Catalysis Today 175 (2011) 157–163

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

In situ DRIFTS study of NO reduction by NH_3 over Fe–Ce–Mn/ZSM-5 catalysts

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ARTICLE INFO

Article history:
Received 1 November 2010
Received in revised form 30 May 2011
Accepted 1 June 2011
Available online 25 June 2011

Keywords:
SCR
Fe–Ce–Mn/ZSM-5 catalysts
Nitric oxide
Ammonia
In situ DRIFTS

ABSTRACT

Fe–Ce–Mn/ZSM-5 catalysts were prepared and performance of catalysts in NO selective catalytic reduction by NH_3 was tested in the temperature range of 100–500 °C. NO conversion reached 96.6% and 98.1% at 200 °C and 300 °C respectively at a GHSV of 30,000 h^{-1}. *In situ* diffuse reflectance infrared transform spectroscopy (DRIFTS) study was carried out for revealing the reaction mechanism. Two possible reaction pathways were proposed. One was that NO_2 could react with $NH_4{}^+$ on Bronsted acid sites and the formed $NO_2[NH_4{}^+]_2$ would react with NO, producing N_2 and H_2O. Another way was that NH_3 was adsorbed and then reacted with NO or HNO_2. Possible intermediate NH_4NO_2 and NH_2NO were unstable and would decompose into N_2 and H_2O. The addition of Mn in Fe–Ce–Mn/ZSM-5 catalysts could contribute to provide more Bronsted acid sites which was beneficial for the adsorption of NH_3. The addition of both Fe and Ce could obviously increase the conversion of NO to NO_2. Introduction of Fe increased the oxidation of NH_3 slightly and the addition of Ce increased the oxidation of NH_3 significantly. The combination of manganese, iron and cerium could significantly enhance the low temperature SCR activity.

1. Introduction

Nitrogen oxides (NO_x) from vehicular and stationary engines remain a major source for air pollution. Selective catalytic reduction (SCR) with hydrocarbon or ammonia in the presence of excess oxygen is an efficient technology for reducing the NO_x emissions. Vanadia-based catalysts in SCR applications have been used extensively for their high activity [1,2]. However, the problems related to toxicity of vanadia, high activity for oxidation of SO_2 to SO_3 and narrow window temperature have caused continuing efforts to develop new catalysts. H-zeolite and ion-exchanged molecular sieves have received much attention for SCR of NO_x by both hydrocarbon and ammonia in recent years [3]. Protons in the catalyst was considered as essential for the aimed reaction [4,5]. Wang et al. [5] noted that framework of zeolite plays an important role in the selective catalytic reduction of NO by hydrocarbons and the incorporation of non-reducible Al^{3+} ions to HZSM5 zeolite significantly enhanced the competitiveness factor attributed to the modification on acidity of the HZSM-5 zeolite. Fe/ZSM-5 catalysts have been reported to be active for the catalytic reduction of nitrogen oxides in the presence of water vapor, even in the presence of SO_2 [6–8]. Long and Yang reported that Fe/ZSM-5 catalysts prepared by the ion exchange method was much more active than the commercial vanadia catalysts and showed nearly 100% NO conversion within the range 450–500 °C; the addition of small amount of cerium further increased the catalyst activity above 500 °C [9]. In order to avoid reheating of the flue gas as well as deposition of dust on the catalyst, highly active catalysts for low temperature SCR have been developed. Manganese oxides have attracted strong interest because of its high SCR activity at low temperature [10,11]. Qi et al. [12] reported that manganese-cerium oxide catalyst yielded over 95% NO conversion at 150 °C at a space velocity of 42,000 h^{-1} and a possible reaction pathway for the SCR reaction on the MnO_x–CeO_2 catalyst was proposed.

In the present work, Fe–Ce–Mn/ZSM-5 catalysts were investigated for the reduction of NO_x by ammonia in the presence of oxygen for the sake of high activity and broad temperature window. The results showed that Fe–Ce–Mn/ZSM-5 catalysts were superior catalysts in the temperature window of 200–400 °C for reduction of NO_x. In this work, *in situ* diffuse reflectance infrared transform spectroscopy (DRIFTS) was carried out to study the reaction mechanism of the SCR reaction.

