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Selective catalytic oxidation (SCO) of ammonia to nitrogen over Fe-exchanged zeolites prepared by sublimation of $FeCl_3$

Gongshin Qi, Joseph E. Gatt, Ralph T. Yang *

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

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Abstract

Fe-exchanged zeolites were prepared by subliming $FeCl_3$ and studied as catalysts for selective catalytic oxidation (SCO) of ammonia to nitrogen in the presence of oxygen. Fe-ZSM-5 prepared by sublimation of $FeCl_3$ at 700 °C showed excellent SCO performances at a very high space velocity ($\mathrm{GHSV} = 2.3 \times 10^5\ \mathrm{h}^{-1}$). Over 99% NH_3 conversion and nearly 100% N_2 selectivity were obtained at 400 °C. Among Fe-ZSM-5 catalysts prepared by subliming at different temperatures (denoted in parentheses, in °C), the catalytic performance decreased in the sequence of Fe-ZSM-5 (700) > Fe-ZSM-5 (600) > Fe-ZSM-5 (500), Fe-ZSM-5 (400), Fe-ZSM-5 (350). Among different Fe-zeolite catalysts prepared by subliming at 700 °C, the catalytic performance decreased in the sequence of Fe-ZSM-5 > Fe-MOR > Fe-FER > Fe-Beta > Fe-Y which are similar to the Fe-zeolites prepared by aqueous ion-exchange method. The activity for the SCR (selective catalytic reduction) of NO with ammonia was also investigated on different Fe-zeolites. The FT-IR results supported the two-step mechanism: NO is an intermediate for N_2 formation, NH_3 was first oxidized to NO by O_2, NO then reacts to the unreacted NH_3 to produce N_2.

Keywords: Selective catalytic oxidation (SCO) of NH_3; Selective catalytic reduction (SCR) of NO; Fe-exchanged zeolites; Fe-ZSM-5; Sublimation of $FeCl_3$; FT-IR

1. Introduction

The removal of ammonia from waste streams is becoming an important problem. Many chemical processes use reactants containing ammonia or produce ammonia as a by-product. They are all plagued with the ammonia emission problem. Selective catalytic oxidation (SCO) of ammonia to nitrogen is potentially an ideal technology for removing ammonia from oxygen-containing waste gases and consequently it has become of increasing interesting in recent years [1–11]. Moreover, ammonia is used effectively in power plants for NO_x ($x = 1$, 2) abatement by selective catalytic reduction (SCR). In order to control the ammonia slip, most processes are carried out under conditions such that $NH_3/NO < 1$, at the expense of decreased NO reduction efficiencies. For improving the NO reduction efficiency, the use of stoichiometric or an excess amount of ammonia is desirable. The SCO of ammonia can be applied to the SCR of NO with ammonia in a secondary bed to oxidize the residual ammonia to N_2, without introducing other reactants into the gas mixture. The SCO process can also be applied to biomass-derived fuels for removing the large amounts of NH_3 impurity [3,4]. Further applications of SCO are the treatment of reformates for fuel cell systems and the deodorization of ammonia-containing gases.

Several types of materials have been reported to be active for SCO of ammonia to N_2, such as Pt, Rh, and Pd exchanged to ZSM-5 [2]; Ni, Fe, and Mn oxides supported on γ-Al_2O_3 [3,4], V_2O_5/TiO_2, CuO/TiO_2, and Cu-ZSM-5 [5]; CuO/Al_2O_3 [6,7]; Cu–Mn/TiO_2 [8]; Fe-exchanged TiO_2-PILC [9]; Fe-exchanged ZSM-5 and other zeolites [10,11]; Fe_2O_3–TiO_2 [12]; and manganese oxide–silica aerogels [13]. These catalysts exhibited activities for N_2 formation under various conditions. Amblard et al. [3] reported that among the transition-metal oxides supported on γ-Al_2O_3, Ni/γ-Al_2O_3, Mn/γ-Al_2O_3, and Fe/γ-Al_2O_3 were the most active and selective catalysts for the SCO reaction. Wöllner et al. [8] reported that Cu/Mn mixed oxides were good catalysts for ammonia oxidation to nitrogen and

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[*] Corresponding author.
E-mail address: yang@umich.edu (R.T. Yang).

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their activities were much higher than the individual component oxides. Cavani and Trifiro [14] studied the SCO of ammonia over V_2O_5/TiO_2 and found that the vanadium oxide supported on the rutile form of TiO_2 was more active and selective to N_2 at low temperatures (i.e., $< 300\,°C$). Among these catalysts, manganese oxides showed interesting activity and selectivity at low temperatures, and Fe-ZSM-5 showed high activities for high-temperature SCO of ammonia (i.e., $> 300\,°C$). In our previous studies, we found that iron-exchanged zeolites had high activities for SCR of NO with ammonia at high temperatures [10,11].

For transition-metal ion-exchanged Y zeolites, pulse reaction results showed that the activity for ammonia oxidation decreased in the sequence of Cu-Y > Cr-Y > Ag-Y > Co-Y > Fe-Y > Ni-Y, Mn-Y, and the main product was nitrogen [1]. Gandhi and Shelef [15] found that $CuMoO_4$ was active for oxidation of NH_3 to N_2 at 450–550 °C, but the activity and/or selectivity to N_2 was inhibited by water vapor. More recently, Li and Armor [2] reported that Pt, Rh, and Pd exchanged to ZSM-5 or supported on Al_2O_3 showed good SCO performance in a wet stream. The metal ion-exchanged ZSM-5 were more active and also less affected by water than the corresponding Al_2O_3-supported catalysts. Also, the noble metal catalysts were more active than V_2O_5/TiO_2 and Co-ZSM-5 [2].

Recently, we studied the SCO reaction on a series of transition-metal (Cr, Mn, Fe, Co, Ni, Cu, or Pd) ion-exchanged ZSM-5 [10]. The results showed that the catalytic performance (i.e., NH_3 conversion and N_2 selectivity) increased in the trend of Co-ZSM-5 $\approx$ Ni-ZSM-5 < Mn-ZSM-5 < H-ZSM-5 < Pd-ZSM-5 < Cr-ZSM-5 < Cu-ZSM-5 < Fe-ZSM-5 at a high gas hourly space velocity ($\text{GHSV} = 2.3 \times 10^5\ h^{-1}$). Nearly 100% of NH_3 conversion to N_2 was obtained at 450 °C on the Fe-ZSM-5.

