

Low-temperature SCR of NO with NH₃ over USY-supported manganese oxide-based catalysts

Gongshin Qi^a, Ralph T. Yang^{a,*}, and Ramsay Chang^b

^a Department of Chemical Engineering, University of Michigan, Ann Arbor, MI 48109-2136, USA

^b Air Pollution Control, Power Generation, Electric Power Research Institute, Palo Alto, CA 94304-1395, USA

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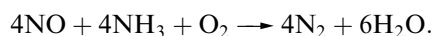
A series of catalysts of manganese oxide, manganese–cerium and iron–manganese oxide supported on USY (ultra-stable Y zeolite) were studied for the low-temperature selective catalytic reduction (SCR) of NO with ammonia in the presence of excess oxygen. It was found that MnO_x/USY have high activity and high selectivity to N₂ in the temperature range 80–180 °C. The addition of iron and cerium oxide increased NO conversion significantly although the single-component Fe/USY and Ce/USY catalysts had low activities. Among the catalysts studied in this work, the 14% Ce–6% Mn/USY showed the highest activity. The results showed that this catalyst yielded nearly 100% NO conversion at 180 °C at a space velocity of 30 000 cm³ g⁻¹ h⁻¹. The only product is N₂ (with no N₂O) below 150 °C. The effects of the concentration of oxygen, NO and NH₃ were studied and the steady-state kinetics were also investigated. The reaction order is 1 with respect to NO and zero with respect to NH₃ on the 14% Ce–6% Mn/USY catalyst at 150 °C.

KEY WORDS: low-temperature SCR; Fe–Mn/USY; Ce–Mn/USY; Mn/USY; SCR of NO with NH₃.

1. Introduction

Nitrogen oxides (NO, NO₂ and N₂O) remain a major source for air pollution. They contribute to photochemical smog, acid rain, ozone depletion and greenhouse effects [1]. Nearly all NO_x (95%) derives from transportation (49%) and power plants (46%) [2]. In recent years, many methods have been used to reduce the emission of nitrogen oxide. Catalytic technologies are attractive because of their low cost and high efficiency [1]. In the case of automotive catalytic converters, CO acts as the main reducing agent for NO [3,4]. Hydrocarbons such as methane, propane or propylene can also be used as reductants [5–9]. However, highly active and stable catalysts have not been found for hydrocarbon selective catalytic reduction (SCR).

The major technology for reducing nitrogen oxide emissions from stationary sources is SCR of NO_x (x = 1, 2) by ammonia. The general reaction is as follows:



Many catalysts have been reported to be active for this reaction [1]. The commercial catalysts for this process are V₂O₅/TiO₂ (anatase) mixed with WO₃ or MoO₃ [10–17]. Although the vanadium-based catalysts are highly active and resistant to SO₂, there are also some disadvantages. This catalyst is active within a narrow temperature window of 300–400 °C, while this temperature range also helps to avoid pore plugging from the deposition

of ammonium sulfate salts such as NH₄HSO₄ and (NH₄)₂S₂O₇ on the catalyst surface. Consequently, it is necessary to locate the SCR unit upstream of the desulfurizer and electrostatic precipitator in order to avoid reheating of the flue gas as well as deposition of dust on the catalyst [1]. The formation of N₂O is another drawback for the vanadium-based catalysts [1].

For the reasons outlined above, there has been much interest in developing highly active catalysts for low-temperature SCR. Such a catalyst would be placed downstream of the desulfurizer and electrostatic precipitator, the temperature at this point being below 200 °C. Success in developing such a catalyst would significantly improve the economics of SCR. Moreover, there is still residual SO₂ remaining after the desulfurizer. Thus, SO₂ resistance needs to be considered.