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doi:10.1016/j.cattod.2011.06.004

2. Experimental

2.1. Catalysts preparation

HZSM-5 powder sample (Si/Al = 25) was kindly supplied by Shanghai Fuxu Molecular Sieve Co. Ltd. (China) and used as the catalyst support. As catalyst sources, ferric nitrate, cerium nitrate and manganese acetate were dissolved in distilled water and then HZSM-5 was added to the solution and impregnated. The impregnated catalysts were first dried at 393 K overnight, followed by calcinations at 773 K in air for 5 h. A series of Fe–Ce–Mn/ZSM-5 catalysts with different Fe/Ce/Mn ratios were prepared and all samples were based on 3 wt% Fe content.

2.2. Catalytic activity measurement

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, 5% O_2, and balance Ar. The reaction over Fe–Ce–Mn/ZSM-5 catalysts was studied between 100 °C and 500 °C at a gas hourly space velocity of 30,000 h^{-1}. The concentration of NO was monitored by a gas analyzer (TH-990S) and the product N_2 by a gas chromatograph (GC9560). In NO–O_2 reacting system, NO_2 was monitored by a chemiluminescent analyzer (Model 42i-HL). The NO conversion and the N_2 selectivity were calculated according to following equations:

$$X_{NO} = \frac{C_{NO_{in}} - C_{NO_{out}}}{C_{NO_{in}}} \times 100\% \quad (1)$$

$$S_{N_2} = \frac{C_{N_2}}{C_{NO_{in}} - C_{NO_{out}}} \times 100\% \quad (2)$$

2.3. DRIFTS experiments

The DRIFT measurements were performed on a Nicolet 6700 spectrometers at 4 cm^{-1} resolution with 64 accumulated scans. In the DRIFTS cell, the catalyst was pretreated at 500 °C in Ar environment for 2 h, and then cooled to required temperature. The background spectrum was recorded in flowing Ar and was subtracted from the sample spectrum.

3. Results

3.1. Activity measurement of catalysts

3.1.1. NH_3–NO–O_2 reacting system

The selective catalytic reduction process was based on the reaction between NO and NH_3 in presence of oxygen:

$$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O \quad (3)$$

$\Delta H^0_{298} = -1627$ kJ/mol [13].

The variations of the NO conversion as a function of the temperature are shown in Fig. 1a. From Fig. 1a, Fe–Ce–Mn/ZSM-5 catalysts were of high SCR activity in the range of 200–400 °C. The catalytic activity increased with increasing temperature. NO conversion reached 96.6% and 98.1% at 200 °C and 300 °C respectively on Fe–Ce–Mn/ZSM-5 catalyst of 1:1:4 molar ratio of Fe:Ce:Mn. The NO conversion decreased above 300 °C due to competitive ammonia oxidation [14]. The variation of small amount of manganese in Fe–Ce–Mn/ZSM-5 catalysts influences the NO conversion. Activities of catalysts were significantly improved at lower temperature due to increasing manganese content. However, more manganese also causes activities to decrease more quickly at higher temperatures. The N_2 selectivity over these samples was shown in the inserted figure. The N_2 selectivity had an obvious decrease probably owing to the production of N_2O with increasing temperatures. The N_2 selectivity calculated on Eq. (2) increased above 300 °C attributed to direct oxidation NH_3 to N_2 by O_2 at higher temperature, as shown Fig. 2b in this article.