It has been found that Fe-exchanged zeolites have high activities and selectivities to N_2 for the SCO of ammonia at high temperatures [11]. It was observed that both NH_3 conversion and N_2 selectivity increased with iron content (with iron-exchange level < 100%) at low temperatures for Fe-ZSM-5 [11]. In order to further increase the activity of SCO, we need to increase the Fe content. Chen and Sachtler [16] have developed a method for the preparation of Fe-ZSM-5 catalysts by subliming $FeCl_3$ into H-ZSM-5. Anhydrous $FeCl_3$ is sublimated into H-form zeolites at high temperatures (e.g., 320 °C), where it reacts with zeolite protons by $H^+ + FeCl_3 = [FeCl_2]^+ + HCl$ until all protons are replaced by $[FeCl_2]^+$. After the reaction, chlorine is removed by washing the samples with deionized water. This method is very effective in obtaining high Fe-exchanged Fe-ZSM-5 catalysts in a reproducible manner. More recently, Krishna et al. [17] studied the Fe-ZSM-5 catalysts prepared by subliming $FeCl_3$ into H-ZSM-5 at different sublimation temperatures for the SCR of NO with ammonia.

In this work, we studied the SCO of ammonia on the Fe-exchanged zeolites prepared by subliming $FeCl_3$ similar to Sachtler's method [16]. For these catalysts, we investigated the effect of the framework types of zeolites which have different pore sizes and different Si/Al ratios, and the effects of different subliming temperatures on the SCO and NH_3-SCR.

2. Experimental

2.1. Preparation of catalysts

The starting materials used for preparation of the catalysts are as follows. NH_4-ZSM-5 (Si/Al $\approx$ 10) was obtained from Alsi-Penta Zeolithe Gmbh (Germany). Mordenites (MOR, Si/Al = 6.4, 10, and 45), NH_4-beta (Si/Al = 12.5), and NH_4-ferrierite (FER, Si/Al = 10) were obtained from Zeolyst International Company. Y zeolite (Si/Al = 2.4) was obtained from Strem Chemicals. The non-NH_4-form zeolites were first converted to NH_4-zeolites by exchanging with 0.5 M NH_4Cl solution (four times) at room temperature. $FeCl_3$ was obtained from Aldrich.

Fe-exchanged catalysts were prepared by chemical vapor ion exchange. This method was similar to that proposed by Chen and Sachtler [16]. $FeCl_3$ (97%, Aldrich) was used as the iron source. During the experiment, 2 g zeolite and 0.5 g $FeCl_3$, separated by glass wool, were loaded into a quartz reactor. Subsequently, the reactor was heated to 350 or 700 °C in flowing He (100 ml/min). $FeCl_3$ was evaporated and then exchanged with H-zeolite according to the following reaction:

$$\text{H-zeolite} + FeCl_3 = [FeCl_2]\text{-zeolite} + HCl. \qquad (1)$$

After 1 h, the sample was removed and then washed with deionized water to eliminate chlorine (detected with silver nitrate solution). The catalysts were dried at 120 °C overnight, then calcined at 500 °C for 6 h in air. Finally, the obtained samples were ground and sieved to 60–100 mesh. The Fe and Al contents in the samples were measured by neutron activation analysis. The iron-exchange level was calculated by 3 (number of iron ions)/(number of aluminum ions) because almost all iron was present as Fe^{3+}. The catalysts are denoted by Fe-zeolite (x), where x is the subliming temperature in °C.

2.2. Catalytic performance measurement

The SCO activity measurement was carried out in a fixed-bed quartz reactor. The reaction temperature was controlled by an Omega (CN-2010) programmable temperature controller. One hundred milligrams of catalyst was used in this work. The reactant gas was obtained by blending different gas flows. The typical reactant gas composition was as follows: 1000 ppm NH_3, 2% O_2, and balance He. The total flow rate was 500 ml/min (ambient conditions). The premixed gases (1.0% NH_3 in He) were supplied by Matheson. A magnetic deflection-type mass spectrometer (AERO VAC, Vacuum Technology Inc.) was used to monitor continuously the effluent gas from the reactor, which contained NH_3

($m/e = 17$ minus the contribution of H_2O), H_2O ($m/e = 18$), N_2 ($m/e = 28$), NO ($m/e = 30$), O_2 ($m/e = 32$) and N_2O ($m/e = 44$). NO_2 ($m/e = 46$) was not detectable with this mass spectrometer. The concentrations of the unreacted NH_3 and the NO_x formed were also continually monitored with a chemiluminescent NO/NO_x analyzer (Thermo Environmental Instruments Inc. Model 42C), in which a high-temperature converter converted NH_3 to NO_x by the reaction $NH_3 + O_2 \rightarrow NO_x + H_2O$. The NH_3 conversion was calculated by $([NO] + 2[N_2] + 2[N_2O])/[NH_3]_0 \times 100\%$, where $[NH_3]_0$ is the initial NH_3 concentration. The selectivity is defined as the percentage conversion of ammonia to N_2, N_2O, and NO. The data were collected when the SCO reaction reached the steady state typically after 20–180 min at each temperature.

The SCR activity measurement was carried out in a fixed-bed quartz reactor. The typical reactant gas composition was as follows: 1000 ppm NO, 1000 ppm NH_3, 2% O_2, and balance He. Typically 50 mg sample was used in each run. The total flow rate was 500 ml/min (under ambient conditions). Thus, a very high GHSV (gas hourly space velocity) was obtained (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 tubing of the reactor system was heat-traced to prevent formation and deposition of ammonium sulfate/bisulfate and ammonium nitrate. The NO and NO_2 concentrations were continually monitored by the chemiluminescent NO/NO_x analyzer. 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 also analyzed by a gas chromatograph (Shimadzu, 8A) at 50 °C with a 5A molecular sieve column for N_2 and a Porapak Q column for N_2O.

2.3. Catalyst characterization

A Micromeritics ASAP 2010 micropore-size analyzer was used to measure the N_2 adsorption isotherms of the samples at liquid N_2 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 N_2 adsorption isotherm using the Barrett–Joyner–Halenda (BJH) formula. Prior to the surface area and pore-size distribution measurements, the samples were degassed in vacuo at 400 °C for 24 h.

