of this variability and to isolating the preparation parameters required to achieve reproducible "good" catalysts. Several additional commercially available NaZSM-5 preparations were also tested with varying results. Evidently subtle differences in surface chemistry of the parent zeolites result from synthesis procedures.

The original Air Products material was a template-free preparation with Na/Al = 1.2. This was normalized to ratios of (Na + Fe)/Al = 1.0 on base-exchange with $10^{-3}$ M $FeC_2O_4$ solution [1]. These catalysts were not poisoned by up to 20% added $H_2O$ nor by 150 ppm of $SO_2$ in the SCR reaction at a temperature of 500 °C for extended periods of time (up to 2500 h at SVH = 40,000). Temperature excursions of 24 h at temperatures as high as 800 °C in SCR did not alter the catalytic behavior on return to 500 °C. All of this and much more is described in our previous publications [1,2]. Notably, the parent zeolite preparation was made in house. The substandard quality of preparations made by other vendors remains an unsolved problem. Sachtler [4] has suggested that "different vendors use different processes in the manufacture of their materials and that two vendors may produce zeolites with the same structure and Si/Al ratios, but with different catalytic properties".

We undertook a variety of approaches to learn the root causes of this variability. These will be described herein, but first let us consider the differences, as we define them, between a "good" catalyst and a "poor" one. Recall that all preparation procedures were designed to make catalysts that approach 100% conversion of $NO_x$ to $N_2$ at $T_{\max}$, to have high selectivity, durability and resistance to the adverse effects of $H_2O$ present in all combustion streams. So our first conclusion was that, despite all indications to the contrary, different parent zeolites of apparently identical composition and crystallinity obtained from different vendors were not the same and led to different catalytic behavior. We supposed that differences in residual Brønsted acid concentrations might be the controlling factor since these sites should be susceptible to hydrothermal attack on the lattice leading to dealumination on reactions with steam at elevated temperatures as found previously [3]. Therefore, templated preparations might be more susceptible to hydrothermal breakdown than $Na^+$-rich non-templated ones, since the former must be made from the HZSM-5 resulting from decomposition of the template. Further, based on earlier work with faujasites [5], we supposed that the base-exchange must be carried out using $Fe^{2+}$ salts with the exclusion of $O_2$.

### *Physical characteristics of "good" versus "poor" catalysts*

(1) "Good" catalysts (figure 1(A)) are invariably selective for formation of $N_2$ versus $CO_2$. Although light-off for the two reactions occurs at virtually the same temperature (~200 °C), the fractional conversion of $NO_x$ to $N_2$ is always higher than that for $i$-$C_4H_{10}$ to $CO_x$. Moreover, $T_{\max}$ for formation of $N_2$ is about 50 °C lower than that for $CO_x$. Comparison with a "poor" catalyst (FeZSM-5-19-162) is made by reference to figure 1(B). Note that here the light-off temperature is about 50 °C higher than for the "good" catalyst (figure 1(A)); the selectivity is reversed and the activity for $N_2$ formation is greatly reduced. Here the conversion to $N_2$ reached only 60% at $T_{\max}$, whereas it approached 100% for the $N_2$ active "good" catalyst. After this experiment, the catalyst was treated with 10% $O_2$ in He for 12 h at 650 °C. As shown by the inverted triangles in figure 1(B), the catalyst was further damaged by this treatment. The "good" FeZSM-5-18-183 was undamaged after 24 h in pure $O_2 + H_2O$ at 800 °C. Note the chief difference between these two catalysts was the parent zeolite. FeZSM-5-18-183 was made from the Air Products NaZSM-5, whereas FeZSM-5-19-162 was made from NaZSM-5 derived from a templated preparation supplied by W.R. Grace.