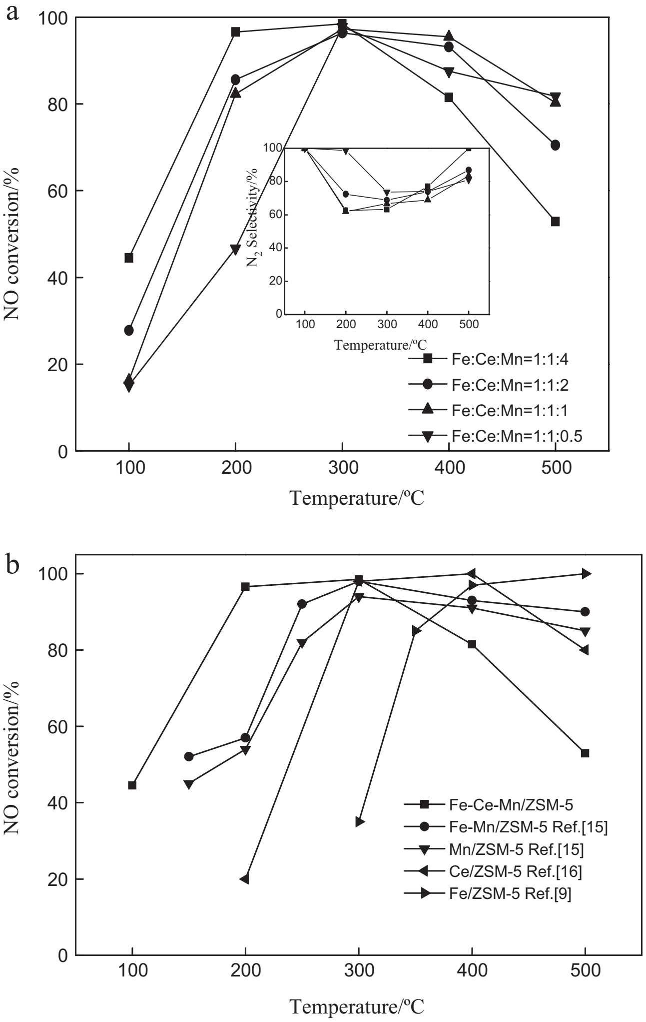

Fig. 1. (a) NO conversion and N_2 selectivity (inserted) over Fe–Ce–Mn/ZSM-5 catalysts of different Mn concentrations. Reaction conditions: 1000 ppm NO, 1000 ppm NH_3, 5% O_2, balance Ar, and GHSV 3.0×10^4 h^{-1}. (b) NO conversion over different catalysts, viz., Fe–Ce–Mn/ZSM-5(Fe:Ce:Mn = 1:1:4, reaction conditions: 1000 ppm NO, 1000 ppm NH_3, 5% O_2, balance Ar, and GHSV 3.0×10^4 h^{-1}), Mn/ZSM-5 and Fe–Mn/ZSM-5 (NO conversion on 5% Mn/ZSM-5 and (0.25) Fe–Mn/ZSM-5 from Ref. [15], reaction conditions: 1000 ppm NO, 1100 ppm NH_3, 5% O_2, balance N_2, and GHSV 1.2×10^4 h^{-1}), Ce/ZSM-5(NO conversion on 50/50 wt% $Ce(Ac)_3$/ZSM-5 from Ref. [16], reaction conditions: 900 ppm NO, 900 ppm NH_3, 3.5% O_2, balance He, and GHSV 4.0×10^4 h^{-1}), Fe/ZSM-5 (NO conversion on Fe(130)/ZSM-5 from Ref. [9], reaction conditions: 1000 ppm NO, 1000 ppm NH_3, 2% O_2, balance He, and GHSV 4.6×10^5 h^{-1}).

Fig. 1b shows the SCR activities of the different catalysts (viz., Fe–Ce–Mn/ZSM-5, Fe–Mn/ZSM-5, Fe/ZSM-5, Mn/ZSM-5, Ce/ZSM-5) with or without Fe, Ce or Mn in the range of 100–500 °C. The SCR activity of the Fe–Ce–Mn/ZSM-5 catalyst was obtained from the experiment in this article. The data of the SCR activity of the other catalysts (viz., Fe–Mn/ZSM-5, Fe/ZSM-5, Ce/ZSM-5, Mn/ZSM-5) were refereed to the references [9,15,16]. It can be observed in Fig. 1b that the low temperature SCR activity of Fe–Ce–Mn/ZSM-5 catalyst was much better than that of the other catalysts. Nearly 100% NO conversion over the Fe–Ce–Mn/ZSM-5 catalyst occurred at 200 °C while the other catalysts had the highest NO conversion at 300 °C or above 300 °C, although the high temperature SCR activity of Fe–Ce–Mn/ZSM-5 catalyst above 300 °C showed obvious

