Catalysis Today 55 (2000) 281–290

www.elsevier.com/locate/cattod

Testing zeolite SCR catalysts under protocol conditions for NO_x abatement from stationary emission sources

Bala Ramachandran, Richard G. Herman *, Sukwon Choi, Harvey G. Stenger, Charles E. Lyman, John W. Sale

Energy Research Center and Zettlemoyer Center for Surface Studies, Sinclair Laboratory, 7 Asa Drive, Lehigh University, Bethlehem, PA 18015, USA

Abstract

In developing higher efficiency catalysts for NO_x abatement from stationary emission sources utilizing selective catalytic reduction (SCR), comparison test conditions, including gas composition and gas flow rates, are needed that approximate industrial operating conditions. Standard tests will be fuel-dependent, i.e. typical flue gas from a coal-fired electrical utility plant might consist of 150–1000 ppm NO, 5% O_2, 13% CO_2, 8% H_2O, and 200–2000 ppm SO_2, while that from a plant utilizing natural gas would contain appreciably more O_2, less NO, and very low SO_2. For low temperature catalysts developed for placement after the electrostatic precipitator (ESP) and desulfurization units, flue gas would essentially be dust- and sulfur-free. Protocols are given for comparison testing of NO_x abatement catalysts using ammonia as the reductant. These test conditions are used in the comparison of Cu-, Fe-, and V- containing ZSM-5 and mordenite catalysts. It was found that initial NO conversion levels were lower than those achieved after a thermal pretreatment of the catalysts. Under the reaction conditions employed, moisture was an inhibitor for the Fe- and V-containing catalysts but was a promoter for the Cu-mordenite catalyst. The V-ZSM-5 catalyst exhibited a stable activity for NO reduction in the presence of H_2O and SO_2 but rapid deactivation was observed in the presence of 10 ppm SO_3. ©2000 Elsevier Science B.V. All rights reserved.

Keywords: Nitric oxide; NO abatement; Zeolites; Selective catalytic reduction; Emissions control

1. Introduction

Nitrogen oxide (NO_x) emissions in the US have been regulated by the US federal government since 1970 under the Clean Air Act (CAA). Title I of the amendments (CAAA) to the act (1990) required states to initiate reasonably available control technology (RACT) standards, based on Environmental Protection Agency (EPA) guidelines, toward achieving required air quality standards. In 1990, EPA estimated that electric utilities accounted for 60% of stationary source NO_x emissions [1]. Title IV of the CAAA, referred to as the Acid Rain Program, set a two-phase schedule, dependent on type of burner, for reducing NO_x emissions by up to 2 million tonnes/yr from designated coal-fired electric utility boilers. Phase I compliance was required by 1 January 1996, with Phase II compliance to be achieved by 2000.

1.1. Approaches to NO_x abatement

Among the technologies being developed, low NO_x burners that minimize thermal formation of NO_x by reducing combustion temperatures and controlling

---

* Corresponding author. Fax: +1-610-758-6555.
E-mail address: rgh1@lehigh.edu (R.G. Herman).

PII: S0920-5861(99)00252-7

flame stoichiometry make an important contribution, and under well-tuned optimized conditions, NO_x reductions of 40% or more can be achieved. However, adverse side effects of this procedure include increased quantities of carbon in the fly ash, larger CO emissions, and corrosion and slagging problems due to localized reducing environments [1]. In general, exhaust gas treatment methods are preferred for NO_x control because they provide for wider range of utility system loads than possible with combustion controls.

Among the methods being investigated to *clean exhaust gas streams of* NO are:

1. Injection of methanol into flue gases to convert NO to NO_2 [2] (potential by-products are CO and CH_2O), which is removed in a 'liquid-modified' wet limestone SO_2 scrubber [3]. Various configurations of the latter step include using a spray dryer with aqueous slurried lime with NaOH as an additive [4–7], where the NO_x removal rate is 35–50% [5–7].
2. Enhanced NO_x removal in wet scrubbers using redox Fe^{2+} chelates has been demonstrated at the Miami Fort Pilot Plant (Ohio), achieving 75% NO_x removal (≈50% in the first stage burner and an additional 50% in the chelate stage) [8].
3. Use of adsorbents, e.g. utilizing γ-alumina impregnated with sodium carbonate in a fluidized bed, where it was found that SO_2 must be present for efficient NO_x removal; when $SO_2/NO_x > 4$ in the flue gas, the NO_x removal efficiency attained was 70–75% [9].
4. Selective non-catalytic reduction (SNCR), using aqueous urea or ammonia injection into the furnace at ≈875–1150°C, can be used to reduce NO_x level by 30–75%. However, >90% NO_x reduction was reported for the NO_x OUT® process under particular conditions [10,11], e.g. at 980°C at refineries and petrochemical plants [12].
5. Concentration of NO followed by SNCR, such as adsorption of NO on supported MgO that is subsequently heated in a regeneration cycle in a reducing atmosphere to reduce NO to N_2, which has attained ≈30% NO_x removal under steady-state operation [13].
6. Selective catalytic reduction (SCR) of NO using ammonia (or other compounds such as hydrocarbons) as the reductant to form nitrogen and water. The principal types of catalysts that have been investigated for SCR are: (a) base metal oxide catalysts, e.g. those containing vanadia, (b) metal ion exchanged zeolites, e.g. Cu-ZSM-5, and (c) supported noble metal catalysts, e.g. Pd/Al_2O_3.