(2) The effects of adding 20% $H_2O$ to the reaction stream are illustrated for a "good" catalyst versus a "poor" one in figure 2. At $T_{\max}$, the "good" catalyst yielded nearly 100% conversion to $N_2$ and was unaffected by the added $H_2O$. When the conversion was lowered by decreasing the temperature, the conversion to $N_2$ again was unaffected by the addition of $H_2O$, while the conversion of $i$-$C_4H_{10}$ to $CO_x$ was inhibited increasing the selectivity. For a "poor" catalyst, as shown, the conversion to $N_2$ was immediately lowered on $H_2O$ addition by a factor of nearly two to a new steady state.

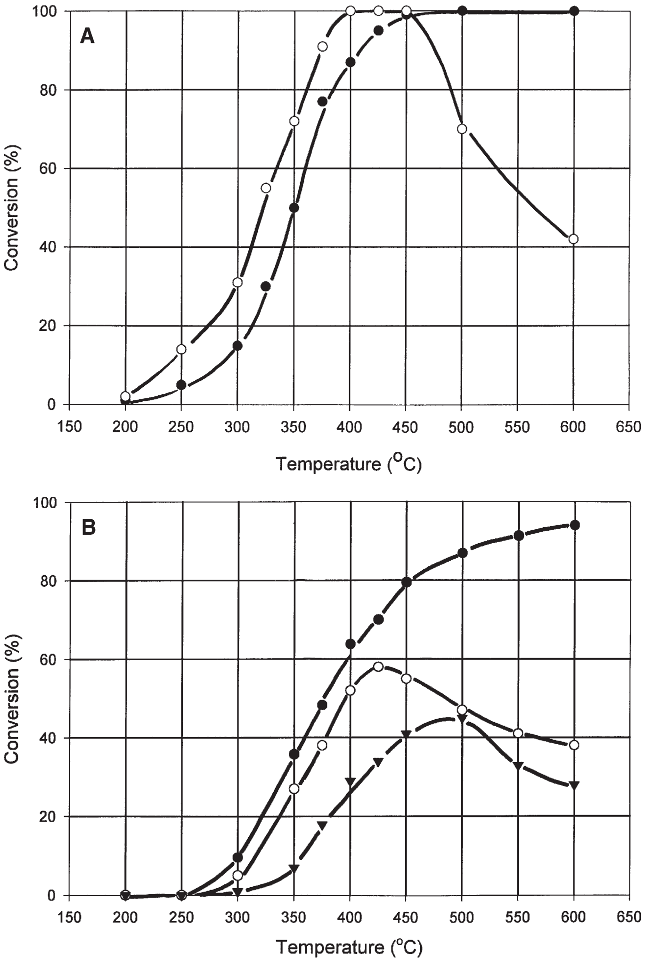

Figure 1. Conversion of NO to $N_2$ and $i$-$C_4H_{10}$ to $CO_2$ at various temperatures: (A) behavior of "good" catalyst FeZSM-5-18-183; (B) profiles for "poor" catalyst FeZSM-5-19-162, where ○ denotes the conversion of NO to $N_2$, and ● the fractional conversion of $i$-butane to $CO_2$. ▼ is the conversion to $N_2$ by the "poor" catalyst after further treatment with 20% $O_2$/He for 13 h at 650 °C (see text for details). The standard feed stream contained 0.2% NO, 0.2% $i$-$C_4H_{10}$, 3% $O_2$ and 20% $H_2$. The space velocity was 42,000 $h^{-1}$ in all cases.

(3) A "good" catalyst invariably has a high Fe loading, viz. Fe/Al $>$ 0.85. Before starting this work, data concerning FeZSM-5 was sparse. The highest loading reported using conventional base-exchange procedures was 70% (Fe/Al = 0.35). This could not be increased by repeated exchange. Our earlier experiments using $FeC_2O_4$ produced ~185% or Fe/Al = 0.93 and were highly active SCR catalysts. This indicated that the ion replacing $Na^+$ was $[Fe–OH]^+$. Our calculation of the distribution of the ions $Fe^{2+}$, $Fe(OH)^+$ and $Fe(OH)_2$ as a function of pH indicated that $Fe(OH)^+$ should be the dominant species present in the $10^{-3}$ M solution of $FeC_2O_4$ over a range

