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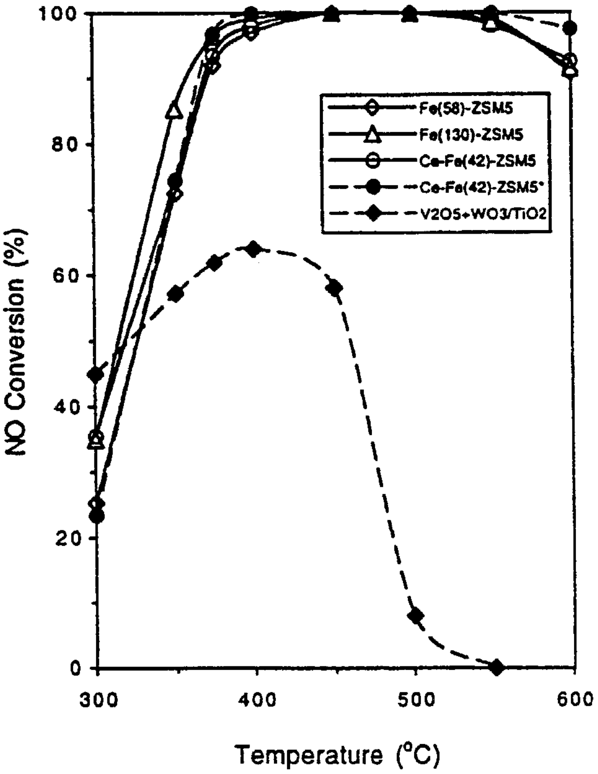

(57) **Abstract:** A catalyst for the selective catalytic reduction of nitrogen oxide compounds with ammonia comprising iron exchanged zeolites. The catalyst may further include promoters ion exchanged, or doped with the zeolites. Preferably the promoter ions are rare earth metals such as cerium.

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ZEOLITE CATALYSTS FOR SELECTIVE CATALYTIC REDUCTION OF NITRIC OXIDE BY AMMONIA AND METHOD OF MAKING

RELATED APPLICATIONS

This application claims priority to U.S. Provisional Patent Application, Serial No. 60/136,626 filed May 27, 1999, the entire disclosure of which is hereby incorporated by reference.

FIELD OF THE INVENTION

This invention relates in general to the field of controlling of nitrogen oxide (NO) emissions from fossil-fuel power plants and engines. More particularly, the invention relates to a catalyst composition for controlling nitrogen oxide emissions from fossil-fuel power plants by selective catalytic reduction (SCR) with ammonia using zeolite catalysts such as Fe-ZSM-5 and Fe-MOR catalysts, and optionally Ce-Fe-ZSM-5 and Ce-Fe-MOR catalysts. The invention also relates to a method of making the same.

BACKGROUND OF THE INVENTION

Nitrogen oxides (NO, NO_2, and N_2O, collectively referred to as "NO_x") present in the exhaust gases from combustion of fossil fuels, continues to be a major source for air pollution. Nitrogen oxides contribute to photochemical smog, acid rain, ozone depletion and greenhouse effects. As a major cause of acid rain, nitrogen oxides additionally contribute to the pollution of water and soil. The current technology for reducing nitrogen oxides emissions from power plants is by selective catalytic reduction (SCR) of NO_x (where x is 1 to 2) with ammonia in the presence of oxygen, to form nitrogen and water. The overall reaction is as follows:

$$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O$$

Many catalysts have been reported to be active for this reaction, such as vanadia and other transition metal oxides (e.g., V_2O5, CuO, Fe_2O_3, Cr_2O_3, Fe_2O_3-Cr_2O_3, Nb_2O_5, and the like), pillared clays and zeolite-type catalysts. For example, in the SCR reaction, a vanadia catalyst $V_2O_5 + WO_3$ (or MoO_3) supported on TiO_2 is commonly used as commercial catalysts. The mechanism of the reaction on the vanadia catalysts has been studied extensively and is reasonably understood although several different mechanisms have been proposed. Although the SCR technology based on vanadia catalysts has been commercialized, problems with this approach still remain. For example, the vanadia catalyst promotes high activity for the oxidation of SO_2 to SO_3, promotes formation of N_2O at high temperatures, and is toxic. Hence there are continuing efforts in developing new catalysts.

H-zeolites and ion-exchanged molecular sieves have received much attention for selective catalytic reduction of NO_x by both hydrocarbon and ammonia in recent years. H-mordenite (MOR) was found active for SCR with ammonia by Pence and Thomas in "Proceedings of the AEC Pollution Control Conference", CONF-721030, 1972, page 15. Since that time, H-form (proton-form), Cu-exchanged, and Fe-exchanged zeolites (examples of such are: mordenite, Y, and ZSM-5), pillared clays, MCM-41 (Mobil molecular sieve) and HMS (a derivative of MCM-41) have been investigated by many groups. The inventors first reported that pillared clays were active for the SCR reaction. Many transition metal ions (such as Cr^{3+} , Cu^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, and the like) have been exchanged with pillared clays. Among them, the Fe-exchanged pillared clays were found to be the most active catalysts. Moreover, the SCR activity of the Fe-exchanged pillared clays was improved by the presence of H_2O and SO_2, which was attributed to an increase in surface acidity due to sulfation of the catalysts. Fe-exchanged zeolites also showed high activities for the SCR reaction.

Komatsu et al. in "Zeolites: A Refined Tool for Designating Catalysis Sites", Elsevier, 1995, page 437, studied the selective catalytic reduction of NO with NH_3 on a Fe-ZSM-5 catalyst, but the activity was only moderate. The inventors believe that its moderate activity could be related to the low iron content in the Fe-ZSM-5 catalyst because the Fe-ZSM-5 was prepared by exchanging Fe^{3+} with ZSM-5 so that only a low exchange level could be reached. More recently, Ma and Grunert, Chem. Commun., 1999, vol. 71, reported the preparation of an over-exchanged Fe-ZSM-5 catalyst by sublimation of $FeCl_3$ vapor into H-ZSM-5, similar to that reported earlier by Chen and Sachtler. The catalyst showed a high SCR activity and was stable in the presence of H_2O and SO_2. However, the maximum NO conversion was still lower than that of over-exchanged Cu-ZSM-5 under the same reaction conditions. The over-exchanged Fe-ZSM-5 also showed a high activity for SCR of NO by iso-butane, reported by Chen and Sachtler, Catal. Today, 1998, Vol. 42, Page

73, earlier. Thus, there is a need in the industry to continue development of catalysts that exhibit improved catalytic activity while minimizing the aforementioned limitations.

OBJECTS AND SUMMARY OF THE INVENTION

Accordingly, it is an object of the present invention to provide an improved catalyst composition for reducing nitrogen oxides emissions.

It is another object of the present invention to provide a method of making an improved catalyst composition for reducing nitrogen oxide emissions.

In summary, the present invention provides a catalyst for selective catalytic reduction of nitrogen oxide compounds with ammonia comprising a composition of iron exchanged zeolites, and mixtures thereof. The composition may further include promoter ions exchanged , or doped, with the zeolites. Preferably the promoter ions are rare earth metals such as cerium (Ce).

One embodiment of the present invention described herein is a catalyst composition comprising iron (Fe) exchanged zeolite catalysts, in particular Fe-ZSM-5, Ce-Fe-ZSM-5, Fe-MOR, Ce-Fe-MOR catalysts and mixtures thereof, for the selective catalyst reduction (SCR) of nitric oxide by ammonia. The Fe exchanged zeolite catalyst compositions of the present invention show remarkable activity for the SCR reaction. Of significant advantage, the Fe-ZSM-5, Fe-MOR, Ce-Fe-ZSM-5 and Ce-Fe-MOR catalysts of the present invention show an activity that is much greater, for example up to about 16 times more active, than conventional commercial catalysts. The catalysts of the present invention function over a broader temperature range, and produces only N_2, as opposed to undesirable N_2O, and H_2O. The catalyst composition of the present invention also show substantially lower activity for oxidation of SO_2 to SO_3, a desirable property. Further, the catalyst of the present invention is resistant to SO_2 and H_2O, and is durable.

In another aspect of the present invention, a method of making an iron exchanged zeolite catalyst is provided.

In one embodiment of the method of the present invention comprises the steps of providing a zeolite starting material of ZSM-5, MOR and other zeolites and exchanging the zeolite starting material with an iron containing material, such as

$FeCl_2$ and other ferrous salts, and carrying out the exchanging step in air at room temperature. In another embodiment, a rare earth metal may be used as a promoter and in this instance the exchanging step further includes exchanging the zeolite starting material with a rare earth promoter, such as a $Ce(NO_3)_3$ solution.

BRIEF DESCRIPTION OF THE DRAWINGS

Additional objects and advantages of the invention will become apparent in reading the detailed description of the invention and the claims and with reference to the figures, in which:

Fig. 1 is a graph of NO_x conversion as a function of temperature showing the catalytic activities for NO_x reduction at certain reaction conditions for various Fe-ZSM-5 catalyst compositions in accordance with the present invention, and compared to a conventional vanadia catalyst.

Fig. 2 is a FT-IR spectra showing ammonia adsorbed on a Fe(58)-ZSM-5 catalyst in accordance with one embodiment of the present invention at various temperatures.

Fig. 3 is a FT-IR spectra showing $NO+O_2/He$ adsorbed on a Fe(58)-ZSM-5 catalyst in accordance with another embodiment of the present invention at various temperatures and then subsequent processing, (a) 200, (b) 300, (c) 300 and (d) 400°C.

Fig. 4 is a FT-IR spectra showing the consumption of NH_4^+ on a Fe(58)-ZSM-5 catalyst at 300 °C in a flow of He containing 1000 ppm NO and 2% O_2 in accordance with another embodiment of the present invention.

Fig. 5 is a graph of NO_x conversion as a function of temperature showing the catalytic activities for selective catalytic reduction of NO_x at certain reaction conditions for various catalyst compositions in accordance with the present invention, and compared to a conventional vanadia catalyst.

Fig. 6 is a graph of NO_x conversion as a function of temperature demonstrating the effect of Si/A ratio on the NO_x conversion of catalyst compositions in accordance with the present invention.