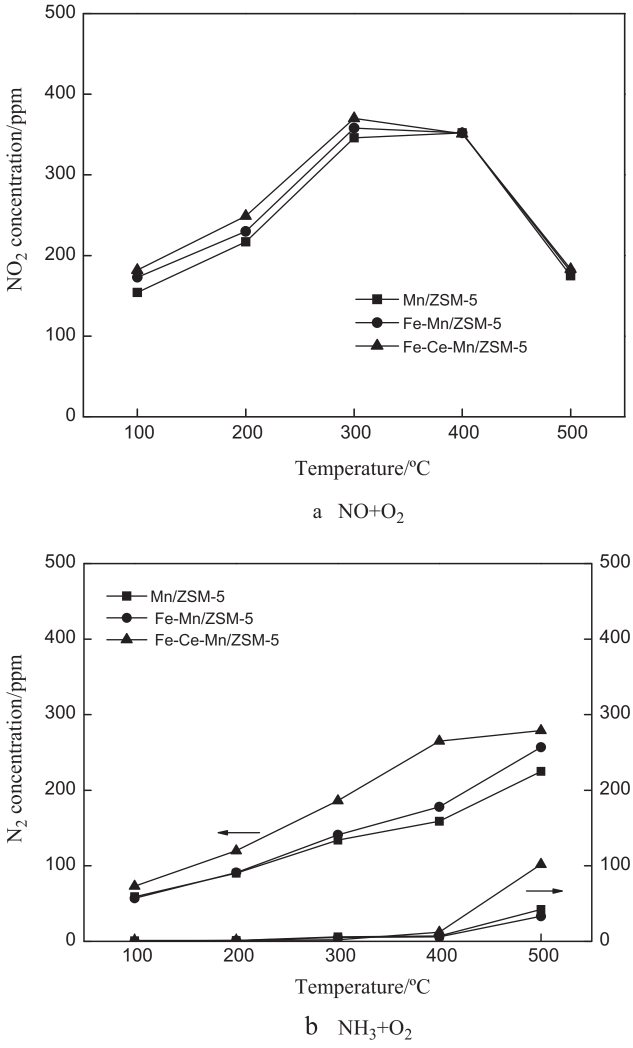

Fig. 2. Reaction of NO–O$_2$ and NH$_3$ -O$_2$ on different catalysts (Fe:Mn = 1:4 in Fe–Mn/ZSM-5, Fe:Ce:Mn = 1:1:4 in Fe–Ce–Mn/ZSM-5). Reaction conditions: (a) 1000 ppm NO, 5% O$_2$, balance Ar, and GHSV 30,000 h^{-1}. (b) 1000 ppm NH$_3$, 5% O$_2$, balance Ar, and GHSV 30,000 h^{-1}.

decrease. The comparison of the NO conversion over the ZSM-5 supported by a single metal (viz., Fe/ZSM-5, Ce/ZSM-5, Mn/ZSM-5) showed that the Mn/ZSM-5 catalyst had the best SCR activity below 300 °C. The NO conversion was increased as the Fe was added into Mn/ZSM-5 catalyst. The NO conversion was further increased in the range of 100–300 °C as the Ce was added into the Fe–Mn/ZSM-5 catalyst. It indicated that the addition of both Fe and Ce was advantageous to improve the SCR activity of the Mn/ZSM-5 catalyst at the lower temperature.

3.1.2. NH_3–O_2 and NO–O_2 reacting system

NH_3 and NO oxidation reactions were also studied as a function of the temperature. NO oxidation reaction is expressed as following stoichiometry:

$$NO + (1/2)O_2 \rightleftharpoons NO_2 \quad (4)$$

$\Delta H^0{}_{298} = -113$ kJ/mol [13].

According to Fig. 2a, more NO_2 was formed over Fe–Mn/ZSM-5 catalyst and Fe–Ce–Mn/ZSM-5 catalyst compared with Mn/ZSM-5 catalyst. The NO_2 concentration over the Mn/ZSM-5 reached 346 ppm at 300 °C. After the Fe was added into the Mn/ZSM-5 catalyst the NO_2 concentration was increased to 358 ppm. After the Ce was added into the Fe–Mn/ZSM-5, the NO_2 concentration was further increased to 370 ppm. While the temperature was increased above 300 °C, the effect of the Fe and Ce on the NO oxidation could be neglected.