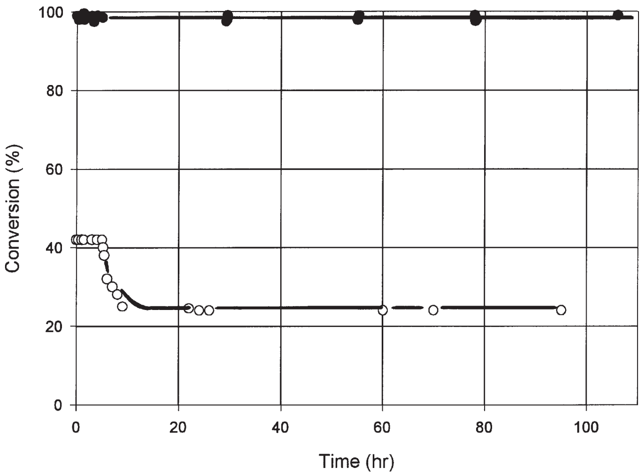

Figure 2. Conversion to $N_2$ (%) versus time on stream (TOS) at $T_{max}$ for "good" catalyst FeZSM-5-18-183 (●), and "poor" catalyst FeZSM-5-19-162 (○). For the first 6.5 h, dry feed was used; then 20% $H_2O$ was added. The "poor" catalyst was severely inhibited by $H_2O$; the "good" catalyst was not affected.

5.0 < pH < 13. However, the possibility of gel formation above a pH of about 7.5 led us to define a useful range 5.0 < pH < 7.0 that we maintained by adding a few drops of dilute NaOH as required (as the reaction proceeded the pH fell). Thus "good" catalysts are strongly overexchanged. However, not all such catalysts are necessarily "good". When a wet preparation is dried and calcined in a pure He stream, a good catalyst may result; if, on the other hand, it is dried and calcined in a stream of 90% He and 10% $O_2$, a "poor" catalyst containing $Fe_3O_4$ and $Fe_2O_3$ may be obtained. Thus, it is important that the preparation not be exposed to $O_2$ before calcination and initiating the SCR reaction. Hence, a second conclusion is that the active phase leading to durability and high activity is formed as the catalyst is dried.

### Recent developments

Clearly, some unusual chemistry is occurring within the zeolite during preparation and pretreatment. This is also affected by the nature of the zeolite itself. Some subtle differences in the parent material may lead to different results on base-exchange and pretreatment. If this problem could be eliminated, the future use of these catalysts would be much more promising.

At the 1997 fall meeting of the American Chemical Society held in Las Vegas, Chen and Sachtler [4] confirmed our earlier observations and described an alternative method of catalyst preparation, viz. sublimation of $FeCl_3$ into dry HZSM-5. Note, however, that this results in the introduction of $Fe^{3+}$ cations into the zeolite rather than $Fe^{2+}$ by our method. Thus $FeCl_3$ reacts with the Brønsted protons of HZSM-5 forming HCl and attaching $Fe^{3+}$ cations to the lattice, i.e., a metathesis reaction. The remaining $Cl^-$ are then removed by hydrolysis. They claimed that this procedure led to the formation of only "good" steam-resistant catalysts regardless of the source of the HZSM-5 and further suggested that their catalyst operated at somewhat lower temperature than ours. We are dubious about this last point. They show a light-off temperature near 250 °C, whereas we found light-off at about 200–250 °C. This parameter is not easy to fix exactly. More to the point, their conversion to $N_2$ at $T_{max} = 350$ °C was about 75% (best case); our catalyst converted nearly 100% of the NO to $N_2$ at 450 °C, but only about 25% at 350 °C. However, if further work confirms that satisfactory catalysts of sufficient durability can be made reproducibly from an HZSM-5, this work [4] will have solved this very practical problem and make possible advances in pollution abatement technology. It may be important to note that loading with Fe can be monitored by the HCl released and that treatment is continued until HCl is no longer evolved. Here it is supposed all of the true Brønsted sites have been removed and the Fe/Al ratio has become unity. This may be critical for achieving steam stability. What is needed is a careful comparison of the catalytic properties of the Sachtler–Chen preparations with good catalysts made and showing the behavior depicted in figures 1 and 2. This must be done by the same workers in the same laboratory using the same equipment and procedures.