Fig. 7 is a graph of NO_x conversion as a function of temperature illustrating the catalytic performance for selective catalytic reduction of NO by ammonia on various Fe-exchanged molecular sieve catalysts in accordance with another embodiment of the present invention.

DESCRIPTION OF PREFERRED EMBODIMENT

The catalyst composition of the present invention is comprised of iron (Fe)-exchanged zeolite catalysts.

In another embodiment of the present invention, the Fe exchanged zeolite catalysts are further exchanged, or doped, with a rare earth metal, preferably cerium (Ce) and oxides tehreof such as CeO_2. Other suitable rare earth metals are La, Pr and oxides thereof such as La_2O_3 and PrOx.

Fe exchanged, and optionally additionally Ce-exchanged, zeolites finding use in the present invention include: ZSM-5, Mordenite (MOR), SAPO, Clinoptilolite, chabazite, ZK-4 and ZK-5, which are all known commercial zeolites. More specifically, the above zeolites having a silicon to aluminum ratio (Si/Al) of about 1 to 100 are included. For purposes of this description, the catalyst compositions of the present invention employ the following catalyst designation: the number in parentheses following the metal atom indicates the metal-exchange level (in percent of ion exchanged) and the number in parenthesis at the end indicates the Si to Al ratio (Si/Al) in the zeolite. Thus, a catalyst designation of Fe(58)-ZSM-5(10) represents a Fe-exchange level of 58% and a Si/Al of 10. The metal exchange level (or percent of ion exchanges) were determined by neutron activation analysis . Of particular advantage the present invention provides a zeolite catalyst composition of Fe-exchanged ZSM-5 catalyst with a Si/Al ratio of 10, which has shown the highest activity among all known catalysts for SCR of NO by ammonia. The catalyst of the present invention are much more active than the commercial vanadia catalysts and do not exhibit the deficiencies associated with the vanadia catalysts. Preferably, the Fe exchanged and optionally additionally Ce doped, zeolites will have a Si to Al ratio in the range of approximately 1 to 100 , and more preferably in the range of approximately 5 to 40.. Preferably, the catalyst of the present invention will exhibit a metal exchange level (in percent of ion exchanges) in the range of approximately 1% to 300% , more preferably in the range of approximately 20% to 150%, with a metal exchange level of approximately 60% being most preferred.

Of particular advantage, the present invention also provides an improved method of making the zeolite catalysts. In one embodiment of the method of the present invention comprises the steps of providing a zeolite starting material of NH_4-ZSM-5 or MOR, and exchanging the zeolite starting material with an iron containing material, such as a $FeCl_2$ solution and other ferrous salts, and carrying out the exchanging step in air at room temperature. In another embodiment, a rare earth metal may be used as a promoter and in this instance the exchanging step further includes exchanging the zeolite starting material with a rare earth promoter, such as a $Ce(NO_3)_3$ solution.

Other suitable iron containing materials include $FeCl_3$, $FeBr_2$, $Fe(CH_3COO)_2$, Fe, and the like. Other suitable rare earth metal promoters include Y, La, Pr, Nd, Sm and Tb and oxides thereof, including Y_2O_3, Nd_2O_3, Sm_2O_3, Gd_2O_3 and TbO_X. The iron containing material will preferably have an Fe concentration in the range of about 0.1 to 15 wt. %. In the case where a $FeCl_2$ solution is used, the Fe concentration is preferably about 1.6 wt. %. When using NH_4-ZSM-5 as the starting material, the Si/Al is preferably about 10.

When employing a promoter such as Ce, the concentration of Fe in the iron containing material may be reduced. In one example, when using a $Ce(NO_3)_3$ solution as a promoter exchanged with the starting material, and a $FeCl_2$ solution, the Fe concentration is preferably about 1.14 wt. %.

Also, when employing the promoter, it is preferred that the promoter be exchanged with the starting material first, and then exchange the zeolite starting material with the Fe containing material. The exchanging step is generally carried out for 0.1 to 72 hours. In another embodiment of the present invention, the starting material is H-ZSM-5, preferably having a Si/Al of about 10. In this embodiment, the Fe containing material is a Fe and HCl solution and the exchanging step is carried out at about 50°C in a flow of helium (He). Preferably the Fe concentration in the Fe containing material is about 2.21 wt. %. Alternatively, H-ZSM-5 may be exchanged with solid $FeCl_3$ at about 320°C in He. In this instance the Fe concentration in the $FeCl_3$ solid is about 8.6 wt. %. Additionally, the Ce promoter may also be employed. In this embodiment, the exchanging step is generally carried out for 0.1 to 24 hours.

The Fe exchanged zeolite catalysts were prepared by using the above methods (methods 1 and 3 are conventional methods, method 2 (Fe+Hcl) is the method of the present invention) and the catalytic activity was evaluated. The catalytic activity experiments were performed at 1 atm with a conventional fixed-bed, flow reactor connected to a chemiluminescent NO_x analyzer. The reaction products were simultaneously analyzed by gas chromatography (GC). Figure 1 shows the percent of NO_x conversion with different catalysts of the present invention, and compared directly with conventional catalyst (i.e. 4.4% V_2O_5- 8.2% WO_3/TiO_2). These results were obtained under the following reaction conditions: 50mg catalyst, 100ppm NO, 1000ppm NH_3, 2%O_2, balance helium (He), and at a gas hourly space velocity (GHSV) of 4.6 x 10^5 l/h at ambient conditions. Surprisingly high NO_x conversions were obtained based on the Fe-ZSM-5 catalysts of the present invention, over a broad temperature window (375-600°C) and under a high GHSV of 4.6x10^5 1/h. At 400-500°C, NO_x conversions reached nearly 100%. Since the maximum NO_x conversion on conventional H-ZSM-5 was only 64% obtained at 600°C under the same reaction conditions, Fe^{3+} in the zeolite framework played an important role in this reaction. It appears that the activities were little influenced by the Fe content between 1.14% by weight to 3.57% by weight in ZSM-5. According to an alternative embodiment of the present invention, it was found that the addition of a small amount (for example 0.054% by wt.) of cerium further increased the activities as shown in Figure 1. In comparison, the conventional catalyst 4.4%V_2O_5+8.2%WO_3/TiO_2 showed substantially lower activities in NO_x reduction under the same conditions, and the NO_x conversions decreased sharply when the temperature was above 450°C (Figure 1) due to oxidation of ammonia by oxygen. However, when the amount of the conventional catalyst was increased from 50 mg to 800 mg while keeping all other conditions identical, the maximum NO_x conversion was increased from 64.0% at 400°C to 99.8% at 375°C. This indicates that the Fe-ZSM-5 catalysts of the present invention were more than 16 times as active as the commercial catalyst as shown in Table 1 below:

Table 1. Results of No_x reduction by NH_3 over Fe-ZSM-5 and 4.4% V_2O_5-8.2%WO_3/TiO_2 catalyst.

Catalyst	Temperature (°C)	NO_x Conversion (%)	Selectivity	
			N_2	N_2O
Fe(130)-ZSM-5	375	96.4	100	0
(50mg)	400	99.1	100	0
	450-500	>99.9	100	0
4.4%V_2O_5-8.2%WO_3TiO_2	350	99.7	97.3	2.7
(800mg)	375	99.8	95.1	4.9
	400	96.0	91.5	8.5

Reaction conditions in Table 1 are: [NO] = [NH_3] = 1000ppm, [O_2] = 2%, He = balance and total flow rate= 500ml/min

The same ratio of 16 can be obtained by comparing the overall, first-order rate constants. In addition, on the Fe-ZSM-5 catalysts, no N_2O was detected in the entire temperature range of 300-600°C, with only N_2 and H_2O as the reaction products. With the conventional V_2O_5+WO_3/TiO_2 catalyst, a significant amount of undesirable N_2O was formed in the reaction. N_2O is known to be the most stable of the greenhouse gases, and it consumes the ozone layer in the atmosphere, and thus its suppression, achieved by the present invention, is a significant advance in the art.

Because combustion gases contain water vapor and sulfur dioxide (along with NO_x, O_2 and other gases), resistance to H_2O and SO_2 is an important factor for SCR catalysts. Accordingly, the effects of H_2O and SO_2 on the catalytic performance of the catalyst of the present invention, and in particular Ce-Fe(42)-ZSM-5 was evaluated. It was found that the effects of H_2O and SO_2 increased the activity and also widened the reaction temperature window. The Ce-Fe-ZSM5 catalyst is also stable in the SCR reaction. During a run of 60 h on stream at 375°C, under the conditions of 100 mg sample, 1000 ppm NO, 1000 ppm NH_3, 2% O_2, 5% H_2O, 500 ppm SO_2 and GHSV = 2.3×10^5 1/h, NO_x conversion remained at ca. 99-100%. Activities for SO_2 oxidation were measured by collecting SO_3 from products as $BaSO_4$ precipitates. The Ce-Fe-ZSM-5 catalyst of the present invention showed a much lower activity for SO_2 oxidation to SO_3 (0.7% vs. 3.8% for 4.4%V_2O_3+8.2%WO_3/TiO_2) at 375°C under the same reaction conditions.