While NO reduction with NH_3 can occur as shown in Eq. (1), both the SCR and SNCR processes are carried out in the presence of air (O_2), as represented by Eq. (2), with the reaction represented by Eq. (3) occurring as a side reaction that is favored by excess oxygen. While N_2O is a non-regulated greenhouse gas, it is more desirable to form only N_2 as the reduction product. In the presence of oxygen, NO can be oxidized to NO_2 (favored by lower reaction temperatures), but NO_2 is also reduced by NH_3, as represented by Eq. (4).

$$6NO + 4NH_3 \Rightarrow 5N_2 + 6H_2O \tag{1}$$

$$4NO + 4NH_3 + O_2 \Rightarrow 4N_2 + 6H_2O \tag{2}$$

$$4NO + 4NH_3 + 3O_2 \Rightarrow 4N_2O + 6H_2O \tag{3}$$

$$2NO_2 + 4NH_3 + O_2 \Rightarrow 3N_2 + 6H_2O \tag{4}$$

Since these reactions do not typically go to completion, the composition of the gas stream (flue gas) must be monitored and the quantity of NH_3 reductant added must be tightly controlled to minimize slip into the exhaust stream. Research in both SCR and SNCR had been reviewed up to 1987 by Bosch and Janssen [14]. More recently, catalytic removal of NO_x has been reviewed by Pârvulescu et al. [15].

In general, SCR is the only large scale process available that can remove >90% NO_x contained in combustion system exhaust gas [1]. The catalyst that is used in most large scale applications is a combination of V_2O_5 and TiO_2 (sometimes promoted with WO_3 or MoO_3) supported on or in a monolith or wire screen plate), where NH_3 is used as the reductant. However, this catalyst has a rather narrow temperature range of utility (typically 300–400°C [16,17]), with WO_3 added to stabilize the catalyst up to 450°C [16] or broaden the temperature window to lower reaction temperatures [18]. It has also been reported that WO_3 and MoO_3 make the catalyst more poison-resistant [18,19].

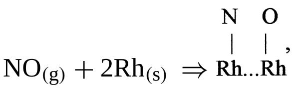
New catalysts that operate at higher and lower temperatures are desired to provide flexibility for placement of the reactor in the unit train. It is noted that a zeolite in the form of extruded monoliths has been utilized for SCR in the configuration of a five catalyst layer train in a TVA high sulfur coal pilot plant with a reactor temperature of 425°C [20]. In addition, a replacement for ammonia is desired because there are severe federal and state restrictions on the storage and transportation of liquid ammonia, particularly in NJ and CA, and NH_3 slippage to the exhaust gas exiting the stack occurs and has to be tightly monitored. Replacement of ammonia by hydrocarbon reductants is being investigated, but these reductants generally require a higher reaction temperature than ammonia. With all catalysts at lower temperatures, NH_3 slippage leads to formation of ammonium bisulfate that can plug the reactor.

1.2. Mechanistic features to be considered for NO abatement

Development of new catalysts or improvements of existing catalysts require a firm knowledge of the chemistry of NO and the functioning of the catalyst components in activating and reducing NO to N_2 and O_2. Nitric oxide, NO, is thermodynamically unstable with respect to its decomposition to elements,

$$2NO_{(g)} \Rightarrow N_{2(g)} + O_{2(g)} \quad \Delta G_{298\,K} = -173\,kJ/mol \tag{5}$$

and yet it is kinetically stable without a suitable catalyst. Among the few catalysts for the above reaction are Rh, Pd, and Pt that are often employed in automotive exhaust three-way catalysts. Decomposition of NO over these noble metals begins with dissociative chemisorption [21–23], e.g.



$$NO_{(g)} + 2Rh_{(s)} \Rightarrow \overset{\overset{N}{|}}{\mathbf{Rh}}\ldots\overset{\overset{O}{|}}{\mathbf{Rh}}, \tag{6}$$

followed by recombination of the chemisorbed atoms to form N_2 and O_2. The latter process occurs only at very high temperatures [21–23], and in real catalytic conditions the surface oxygen still has to be removed by reduction. The effective catalytic action of $Rh^{\bullet}$ is due to its ability to attack both ends of the NO molecule, to the weak bonding of the surface nitride, and to the reducibility of surface O. Rh catalysts by themselves do not work in excess O_2 because bulk oxides are formed irreversibly with loss of catalytic activity.

Ever since Iwamoto et al. [24,25] found that Cu-ZSM-5 zeolites exhibited higher catalytic activity for NO decomposition than any zeolite catalysts studied previously, NO decomposition studies have mainly been centered on this zeolite. Early insight into the NO decomposition reaction over this catalyst was provided by Li and Hall [26,27] and by Iwamoto and Hamada [28]. For example, in flowing 2.1% NO/He ($GHSV \approx 2000\,h^{-1}$), 60–70% of the NO was converted mainly to N_2 and O_2 in the 425–575°C range (maximum at ≈500°C) over fully exchanged Cu-ZSM-5 zeolite [25]. By comparison, 87% exchanged Cu-mordenite exhibited maximum NO decomposition at 550°C, while the maximum activity of 64% exchanged Cu-ferrierite occurred at ≈600°C. It was proposed that the temperature needed to achieve NO decomposition was determined by the desorption temperature of the oxygen formed via NO decomposition [25]. After room temperature NO adsorption, temperature programmed desorption (TPD) (in flowing He) indicated that NO began to desorb at ≈60°C and exhibited a maximum desorption rate at ≈120°C. However, O_2 did not begin to desorb from Cu-ZSM-5 until 300°C, with a desorption maximum at 380°C, while Cu-ferrierite exhibited a maximum O_2 desorption at ≈410°C [25]. It was shown that at 500°C, O_2 and H_2O inhibit the NO decomposition reaction to different degrees, but the inhibition was reversible [26].