Table 1
Flow microbalance experiments made at several temperatures over two good catalysts prepared by base-exchange of NaZSM-5 with $FeC_2O_4$. As prepared, these catalysts contain only $Fe^{2+}$ cations.

| Temperature (°C) | Treatment | $\Delta O/Fe$ | |
|---|---|---|---|
| | | FeZSM-5-18-183 | FeZSM-5-18-198 |
| 500 | $O_2$ | +0.46 | +0.49 |
| | He | −0.05 | −0.01 |
| | $H_2$ | −0.42 | −0.48 |
| | He | −0.01 | −0.02 |
| 950 | $O_2$ | +0.45 | +0.49 |
| | He | −0.05 | −0.01 |
| | $H_2$ | −0.44 | −0.48 |
| | He | −0.01 | −0.02 |
| 1050 | $O_2$ | +0.94 | +1.00 |
| | He | −0.07 | −0.02 |
| | $H_2$ | −1.01 | −0.97 |

The question arises: why does not it matter whether the cation valence introduced is $Fe^{2+}$ or $Fe^{3+}$? To understand this question, flow microbalance experiments were made and the results for two "good" catalysts, FeZSM-5-18-183 and FeZSM-5-18-198 are listed in table 1. These data are supplemented by Mössbauer data obtained in Professor Dumesic's laboratory.

It has been known for many years [5] that, when $Fe^{2+}$ ions are exchanged into zeolites, a reversible 1e redox couple, $Fe^{2+} \rightleftharpoons Fe^{3+}$, is established. $Fe^{2+}$ can be oxidized at elevated temperatures to $Fe^{3+}$, and the latter can be reduced back to $Fe^{2+}$ by simply changing the gas flowing over the catalyst from $O_2$ to $H_2$ or CO. Lower valence states cannot be achieved below 1000 °C because of the stability of the $Fe^{2+}$ ions required to charge-balance the lattice. Hence, $Fe^{2+}$ zeolites prevent dealumination and resist hydrothermal destruction.

When CO is used as a reducing agent, one $CO_2$ molecule results from the removal of an oxygen atom from the $Fe^{3+}$ site where it was deposited in the oxidation step. Moreover, the removal of this oxygen effects the reduction of two $Fe^{3+}$ to two $Fe^{2+}$ ions, suggesting that it is a bridging oxygen bound to two $Fe^{3+}$ cations, i.e., these sites are at least paired. Thus, table 1 shows that, starting with the $Fe^{2+}$ form, treatment with $O_2$ in the first step effects a weight increase corresponding to oxidation of over 90% of the $Fe^{2+}$ to $Fe^{3+}$. Simply flushing this preparation with pure He causes a loss in weight of approximately 10% of this increase, while reduction with $H_2$ removed the remainder. Almost identical results were obtained when the temperature was raised to 950 °C, but at 1050 °C, the data suggest the formation of iron oxides during the oxidation step, much as was observed with CoZSM-5 at lower temperatures [6]. The formation of $Co_3O_4$ or $Fe_3O_4$ corresponds to the introduction of a ferromagnetic phase that is easily detected by magnetic measurements [6,7].