The mechanism of NO_x reduction by NH_3 on the catalyst of the present invention was studied by *in situ* FT-IR. A Fe-ZSM5 sample (20 mg) was pressed as a self-supporting wafer and loaded in an infrared cell with Si windows. The sample was pretreated at 500°C for 15 minutes in a flow of He and then cooled to 100°C for adsorption of NH_3. After the sample adsorbed NH_3 (1000 ppm NH_3 in He) for 30 minutes followed by purging with He, NH_4^+ coordination in ZSM-5 was formed as shown in Figure 2, at bands at 3351-2730, 2154, 1944 and 1466 cm^{-1}. The negative peak at 3608 cm^{-1} was due to consumption of OH groups because the background spectrum was from the He-pretreated FE-ZSM5. An increase in temperature resulted in desorption of NH_4^+ from the sample. However, some NH_4^+ ions still remained in the Fe-ZSM-5 catalyst at 450°C (Figure 2). This suggests that strong Brønsted acid sites existed on the sample. In a separate experiment, when the Fe-ZSM-5 was exposed to 1000 ppm NO and 2% O_2 at 200°C, three bands at 1880, 1624 and 1580 cm^{-1} were detected as illustrated in Figure 3. This can be assigned to weakly adsorbed NO, NO_2 and NO_3^- species, respectively. This result suggests that NO was oxidized to NO_2 by O_2 on this surface. After purging with He for 5 min at 400°C, all of the bands vanished. In another experiment, NH_3 was first adsorbed on the Fe-ZSM-5 to form NH_4, and the sample was subsequently exposed to NO/O_2/He at 300°C. The NH_4^+ bands vanished gradually in 5 minutes, as illustrated in Figure 4. This indicates that NH_4^+ reacted with NO/NO_2 to form N_2, as identified by gas chromatography. When the Fe-ZSM-5 was exposed to the reactant mixture ($NO+NH_3+O_2$/He) at 250-450°C, only adsorbed NH_4^+ ions were detected. The above results taken together indicate the following scheme for NO reduction by NH_3 on the Fe-ZSM-5 catalyst of the present invention. NH_3 is first activated to NH_4^+ on Brønsted acid sites of the zeolite, then weakly adsorbed and gaseous NO and NO_2 (resulting from NO oxidation by O_2) and NO_3^- species react with NH_4^+ to form N_2 and H_2O. The reaction between NO_2 (NO_{3-}) and NH_4^+ is much faster than that between NO and O_2.

The high activity of the inventive catalyst could be attributed to its strong Brønsted acidity (thus a high concentration of NH_4^+ ions) and a high activity for oxidation of NO to NO_2. It is well known that both Brønsted acidity and the formation of NO_2 are important for the SCR reaction on zeolite-type catalysts.

In an alternative embodiment of the present invention, a series of Fe-exchanged zeolite were studied as catalysts for the selective catalytic reduction (SCR) of NO with ammonia. It was found that Fe-ZSM-5 and Fe-mordenite catalysts were highly active for the SCR reaction. Nearly 100% NO conversions were obtained at 400-550°C under conditions with a high space velocity (GHSV=4.6×10^5 1/h). However, Fe-Y and Fe-MCM-41 with larger pore sizes showed lower activities for this reaction. For Fe-ZSM-5 catalysts, the SCR activity decreased with increasing Si/Al ratio in the zeolites. As Fe-exchange level in the Fe-ZSM-5 catalysts was increased from 58 to 252%, NO conversion increased at lower temperatures (e.g., 300°C), but decreased at higher temperatures (e.g., 600°C). The addition of cerium to Fe-ZSM-5 further increased the SCR activity and durability in the presence of H_2O and SO_2. Compared with the commercial vanadia catalyst, the Fe-ZSM-5 catalyst was 16 times more active; it also functioned in a broader temperature window, produced only N_2 rather than N_2O and H_2O, and showed a substantially lower activity for oxidation of SO_2 to SO_3.

A number of experiments were performed to demonstrate the present invention. The experiments are provided herein for illustration purposes only and are in no way intended to limit the scope of the invention.

EXPERIMENTAL

Preparation of Catalyst. The starting materials used for preparation of the catalysts are as follows. NH_4-ZSM-5 (Si/Al = 10) was obtained from Air Products and Chemicals Inc. The other NH_4-form zeolites were prepared from Na-form zeolites by exchanging with 0.5 M NH_4Cl solution (three times) at room temperature. ZSM-5 (Si/Al = 40) and ZSM-5 (Si/Al = 100) were kindly supplied by Exxon. Mordenite (MOR, Si/Al = 6.4) and Y zeolite (Si/Al = 2.4) were obtained from Zeolyst International Company and Strem Chemicals, respectively. Al-MCM-41 (Si/Al = 10) was prepared according to the procedure described elsewhere. $FeCl_2\cdot4H_2O$ (99%), $FeCl_3$ (99%) and $Fe(NO_3)_3\cdot9H_2O$ (98.5%) were obtained from Aldrich. Iron powder and HCl solution (2.00 M) were supplied by Fisher.

The Fe-exchanged zeolite catalysts were prepared using the method of the present invention. In each experiment, 2 g NH_4-ZSM-5 (Si/Al = 10, 40 and 100), NH_4-MOR, or NH_4-Y was added to 200 ml of 0.05 M $FeCl_2$ solution with constant stirring. After 24 hours, the mixture was filtered and washed five times with deionized water. Ce(0.8)-Fe(42)-ZSM-5 was obtained from 3g NH_4-ZSM-5 exchanged with 200 ml 0.05 M $Ce(NO_3)_3$ solution, followed by exchanging with 200 ml 0.05 M $FeCl_2$ solution. The exchange processes were performed at room temperature for 1 day. Fe(93)-ZSM-5(10) was prepared by exchanging NH_4-ZSM-5 (Si/Al = 10) with $FeCl_2$ solution three times. Table 2 sets forth the preparation conditions and iron content of the various Fe-exchanged zeolite catalysts according to one embodiment of the present invention, as well as conventional catalysts:

Table 2. Preparation conditions and iron contents of Fe-exchanged zeolite catalyst.

Sample	Si/Al	Fe Content (wt.%)	ion-exchange extent (%)	Preparation Condition
Fe(58)-ZSM-5 (10)	10/1	1.59	57.7	Exchanging NH_4-ZSM-5 with $FeCl_2$ solution for 24 hours at room temperature (once)
Ce-Fe(42)-ZSM-5 (10)	10/1	1.17	42.3	Exchanging NH_4-ZSM-5 with $Ce(NO_3)_3$, then $FeCl_2$ solution for 24 hours at room temperature (once)
Fe(93)-ZSM-5 (10)	10/1	2.56	93.0	Exchanging NH_4-ZSM-5 with $FeCl_2$ solution for 24 hours at room temperature (three times)
Fe(130)-ZSM-5 (10)	10/1	3.58	130	Exchanging H-ZSM-5 with Fe+HCl solution at 50°C for 10 days in He
Fe(252)-ZSM-5 (10)	10/1	6.94	252	Exchanging H-ZSM-5 with $FeCl_3$ vapor at 320°C

Fe(57)-ZSM-5 (40)	40/1	0.43	57.3	Exchanging NH$_4$-ZSM-5 with FeCl$_2$ solution for 24 hours at room temperature (once)
Fe(65)-ZSM-5 (100)	100/1	0.20	65.3	Exchanging NH$_4$-ZSM-5 with FeCl$_2$ solution for 24 hours at room temperature (once)
Fe(60)-MOR (6.4)	6.4/1	2.41	59.6	Exchanging NH$_4$-mordenite with FeCl$_2$ solution for 24 hours at room temperature (once)
Fe(67)-Y (2.4)	2.4/1	5.59	66.9	Exchanging NH$_4$-Y with FeCl$_2$ solution for 24 hours at room temperature (once)
Fe(85)-MCM-41 (10)	10/1	2.33	84.7	Exchanging H-Al-MCM-41 with Fe+HCl solution at 25°C for 3 days in a flow of He

In order to prepare over-exchanged Fe-ZSM-5 (i.e., where Fe-exchange level is above 100%), two other methods were used. Fe(130)-ZSM-5(10) was obtained from exchanging 2 g H-ZSM-5 with a mixed solution that contained 200 ml 0.1 M HCl and 0.73 g iron powder. The ion-exchange was performed at 50°C for 10 days in a flow of He, in order to prevent oxidation of the ferrous ion to the ferric form. Fe(252)-ZSM-5(10) was prepared by a sublimation of FeCl$_3$ vapor into H-ZSM-5 at 320°C for 2 hours, followed by hydrolytic removal of chlorine, by following the procedure given by Chen and Sachtler. H-ZSM-5 was prepared by calcining NH$_4$-ZSM-5 at 500°C for 3 h. Fe(85)-MCM-41(10) was prepared by exchanging H-Al-

MCM-41 (Si/Al = 10) with a solution containing 200 ml 0.1M HCl and 0.73g Fe at room temperature for 3 days in a flow of He. The obtained catalysts were first dried at 120°C in air for 12 h, then calcined at 600°C for 6 h. Fe^{2+} in the catalysts was oxidized to Fe^{3+}. Finally, the obtained samples were ground to 60-100 mesh. The Fe and Al contents in the samples were measured by neutron activation analysis. The iron exchange extent was calculated by 3 × (number of iron ions) / (number aluminum ions). The preparation of the catalysts and the resulting Fe contents are summarized in Table 2.

In addition to the Fe-exchanged catalysts of the present invention, 2.27 wt.%Fe_2O_3/H-ZSM-5 and $V_2O_5+WO_3/TiO_2$ catalyst (4.4 wt.%V_2O_5+8.2 wt.%WO_3/TiO_2) were also used for comparison. The catalysts were prepared by incipient wetness impregnation. The $V_2O_5+WO_3/TiO_2$ catalyst had nearly identical SCR activity and behavior as that of the commercial SCR catalyst supplied by a major catalyst manufacturer.

Catalytic Activity Measurement. The SCR activity measurement was carried out in a fixed-bed quartz reactor, using 50 mg (0.065 ml) of catalyst. The flue gas was simulated by blending different gaseous reactants to represent the various emission gases. Two sets of flowmeters were used to control the flow rates of the individual reactants. Helium, NH_3/He (premixed), and No/He (premixed) gases were controlled by rotameters, whereas SO_2/He (premixed) and O_2 were controlled by mass flowmeters (FM 4575 Linde Division). The typical reactant gas composition was as follows: 1000 ppm NO, 1000 ppm NH_3, 2% O_2, 500 ppm SO_2 (when used), 5% water vapor (when used), and balance He. The total flow rate was 500 ml/min (ambient conditions) and thus a very high GHSV was obtained, i.e. 4.6×10^5 1/h. The premixed gases (1.01% NO in He, 1.00% NH_3 in He, and 0.99% SO_2 in He) were supplied by Matheson. Water vapor was generated by passing He through a heated gas-wash bottle containing deionized water. The tubings of the reactor system were wrapped with heating tapes to prevent formation and deposition of ammonium sulfate/bisulfate and ammonium nitrate. The NO and NO_2 concentrations were continually monitored by a chemiluminescent NO/NO_x analyzer (Thermo Electron Corporation, Model 10). To avoid errors caused by the oxidation of ammonia in the converter of the NO/NO_x analyzer, an ammonia trap containing a phosphoric acid solution was installed before the sample inlet to the chemiluminescent analyzer. The products were also analyzed by a gas chromatograph (Shimadzu, 14A) at 50°C with 5A molecular sieve column for N_2 and Porapak Q column for N_2O. Hence the nitrogen balance and the product selectivities for N_2 and N_2O could be obtained. During the reaction, the temperature was increased from room temperature to 600°C step by step. At each temperature point, in 50°C intervals (i.e., 250, 300, 350, 400, 450, 500, 550 and 600°C), data was obtained when the SCR reaction reached steady state after five minutes.