Similar TPD experiments were carried out with a Co-A zeolite after NO adsorption at ambient temperature [29,30]. While maintaining a *dynamic* vacuum during TPD, NO began to desorb at ≈50°C and exhibited a broad maximum in the TPD curve at 110–160°C. While small quantities of N_2 and N_2O were observed, no O_2 desorption was observed up to the maximum temperature of 350°C that was utilized in these studies [30]. Therefore, for efficient NO conversion at low reaction temperatures, a means to achieve removal of oxygen from the surface of the active zeolite catalysts must be implemented, e.g. by reduction. Reduction of oxygen results in the formation of water as a product. However, it is generally accepted that catalysts under study for low temperature NO reduction, as well as decomposition, exhibit only low activity when water vapor is present in the reactant stream because of competitive adsorption.

Table 1
Typical concentrations and ranges of emissions in flue gases from efficient electric power generation plants as a function of the fuel utilized

	Natural gas	Fuel oil[a]	Coal
NO_x (ppm)	25–160	100–600	150–1000
SO_x (ppm)	Neg. (<0.5–20)	(1000) 200–2000	(400) 200–2000
CO_2 (%)	9 (5–12)	12 (12–14)	13 (10–15)
O_2 (%)	3–18	2–5	5 (3–5)
H_2O (%)	15 (8–19)	10 (9–12)	8 (7–10)
N_2	Balance	Balance	Balance

[a] Dependent on fuel oil, e.g. No. 6 fuel oil.

In previous literature reports, a wide variety of testing conditions have been used in the large number of investigations of NO abatement catalysts, and direct comparisons of results are usually impossible to make. Therefore, in the present work a protocol for testing catalysts is described that was based on typical flue gas compositions found at electric power plants. These compositions, tabulated in Table 1, can be used for comparison testing of catalysts for NO reduction.

2. Experimental

Reactor systems have been constructed for both powdered and pelleted laboratory-scale catalysts and for bench-scale and commercial monolith and plate-type catalysts. A schematic of the former quartz reactor system used in this work is shown in Fig. 1. It was found that the Drierite water removal column was not needed for accurate analyses, so this trap was not usually utilized.

Laboratory catalysts that were investigated included ZSM-5 zeolite catalysts prepared by ion exchange of 1/16 in. diameter (≈1/4 in. long) H-ZSM-5 pellets obtained from UOP and H-mordenite pellets of the same size obtained from Zeolyst. These pelleted catalysts contained an alumina binder. The mordenite itself had a Si/Al ratio of 6.4, while the pelleted catalyst has a Si/Al ratio of 5.1. The ion exchange of the catalysts was carried out from dilute aqueous solutions of $Cu(NO_3)_2$, $VOCl_3$, or $Fe(NH_3)_4(NO_3)_2$ at ambient temperature with continuous stirring, usually for 4–6 days. The filtered pellets were washed with distilled water, air-dried for 15 h, dried at 70°C for 4 h, and subsequently calcined at 500°C for 15 h. The metal loading of the catalysts was nominally 1.5–2.0 wt.% metal. The surface area of the calcined Cu-mordenite catalyst was 375 m^2/g.

Testing of the zeolite catalysts was carried out at approximately ambient pressure in a vertical downflow quartz tube reactor. The catalyst, generally 10 ml, was supported in the reactor on a porous glass fritted disc. The reaction conditions utilized in this study were the following:

$NO = 400$ ppm (dry basis)
$NH_3 = 400$ ppm (dry basis)
$O_2 = 5$ vol% (dry basis)
$CO_2 = 13$ vol% (dry basis)
$H_2O = 8$ vol% (wet basis)
$N_2 =$ balance.

Conversion vs reaction temperature testing of all catalysts was carried out once or twice in a dry gas mixture before injection of water was begun to determine the conversion/temperature relationship for the catalysts in a wet atmosphere. The usual procedure involved heating the catalyst to the highest reaction temperature, e.g. 500°C, and then sequentially lower the temperature and obtained steady-state conversions at each temperature.

Each of the first four gases were fed into the reactor gas manifold and controlled by a separate calibrated flowmeter. The NO, NH_3, and O_2 were utilized as mixtures in N_2, while CO_2 was added as the pure gas. When water was injected into the gas mixture, it was fed by means of an ISCO pump into the preheater zone prior to entering the reactor. The final gas hourly space velocity (GHSV) was 10,000 h^{-1} unless stated otherwise. Temperature of the catalyst was monitored by an axial thermocouple in the reactor. Total gas flow was monitored by a bubble meter. In the exit stream, NO was determined by a chemiluminescence detector and NH_3 was periodically monitored by an ion selective electrode.

3. Results

3.1. Activities of Cu-ZSM-5 and Cu-mordenite catalysts

The Cu-ZSM-5 catalyst is probably the most studied zeolite for NO reduction using a wide variety of reductants under a wide range of reaction conditions. In