### *Mössbauer data*

A series of Mössbauer spectra were recorded (figure 3) using "good" catalyst FeZSM-5-18-183. Comparison is made with solid $FeC_2O_4$ as a reference, figure 3(A), versus the freshly prepared "good" catalyst, figure 3(B). These spectra demonstrate that the iron is present as high spin $Fe^{2+}$ ions having nearly identical spectral parameters as those shown in table 2. After using the catalyst in the SCR reaction, however, the spectra show the $Fe^{2+}$ ions have been mostly oxidized to $Fe^{3+}$. Only remnants of the $Fe^{2+}$ doublet remain depicted by the dotted line. As shown in table 2, both the isomer shift and the quadrupole splitting correspond closely to those recorded for other ferric compound. It can be concluded, therefore, that the redox reaction involving the transfer of oxygen from one molecule to another is occurring via the catalyst operating near its completely oxidized state. These data indicate that the ratio $Fe^{3+}/Fe^{2+}$ is nearly 40/1, i.e., about 2.5% $Fe^{2+}$. These

Table 2
Mössbauer parameters derived from spectra of figures 3 and 4.

| Sample used | Drying temp. (°C) | IS (mm/s) | QS (mm/s) | Derived from figure no. |
|---|---|---|---|---|
| $FeC_2O_4 \cdot 2H_2O$ | RT | 1.200 | 1.707 | 3A |
| FeZSM-5-18-183 | RT | 1.205 | 1.717 | 3B |
| FeZSM-5-18-183[a] | 500 | 0.483 | 2.587 | 3C |
| | 500 | 1.005 | 1.711 | 3C |
| FeZSM-5-19-162 | RT | 1.19 | 1.72 | 4A |
| FeZSM-5-19-162 | 225 | 1.08 | 1.73 | 4B |
| FeZSM-5-19-162 | 300 | 1.11 | 1.80 | 4C |
| FeZSM-5-19-162 | 400 | 0.92 | 1.69 | 4D |
| FeZSM-5-19-162 | 500 | 0.94 | 1.69 | 4E |

[a] Both the $Fe^{2+}$ and the $Fe^{3+}$ doublets appeared after the FeZSM-5 was used in the SCR reaction. The latter dominated by a ratio of about 40 to 1.