SO_3 Analysis. To measure the amount of SO_3 from SO_2 oxidation during the SCR reaction, a conventional wet analysis method was adopted. With the same reactor used for measuring the catalyst SCR activity, the effluent was bubbled through a solution containing $BaCl_2$ and HCl. After 12-24 hour runs at 375°C under the conditions of 1000 ppm NO, 1000 ppm NH_3, 2% O_2, 5% H_2O, 500 ppm SO_2 and GHSV = 4.6×10^5 1/h, the SO_3 was quantitatively captured and precipitated as $BaSO_4$. Considering that a small amount of ammonium sulfates (resulting from the reaction of SO_3, H_2O and NH_3) might stay in the tubing between the SCR reactor and $BaCl_2$ solution after the reaction. The $BaSO_4$ precipitate was collected on an ashless filter paper which was burned along with the precipitate in a crucible, so the amount of the precipitate was accurately measured.

Catalytic performance of Fe-ZSM-5. The SCR activities of H-ZSM-5, Fe_2O_3/H-ZSM-5, Fe-ZSM-5, and V_2O_5+WO_3/TiO_2 catalysts are shown in Figure 5. Under the conditions with a high GHSV (i.e. 4.6×10^5 1/h), the H-ZSM-5(10) catalyst showed moderate activity. NO conversion increased from zero to 65% when the reaction temperature was increased from 250 to 600°C. This is in good agreement with the previous result that H-ZSM-5 was active for the SCR reaction at high temperatures. After 2.27 wt.% Fe_2O_3 was doped on the H-ZSM-5, NO conversions were improved at lower temperatures, but the highest NO conversion was only 70% at 550°C. However, when the same amount of iron ions were exchanged to ZSM-5 in accordance with the present invention, surprisingly high NO conversions were obtained on the Fe(58)-ZSM-5(10) catalyst, which also gave a broad temperature window (Figure 5). Nearly 100% NO conversion was obtained at 400-550°C on the Fe-ZSM-5 catalyst of the present invention. The above results indicate clearly that Fe^{3+} in the catalyst played an important role for the SCR reaction. By comparison, the commercial V_2O_5+WO_3/TiO_2 catalyst showed substantially lower NO conversions under the same conditions, and the NO conversions decreased sharply when the temperature was above 450°C (Figure 5) due to oxidation of ammonia by oxygen. However, when the amount of the commercial catalyst was increased from 50 mg to 800 mg while keeping all other conditions identical, the maximum NO conversion was increased from 57.0% at 400°C to 99.8% at 375°C. This indicates that Fe-ZSM-5 catalysts were more than 16 times as active as the commercial catalyst. The SCR activity can also be represented quantitatively by the first-order rate constant (k), since the reaction is known to be first order with respect to NO under stoichiometric NH_3 conditions on a variety of catalysts. By assuming a plug flow reactor (in a fixed bed of catalyst) and free of diffusion limitation, the rate constant can be calculated from the NO conversion (X) by

$$k = -\frac{F_0}{[NO]_0 W} \ln(1-X) \tag{1}$$

where F_0 is the molar NO feed rate, $[NO]_0$ is the molar NO concentration at the inlet (at the reaction temperature), and W is the catalyst amount (g). From the NO conversions and reaction conditions, first-order rate constants could be calculated. The k values of the inventive Fe(58)-ZSM-5(10) catalyst were 2078 and 2793 $cm^3/g/s$ at 400 and 450°C, respectively. By comparison, the k values for the commercial vanadia catalyst were only 417 $cm^3/g/s$ at 400°C and 386 $cm^3/g/s$ at 450°C. In addition, on the inventive Fe(58)ZSM-5(10) catalyst, no N_2O was detected in the entire temperature range of 250-600°C, with only N_2 and H_2O as the reaction products. With the conventional V_2O_5+WO_3/TiO_2 catalyst, a significant amount of N_2O was formed at high temperatures (e.g., 5% of N_2O yield was obtained at 375°C). The nitrogen balance in this work was above 95%. The maximum SCR activity on the Fe-ZSM-5 catalyst was also superior to any other catalysts reported in the literature.

Effect of Fe content on SCR activity over Fe-ZSM-5(10) catalysts. The effect of the Fe content on the SCR activity is summarized in Table 3.

Table 3. Catalytic performance of Fe-ZSM-5(Si/Al=10) catalyst at different ion exchange percentages in the absence of H_2O and SO_2.[a]

Catalyst	Temperature (°C)	NO Conversion to N_2 (%)	k_b ($cm^3/g/s$)
Fe(58)-ZSM-5 (10)	300	27.0	101
	350	72.5	450
	400	99.6	2080
	450	>99.9	2790
	500	>99.9	2990
	550	99.2	2220
	600	92.0	1230
Fe(93)-ZSM-5 (10)	300	33.0	128
	350	82.0	597
	400	99.0	1730
	450	>99.9	2790
	500	>99.9	2990
	550	95.6	1260
	600	91.0	1180
Fe(130)-ZSM-5 (10)	300	35.0	138
	350	85.4	670
	400	99.1	1770
	450	>99.9	2790
	500	>99.9	2990
	550	98.6	1970
	600	91.5	1200
Fe(252)-ZSM-5 (10)	300	57.0	270
	350	97.0	1220
	400	99.7	2.19
	450	95.0	1210
	500	90.0	995
	550	86.0	905
	600	67.0	541
Ce(0.8)-Fe(42)-ZSM-5 (10)	300	35.5	131
	350	74.5	476
	400	>99.9	2600
	450	>99.9	2790
	500	>99.9	2990
	550	99.0	2119
	600	92.5	1265

[a] Reaction conditions: 0.05g catalyst, [NO] = [NH_3] = 1000 ppm, [O_2] = 2%, He = balance, total flow rate = 500 ml/minute and GHSV = 4.6 X 10^5 1/h.

[b] First-order rate constant, as defined in the text, calculated by Equation 1.

At low temperatures (e.g., 300°C), both NO conversion and the first-order rate constant (k) increased with increasing Fe content on the Fe-ZSM-5(10) catalysts. But at higher temperatures (> 550°C), they dropped more rapidly with an increase in Fe content. This may be related to oxidation of NH_3 by O_2 at high temperatures because a high iron content on the catalyst may be beneficial to oxidation of NH_3. At 400-500°C, NO conversion reached nearly 100% on the Fe-ZSM-5(10) catalysts with 58-130% of Fe-exchange level. Also, no N_2O was detected by GC during the reaction for these catalysts.

Effect of Si/Al ratio on SCR activity over Fe-ZSM-5 catalysts. It is known that the Si/Al ratio in zeolites affects their acidity-basicity and cation exchange capacity. The effect of Si/Al ratio on SCR activity over the catalysts of the present invention was studied. As shown in Figure 6, the ratio of Si/Al had a strong effect on NO conversion for the Fe-ZSM-5 catalysts. With an increase in Si/Al ratio, NO conversions decreased rapidly at the temperature range of 250-600°C (Figure 6). High NO conversions were obtained over Fe(58)-ZSM-5 (Si/Al = 10), but very low NO conversions were obtained on Fe(65)-ZSM-5 (Si/Al = 100). These results indicate that the Fe-ZSM-5 catalysts with low Si/Al ratio in the range of about 1 to 40 is favorable to a high NO conversion.

SCR activities on different Fe-exchanged molecular sieves. The SCR activity on other different Fe-exchanged molecular sieves (Fe-MOR, Fe-Y, and Fe-MCM-41) were also studied by the inventors. The results are shown in Figure 7. Like the Fe(58)-ZSM(10) catalyst, the Fe(60)-MOR(6.4) catalyst also showed high activities and a broad temperature window. Also, no N_2O was detected in the entire temperature range. In comparison, Fe(67)-Y(2.4) was less active than the above two catalysts. The lowest SCR activity was found on Fe(85)-MCM-41(10) catalyst. The maximum NO conversion on the Fe-MCM-41 catalyst was only 25.5% at 550°C under the condition with 4.6×10^5 1/h. The above results suggest that the structure of molecular sieves has a strong effect on the SCR activity.

Effect of Ce Promoter. In accordance with an alternative embodiment of the present invention, a Ce promoter is added to the catalyst composition. Specifically, Ce and Fe are exchanged with the zeolite. Table 3 shows the catalytic activity for a Ce(0.8)-Fe(42)-ZSM-5(10) catalyst in accordance with this alternative embodiment of the invention. As shown the Ce exchanged catalyst was also very active in the SCR reaction. NO conversions reached near 100% at 400-500°C. As compared with Fe(58)-ZSM-5, the addition of cerium increased SCR activity at lower temperatures (>400°C).

Effect of H_2O + SO_2 on SCR activity. Because resistance to H_2O and SO_2 is an important factor for SCR catalysts, we studied the effect of H_2O and SO_2 on the catalytic performance over the Fe-ZSM-5 catalysts (Table 4). The results are shown in Table 4.

Table 4. Catalytic performance of Fe-ZSM-5(Si/Al=10) catalyst in the presence of H_2O and SO_2.[a]

Catalyst	Temperature (°C)	NO Conversion to N_2 (%)	$k_b/10^3$ ($cm^3/g/s$)
Fe(58)-ZSM-5 (10)	300	20.0	72
	350	70.0	419
	400	>99.9	2600
	450	>99.9	2790
	500	>99.9	2990
	550	>99.9	3180
	600	94.0	1370
Fe(130)-ZSM-5 (10)	300	30.0	114
	350	81.8	594
	400	>99.9	2600
	450	>99.9	2790
	500	>99.9	2990
	550	>99.9	3180
	600	95.0	1460
Ce(0.8)-Fe(42)-ZSM-5 (10)	300	23.5	85.8
	350	74.5	476
	400	>99.9	2600
	450	>99.9	2790
	500	>99.9	2990
	550	>99.9	3180
	600	97.7	1842

[a] Reaction conditions: 0.05g catalyst, [NO] = [NH_3] = 1000 ppm, [O_2] = 2%, [H_2O] = 5%, [SO_2] = 500 ppm, He = balance, total flow rate = 500 ml/minute and GHSV = 4.6 X 10^5 l/h.