Some transition metal-containing catalysts have been investigated for the low-temperature SCR reaction, such as chromia [2], NiSO₄/Al₂O₃ [18], MnO_x/Al₂O₃ [19], V₂O₅/activated carbon [20], iron–silica aerogels [21], MnO_x/NaY [22] and other oxides [23]. They showed various SCR activities below 200 °C under different conditions. Recently, we found that Fe–Mn-based transition metal oxides [24] were highly active for low-temperature SCR of NO with NH₃ with 100% selectivity to N₂ at a high space velocity. Much work has been focused on zeolite-based catalysts for medium-temperature SCR of NO with ammonia, but few studies have been done for the low-temperature SCR of NO with ammonia with zeolite-based catalysts. As SCR catalysts, zeolites generally lack resistance to moisture, which is always present in exhaust gases. In this work, we selected

* To whom correspondence should be addressed.
E-mail: yang@umich.edu

ultra-stable Y (USY) zeolite as the support. This was doped with manganese oxide, and further promoted by adding Ce and Fe oxides.

2. Experimental

The catalyst support was H-type ultra-stable Y zeolite (H-USY, Si/Al = 195, Tosoh Corporation, HSZ-390HUA). The catalyst was impregnated by incipient wetness with an aqueous solution of manganese acetate, iron nitrate and/or cerium nitrate. The impregnated sample was first dried at 120 °C for 12 h, followed by calcination at 500 °C in air for 6 h. The metal contents (%) of Fe, Mn and Ce are based on the support.

The SCR activity measurement was carried out in a fixed-bed quartz reactor. The reaction conditions were as follows: 0.2 g sample, 1000 ppm NO, 1000 ppm NH₃, 2% O₂, 2.5% water vapor (when used), 100 ppm SO₂ (when used), balance He, 100 ml/min total flow rate. The premixed gases (1.01% NO/He, 1.00% NH₃/He and 0.99% SO₂/He) were supplied by Matheson. Water vapor was generated by passing He through a gas-wash bottle containing deionized water. The tubings of the reactor system were heat traced to prevent formation and deposition of ammonium sulfate/bisulfate and ammonium nitrate. The NO and NO₂ concentrations were continually monitored by a chemiluminescent NO/NO_x analyzer (Model 42C, Thermo Environmental Instruments Inc.). To avoid errors caused by the oxidation of ammonia in the converter of the NO/NO_x analyzer, an ammonia trap containing phosphoric acid solution was installed before the sample inlet to the chemiluminescent analyzer. The products were analyzed by a gas chromatograph (Shimadzu, 8A) at 50 °C with a 5A molecular sieve column for N₂ and a Porapak Q column for N₂O. All the data were obtained after 60–200 min when the SCR reaction reached steady state.

Steady-state kinetics studies were carried out in a fixed-bed quartz flow reactor. The reaction temperature was controlled by an Omega (CN-2010) programmable temperature controller. An amount of 75 mg of catalyst was used in this work. The flue gas was simulated by blending different gaseous reactants. The typical reactant gas composition was as follows: 400–2000 ppm NO, 400–2000 ppm NH₃, 2% O₂ and balance He. The total flow rate was 500 ml/min (ambient conditions). The instrument is the same as for the catalytic activity measurement mentioned above.

A Micromeritics ASAP 2010 micropore size analyzer was used to measure the N₂ adsorption isotherms of the samples at liquid N₂ temperature (−196 °C). The specific surface area was determined from the linear portion of the BET plot. The pore size distribution was calculated from the desorption branch of the N₂ adsorption isotherm using the Barrett–Joyner–Halenda (BJH) formula. Prior to the surface area and pore size

distribution measurements, the samples were degassed in vacuum at 400 °C for 24 h.

Powder X-ray diffraction (XRD) measurements were carried out using a Rigaku Rotaflex D/Max-C system with CuKα (λ = 0.1543 nm) radiation. The samples were loaded on a sample holder with a depth of 1 mm.

3. Results and discussion

The BET surface area, pore volumes and pore sizes of the USY-supported catalysts are summarized in table 1. The surface area and pore volume of H-USY are 858 m²/g and 0.346 cm³/g, respectively. After doping with manganese oxide, both the surface area and pore volume of the 10% Mn/USY sample decrease significantly to 595.45 m²/g and 0.2647 cm³/g, respectively. From table 1 we can see that after doping Ce or Fe on Mn/USY, the surface area and pore volume of Ce–Mn/USY and Fe–Mn/USY samples increase significantly, which may be related to the high activities for Ce–Mn/USY and Fe–Mn/USY catalysts.