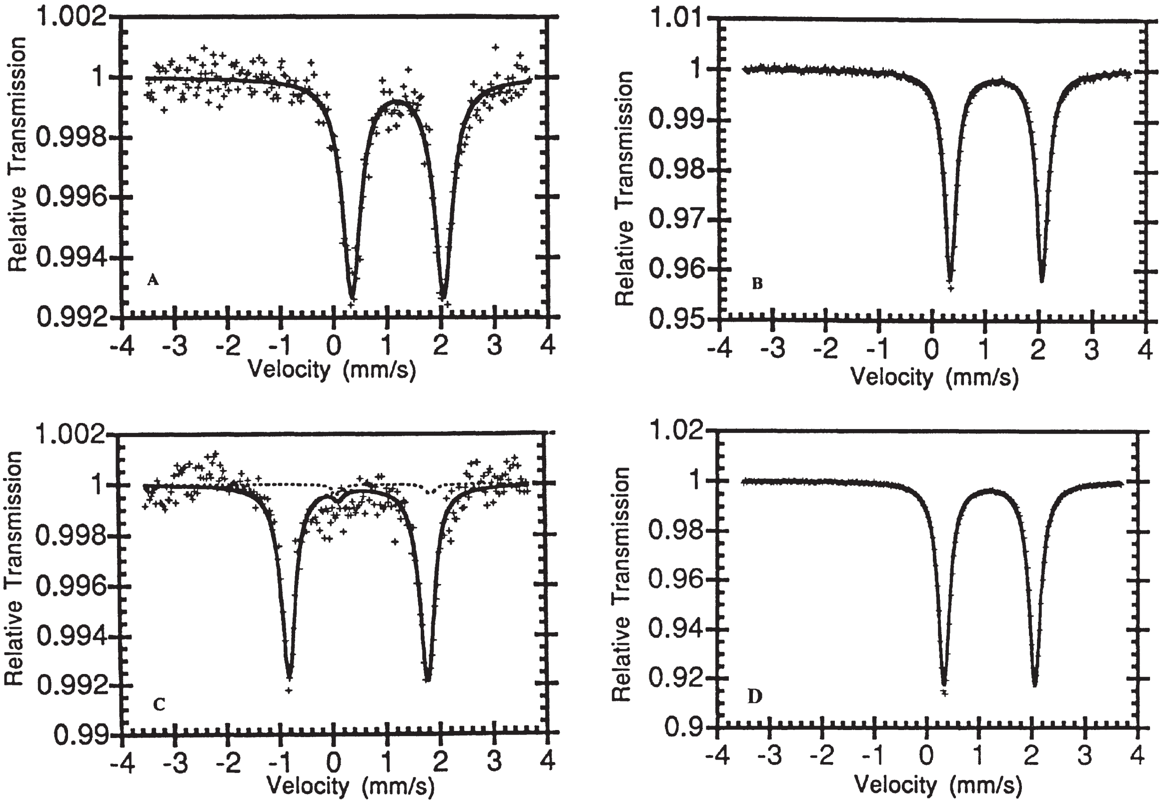

Figure 3. Mössbauer spectra obtained from "good" catalysts: (A) pure solid $FeC_2O_4$; (B) freshly prepared FeZSM-5-18-183; (C) following (B), the SCR reaction was carried out for 3 h at 500 °C using the standard feed. Spectrum (D) was recorded from a bimodal preparation of fresh FeZSM-5-18-218, i.e., FeZSM-5-18-200 plus some occluded $FeC_2O_4$.