The powder X-ray diffraction (XRD) measurements were carried out with a Rigaku Rotaflex D/Max-C system with Cu-K_α ($\lambda = 0.1543$ nm) radiation. The samples were loaded on a sample holder with a depth of 1 mm.

In each H_2-TPR (temperature-programmed reduction) experiment, a 50-mg sample was loaded into a quartz reactor and then pretreated in O_2/He (100 ml/min) at 500 °C for 0.5 h. The sample was then cooled down to room temperature in O_2/He flow. The reduction of the sample was carried out from room temperature to 700 °C in a flow of 5.32% H_2/N_2 (40 ml/min) at 10 °C/min. The consumption of H_2 was monitored continuously with a thermal conductivity detector. The water produced during reduction was trapped in a 5 A molecular sieve column.

2.4. FTIR studies

Infrared spectra were recorded on a Nicolet Impact 400 FTIR spectrometer with a TGS detector. A self-supported wafer of 1.3 cm diameter was prepared by pressing a 15-mg sample and then loaded into an IR cell with BaF_2 windows. The wafers could be pretreated in situ in the IR cell. The wafers were first treated at 400 °C in a flow of high purity 20% O_2/He for 0.5 h and then cooled to room temperature. At each temperature, the background spectrum was recorded in flowing He and was subtracted from the sample spectrum that was obtained at the same temperature. Thus the IR absorption features that originated from the structure vibrations of the catalyst were eliminated from the sample spectra. In the experiment, the IR spectra were recorded by accumulating 100 scans at a spectra resolution of 4 cm^{-1}.

3. Results

3.1. Characterization of catalysts

Fig. 1 shows the XRD patterns of different Fe-ZSM-5 catalysts prepared at different temperatures and pure HZSM-5. The XRD patterns of Fe-ZSM-5 catalysts prepared at different temperatures are similar to the patterns of HZSM-5, and no peak for Fe_2O_3 species was observed. This indicated that Fe_2O_3 was dispersed well on the framework of ZSM-5.

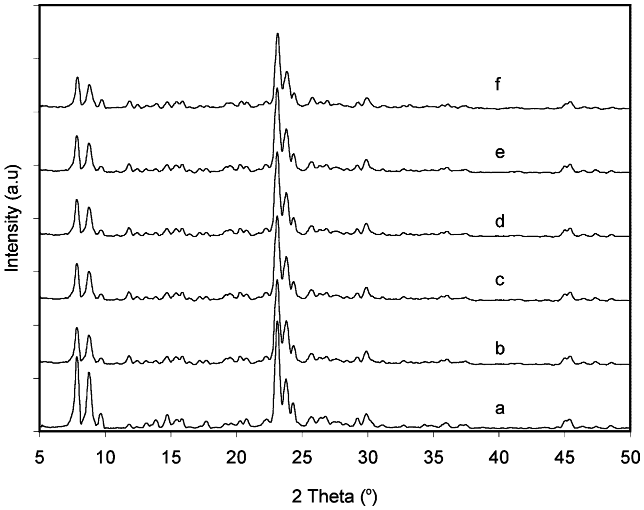

Fig. 1. XRD profiles of Fe-ZSM-5 catalysts prepared by different subliming temperatures (a) H-ZSM-5, b) Fe-ZSM-5 (350), (c) Fe-ZSM-5 (400), (d) Fe-ZSM-5 (500), (e) Fe-ZSM-5 (600), (f) Fe-ZSM-5 (700).

Table 1
Characterization of the catalysts

Sample	BET surface area (m^2/g)	Pore volume (cm^3/g)
Fe-ZSM-5 (350)	313.02	0.073
Fe-ZSM-5 (400)	313.35	0.073
Fe-ZSM-5 (500)	300.77	0.072
Fe-ZSM-5 (600)	292.13	0.081
Fe-ZSM-5 (700)	257.22	0.078
Fe-MOR (700)	366.49	0.13
Fe-FER (700)	299.90	0.084
Fe-Beta (700)	487.63	0.54
Fe-Y (700)	145.15	0.048

The BET surface areas and pore volumes of the Fe-zeolite catalysts are summarized in Table 1. After iron exchange and calcinations at different temperatures for 6 h, the surface areas of Fe-ZSM-5 decreased from 313 to 257 cm^2/g. As the calcination temperature increased, the surface area decreased. Table 2 shows the Fe contents for Fe-ZSM-5 samples obtained by sublimation of $FeCl_3$ at different temperatures.

Fig. 2 shows the H_2-TPR profiles of Fe-ZSM-5 obtained by subliming at 350 and 700 °C. Before the reduction, the samples were pretreated in O_2/He at 400 for 30 min. A peak at 400 °C and a shoulder at 520 °C were observed on the TPR profiles for both catalysts, which can be attributed to the reduction of iron species at two different sites. Integrations of area of the TPR peaks yielded an H_2/Fe molar ratio of close to 0.5. This indicates that almost all of the iron was located at exchange sites where it could only be reduced from +3 to +2 under this reduction condition. The result above is consistent with the literature results [16,17].

3.2. *SCO performance on different Fe-ZSM-5 prepared at different temperatures*

The catalytic performance of Fe-ZSM-5 prepared by subliming at different temperatures for the SCO of NH_3 is summarized in Table 3. Under the conditions of 1000 ppm NH_3, 2% O_2, and GHSV $= 2.3 \times 10^5\ h^{-1}$, these catalysts showed various ammonia conversions at different temperatures. NH_3 conversion increased with reaction temperature and all of the catalysts showed very high NH_3 conversions. In all cases, N_2 was the main product for ammonia oxidation, no N_2O was detected at any of the temperatures studied, and NO was detected at lower temperatures for all the catalysts. Among them, Fe-ZSM-5 sublimed at 700 °C showed the highest activities for NH_3 oxidation to N_2 at 350–450 °C. N_2 selectivity increased with increasing temperature. The conversion of ammonia for the different Fe-ZSM-5 catalysts decreased in the sequence of Fe-ZSM-5 (700) > Fe-ZSM-5 (600) > Fe-ZSM-5 (500), Fe-ZSM-5 (400), Fe-ZSM-5 (350).