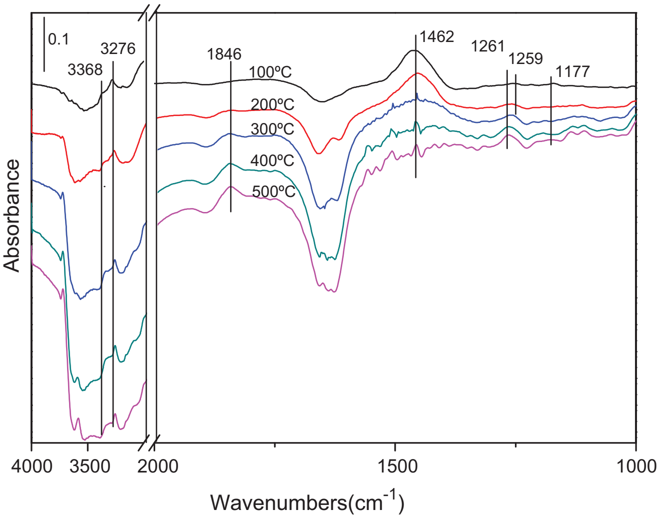

Fig. 3. DRIFT spectra of Fe–Ce–Mn/ZSM-5 catalyst (Fe:Ce:Mn = 1:1:4) treated in flow of 1000 ppm NH_3 and 5% O_2 at 100 °C for 30 min and then purged by Ar at different temperature.

From Fig. 2b, NH_3 was gradually oxidized over different catalysts (viz., Mn/ZSM-5, Fe–Mn/ZSM-5, Fe–Ce–Mn/ZSM-5) as the temperature was increased. As the Fe was added into the Mn/ZSM-5 catalyst the oxidation of NH_3 was slightly increased. As a comparison, the oxidation of NH_3 could be significantly increased as the Ce was further added into the Fe–Mn/ZSM-5. It indicated that Ce had more important effect on the improvement of the oxidation of NH_3. Fig. 2b also indicates that the NH_3 is more oxidized to N_2 [17] rather than to NO. The reaction of NH_3 to N_2 can be expressed as follows:

$$2NH_3 + (3/2)O_2 \rightarrow N_2 + 3H_2O \quad (5)$$

$\Delta H^0{}_{298} = -633$ kJ/mol [13]

When the temperature was higher than 300 °C, NO formation increased more quickly. This showed that the ammonia was over-oxidized to NO. NH_3 oxidation is a competitive reaction with SCR reaction [14,18]. This may be the reason that the SCR activities of Fe–Ce–Mn/ZSM-5 catalysts decreased above 300 °C in Fig. 1a.

3.2. DRIFT studies

3.2.1. Temperature-programmed desorption of pre-adsorbed NH_3 and O_2

Fig. 3 shows the DRIFT spectra of Fe–Ce–Mn/ZSM-5 catalysts treated in flow of 1000 ppm NH_3 and 5% O_2 for 30 min and then purged by Ar from 100 °C to 500 °C at 10 °C/min. After co-adsorption of NH_3 and O_2 for 30 min and then purged by Ar for 30 min at 100 °C, a strong band at 1462 cm^{-1} and weak bands at 1259, 1177, 3368, 3276 and 1600–1570 cm^{-1} were observed. The band at 1462 cm^{-1} could be due to $NH_4{}^+$ species on Bronsted acid sites [19–22]. The bands at 1259, 1177 and 1600–1570 cm^{-1} could be attributed to coordinated NH_3 on Lewis acid sites [12,22–24]. With increasing temperature, the intensity of the adsorbed ammonia species decreased. Meanwhile, new bands at 1846 cm^{-1} and 1261 due to nitrosyl NO$^-$ [12] species were observed and the intensity increased with increasing temperature. That mean NH_3 was over-oxidized at high temperature. NH_3 over-oxidation to NO or N_2 was a competitive reaction with SCR reaction [14,18] and would reduce the SCR activity. Above 300 °C, ammonia species decreased so much

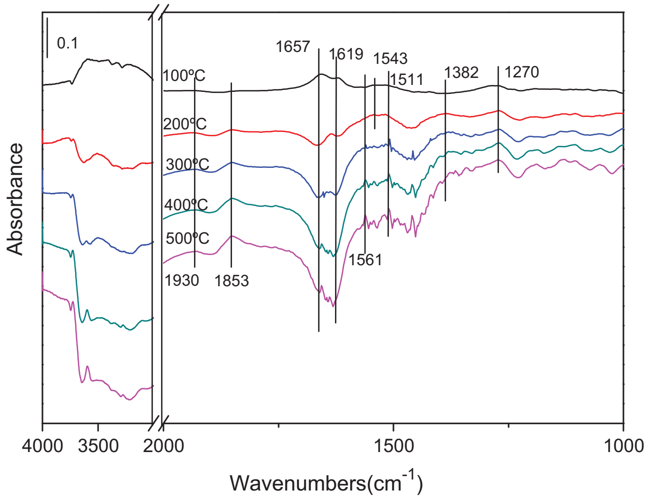

Fig. 4. DRIFT spectra of Fe–Ce–Mn/ZSM-5 catalyst (Fe:Ce:Mn = 1:1:4) treated in flow of 1000 ppm NO and 5% O_2 at 100 °C for 30 min and then purged by Ar at different temperature.

as nearly could not be detected. This was consistent with the results that more NO was detected due to NH_3 over-oxidation at higher temperature from Fig. 2b and the SCR activities over Fe–Ce–Mn/ZSM-5 catalysts decreased above 300 °C from Fig. 1a.