[b] First-order rate constant, as defined in the text, calculated by Equation 1.

At low temperatures (e.g., 300°C), NO conversions and first-order rate constants (k) decreased in the presence of H_2O and SO_2 on Fe(58)-ZSM-5(10), Fe(130)-ZSM-5(10) and Ce(0.8)-Fe(42)-ZSM-5(10) catalysts. But at high temperatures, it was found that H_2O and SO_2 increased SCR activities and also widened the temperature windows for the two catalysts (Tables 3 and 4). However, after a run of 60 hours on stream at 375°C, under the conditions of 100 mg sample, 1000 ppm NO, 1000 ppm NH_3, 2% O_2, 5% H_2O and 500 ppm SO_2, the activity on Fe(58)-ZSM-5(10) decreased from 99.5 to 80.0%. By comparison, NO conversion on the inventive Ce(0.8)-Fe(42)-ZSM-5(10) was only changed from 99.9 to 99.0%. This indicates that the Ce-Fe-ZSM-5 was stable in the SCR reaction and cerium plays a stabilization role for Fe-ZSM-5.

SO_2 Oxidation Activity. Using the wet chemical method described in the foregoing to quantitatively measure the amounts of SO_3 generated in the reaction effluents, SO_2 conversions at 375°C for Fe(58)-ZSM-5(10), Ce(0.8)-Fe(42)-ZSM-5(10) and 4.4%V_2O_5+WO_3/TiO_2 were obtained. The conversion for SO_2 to SO_3 was about 0.7% for Fe(58)-ZSM-5(10) and Ce(0.8)-Fe(42)-ZSM-5(10), which was much lower than that (3.8%) on the vanadia catalyst under the same reaction conditions.

The foregoing demonstrates that the Fe exchanged zeolite, and optionally additionally exchanged with Ce, catalysts of the present invention have higher activities than all known catalysts for the SCR reaction of NO with ammonia. In particular, for Fe-ZSM-5(10) catalysts, when the Fe-exchange level was increased from 58 to 252%, the NO conversion increased at lower temperatures (e.g., 300°C) but decreased at high temperatures (>500°C, Table 2). This is in good agreement with our previous result on Fe-TiO_2-PILC catalysts that NO conversion at high temperatures decreased with an increase in iron content, but is contrary to the result reported by Ma and Grunert that the SCR activity on Fe-ZSM-5 with an exchange degree of < 100% was inferior to that on the over-exchanged Fe(300)-ZSM-5(14). Over-exchanged Fe-ZSM-5 catalysts have attracted much attention for the SCR of NO with hydrocarbon because they were highly active and resistant to H_2O and SO_2 as compared with the Cu-ZSM-5 catalysts. Feng and Hall first reported that Fe(183)-ZSM-5(19) prepared by an ion-exchange from oxalate salt was an active and durable SCR catalyst with iso-butane as the reductant. The SCR activity of Fe(183)-ZSM-5(19) was much higher than that of under-exchanged Fe-ZSM-5 catalysts (i.e., ion-exchange level < 100%). Chen and Sachtler studied the same reaction on Fe(300)-ZSM-5 catalysts prepared by using anaerobic sublimation of volatile $FeCl_3$ to H-ZSM-5. They also reported high activity and durability of the over-exchanged Fe-ZSM-5 catalysts for SCR with hydrocarbons. Using the procedure of Chen and Sachtler, Ma and Grunert prepared an over-exchanged Fe(300)-ZSM-5(14) catalyst and investigated its catalytic performance for the SCR of NO with ammonia. They also concluded that the SCR activity of the over-exchanged catalyst was superior to that of under-exchanged Fe-ZSM-5 catalysts obtained by conventional aqueous exchange. But the maximum NO conversion on the Fe(300)-ZSM-5(14) in their work was below 85% under the condition with a lower space velocity of 3.04×10^5 1/h, which was significantly lower than that (near 100%) on the Fe(58)-ZSM-5(10) catalyst of the present invention obtained at a higher space velocity (4.6×10^5 1/h) as tested herein. It is noted that, although over-exchange is important for Fe-ZSM-5 catalysts to obtain a high activity for SCR with hydrocarbons, it may not be necessary for SCR with ammonia. The mechanisms for these two SCR reactions are very different. The SCR reaction with hydrocarbons generally involves the adsorption/oxidation of nitrogen oxides and hydrocarbons. The surface acidity of catalyst does not play an important role and no direct relationship between catalytic activity and acidity has been found for this reaction of SCR with hydrocarbon. Conversely, for the SCR reaction of NO with ammonia, the subject of the present invention, the reaction path involves the adsorption of ammonia on the Brønsted or Lewis acid sites and reaction between the ammonia adspecies and nitrogen oxides. In this reaction, surface acidity is important because strong acidity is beneficial to NH_3 adsorption. Work has demonstrated that there is a direct correlation between SCR activity and surface acidity for many catalysts (e.g., V_2O_5+WO_3/TiO_2, pillared clay and zeolite catalysts), and an increase in surface acidity improves the catalytic activity. The results obtained by the inventors, indicated that a higher Fe-exchange level did not result in a higher acidity. However, a higher iron content may increase the activity for oxidation of ammonia by oxygen at high temperatures. This will result in a decrease in NO conversion at high temperatures over the Fe-ZSM-5(10) catalysts with higher iron contents. Komatsu et al. reported that the oxidation activity of ammonia by oxygen increased with copper content on Cu-ZSM-5 and the catalysts with higher copper contents also showed lower NO conversions at high temperatures for the SCR reaction of NO with ammonia.

The above results also indicated that the ratio of Si/Al in ZSM-5 had a strong effect on NO conversion for the Fe-ZSM-5 catalysts. Although the ion-exchange level for Fe(58)-ZSM-5(10), Fe-(57)-ZSM-5(40) and Fe(65)-ZSM-5(100) were close, NO conversions decreased sharply with increasing Si/Al ratio (Figure 6). It is known that ZSM-5 with a lower Si/Al ratio has a higher Brønsted acidity so that a high SCR activity will be achieved on the Fe-ZSM-5 catalyst. For different Fe-exchanged molecular sieves, NO conversions were found to decrease in an order of Fe(58)-ZSM-5(10) > Fe(60)-MOR(6.4) > Fe(67)-Y(2.4) >> Fe(85)-MCM-41(10) (Figure 7). This indicates that the structure of molecular sieve played an important role for the SCR reaction with ammonia. ZSM-5 has a unique pore structure that consists of two intersecting channel systems: one straight and the other sinusoidal and perpendicular to the former. Both channel systems have ten-membered-ring elliptical openings (0.52-0.57 nm in diameter). The mordenite pore structure consists of elliptical and noninterconnected channels parallel to the c-axis of the orthorhombic structure. Their openings are limited by twelve-membered rings (0.6-0.7 nm). Y-zeolite is a faujasite-type zeolite with 1.5-3.0 of Si/Al ratio, whose large cavities of 1.3 nm in diameter (supercages) are connected to each other through apertures of 1.0 nm. By comparison, MCM-41, a new member of molecular sieve family, shows a regular hexagonal array of uniform pore openings with pore dimensions between 1.5 and 10 nm. The average pore diameter of the Al-MCM-41(10) was 4.3 nm. Hence, the pore sizes of the above molecular sieves increase according to a sequence of ZSM-5 < MOR < Y < MCM-41, but the SCR activities on the above Fe-exchanged zeolites decreased in this order. However, large pore diameter is clearly beneficial to diffusion rates for the SCR reaction. This contradiction suggests that the SCR reaction could be free of diffusion limitation and the SCR reaction was achieved at pore openings near the crystallite surfaces. For the H-ZSM-5 catalyst, Eng and Bartholomew proposed a scheme for reducing NO to N_2 by ammonia. One pair of HN_4^+ ions (i.e., two NH_3 molecules adsorbed onto neighboring Brønsted acid sites) reacts with one NO_2 molecule (resulting from oxidation of NO by O_2) to form a complex, which subsequently reacts with another

NO molecule to produce N_2 and H_2O. They suggested that the oxidation of NO to NO_2 was the rate-limiting step for the reaction. According to the above catalytic performance results, it seems that Fe-exchanged zeolites also follow this reaction pathway. Fe^{3+} ions on the catalysts increased the oxidation rate of NO to NO_2 and thus increased the SCR activity significantly as compared with H-ZSM-5 (Figure 5). A small pore diameter and a low Si/Al ratio in molecular sieves would promote the formation of NH_4^+ pairs, so that Fe-ZSM-5(10) and Fe-MOR(6.4) catalysts showed high activities. On the contrary, pairs of NH_4^+ would be difficult to form on Fe-exchanged molecular sieves with large pore sizes and high Si/Al ratios (due to a lack of adjacent acid sites) thus very low SCR activities were obtained on Fe(85)-MCM-41(10) and Fe(65)-ZSM-5(100) catalysts.

In summary, the present invention of Fe exchanged zeolite catalysts (which may be optionally exchanged with Ce) are shown to be highly reactive for the SCR reaction of NO with ammonia. Nearly 100% NO_x conversion was obtained at 400-550°C under conditions with a high space velocity (GHSV = 4.6×10^5 1/h). But conventional catalyst of Fe-Y(Si/Al = 2.4) and Fe-MCM-41(Si/Al = 10) with larger pore diameters showed lower activities for this reaction. For Fe-ZSM-5 catalysts of the present invention, the SCR activity also decreased with increasing Si/Al ratio in the zeolites. The addition of cerium to Fe-ZSM-5 further increases the SCR activity and durability in the presence of H_2O and SO_2. As compared with the commercial vanadia catalyst, the Fe-ZSM-5(10) catalysts were much more active; they functioned in a broader temperature window and produced only N_2 (rather than N_2) and H_2O; they also showed a substantially lower activity for oxidation of SO_2 to SO_3.