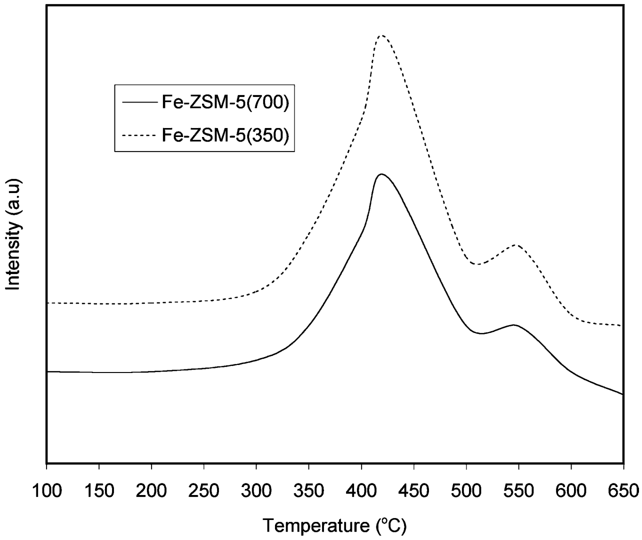

Fig. 2. H_2-TPR profiles of Fe-ZSM-5 catalysts.

3.3. *SCO performance on different Fe-zeolites*

The catalytic performance of different Fe-zeolites prepared by subliming at 700 °C for the SCO of NH_3 is summarized in Table 4. Under the conditions of 1000 ppm NH_3, 2% O_2, and GHSV $= 2.3 \times 10^5\ h^{-1}$, these catalysts showed various ammonia conversions at different temperatures. Among them, Fe-ZSM-5 and Fe-MOR showed the highest activities. Small amounts of NO were observed. The lowest SCO activities were obtained on Fe-Y and Fe-Beta. With increasing temperature, more NO was produced on Fe-FER and Fe-MOR, while on Fe-Y and Fe-Beta the NO product decreased after the temperature was higher than 450 °C. These results suggest that the structure of zeolite has a strong effect on the SCO of NH_3 to N_2 for the Fe-exchanged zeolites. The maxi-

Table 2
Catalyst preparation conditions and Fe ion-exchange percentage

Catalysts	Activation in He (°C/h)	$FeCl_3$ sublimation (°C/h)	Fe content (wt%)	Ion exchange[a] (%)	TOF[b] ($\times 10^3/s$)
Fe-ZSM-5 (350)	600/1	350/2	4.5	240	1.25
Fe-ZSM-5 (400)	600/1	400/2	5.0	267	1.26
Fe-ZSM-5 (500)	600/1	500/2	4.7	252	1.26
Fe-ZSM-5 (600)	600/1	600/2	5.0	267	2.54
Fe-ZSM-5 (700)	600/1	700/2	3.6	192	3.64

[a] Determined from neutron activation analysis.

[b] Overall TOF (turnover frequency) is defined as the number of NH_3 molecules converted per Fe per second at 350 °C, 1000 ppm NH_3, 2% O_2 at $2.3 \times 10^5\ h^{-1}$.

Table 3
Catalytic performance of SCO over Fe-ZSM-5 prepared by subliming at different temperatures

Catalyst	Temperature (°C)	NH_3 conversion (%)	Selectivity (%)		
			N_2	N_2O	NO
Fe-ZSM-5 (350)	300	6	91	0	9
	350	27	96	0	4
	375	46	97	0	3
	400	95	98	0	2
	425	95	100	0	0
	450	99	100	0	0
Fe-ZSM-5 (400)	300	6	91	0	9
	350	29	96	0	4
	375	47	97	0	3
	400	94	98	0	2
	425	96	100	0	0
	450	99	100	0	0
Fe-ZSM-5 (500)	300	6.4	92	0	8
	350	30	96	0	4
	375	52	98	0	2
	400	94	99	0	1
	425	95	100	0	0
	450	99	100	0	0
Fe-ZSM-5 (600)	300	10	96	0	4
	350	61	99	0	1
	375	86	99	0	1
	400	99	100	0	0
	425	99	100	0	0
	450	100	100	0	0
Fe-ZSM-5 (700)	300	15	96	0	4
	350	63	99	0	1
	375	90	100	0	0
	400	100	100	0	0
	425	100	100	0	0
	450	100	100	0	0

Reaction conditions: 0.1 g catalyst, $[NH_3] = 1000$ ppm, $[O_2] = 2\%$, He = balance, total flow rate = 500 ml/min and GHSV = $2.3 \times 10^5\ h^{-1}$.

Table 4
Catalytic performances of SCO over various Fe-exchanged zeolites

Catalyst[a]	Temp. (°C)	NH_3 conv. (%)	Selectivity (%)			N_2 yield (%)
			N_2	N_2O	NO	
Fe-FER (ferrierite)	350	18	95	0	5	17
	375	36	92	0	8	33
	400	62	90	0	10	56
	425	84	88	0	12	74
	450	99	85	0	15	84
Fe-ZSM-5	350	63	96	0	4	60
	375	90	99	0	1	89
	400	100	100	0	0	100
	425	100	100	0	0	100
	450	100	100	0	0	100
Fe-MOR (mordenite)	350	26	88	0	12	23
	375	48	94	0	6	45
	400	74	97	0	3	72
	425	92	99	0	1	91
	450	99	100	0	0	99
Fe-Y	350	12	89	0	11	10.6
	375	28	84	0	16	23.5
	400	50	76	1	23	38
	425	78	69	6	25	53.8
	450	90	79	0	21	71.1
Fe-Beta	350	13	95	0	5	12.3
	375	26	93	0	7	24.2
	400	44	88	0	12	38.7
	425	70	86	0	14	60.2
	450	89	92	0	8	81.9

Reaction conditions: 0.1 g catalyst, $[NH_3] = 1000$ ppm, $[O_2] = 2\%$, He = balance, total flow rate = 500 ml/min and GHSV = $2.3 \times 10^5\ h^{-1}$.

[a] Catalysts prepared by subliming at 700 °C.

mum N_2 yield by the Fe-exchanged zeolites decreased in the sequence of Fe-ZSM-5 > Fe-MOR > Fe-FER > Fe-Beta > Fe-Y. The selectivity for N_2O was too low to be detected for all the catalysts.