The XRD patterns of the MnO_x/USY catalysts are shown in figure 1. It can be seen that the pure USY support has several strong peaks, while after doping the intensities of the peaks decrease significantly. For 14% Ce/USY and 10% Fe/USY, very weak peaks of the CeO₂ and Fe₂O₃ phases can be observed, while for 10% Mn/USY manganese phase cannot be detected. Based on the results of Fabrizioli *et al.* [21], MnO₂ and Mn₂O₃ were detected on MnO_x/NaY catalyst calcined at 500 °C. Thus, we may conclude that MnO₂ and Mn₂O₃ should coexist on the MnO_x/USY catalyst. The XRD patterns of Fe–Mn, Ce–Mn oxides supported on USY are also shown in figure 1; no visible phases of Fe, Ce and Mn can be observed. This may be due to the weakly crystalline nature (amorphous) of the metal oxides. From figure 1 we can see that coexistence of the manganese and cerium/iron oxides enhances the dispersion, thereby reducing the crystallinity of both, which indicates that there are strong interactions between these two metal oxides.

Based on our previous study, we found that Fe–Mn-based transition metal oxides were highly active for low-temperature oxidation of NO to NO₂ and SCR of

Table 1
Characterization of the catalysts

Samples	BET surface area (m ² /g)	Pore volume (cm ³ /g)	Pore diameter (Å)
USY	858	0.3476	28.86
10% Mn/USY	595	0.2647	28.82
10% Fe/USY	692	0.3100	28.87
14% Ce/USY	625	0.2766	28.14
10% Mn–10% Fe/USY	678	0.2719	27.34
6% Mn–14% Ce/USY	723	0.3116	27.48

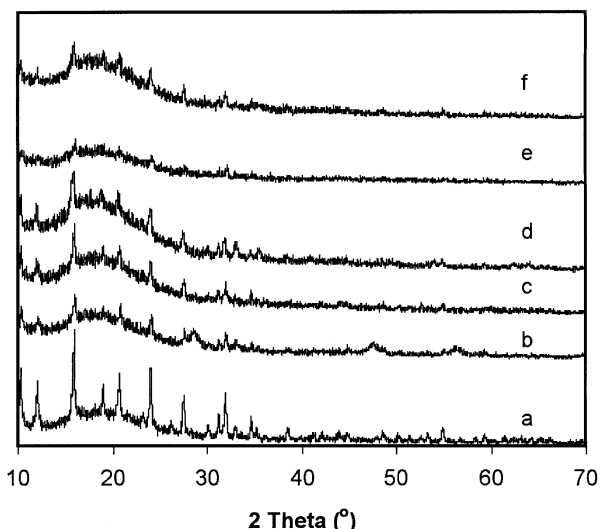


Figure 1. XRD patterns of USY-supported manganese oxide-based catalysts: (a) USY, (b) 14% Ce/USY, (c) 10% Mn/USY, (d) 10% Fe/USY, (e) 14% Ce-6% Mn/USY, (f) 10% Fe-10% Mn/USY.

NO by ammonia [24]. The Fe-exchanged ZSM-5 was active for SCR of NO with ammonia at high temperatures. In this work we investigated the effect of Fe, Ce oxide on Mn/USY catalyst for the SCR of NO with ammonia. Steady-state NO conversion data obtained with catalysts doped with Ce or Fe and at various temperatures are shown in figure 2, and compared with the activity of the 10% Mn/USY catalyst. The results in figure 2 show that the addition of Fe, Ce increased NO conversion significantly although the 10% Fe/USY and 14% Ce/USY catalysts had low activities for low-temperature SCR (not shown). For the 10% Mn/USY catalyst, at 80 °C, only 30% NO conversion was reached. After doping with Ce or Fe, the conversions at 80 °C were 43 and 50%, respectively. From the results we can see that at 180 °C, 98% NO conversion was reached on the 14% Ce-6% Mn/USY catalyst. Among all the catalysts, at reaction temperatures below 150 °C, no