CLAIMS

What is claimed is:

1. A catalyst for selective catalytic reduction of nitrogen oxide compounds with ammonia, comprising:

a composition of iron exchanged zeolites, and mixtures thereof.

2. The catalyst of Claim 1 wherein said composition further comprises promoter ions exchanged with said zeolites.

3. The catalyst of Claim 1 wherein said zeolite is selected from the group of chabazite, clinoptilolite, ZK-4, ZK-5, ZSM-5 and mordenite (MDR).

4. The catalyst of Claim 2 wherein said promoter ions are selected from the group of Ce, La, Pr, Y, Nd, Sm, Gd, Tb and oxides thereof.

5. The catalyst of Claim 1 wherein said zeolite is ZSM-5.

6. The catalyst of Claim 1 wherein said zeolite is mordenite (MOR).

7. The catalyst of Claim 1 wherein said catalyst is comprised of Fe-ZSM-5 or Ce-Fe-ZSM-5.

8. The catalyst of Claim 1 wherein said catalyst is comprised of Fe-ZSM-5 and has a Si/Al ratio in the range of approximately 1 to 100.

9. The catalyst of Claim 1 wherein said catalyst is comprised of Fe-ZSM-5 and has a Si/Al ratio of approximately 10.

10. The catalyst of Claim 1 wherein said catalyst is comprised of Ce-Fe-ZSM-5 and has a Si/Al ratio in the range of approximately 1 to 100.

11. The catalyst of Claim 1 wherein said catalyst is comprised of Ce-Fe-ZSM-5 and has a Si/Al ratio of approximately 10.

12. The catalyst of Claim 1 wherein the percent of iron ions exchanged is in the range of approximately 1% to 300%.

13. The catalyst of Claim 1 wherein the percent of cerium ions exchanged is in the range of approximately 1% to 300%.

14. The catalyst of Claim 2 wherein the promoter ions are provided by rare earth metal compounds selected from the group of Y_2O_3, Nd_2O_3, Sm_2O_3, Gd_2O_3, TbO_x, CeO_2, La_2O_3, or PrO_x.

15. The catalyst of Claim 1 wherein said catalyst is selected from the group of:
Fe(58)-ZSM-5 (10); Ce-Fe(42)-ZSM-5 (10); Fe(93)-ZSM-5 (10); Fe(130)-ZSM-5 (10); Fe(252)-ZSM-5 (10); Fe(57)-ZSM-5 (40); Fe(65)-ZSM-5 (100); and Fe(60)-MOR(6.4).

16. The catalyst of Claim 4 wherein said rare earth ions are present in a concentration in the range of about 0.1 to 15 wt. %.

17. A method of making an iron exchanged zeolite catalyst for the selective catalytic reduction of nitrogen oxide compounds with ammonia, comprising the steps of:

providing a zeolite starting material;

exchanging said zeolite starting material with an iron containing material; and

carrying out said exchanging step in air or inert gas at room temperature.

18. The method of Claim 17 wherein said exchanging step further includes exchanging the zeolite starting material with a promoter ion.

19. The method of Claim 17 wherein said iron containing material is selected from the group of $FeCl_2$, Fe and other ferrous salts.

20. The method of Claim 18 wherein said promoter ions are rare earth metal ions selected from the group of Ce, La, Pr, Y, Nd, Sm, Gd and Tb.

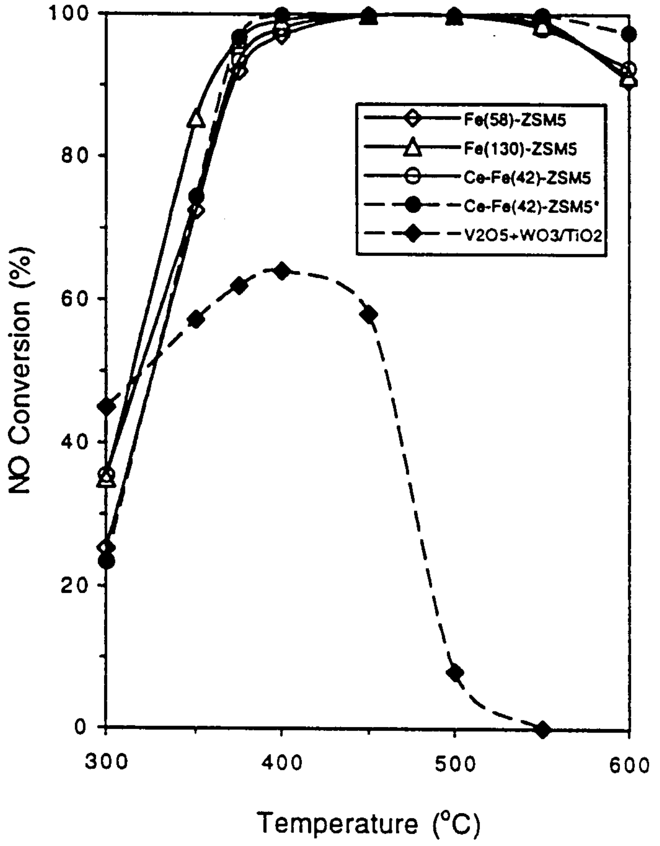
100
80
60
40
20
0
NO Conversion (%)
300
400
500
600
Temperature (°C)
Fe(58)-ZSM5
Fe(130)-ZSM5
Ce-Fe(42)-ZSM5
Ce-Fe(42)-ZSM5*
V2O5+WO3/TiO2

Fig. 1

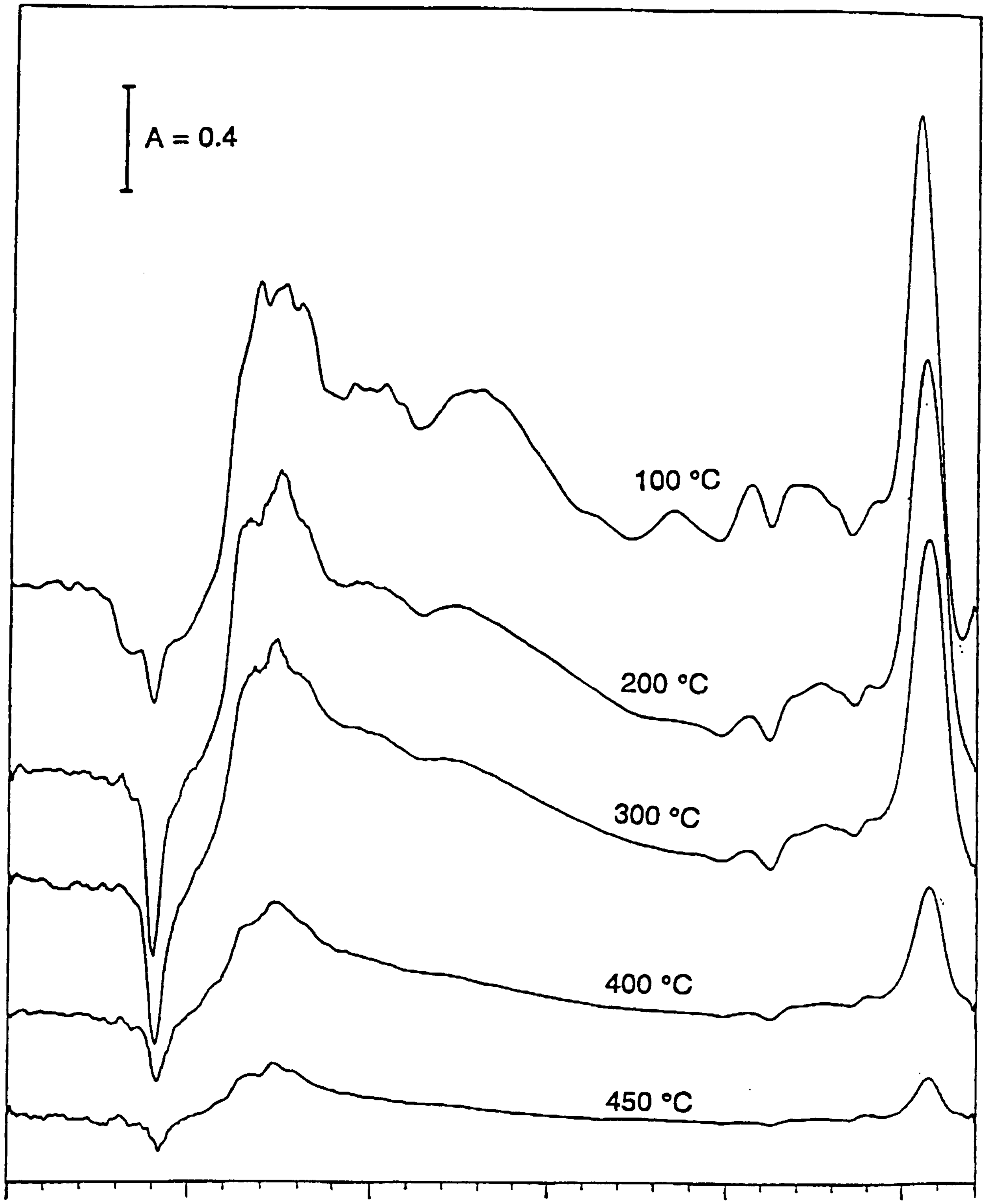
A = 0.4
100 °C
200 °C
300 °C
400 °C
450 °C
3500
3000
2500
2000
1500
Wavenumbers (cm-1)