3.2.2. Temperature-programmed desorption of pre-adsorbed NO and O_2

Fig. 4 shows the DRIFT spectra of Fe–Ce–Mn/ZSM-5 catalysts treated in flow of 1000 ppm NO and 5% O_2 for 30 min and then purged by Ar from 100 °C to 500 °C at 10 °C/min. After NO and O_2 were passed over the sample and then purged by Ar at 100 °C, bands at 1657, 1619, 1543, 1511 and 1270 cm^{-1} appeared and weak bank at 1930 cm^{-1} could be detected. The bands at 1657, 1543, 1511 and 1270 cm^{-1} could be attributed to nitrate species [12,20]. These species should be produced by NO oxidation. The bands at 1930, and 1619 cm^{-1} could be attributed to gas phase or weekly adsorbed NO and NO_2, respectively [12,25]. Purging at 200 °C caused the disappearance of bands at 1657 and 1619 cm^{-1}. Bands at 1930, 1543, 1511 and 1270 cm^{-1} became sharpened. New bands at 1853 cm^{-1} due to nitrosyl and 1382 cm^{-1} due to nitrate could be detected. Continuous purging at increasing temperature until 500 °C caused the decrease of intensity of bands at 1930, 1543, 1382 and 1270 cm^{-1}. The intensity of bands at 1853 and 1511 cm^{-1} remained nearly unchanged.

3.2.3. NH_3 adsorption on Fe–Ce–Mn/ZSM-5

The DRIFT spectra of 1000 ppm NH_3/Ar on Fe–Ce–Mn/ZSM-5 catalyst at 200 °C are shown in Fig. 5. Immediately after introducing NH_3 into the IR cell (time = 2 min), large band at 1468 cm^{-1} was detected which could be attributed to $NH_4{}^+$species on Bronsted acid sites [19,20]. With increasing time, band at 1740 cm^{-1} and several weak bands at 1259, 1177 cm^{-1} and a broad band in the range of 1600–1570 cm^{-1} appeared. The intensity of the band at 1468 cm^{-1} increased. The band at 1740 cm^{-1} could be attributed to NO_x adspecies, e.g., N_2O_4 [26–28] resulted from ammonia oxidation. The band at 1740 cm^{-1} would disappear and N_2O_4 would be further converted into nitrate adspecies when NO and O_2 were introduced as the following Fig. 7 in this article. The bands at 1259,1177 and 1600–1570 cm^{-1} could be due to coordinated NH_3 on Lewis acid sites [12,22–24]. The bands at 3351, 3276 and 3188 cm^{-1} attributed to N–H stretching vibration modes of NH_3 [23,24] were found and showed progressive increase in intensity. At the same time, the intensities of the negative bands at 3665, 3508 and 1630 cm^{-1} ascribed to O–H stretching vibration modes due to the interaction of surface hydroxyls with NH_3 [23,29] also became strong. From Fig. 5, it could be also observed that the intensity of all above bands was nearly no variation after the sample was purged for 30 min by Ar. It indicated that the ammonia adspecies and N_2O_4 adsorbed on the Fe–Ce–Mn/ZSM-5 catalyst were stable.

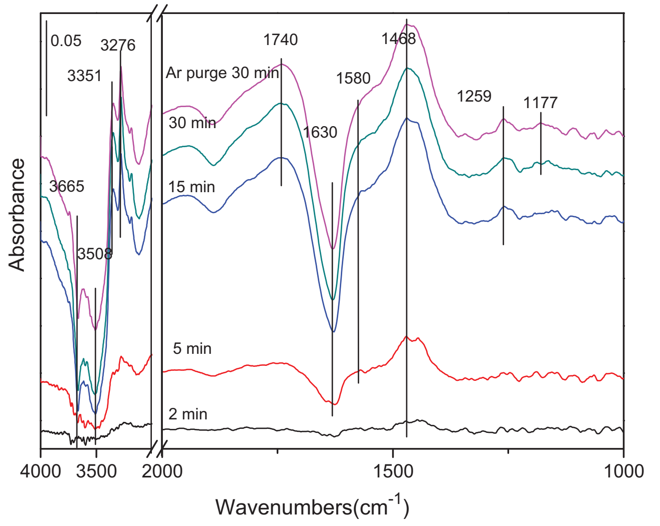

Fig. 5. DRIFT spectra of Fe–Ce–Mn/ZSM-5 catalyst (Fe:Ce:Mn = 1:1:4) exposed to1000 ppm NH_3 for various times and then purged by Ar for 30 min at 200 °C.