3.4. Catalytic performance of SCR of NO with ammonia over Fe-zeolite catalysts

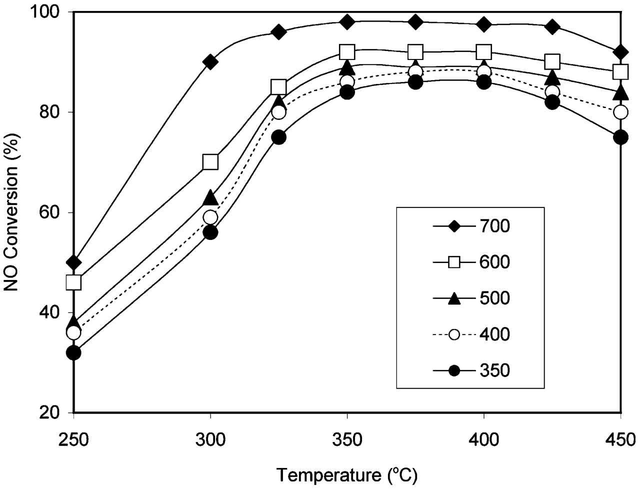

Fig. 3. NO conversions over Fe-ZSM-5 catalysts at different temperatures. Reaction conditions: catalyst 0.05 g, $[NO] = [NH_3] = 1000$ ppm, $[O_2] = 2\%$, He = balance, total flow rate = 500 ml/min, GHSV = $4.6 \times 10^5\ h^{-1}$.

Selective catalytic reduction of NO with ammonia was also studied on various Fe-based catalysts to demonstrate the relationship between the SCR reaction and the ammonia oxidation reaction. Fig. 3 shows the NO conversion on the various Fe-ZSM-5 catalysts prepared by subliming at different temperatures. All the catalysts showed high activities and high selectivities to N_2. The subliming temperature affected the activity significantly, particularly at higher temperatures. A higher subliming temperature led to a higher activity for the SCR reaction. This is very similar to the SCO reaction. The order of the different activities of the catalysts is Fe-ZSM-5 (700) > Fe-ZSM-5 (600) > Fe-ZSM-5 (500) > Fe-ZSM-5 (400) > Fe-ZSM-5 (350). Fig. 4 shows the NO conversion on the various Fe-zeolite catalysts prepared by subliming at 700 °C. Among them, Fe-ZSM-5 and Fe-MOR showed the highest activities. The lowest SCR activities were obtained on Fe-Y and Fe-Beta. These results suggest that the structure of zeolites also has a strong effect on the SCR of NO with NH_3 to N_2 for the Fe-exchanged

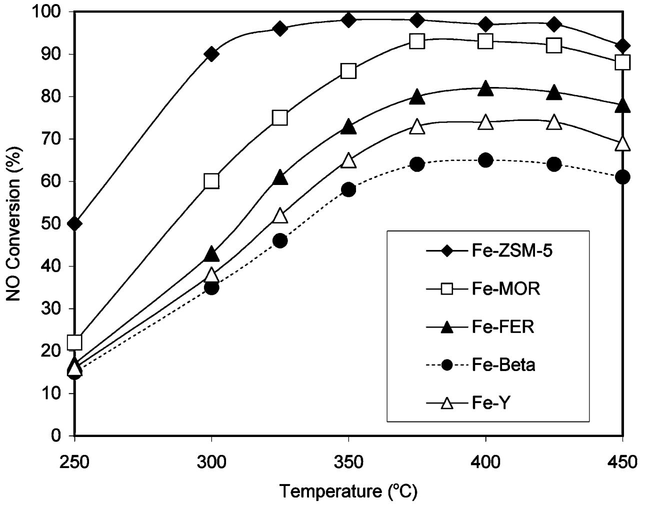

Fig. 4. NO conversions over Fe-zeolite catalysts at different temperatures. Reaction conditions: catalyst 0.05 g, [NO] = [NH_3] = 1000 ppm, [O_2] = 2%, He = balance, total flow rate = 500 ml/min, GHSV = 4.6 × 10^5 h^{-1}.

zeolites. More importantly, a link between the NH_3 SCO reaction and the NO SCR reaction became obvious.

3.5. Effect of H_2O and SO_2 on NH_3 conversion for Fe-ZSM-5 (700)

Since the waste streams usually contain water vapor and small amounts of SO_2, we further studied the effects of H_2O and SO_2 on the catalytic performance of Fe-ZSM-5 (700) for SCO of ammonia. For Fe-ZSM-5 (700), when 500 ppm SO_2 and/or 2.5% H_2O was added to the reactants, NH_3 conversion was decreased only slightly by H_2O (Fig. 5). SO_2 and $H_2O + SO_2$ decreased NH_3 conversion at 350–450 °C, but the decrease was less significant at high temperatures. N_2 was again the dominant product for NH_3 oxidation in the presence of H_2O and/or SO_2.

3.6. FT-IR study

The IR spectra of Fe-ZSM-5 (700) and Fe-ZSM-5 (350) at room temperature are shown in Fig. 6. The IR spectra of both samples are almost the same, several bands at 1630, 1870, 1990, and 3740 cm^{-1} are observed. The weak band at 3740 cm^{-1} can be assigned to hydroxyl stretching vibration of the Si-OH group at crystal termination [18]. The bands at 1990 and 1870 cm^{-1} are due to the zeolite overtone bands [19]. The band at 1630 cm^{-1} and the broad absorption at 3000–3400 cm^{-1} are due the adsorbed water. The band at 3610 cm^{-1} due to OH stretching of the Brønsted acid [19, 20] which is very small and is in accordance with the results obtained by Chen and Sachtler [16].