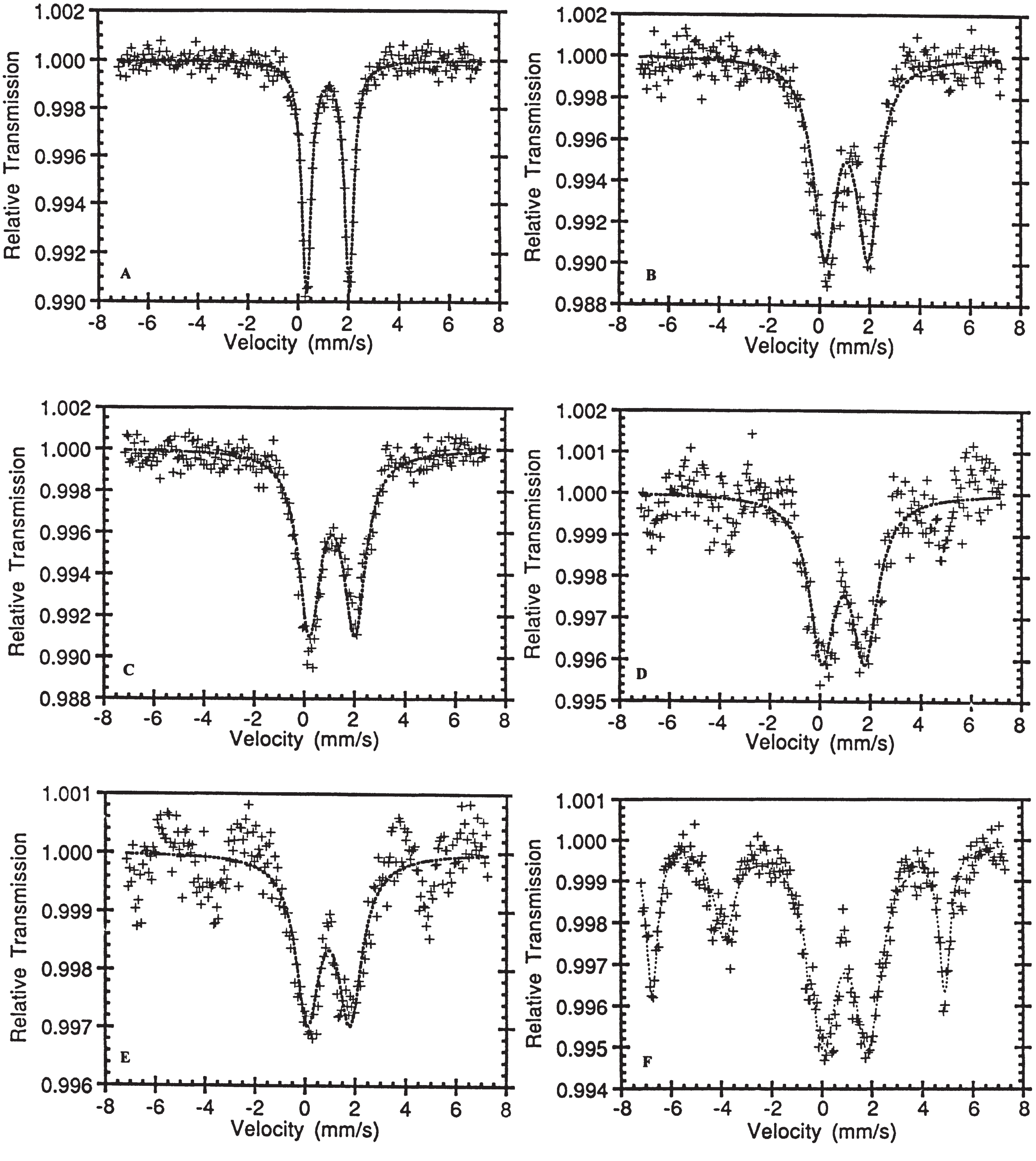

Figure 4. Spectrum (A) was obtained from "poor" fresh catalyst FeZSM-5-19-162. Again, like the "good" catalyst, this spectrum showed only the clean $Fe^{2+}$ doublet. Following (A), the catalyst was treated in flowing He at 225 °C (B), 300 °C (C), 400 °C (D), and 500 °C (E). With the "poor" catalyst, evidence of lattice breakdown appeared distinctly in spectra from samples treated at 400 °C and above. Spectrum (F) was recorded from a sample of FeZSM-5-19-162 after treatment for 12 h in 10% $O_2$ in He at 650 °C. Interestingly, the appearance of the oxide bands in the wings was not accompanied by evidence of oxidation of the $Fe^{2+}$ cations to the $Fe^{3+}$ state.

data suggest that it should make no real difference whether in preparation $Fe^{3+}$ or $Fe^{2+}$ are loaded onto the exchange sites. The iron is reduced or oxidized to its optimum operational condition during the early minutes on stream during SCR.

Figure 3(D) was obtained from another "good" catalyst having still higher loading. Again, the spectrum reveals only high spin $Fe^{2+}$ ions. Of course, the ratio of $Fe^{2+}/Fe^{3+}$ is controlled by the gas composition with the kinetics governed by this ratio [14]. It is, therefore, established that under our experimental conditions, the freshly made catalysts, calcined in pure He, are durable and contain exclusively $Fe^{2+}$ ions. These are stable against further reduction, but can readily be oxidized to the $Fe^{3+}$ state. Further oxidation does not occur below 1000 °C.

A second set of experiments is presented in figure 4. The "poor" catalyst FeZSM-5-19-162 was treated with pure He at several temperatures. The freshly prepared catalyst, figure 4(A), appeared normal; only the sharp high spin $Fe^{2+}$ doublet was recorded. Changes occurred as the catalyst was dehydrated at increasingly higher temperature. Most of the loosely bound water of hydration was removed by the treatment at 300 °C. Note, the scatter in the points on the wings of the spectra recorded after 400 and 500 °C treatments, where evidence of formation of other Fe compounds appears (figure 4 (D) and (E)). After obtaining figure 4(E), the catalyst was treated for 12 h in 10% $O_2$ in He at 600 °C, and now the extra bands in the wings of the $Fe^{2+}$ doublet became well resolved, showing segregation of another iron oxide phase. Surprisingly, the $Fe^{3+}$ doublet did not appear in these experiments as expected.