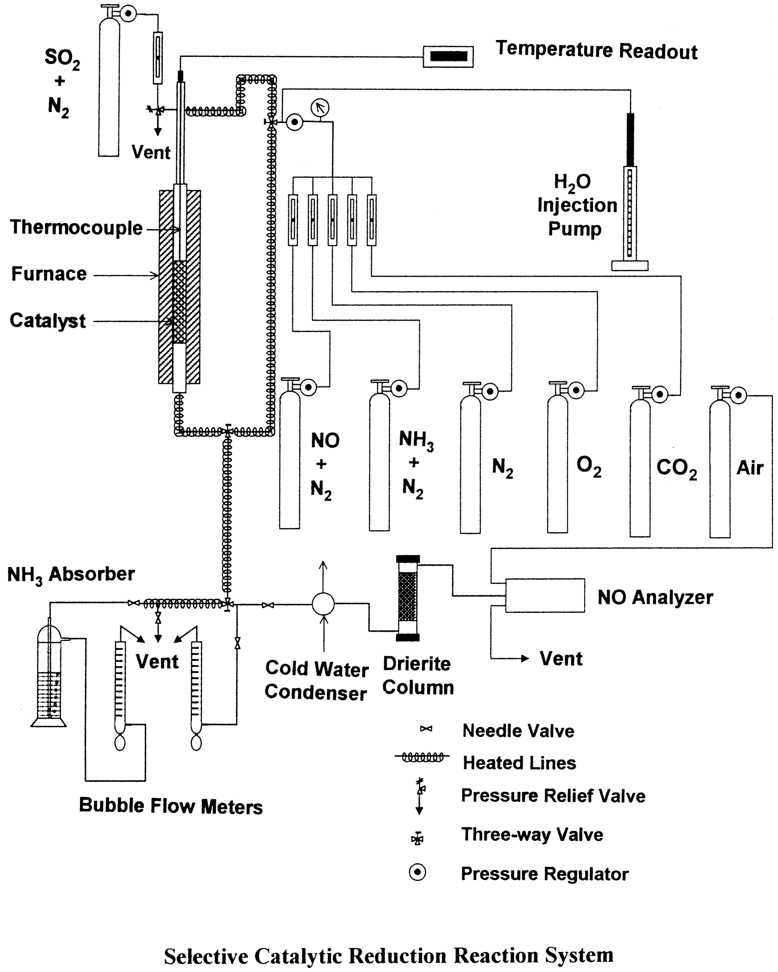


Fig. 1. Schematic of the continuous downflow selective catalytic reduction testing system for NO abatement catalysts.

contrast to most reported studies, the reactant mixture employed here contained oxygen and carbon dioxide, and in some cases moisture, in addition to nitric oxide and ammonia. Upon increasing the reaction temperature from 150 to 325°C, the conversion of NO from the standard reaction mixture containing moisture increased over the Cu-ZSM-5 until 100% conversion was achieved at 325°C, as shown in Fig. 2. It is noted that about 70% NO reduction was achieved at 190°C. Although only two data points are shown for the Cu-mordenite catalyst, very high NO conversion was also achieved in the presence of moisture with this catalyst at 250°C, as shown in Fig. 2.

A fresh portion of the Cu-mordenite catalyst was loaded into the reactor and tested for NO reduction in the absence of moisture. As shown in Fig. 2, without the presence of moisture in the reaction mixture, a very broad maximum in NO conversion as a function of reaction temperature was observed, and the activity of this catalyst never exceeded 60% NO conversion at any temperature. After this test, the catalyst was cooled to ambient temperature and stored overnight in the reactor under dry air.

The effect of water vapor on the activity of this Cu-mordenite catalyst was probed further by starting and stopping the injection of water into the inlet

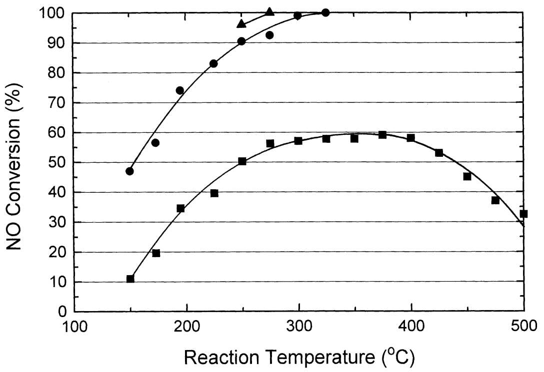


Fig. 2. Catalytic activities of the Cu-ZSM-5 (●) and Cu-mordenite (▲) catalysts for NO removal from a gas mixture (dry basis) of NO = 400 ppm, NH_3 = 400 ppm, O_2 = 5 vol%, CO_2 = 13 vol%, with balance of N_2, with moisture added to give H_2O = 8 vol% and a final GHSV = 10,000 h^{-1}. Also shown is the activity curve of the Cu-mordenite (■) catalyst in the absence of moisture in the reactants.

reaction mixture. The testing was initiated by establishing the flow of reactants in the absence of moisture and heating the catalyst to 275°C. The NO conversion was 96%, which was much higher than that observed in the first dry test, as shown in Fig. 2. Moisture was added to 8 vol%, and the activity gradually increased to nearly 100% NO conversion, as shown in Fig. 3. Maintaining the presence of moisture, the temperature was lowered to 250°C, and the NO conversion level decreased from 100 to 96%. Upon briefly stopping the injection of water, the activity decreased, but it increased upon again adding moisture to the reactants. This behavior was repeatable, as shown in Fig. 3. After about 1050 min of testing of the Cu-mordenite catalyst, the final removal level of NO was over 96% in the gas stream containing 8 vol% moisture.

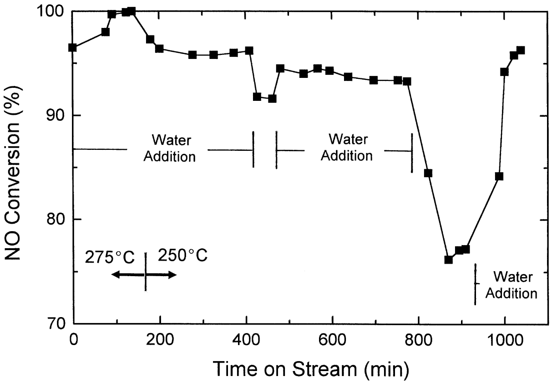


Fig. 3. Catalytic activity of the Cu-mordenite (■) catalyst for NO removal from a gas mixture (dry basis) of NO = 400 ppm, NH_3 = 400 ppm, O_2 = 5 vol%, CO_2 = 13 vol%, with balance of N_2. Moisture was added to give H_2O = 8 vol% and a final GHSV = 10,000 h^{-1}. Testing was begun at 275°C and then the temperature was decreased to 250°C. The addition of moisture was briefly stopped after 410 and 790 min on steam and then restarted.