The IR spectra of ammonia adsorbed on Fe-ZSM-5 (700) at different temperatures are shown in Fig. 7. After the sample was treated in flowing 1000 ppm NH_3/He for 30 min and then purged with He for 30 min at 30 °C, a strong band around 1470 cm^{-1} and several weak bands at 1705, 1630, and 1280 cm^{-1} were observed. The bands at 1705 and 1470 cm^{-1} are due to the symmetric and asymmetric bending vibrations, respectively, of NH_4^+ that is chemisorbed on the Brønsted acid sites, while the bands at 1630 and 1280 cm^{-1} may be assigned to symmetric and asymmetric bending vibration of the N–H bonds in NH_3 coordinately linked to the Lewis acid sites [21,22]. The above results indicated that there are many more Brønsted acid sites than Lewis acid sites on the Fe-ZSM-5. With increasing temperatures, the intensities of the 1630 and 1270 cm^{-1} bands increased while the intensities of the 1470 and 1705 cm^{-1} bands decreased. This result indicated that some NH_3 species have desorbed and some of NH_4^+ species were transformed to coordinately adsorbed NH_3 on Fe-ZSM-5.

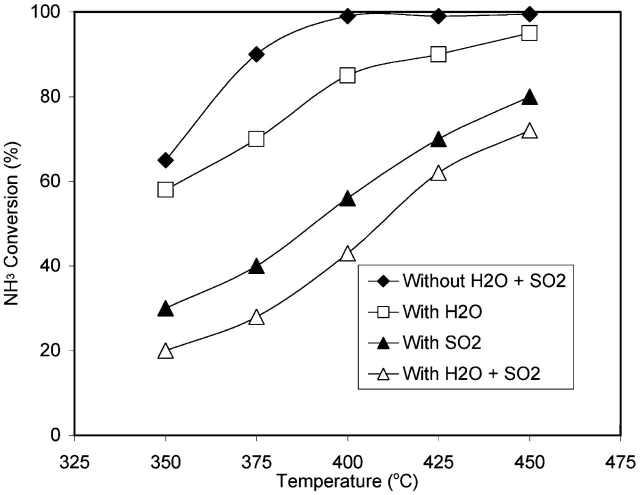

Fig. 5. Effect of H_2O and SO_2 on NH_3 conversion for Fe-ZSM-5 (700). Reaction conditions: catalyst 0.1 g, [NH_3] = 1000 ppm, [O_2] = 2%, He = balance, 500 ppm SO_2 (when used), 2.5% water vapor (when used), total flow rate = 500 ml/min, GHSV = 2.3 × 10^5 h^{-1}.

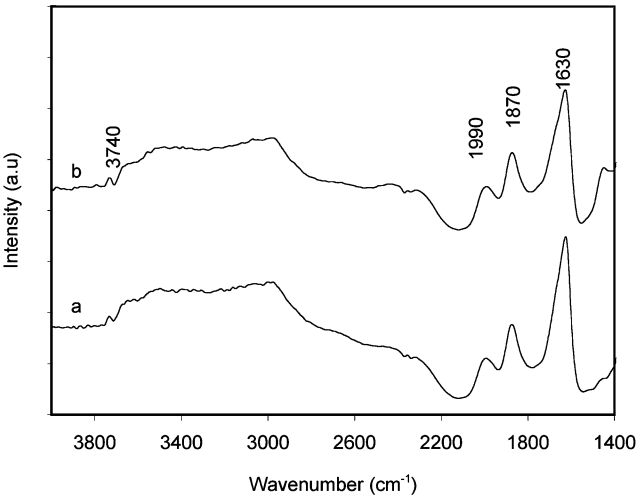

Fig. 6. IR spectra of Fe-ZSM-5 (700) and Fe-ZSM-5 (350) at 30 °C with empty cell as background. (a) Fe-ZSM-5 (700) and (b) Fe-ZSM-5 (350).

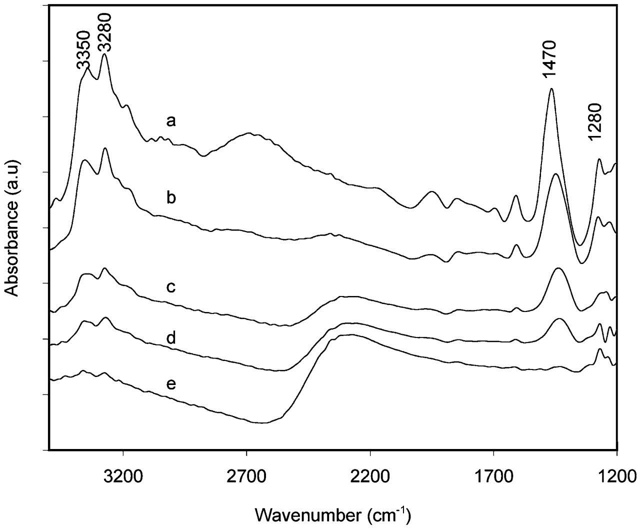

Fig. 7. IR spectra of Fe-ZSM-5 (700) treated in flowing 1000 ppm NH_3/He at 30 °C for 30 min and then purged by He at (a) 30, (b) 100, (c) 200, (d) 300, and (e) 400 °C.

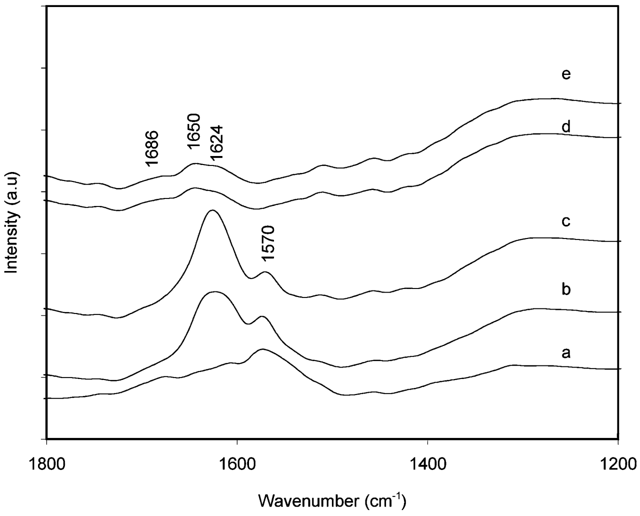

Fig. 8. IR spectra of Fe-ZSM-5 (700) treated in flowing 1000 ppm NO/He + 2% O_2 at 30 °C for 30 min and then purged by He at (a) 30, (b) 100, (c) 200, (d) 300, and (e) 400 °C.