Both figures 3 and 4 show the sharp symmetric doublet for the freshly prepared (hydrated) $Fe^{2+}$. It is supposed that here the cation is in its most symmetric state. As the samples were dehydrated at increasingly higher temperatures, the symmetry around the cation decreased. Concomitantly the scatter in the individual points increased, and the shapes of the doublets changed. This is reflected in the decrease in both the IS and QS parameters. The Mössbauer parameters for these two sets of samples are collected in table 2 (A and B). In both cases, catalysts treated at/or below 300 °C had larger IS and QS values than samples heated to higher temperatures. However, the accuracy of these values is not high, because the sample weight was smaller than desired and the $^{60}$Co source was getting weak, requiring inconveniently long collection times to accumulate the data. Hence we must conclude that the preparation of a "good" versus a "poor" catalyst is a function of the iron loading and the pretreatment following base-exchange. Multiple splitting is one characteristic of a "poor" catalyst, although the underlying cause–effect relationship is not yet understood.

Neither the work of Chen and Sachtler [8] nor our own has adequately defined the nature of the active catalytic site. Both models do, however, have the advantage of simplicity and supply a rationale for the active oxygen that must be reversibly transferred from one molecule to another during the SCR reaction. These are the bridging oxygen held between two lattice-bound Fe ions. When $Fe^{2+}$ ions are exchanged into the zeolite, a reaction with $O_2$ can occur supplying the oxygen atoms to fill these vacant sites and oxidize two adjacent $Fe^{2+}$ to $Fe^{3+}$, but what happens with the other oxygen? Evidently, these adsorbed O atoms must have a high surface mobility. The observation of table 1 that 10% of the adsorbed oxygen can be pumped off isothermally suggests the presence of a loosely held form of adsorbed O atoms that are effectively part of the lattice oxygen. This picture is supported by tracer data [9]. A further complication is that the redox couple is $Fe^{2+} \rightleftharpoons Fe^{3+}$.

The evolution of the surface chemistry of CuZSM-5 is fairly well understood [10]. $Cu^{2+}$ ions are introduced into the zeolite mainly as $Cu(OH)^{+}$ during the exchange reaction. These may dehydrate forming the oxygen-bridged species or may be *reduced* to $Cu^{+}$ ions on the exchange sites and, of course, can be reoxidized. With FeZSM-5 the situation is different. $Fe^{2+}$ ions are again introduced as $Fe(OH)^{+}$, and, of course, these may dehydrate to form an oxygen-bridged species. However, the $Fe^{2+}$ ions cannot be further reduced, i.e., the bridged oxygen cannot be removed, so it cannot serve as the oxygen transfer site. The redox couple is now $Fe^{2+} \rightleftharpoons Fe^{3+}$, so that an additional oxygen must be held by the exchange site. Chen and Sachtler [4,11] suggest that the species may be $(HO)_2Fe–O–Fe(OH)_2$ (for which there is no real evidence). Possibly, a better way of describing the site is to postulate that the divalent dication supplies electrons to oxygens held remotely by the expanded [9] lattice.

Recently, Joyner and Stockenhuber [12] studied FeZSM-5 made by base-exchange of HZSM-5 (Si/Al = 36) with $Fe(NO_3)_3$. Their EXAFS data suggested that clusters of perhaps four $Fe^{3+}$ ions, all connected with bridging oxygens, were formed by analogy with ferredoxin II. These clusters were suggested to be the active sites.

Clearly, much more study of the FeZSM-5 system will be required before it can be understood in detail how the ELO of these polyvalent systems is held and functions in catalysis. Detailed systematic Mössbauer studies should help. An additional incentive is to develop some understanding of the hydrophobic nature of the active sites, the resistance to poisoning by the high concentration of $H_2O$ normally present in exhaust gas streams, and hence to durability of these catalysts. Whatever is the chemistry of FeZSM-5 surface, it certainly has unique properties, e.g., it was recently reported [13] that FeZSM-5 functioned in a similar way as cytochrome P-450 in olefin epoxidation and in the oxidation of $CH_4$.

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