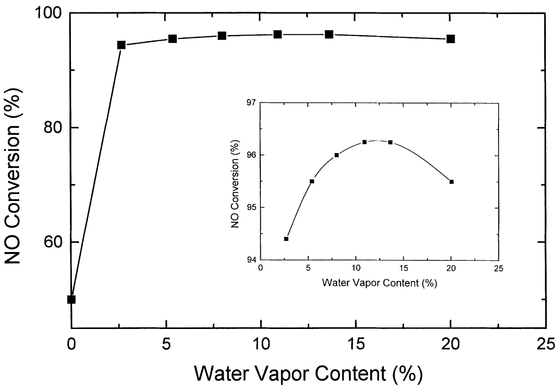


Fig. 4. Activity of the Cu-mordenite (■) catalyst for NO removal at 250°C as a function of the moisture content of a gas mixture (dry basis) of NO = 400 ppm, NH_3 = 400 ppm, O_2 = 5 vol%, CO_2 = 13 vol%, with balance of N_2 (GHSV = 10,000 h^{-1}).

The Cu-mordenite catalyst showed a pronounced positive effect of having moisture in the gas mixture. It was observed that the quantity of water vapor present did not significantly alter the NO conversion level observed at 250°C, as long as it was present (Fig. 4). However, the effect was systematic as shown by the figure insert.

3.2. Activities of H-mordenite and Fe-mordenite catalysts

For comparison, the H-mordenite as received and an Fe-mordenite were tested for NO reduction activity under the same reaction conditions as used for the Cu-zeolite catalysts. In the absence of moisture, the Fe-mordenite catalyst exhibited activity (Fig. 5) that was very similar to that observed with the Cu-mordenite catalyst (Fig. 2). Again a broad maximum in NO conversion occurred as the reaction temperature was increased, but the high activity extended to higher temperatures than observed with the Cu-mordenite catalyst. The H-mordenite catalyst exhibited similar activity at low temperature, but the

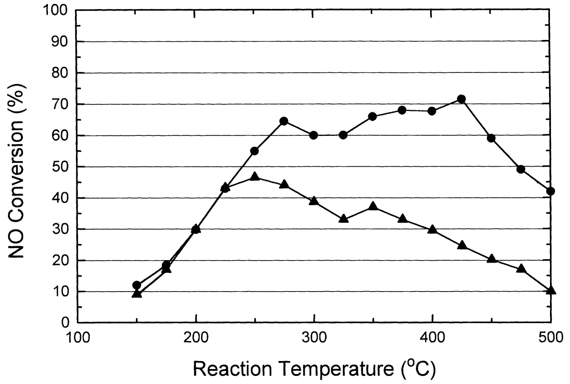


Fig. 5. Catalytic activities of the Fe-mordenite (●) and H-mordenite (▲) catalysts for NO removal from a gas mixture (dry basis) of NO = 400 ppm, NH_3 = 400 ppm, O_2 = 5 vol%, CO_2 = 13 vol%, with balance of N_2 (GHSV = 10,000 h^{-1}) as functions of the reaction temperature.

NO conversion steadily decreased as the temperature was increased above 250°C, as shown in Fig. 5.

These same catalysts were retested using the identical reaction conditions. At 300°C in the dry reactant mixture, the Fe-mordenite catalyst exhibited a NO conversion level of 84% (Fig. 6), which was appreciably higher than the 60% conversion initially observed (Fig. 5). Similarly, the H-mordenite catalyst exhibited an enhanced activity upon retesting at 250°C, increasing from 47 to 69% NO reduction. Upon addition of moisture to the inlet gas stream to 8 vol% after the first data points at time on stream = 0, the activities of both catalysts decreased, at shown in Fig. 6. Upon increasing the temperature of the Fe-mordenite catalyst from 300 to 325°C about 25 min after the water addition had been initiated, the activity increased to approximately the level observed before moisture was added to the gas mixture, i.e. ≈85%. Terminating the water addition over this catalyst after about 325 min on stream led to an increase in the NO conversion to 99%. The effects of moisture on the conversion of NO over the H-mordenite catalyst followed the same trends but with slower response times, as shown in Fig. 6 (▲).

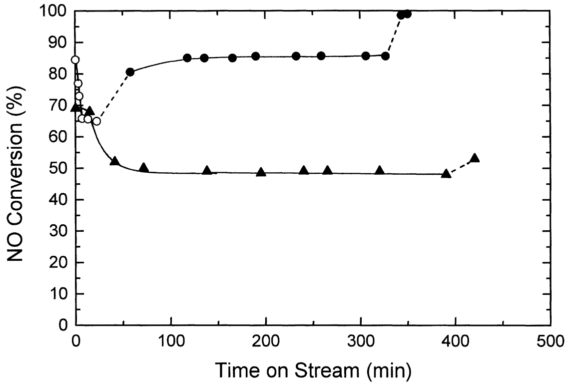


Fig. 6. Catalytic activities of the Fe-mordenite catalyst at 300°C (○) and 325°C (●) for NO reduction, where the initial and final data points are in the absence of moisture. The reactant gas mixture (dry basis) consisted of NO = 400 ppm, NH_3 = 400 ppm, O_2 = 5 vol%, CO_2 = 13 vol% prior to the addition of 8 vol% H_2O, with balance of N_2 (GHSV = 10,000 h^{-1}). Also shown is the activity of the H-mordenite (▲) catalyst for NO removal for the same reaction conditions at 250°C, where the first and last data points were obtained with no moisture present in the reactant gas mixture.