Fig. 8 shows the IR spectra of Fe-ZSM-5 (700) treated in flowing NO + O_2 and then purged by He at different temperatures. After the Fe-ZSM-5 (700) was heated to 100 °C in He, the bands at 1686 and 1570 cm^{-1} decreased sharply, while the band at 1624 cm^{-1} increased significantly. The band at 1686 cm^{-1} was probably due to adsorbed N_2O_3 species since it is close to the IR band at 1690 cm^{-1} for gaseous N_2O_3 [24]. The bands at 1624 and 1570 cm^{-1} can be assigned to adsorbed NO_2 and nitrate species, respectively [23,25–27]. This result indicated that N_2O_3 and nitrate adspecies desorbed or transformed to NO_2 adspecies. As the temperature was further increased above 300 °C, the 1624 cm^{-1} band also decreased.

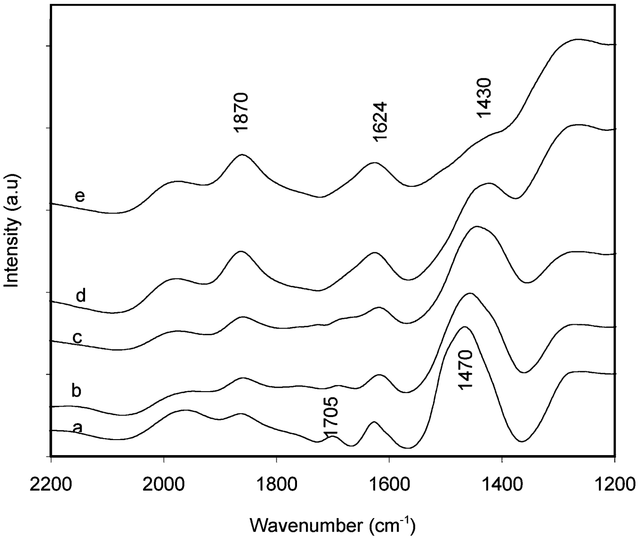

Fig. 9. IR spectra of Fe-ZSM-5 (700) treated in flow of 1000 ppm NH_3 + 2% O_2/He at (a) 30, (b) 100, (c) 200, (d) 300, and (e) 400 °C.

The IR spectra of the reaction between ammonia and oxygen are shown in Fig. 9. Fe-ZSM-5 (700) was first treated with O_2/He at 400 °C for 30 min followed by cooling to 30 °C. Then 1000 ppm NH_3 and 2% O_2/He were introduced into the IR cell and IR spectra were recorded as a function of temperature. As the temperature increased, the intensity of NH_4^+ species decreased and the peak at 1870 cm^{-1} was observed. The band at 1870 cm^{-1} can be attributed to the adsorbed NO species on Fe^{2+} sites [20,23,31].

4. Discussion

The results discussed above show that Fe-exchanged zeolites prepared by subliming $FeCl_3$ are highly active for the SCO of ammonia to nitrogen in the presence of oxygen. Table 3 shows the ammonia conversions on Fe-ZSM-5 catalysts by subliming at different temperatures in the absence of water and SO_2. All the catalysts showed high activities. The best catalyst was prepared by subliming at 700 °C. More than 99% NH_3 conversion and nearly 100% N_2 selectivity were obtained on Fe-ZSM-5 (700) at 400 °C under the condition of GHSV $= 2.3 \times 10^5\ h^{-1}$. A comparison has been made for the Fe-ZSM-5 catalysts prepared by subliming at different temperatures, given in Tables 2 and 3. It is clearly seen from Tables 2 and 3 that the subliming temperature has a significant effect on the catalytic activities on SCO of ammonia. Fe-ZSM-5 (700) has the highest TOF, indicating that this catalyst contains the most active iron species. The process during the catalyst preparation can be described as follows [17]. It is known that $FeCl_3$ at 320 °C will be present as a dimmer (Fe_2Cl_6) [28]. The ion exchange could proceed according to the following reactions:

$$Fe_2Cl_6 + \text{H-ZSM-5} \rightarrow Fe_2Cl_5\text{-ZSM-5} + HCl, \tag{2}$$

$$Fe_2Cl_5\text{-ZSM-5} \rightarrow \text{Fe-ZSM-5} + FeO_x + 5HCl, \tag{3}$$

where the framework and surface hydroxyls also participate in the reaction.

At 700 °C, $FeCl_3$ will be present as a monomer ($FeCl_3$), and the low iron content of the Fe-ZSM-5 catalyst (see Table 2) could be due to the rapid ion-exchange process at 700 °C:

$$FeCl_3 + \text{H-ZSM-5} \rightarrow FeCl_2\text{-ZSM-5} + HCl. \quad (4)$$

Kaucky et al. [29] and Sobalik et al. [30] have proposed the presence of α, β, and γ sites in ZSM-5 which are located at straight channels, at the intersection of the straight and sinusoidal channels and in a boat-shaped site in sinusoidal channels, respectively. The dimer (Fe_2Cl_6) preferentially occupies the α position along with β and γ positions [17]. Fe-ZSM-5 catalyst prepared by high temperature resulted in preferential occupation of γ positions. Although the α and β sites presented in straight channels and intersections are easily available, these positions were not extensively occupied when the materials were prepared by sublimation or treated at 700 °C because the $FeCl_2$ is bound weakly at α and β positions and migrates to the more stable γ positions or migrates out to the crystal surface [17]. Sobalik et al. [30] have proposed that, in Co-ZSM-5, the α-type Co ions exhibit the weakest bonding followed by β sites of medium strength of bonding to framework oxygens. The γ sites showed highest strength Co ions bound to the framework oxygens, similar to the above observation.

The catalytic performance, especially N_2 selectivity, was found to decrease in a trend of Fe-ZSM-5 > Fe-MOR > Fe-FER > Fe-Beta > Fe-Y (Table 4). More than 99% NH_3 conversion and nearly 100% N_2 selectivity were obtained on Fe-ZSM-5 at 400 °C under the condition of GHSV $= 2.3 \times 10^5\ h^{-1}$. The difference in the SCO performance may be related to the various pore structure and size and surface acidity for the Fe-exchanged zeolites. 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 10-member 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 12-member rings (0.6–0.7 nm). It appears that zeolites with narrow, channel pore structures favor ammonia oxidation to nitrogen by oxygen [11].