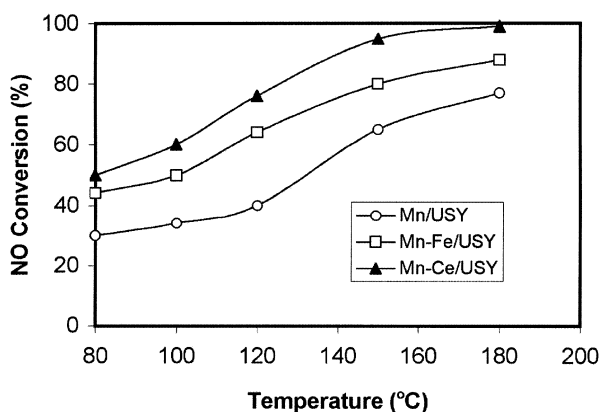


Figure 2. NO conversion on different USY-supported MnO_x-based catalysts. Reaction conditions: [NO]=[NH₃]=1000 ppm, [O₂]=2%, He balance, total flow rate = 100 ml/min, catalyst = 0.2 g.

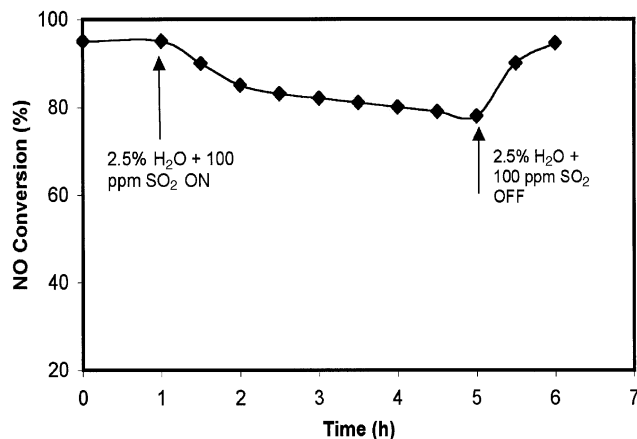


Figure 3. NO conversion on the 14% Ce-6% Mn/USY catalyst in the presence of SO₂ + H₂O. Reaction conditions: 0.2 g catalyst, temperature = 150 °C, [NO]=[NH₃]=1000 ppm, [O₂]=2%, [SO₂]=100 ppm, [H₂O]=2.5%, He = balance, total flow rate = 100 ml/min.

N₂O production was detected; at 180 °C, a trace amount of N₂O was detected (<0.2%).

It is noted that there remain small concentrations of SO₂ in combustion gases even after the desulfurizer. Effects of SO₂ on the SCR activity are also important for low-temperature SCR catalysts. The effect of SO₂ + H₂O on the SCR activity of the 14% Ce-6% Mn/USY catalyst is illustrated in figure 3. Our results show that, when 100 ppm SO₂ and 2.5% H₂O were added to the reaction gas and the reaction temperature and space velocity were kept at 150 °C and 30000 cm³ g⁻¹ h⁻¹, respectively, the NO conversion on Ce-Mn/USY decreased slowly to 80% at 150 °C in 4 h and seemed to level off. This is consistent with the previous observation that MnO_x catalysts were deactivated by SO₂ [18]. In the presence of SO₂, SO₂ can be oxidized to SO₃ by O₂. The SO_x compounds (SO₂ + SO₃) are adsorbed on the transition metal oxides and they are difficult to desorb at low temperatures. The occupation of the active sites by metal sulfates and ammonium sulfates would consequently decrease the SCR activity. After the H₂O and SO₂ were cut off, the activity was quickly restored to nearly the original value.

For determining the order of reaction with respect to NO, the concentration of NH₃ was kept constant at 1000 ppm, while the concentration of NO was varied from 400 to 2000 ppm. Similarly, in determining the order with respect to NH₃, the concentration of NO was kept at 1000 ppm, while the concentration of NH₃ was varied between 400 and 2000 ppm. Since the flow rate was 500 ml/min and only 75 mg of catalyst was used, less than 15% NO conversion was obtained at 150 °C in these experiments. Therefore, the reactor may be treated as a differential reactor. The experimental results for the rate of NO conversion as a function of nitric oxide and ammonia concentration are presented in figures 4 and 5, respectively. The rate of NO conversion increased with NO concentration, but it was