3.3. Activity of V-ZSM-5 and V-mordenite catalysts

Vanadium-containing zeolite catalysts were prepared and tested for NO reduction activity using the standard testing conditions with and without 8 vol% moisture present. Under dry conditions, a V-ZSM-5 catalyst exhibited 65% NO conversion at 175°C and 79% conversion at 200°C. Upon addition of moisture to the reactant stream, the NO conversion levels decreased to 49.5 and 64% at 175 and 200°C, respectively. Using a fresh batch of the V-ZSM-5 catalyst with a moisture-containing gas mixture, it was observed that upon sequentially increasing the reaction temperature, a maximum of NO conversion was obtained at 225°C, as shown in Fig. 7. Upon retesting, the activity of the catalyst increased more rapidly as the temperature was sequentially increased, reaching 98% NO conversion at 200°C. The V-mordenite catalyst exhibited an activity curve that was significantly shifted to higher temperatures, and no further investigation of this catalyst was carried out.

The deactivation behavior of the V-ZSM-5 catalyst was studied in the presence of 400 ppm SO_2. With a reactant mixture containing 400 ppm NO and 400 ppm NH_3, plus O_2, CO_2, and N_2, but no moisture, the initial activity at 200°C was 80.5% NO reduction, as shown in Fig. 8. Upon addition of 8 vol% moisture to the gas stream, the NO conversion level immediately decreased to about 50% but gradually increased to approximately 60%. Periodic removal of SO_2 from the

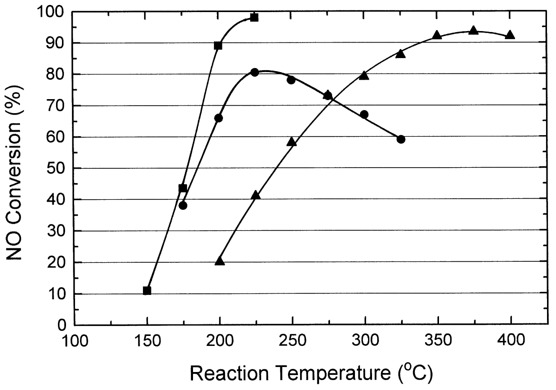


Fig. 7. Catalytic activities of the V-ZSM-5 catalyst during a first temperature sweep (●) and during a second test (■) as a function of the reaction temperature for NO removal from a gas mixture (dry basis) of NO = 400 ppm, NH_3 = 400 ppm, O_2 = 5 vol%, CO_2 = 13 vol%, with balance of N_2 and moisture added to give H_2O = 8 vol% and a final GHSV = 10,000 h^{-1}. Also shown is the activity curve of the V-Mor catalyst (▲) under the same wet reaction conditions.

reactants hardly affected the NO removal level (open circles in Fig. 8), with usually only a slight increase in the NO conversion.

The effect of moisture on the activity of the catalyst was more pronounced. Periodic termination of water injection into the SO_2-containing gas mixture showed that over 80% NO reduction was immediately achieved in the absence of moisture (solid triangles in Fig. 8), indicating no loss of activity under dry reaction conditions and that the inhibition of NO conversion by water vapor was reversible.

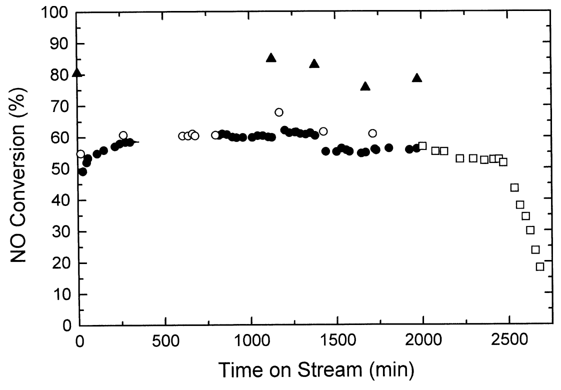


Fig. 8. Catalytic activities for NO removal over a second V-ZSM-5 catalyst at 200°C in the presence of 400 ppm SO_2 and 8 vol% H_2O vapor (●) in a gas mixture (dry basis) of NO = 400 ppm, NH_3 = 400 ppm, O_2 = 5 vol%, CO_2 = 13 vol%, with balance of N_2 as a function of time on stream (GHSV = 10,000 h^{-1}). There was little effect on the NO conversion level when SO_2 was removed from the reactant stream (○). About 80% NO conversion was observed when the addition of both SO_2 and H_2O vapor was terminated (▲). After 1975 min on stream, 10 ppm SO_3 was added to the reaction mixture containing both H_2O and SO_2 (□).

After 1400 min on steam, a reactor malfunction results in a decrease of about 5% in NO conversion, but the intrinsic activity appeared to be steady both before and after the malfunction. Fig. 8 demonstrates that the activity was stable until 10 ppm SO_3 was continuously added to the reactant gas mixture. The SO_3 addition was achieved by replacing the injection of water via an ISCO pump with injection of an appropriate concentration of dilute sulfuric acid solution (to give 10 ppm SO_3) using a different ISCO pump. Upon exposure to SO_3, gradual deactivation of the V-ZSM-5 catalyst occurred for about 8 h; thereafter a rapid deactivation was observed, as is evident in Fig. 8.

4. Discussion

In the absence of moisture, the initial activities for NO reduction were Cu-mordenite ≈ Fe-mordenite > H-mordenite, see Figs. 2 and 5. The dependence of NO conversion on the reaction temperature exhibited a broad maximum in activity as expected. Above 400°C, the activity declined significantly as the temperature was increased. This is consistent with NH_3 oxidation to NO at the higher reaction temperatures.

Using NO conversion data below 300°C, Arrhenius plots were used to determine the apparent activation energies of the NO reduction reaction with NH_3. The values obtained were in the range of 9.5–12 kcal/mol. This is consistent with the values of 12.9 and 10.2 kcal/mol previously obtained with Cu-mordenite [31] and Cu-ZSM-5 [32], respectively.