It is known that ammonia molecules can adsorb on the Brønsted acid and Lewis acid sites of zeolites to generate, respectively, NH_4^+ ions and coordinated NH_3. Our previous IR spectra showed that the NH_4^+ ions (at 1470 cm^{-1}) and the coordinated NH_3 (at 1280 cm^{-1}) can be detected on Fe-ZSM-5 catalyst. Our previous XPS and ESR data [32] on Fe-ZSM-5 indicated that iron cations were present mainly as Fe^{3+} ions with tetrahedral coordination, along with a small amount of Fe^{2+} and aggregated Fe^{3+} ions. Also, the Fe^{3+} ions could be partially reduced to Fe^{2+} ions by H_2 at 300–600 °C (Fig. 2), but the oxidation was reversible when O_2 was introduced into the reduced catalyst at 500 °C [32]. The variable valence of iron cations in the Fe-exchanged zeolites might be beneficial to oxygen adsorption and activation under the SCO reaction conditions. The oxygen adspecies, e.g., O_2^-, $O_2^{\delta-}$ ($1 < \delta < 2$), and O_2^{2-}, have been observed on O_2-adsorbed Fe_2O_3 by IR spectroscopy [33]. The high cation capacities would lead to more iron ions in the Fe-exchanged zeolites, which provide more active sites for oxygen adsorption and activation. Consequently, high activities for ammonia oxidation to N_2 are expected on the catalysts with high iron contents. The vapor-phase exchange can provide the higher exchange level of iron which results in the high activity of SCO.

It is also noted that Fe-exchanged zeolites also showed excellent activities for the selective catalytic reduction of NO to N_2 with ammonia as reductant (Figs. 3 and 4). But the SCR activity was higher than the SCO activity for the same catalyst, which was attributed to a higher reactivity of NH_3 with NO_x than with O_2 [34]. Our results indicated that almost all of NO was reduced to N_2 by ammonia on Fe-ZSM-5 at 350–450 °C under the condition of GHSV $= 4.6 \times 10^5\ h^{-1}$ (Figs. 3 and 4). This catalysts were much more active than Fe-Y, Fe-Beta, e-FER which are in line with their relative SCO performance (e.g., N_2 selectivity) obtained in this work and others [11]. By comparing the SCR activity with SCO performance for the various Fe-exchanged zeolites, it can be seen that there is a good correlation between the SCR activity and the N_2 selectivity for the SCO reaction; i.e., the higher SCR activity, the higher the N_2 selectivity. This conclusion indicates that when NO (the main byproduct) is generated during the SCO reaction, it can be further reduced to N_2 by unreacted ammonia through the SCR reaction. Similar results were also obtained on V_2O_5/TiO_2, which showed both high SCR activity and N_2 selectivity of SCO [1,2,5].

The FT-IR spectra indicate that NH_3 were adsorbed on Fe-ZSM-5 catalysts after the sample was treated with NH_3. NH_3 molecules were adsorbed on the Brønsted acid and Lewis acid sites of catalyst to generate NH_4^+ ions and coordinated NH_3, respectively (Fig. 7). In addition to the NH_4^+ ions and coordinated NH_3, NH_2 species were also detected in the IR spectra, which indicated that hydrogen abstraction took place for some ammonia species. The IR spectra of $NO + O_2$ adsorbed on Fe-ZSM-5 were also studied. NO_2, nitrate, and N_2O_3 species could be observed. With increasing temperature, the bands due to nitrogen oxides adspecies decreased (Fig. 8). The NO_2 adspecies was dominant at 100–300 °C. The IR spectra in the flow of NH_3 and O_2 were also studied (Fig. 9). With increasing temperature, the intensity of adsorbed ammonia species decreased while the band at 1870 cm^{-1} increased. From Fig. 9, the band at 1510 cm^{-1} cannot be detected, which may have resulted from the high reaction rate between NH_2 and NO species.

For the SCO reaction, two pathways for oxidation of NH_3 to N_2 have been proposed in the literature. One is a direct route by the recombination of 2 NH_2 species to NH_2–NH_2 and then oxidation of NH_2–NH_2 to N_2 [35]. The other is a two-step route that involves oxidation of NH_3 to NO_x and then reduction of NO_x to N_2 by NH_3 [1,4]. According to our catalytic performance and FT-IR results, it seems that the SCO reaction on the Fe-exchanged zeolites takes place by the two-step route; i.e., NO is an intermediate for N_2 formation. NH_3 was first oxidized to NO by O_2. This reaction occurs either on the catalyst surface or in the gaseous phase, or both. Our empty-tube results showed that NH_3 conversions were 23–55% at 350–450 °C under the condition of $\mathrm{GHSV} = 2.3 \times 10^5\ \mathrm{h}^{-1}$, with NO as the predominant product. Subsequently, the NO reacts with unreacted NH_3 to produce N_2 through the SCR reaction. Therefore, good SCR catalysts are expected to have high N_2 selectivities for the SCO reaction.

5. Conclusions

Based on the above results, it can be concluded that Fe-exchanged zeolites prepared by vapor-phase exchange method are highly active for the SCO of ammonia to nitrogen. Fe-ZSM-5 and Fe-mordenite (MOR) showed excellent SCO performances at a very high space velocity ($\mathrm{GHSV} = 2.3 \times 10^5\ \mathrm{h}^{-1}$). Over 99% NH_3 conversion and nearly 100% N_2 selectivity were obtained. Among different subliming temperature, the catalytic performance decreased in the sequence of Fe-ZSM-5 (700) > Fe-ZSM-5 (600) > Fe-ZSM-5 (500), Fe-ZSM-5 (400), Fe-ZSM-5 (350). Among different Fe-zeolites catalysts by subliming at 700 °C, the catalytic performance decreased in the sequence of Fe-ZSM-5 > Fe-MOR > Fe-FER > Fe-Beta > Fe-Y. For the Fe-exchanged zeolites, there existed a good correlation between the N_2 selectivity for the SCO reaction and the activity for the SCR (selective catalytic reduction) of NO with ammonia; i.e., the higher the SCR activity, the higher the SCO N_2 selectivity. The FT-IR results supported the two-step mechanism: NO is an intermediate for N_2 formation and NH_3 was first oxidized to NO by O_2.

Acknowledgments

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