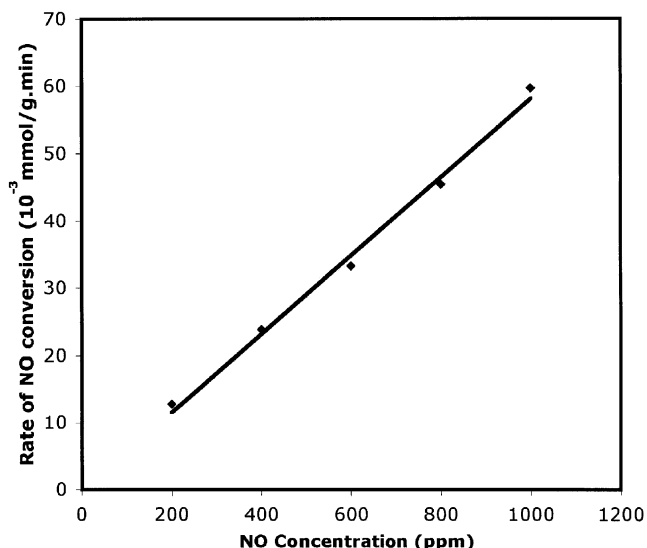


Figure 4. Dependence of NO conversion rate on NO concentration on 14% Ce-6% Mn/USY at 150 °C under the conditions of 75 mg catalyst, 1000 ppm NH₃, 200–1000 ppm NO, 2% O₂ and 500 ml/min total flow rate, He = balance.

almost unchanged with an increase in the NH₃ concentration. The intrinsic reaction rate of NO conversion as a function of reactant concentrations can be expressed as

$$\text{Rate of NO conversion} = k[\text{NO}]^x[\text{NH}_3]^y[\text{O}_2]^z. \quad (1)$$

The reaction order x with respect to NO was calculated to be nearly 1, while the reaction order y with respect to NH₃ was nearly zero at 150 °C.

Previous studies of SCR catalysts have shown the importance of oxygen in the SCR of NO with NH₃ [1]. The effect of oxygen on catalytic activity was also studied in this work. As shown in figure 6, Mn-Ce/USY showed a low activity for the reduction of NO by NH₃ at 150 °C in the absence of oxygen. However, when a small

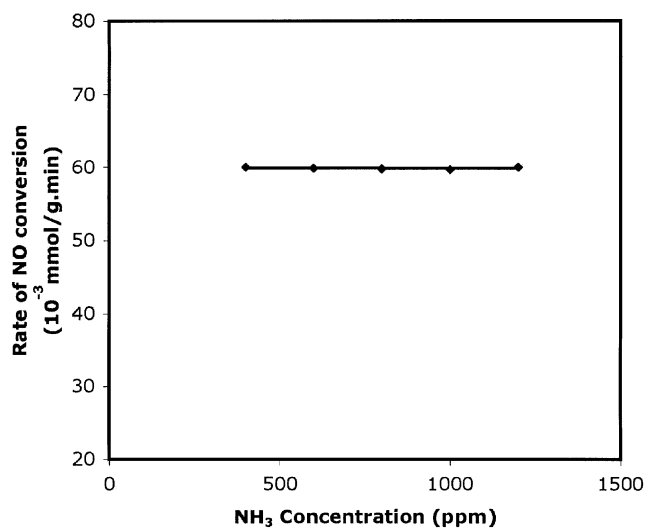


Figure 5. Dependence of NO conversion rate on NH₃ concentration on 14% Ce-6% Mn/USY at 150 °C under the conditions of 75 mg catalyst, 1000 ppm NO, 400–1000 ppm NH₃, 2% O₂ and 500 ml/min total flow rate, He = balance.