4.1. Higher activity of catalysts tested a second time

The catalysts tested in this study were calcined at 500°C for 15 h after being prepared. However, they were stored in sample bottles for short periods of time and loaded into the reactor under ambient conditions prior to being tested. Thus, some degree of hydration could occur before the testing. In all cases, the initial temperature sweeps for catalyst screening under dry reaction conditions produced lower catalytic activities than second and third sweeps of the same catalyst. This was also observed with the V-ZSM-5 catalyst where testing was initiated with a moisture-containing reactant gas mixture (Fig. 7).

Similar behavior was observed with a Cu-Y zeolite, where it was observed that in situ dehydration at 250°C for 3 h in flowing argon, pretreatment in flowing 5% NH_3/Ar at 400°C for 3 h followed by ambient temperature oxidation in dry air, or treatment in flowing NO/NH_3/Ar at 200°C for 3 h followed by ambient temperature oxidation in dry air produced a significant increase in NO conversion using $[NO] = [NH_3] = 1500$ ppm [33]. Thus, our subsequent studies with zeolite catalysts, to be described elsewhere, have utilized a moisture-free test pretreatment procedure.

4.2. Roles of oxygen and moisture

It has been previously reported that the presence of oxygen inhibits NO *decomposition*, e.g. over Cu/ZSM-5 [26,27,34], because of competitive adsorption of oxygen on the catalytically active sites [35]. In contrast, the *reduction* of NO is negligible in the absence of oxygen in the reactant mixture over zeolite catalysts [36–38]. Thus, oxygen plays an important role [14] in promoting the reduction of NO by NH_3, as represented by Eq. (2). In the absence of ammonia, it has also been reported that zeolites, e.g. H-ZSM-5 and H-mordenite catalysts [36,37,39,40], are capable of oxidizing NO to NO_2 in the presence of oxygen. This has also been shown with Cu-ZSM-5 catalysts [41]. However, the degree of NO conversion decreased as the NO concentration in the reactant decreased and a minimum in conversion was usually observed at 200°C [39]. Exchange of the H-mordenite with Cu poisoned the NO oxidation reaction but promoted the NO reduction with NH_3 reaction in the presence of O_2 [36]. Therefore, the strongly acid catalysts contain oxidation sites, but reduction of NO is greatly enhanced by oxygen, as well as by replacement of the acid sites by transition metal cations such as Cu.

In the presence of moisture at about 250°C, the activity order was Cu-mordenite > Cu-ZSM-5 > Fe-mordenite ≈ V-mordenite > H-mordenite. The effect of the presence of moisture was different over the different catalysts, as will be noted below. It is generally observed that water vapor inhibits NO decomposition [42] and NO reduction with NH_3 [15] over Cu-zeolites to some extent. However, Figs. 3 and 4 show that the level of NO conversion over Cu-mordenite was higher in the presence of H_2O than in the dry reactant gas mixture. Similar behavior was observed with a Cu-ZSM-5 catalyst when moisture was added to a reactant mixture containing 0.6% NO, 0.6% NH_3, and 3.3% O_2 [43]. With additions of H_2O corresponding to 3 and 9%, enhancements in NO conversion to N_2 on the order of 10–20% were achieved in the reaction temperature range of 200–300°C [43]. For NO reduction with propane (1000 ppm NO, 500 ppm propane, 2% O_2) over a Sn-ZSM-5 catalyst, addition of 5.7% H_2O increased the NO conversion by about 25% at 400°C [44], where the water effect was reversible. No speculation of the cause of this behavior with these catalysts has been provided, and this is an area where systematic study needs to be carried out.

4.3. Vanadium zeolite catalysts for NO reduction

It was shown that the V-ZSM-5 catalyst achieved appreciable NO conversion levels at low reaction temperatures in the presence of moisture. Water inhibited the NO reduction reaction, but this effect was reversible (Fig. 8). In the presence of 8% moisture, 400 ppm SO_2 caused little additional inhibition of the activity, and the activity of the catalyst was maintained. In contrast, addition of 10 ppm SO_3 to the reactant gas mixture caused a large, but delayed, decrease in the NO conversion. This is consistent with formation of ammonium (bi)sulfate on the catalyst surface and eventually plugging of the zeolite pores.

5. Conclusions

Protocol reaction conditions have been proposed for comparing catalysts for stationary power plant NO abatement applications. To achieve high, steady-state, reproducible activity for NO reduction with NH_3, transition metal zeolite catalysts should be thermally pretreated. Under the reaction conditions utilized, it was shown that moisture was a promoter for NO reduction over Cu-mordenite, while it was an inhibitor over H-, Fe-, and V-zeolite catalysts. The V-ZSM-5 catalyst is a promising catalyst for NO reduction in the presence of SO_2, but it is poisoned by SO_3. The later probable deactivation mechanism of ammonium (bi)sulfate formation would affect all low temperature catalysts when both NH_3 and SO_3 are present.

Acknowledgements

This research was supported in part by Allegany Power Systems, Ontario Hydro, Pennsylvania Power and Light Co., GPU Generation, Inc., and Southern Company Services, the Pennsylvania Infrastructure Technology Alliance, and Lehigh University.