FIG - 2

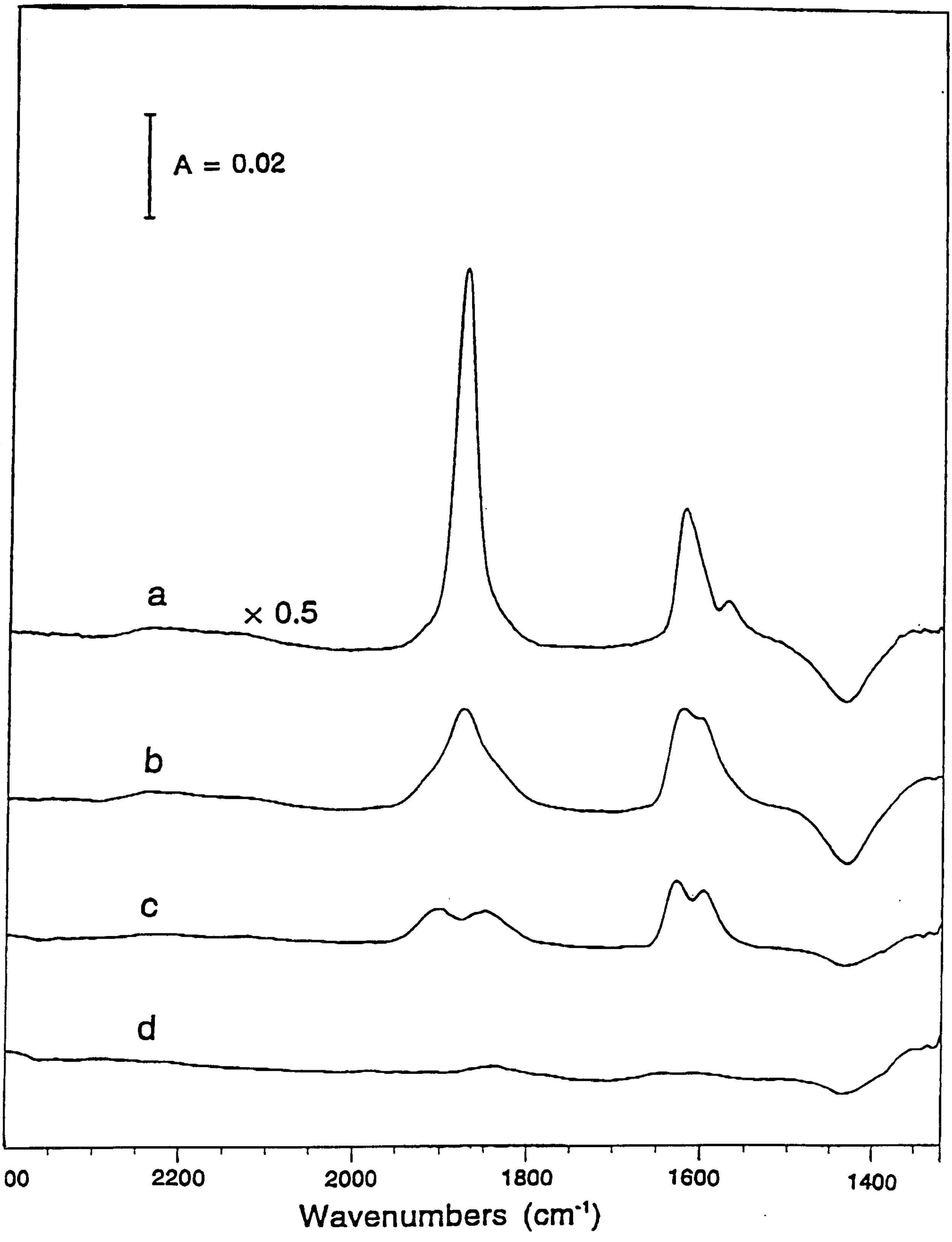

FIG – 3

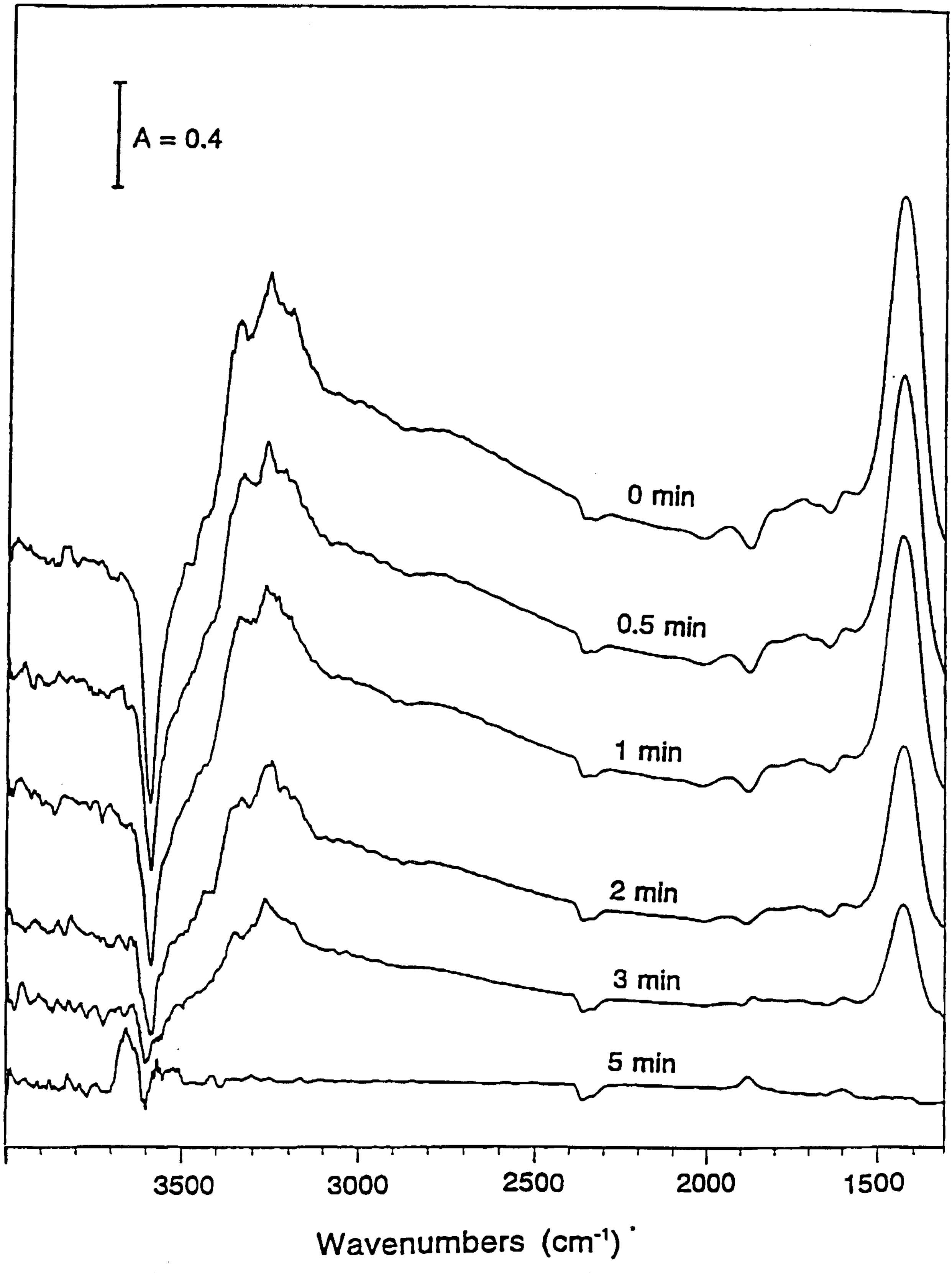
A = 0.4
0 min
0.5 min
1 min
2 min
3 min
5 min
3500
3000
2500
2000
1500
Wavenumbers (cm^{-1})

FIG - 4

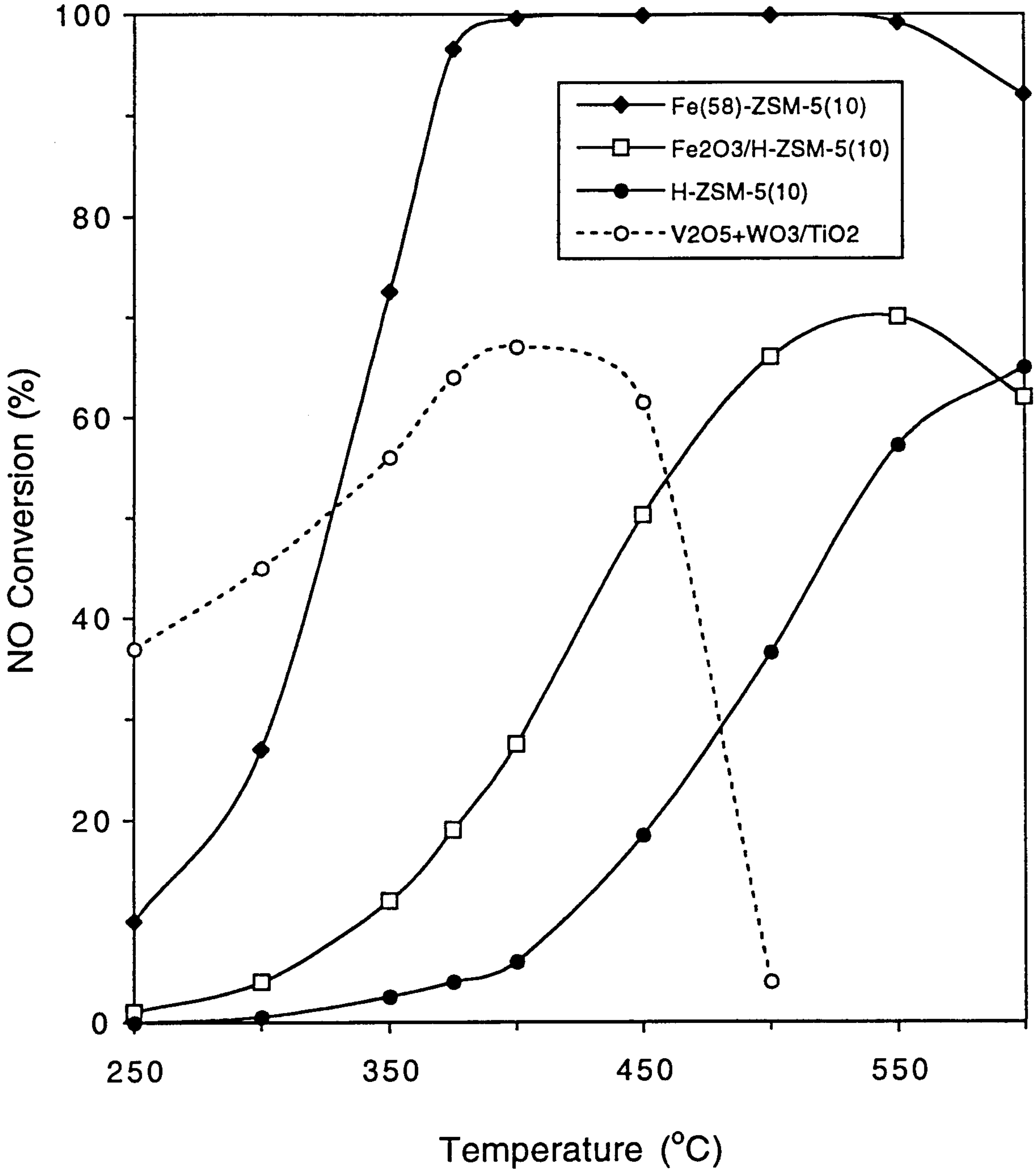
Fe(58)-ZSM-5(10)
Fe2O3/H-ZSM-5(10)
H-ZSM-5(10)
V2O5+WO3/TiO2
NO Conversion (%)
100
80
60
40
20
0
250
350
450
550
Temperature (°C)