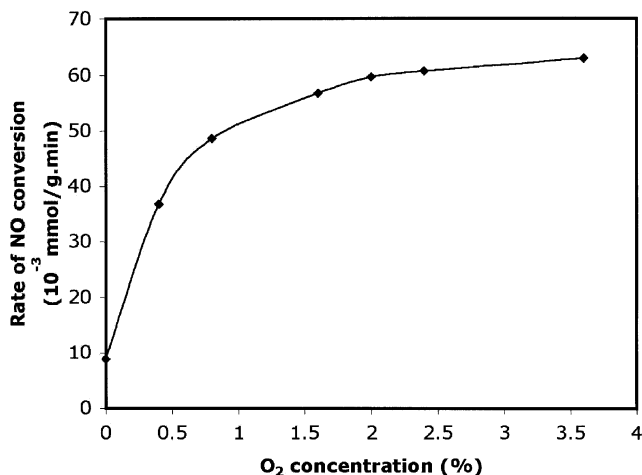


Figure 6. Effect of O₂ concentration on NO conversion rate on 14% Ce-6% Mn/USY catalyst at 150 °C. Reaction conditions: 75 mg catalyst, [NO] = [NH₃] = 1000 ppm, [O₂] = 0–4%, He = balance, total flow rate = 500 ml/min.

concentration of O₂ was introduced to the reactants, NO_x conversion increased sharply. When O₂ concentration was more than 2%, the NO_x conversion showed nearly no change. This indicated that O₂ played a significant promoting role in the SCR reaction. According to equation (1) and the above data, the reaction order (z) with respect to O₂ was calculated to be 0.43 at 150 °C. It is approximately half-order with respect to O₂. By comparison, previous results showed that the reaction order with respect to O₂ was 1/2 for a Mn₂O₃-WO₃/γ-Al₂O₃ catalyst [25]. According to the foregoing results, the SCR reaction can be considered to be approximately first order with respect to NO, zero order with respect to NH₃ and one-half order with respect to O₂. The reaction rate of NO consumption is expressed as

$$r_{\text{NO}} = k[\text{NO}][\text{O}_2]^{0.5}. \quad (2)$$

This rate equation is valid only when the oxygen partial pressure is below approximately 0.5 at%. For the results of experiments listed in table 2, the partial pressures were all above 2 at%. Under such conditions, the following rate equation applies:

$$r_{\text{NO}} = k[\text{NO}]. \quad (3)$$

Since the amount of oxygen is in excess, if the reaction is free of diffusion limitation, the apparent rate constant (k) and NO conversion (X) will have a relationship as follows:

$$k = -F_0 \ln(1 - X) / ([\text{NO}]_0 W) \quad (4)$$

where F_0 is the molar NO feed rate, $[\text{NO}]_0$ is the molar NO concentration at the inlet (at the reaction temperature) and W is the amount of catalysts (g).

A summary comparison has been made for the USY-supported Mn-based catalysts with other high-activity catalysts that were reported in the literature (table 2). In order for a fair comparison, the first-order rate

Table 2
Performance of various catalysts for low-temperature SCR of NO with NH₃

Catalyst	Feed composition			<i>T</i> (K)	<i>X</i> _{NO} ^a (%)	SV (cm ³ g ⁻¹ h ⁻¹)	<i>k</i> ^b (cm ³ g ⁻¹ s ⁻¹)	Ref.
	NO (ppm)	NH ₃ (ppm)	O ₂ (%)					
5% V ₂ O ₅ /AC	500	560	3.3	523	79.7	90 000	69.96	[18]
MnO _x /Al ₂ O ₃	500	550	2	423	63	24 000	9.40	[19]
MN ₂ O ₃ -WO ₃ /γ-Al ₂ O ₃	500	550	10	423	45	91 400	21.54	[20]
15MnNaY775 ^b	1000	1000	5	443	82	48 000	33.98	[21]
10% Mn-14% Ce/USY	1000	1000	2	353	50	30 000	6.84	This work
				373	59		9.31	This work
				393	78		16.64	This work
				423	87		24.13	This work
				453	98		49.55	This work

^a NO conversion.

^b First-order rate constant.

^c The feed contained 7% H₂O.

constants, *k*, were calculated by equation (3), assuming no diffusion limitation. The vanadia/carbon system had a high activity [20], but it was at a high temperature (523 K) and clearly some carbon combustion was involved. The results show that the Ce-Mn/USY catalyst is substantially more active than all other catalysts.

4. Conclusion

Based on the above results, it can be concluded that cerium-promoted MnO_x/USY showed good low-temperature SCR performance. On the 14% Ce-6% Mn/USY, nearly 100% NO conversion was obtained at 180 °C at high space velocity. The product was only N₂ when the temperature is below 150 °C.

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