References

[1] J.E. Staudt, Hazmat World, May 1993.
[2] R.K. Lyon, J.A. Cole, J.C. Kramlich, S.L. Chen, Combustion and Flame 81 (1990) 30.
[3] J.N. Pont, A.B. Evans, G.C. England, R.K. Lyon, W.R. Seeker, U.S. DOE-PETC Contractors' Review Meeting, Pittsburgh, PA, 27–30 July 1992.
[4] K. Felsvang, P. Morsing, P. Veltman, EPA/EPRI Symp. on Flue Gas Desulfurization, New Orleans, LA, 1–4 November 1983.
[5] J.M. Markussen, J.T. Yeh, C.J. Drummond, AIChE Spring National Meeting, New Orleans, LA, 6–10 April 1986.
[6] H.S. Huang, P.S. Farber, C.D. Livengood, J.T. Yeh, J.M. Markussen, C.J. Drummond, AIChE Spring National Meeting, Houston, TX, 29 March to 2 April 1987.
[7] J.M. Markussen, H.W. Pennline, U.S. DOE-PETC Contractors' Review Meeting, Pittsburgh, PA, 27–30 July 1992.
[8] K. Smith, L. Benson, S. Tseng, M. Babu, P. Bergman, Proc. 9th Int. Pittsburgh Coal Conf., Pittsburgh, PA, 1992, p. 895.
[9] J.L. Haslbeck W.T. Ma, Proc. 9th Int. Pittsburgh Coal Conf., Pittsburgh, PA, 1992, p. 848.
[10] M.L. Lin, D.V. Diep, L. Dubin, Nalco Fuel Tech. Bulletin NFT-26, 1991.
[11] M.L. Lin, D.V. Diep, L. Dubin, Proc. 8th Int. Pittsburgh Coal Conference, Pittsburgh, PA, 1991.
[12] M.L. Lin, J.R. Comparato, W.H. Sun, Div. Pet. Chem., ACS 39 (1994) 181, Preprints.
[13] S.G. Nelson, D.A. Van Stone, S.G. Nelson Jr., Proc. 9th Int. Pittsburgh Coal Conf., Pittsburgh, PA, 1992, p. 901.
[14] H. Janssen, F Bosch, Catal. Today 2 (1988) 369.
[15] V.I. Pârvulescu, P. Grange, B. Delmon, Catal. Today 46 (1998) 233.
[16] R.M. Heck, J.M. Chen, B.K. Speronello, L. Morris, ACS Symp. Ser. 552 (1994) 215.
[17] H. Gutberlet, B. Schallert, Catal. Today 16 (1993) 207.
[18] J.P. Yang, R.T. Chen, Appl. Catal. A 80 (1992) 135.
[19] E. Hums G.W. Spitznagel, Div. Pet. Chem., ACS 39 (1994) 130, preprint.
[20] C. Huang, J. Hargis, L. Fuller, R. Mallory, J. Jarvis, B. Stapper, E. Cichanowicz, Proc. EPA/EPRI Joint Symp., 1993, 20pp.
[21] R.M. Comrie, C.M. Lambert, Surface Sci. 46 (1974) 61.
[22] G. Bonzel, H.P. Pirug, J. Catal. 50 (1977) 64.
[23] D. Lorimer, A.T. Bell, J. Catal. 59 (1979) 223.
[24] M. Iwamoto, H. Furukawa, S. Kagawa, in: Y. Murakami (Ed.), New Developments in Zeolite Science Technology, Elsevier, Amsterdam, 1986, p. 943.
[25] M. Iwamoto, H. Yahiro, K. Tanda, in: R. Inui (Ed.), Successful Design of Catalysts, Elsevier, Amsterdam, 1988, p. 219.
[26] Y. Li, W.K. Hall, J. Phys. Chem. 94 (1990) 6145.
[27] Y. Li, W.K. Hall, J. Catal. 129 (1991) 202.
[28] M. Hamada, H. Iwamoto, Catal. Today 10 (1991) 57.
[29] K. Klier, R.G. Herman, S. Hou, Proc. Eighth Annual Coal Preparation, Utilization, and Environmental Control Contractors Conference, U.S. Department of Energy, Pittsburgh Energy Technology Center, 1992, p. 593.
[30] K. Klier, R.G. Herman, S. Hou, Zeolites and related microporous materials: state of the art 1994, in: J. Weitkamp, H.G. Karge, H. Pfeifer, W. Holderich (Eds.), Studies in Surface Science and Catalysis, Elsevier, Amsterdam, vol. 84, 1994, p. 1507.
[31] I.S. Nam, J.W. Eldridge, J.R. Kittrell, Catalysis 1987, in: J.W. Ward (Ed.), Studies in Surface Science and Catalysis, Elsevier, Amsterdam, vol. 38, 1988, p. 589.
[32] T. Komatsu, M. Nunokawa, I.S. Moon, T. Takahara, S. Namba, T. Yashima, J. Catal. 148 (1994) 427.
[33] W. Hwang, S.-J. Wang, Appl. Catal. B, Environ. 5 (1995) 187.
[34] M. Iwanoto, H. Yahiro, K. Tanda, N. Mizuno, Y. Mine, S. Kagawa, J. Phys. Chem. 95 (1991) 3727.
[35] J.W. Hightower, D.A. Van Leirsbung, in: R.L. Klimish, J.G. Larson (Eds.), The Catalytic Chemistry of Nitrogen Oxides, Plenum Press, London, 1975, p. 63.
[36] J.G.M. Brandin, L.A.H. Anderson, C.U.I. Odenbrand, Catal. Today 4 (1989) 187.
[37] D.M. Sill, G. Lukyanov, J.L. D'Itri, W.K. Hall, J. Catal. 153 (1995) 265.
[38] M. Richter, R. Eckelt, B. Parlitz, R. Fricke, Appl. Catal. B, Environ. 15 (1998) 129.
[39] C.U.I. Odenbrand, L.A.H. Anderson, J.G.M. Brandin, S. Järas, Catal. Today 4 (1989) 155.
[40] I. Halasz, A. Brenner, K.Y.S. Ng, Catal. Lett. 34 (1995) 151.
[41] M. Shelef, C.N. Montreuil, H.W. Jen, Catal. Lett. 26 (1994) 277.
[42] M. Shelef, Chem. Rev. 95 (1995) 209.
[43] J.A. Sullivan, J. Cunningham, M.A. Morris, K. Keneavey, Appl. Catal. B, Environ. 7 (1995) 137.
[44] Y. Hirao, C. Yokoyama, M. Misono, J. Chem. Soc., Chem. Commun. (1996) 597.