FIG-5

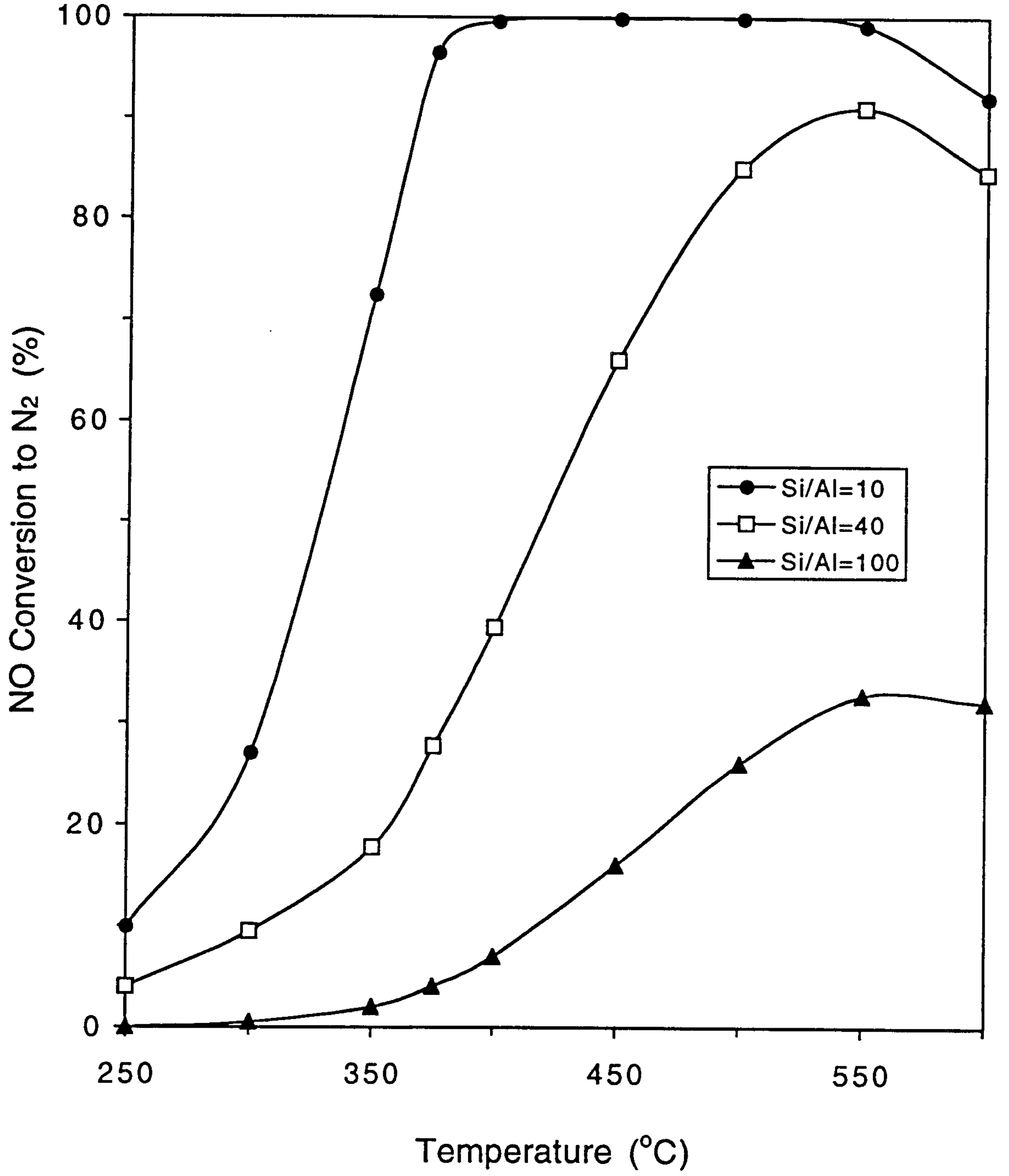
100
80
60
40
20
0
250
350
450
550
NO Conversion to N₂ (%)
Temperature (°C)
Si/Al=10
Si/Al=40
Si/Al=100

FIG. 6

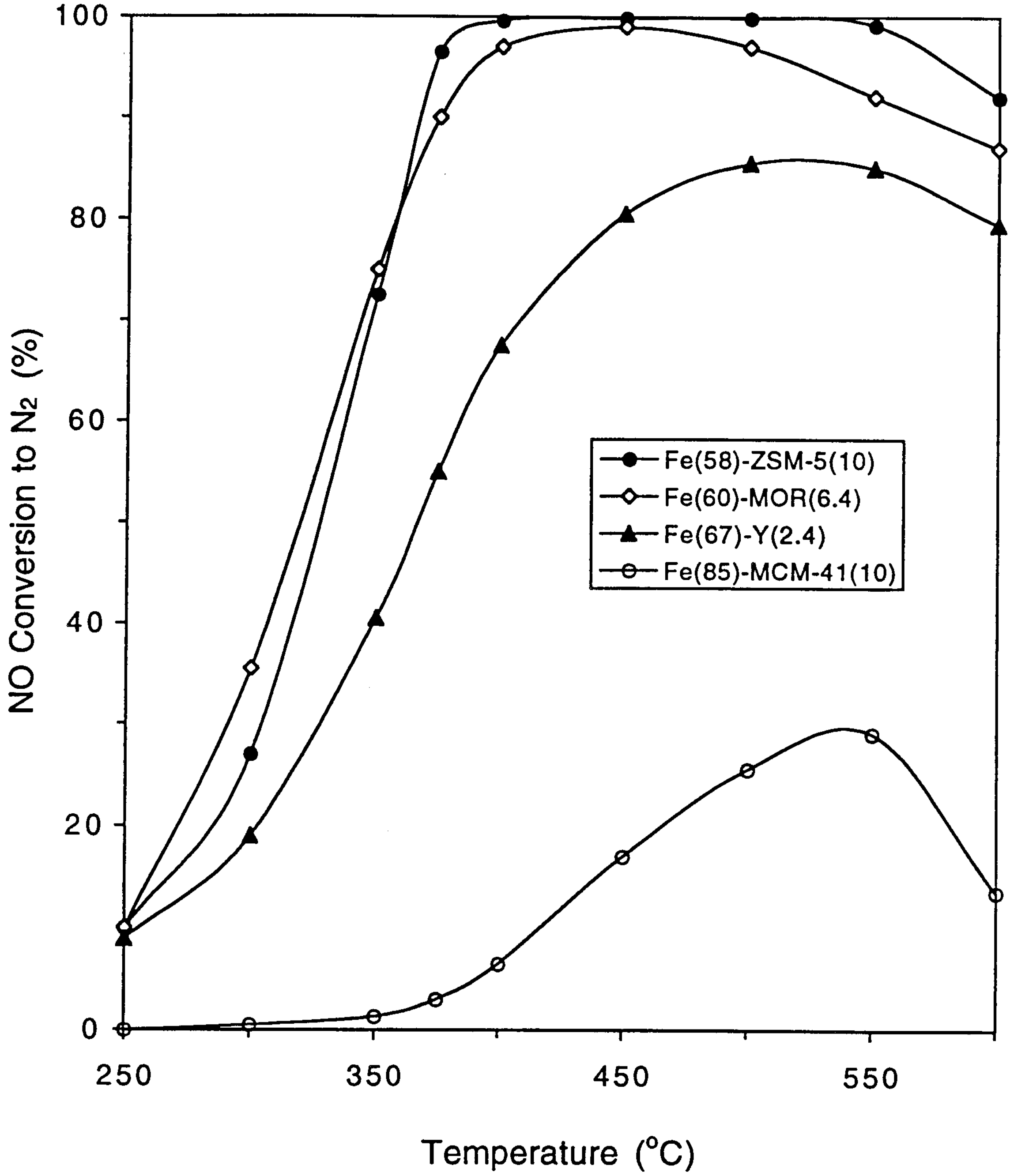
100
80
60
40
20
0
NO Conversion to N₂ (%)
250
350
450
550
Temperature (°C)
Fe(58)-ZSM-5(10)
Fe(60)-MOR(6.4)
Fe(67)-Y(2.4)
Fe(85)-MCM-41(10)

FIG – 7

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/14830

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) :B01J 29/072, 29/40, 29/42, 29/46
US CL : 502/64, 66, 71, 74, 77
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 502/64, 66, 71, 74, 77

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5,543,125 A (UCHIDA et al.) 06 August 1996, col. 18-20.	1-20
A	US 5,520,895 A (SHARMA et al.) 28 May 1996, col. 17-18.	1-20
X	US 5,116,586 A (BAACKE et al.) 26 May 1992, see the examples and col. 2, lines 28-38.	1-20
X	US 5,271,913 A (IIDA et al.) 21 December 1993, see the claims.	1-20

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

*	Special categories of cited documents:
"A"	document defining the general state of the art which is not considered to be of particular relevance
"E"	earlier document published on or after the international filing date
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O"	document referring to an oral disclosure, use, exhibition or other means
"P"	document published prior to the international filing date but later than the priority date claimed
"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&"	document member of the same patent family

Date of the actual completion of the international search
27 AUGUST 2000

Date of mailing of the international search report
06 SEP 2000

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