3.2.4. Co-adsorption of NO and O_2 on Fe–Ce–Mn/ZSM-5

The catalyst was treated with 1000 ppm NO and 5% O_2 at 200 °C for 30 min, followed by purging with Ar for 30 min. Then the spectra of Fe–Ce–Mn/ZSM-5 catalyst (Fig. 6) were recorded. Flowing NO and O_2 produced the bands at 1879, 1621, 1543, 1360, 1125 cm^{-1}. The bands at 1879 cm^{-1} and 1621 cm^{-1}could be assigned to gas phase or weekly adsorbed NO and NO_2, respectively [12,25]. The band at 1543 cm^{-1} was assigned to nitrate species and 1125 cm^{-1} to nitrosyl NO^- species, which could be oxidized to nitrate or nitrite species in the presence of oxygen [12]. The band at 1360 cm^{-1} could be attributed to M–NO_2 nitro compounds [20,30]. Some negative bands around 3733 cm^{-1} were also found, which could be assigned

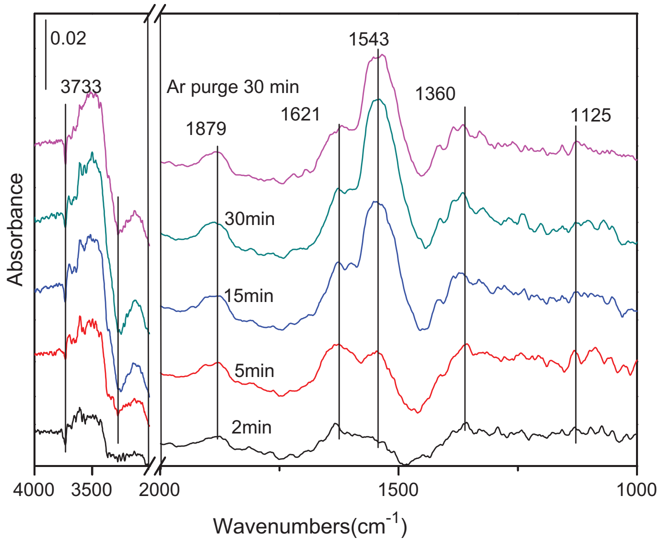

Fig. 6. DRIFT spectra of Fe–Ce–Mn/ZSM-5 catalyst (Fe:Ce:Mn = 1:1:4) exposed to1000 ppm NO and 5% O_2 for various times and then purged by Ar for 30 min at 200 °C.

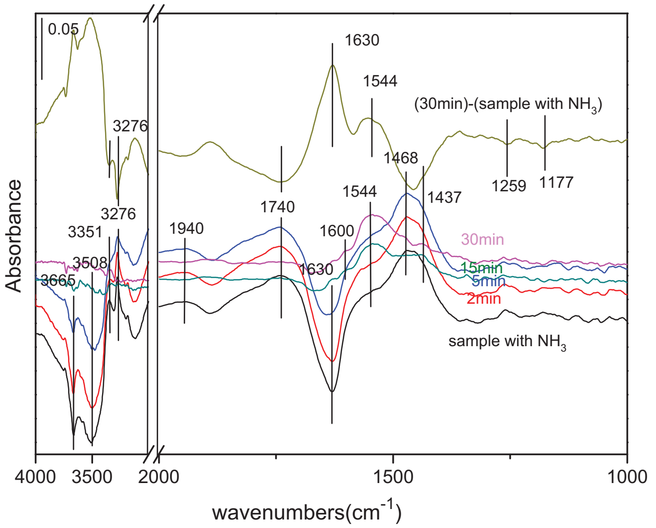

Fig. 7. DRIFT spectra of NH_3-adsorbed Fe–Ce–Mn/ZSM-5 catalyst (Fe:Ce:Mn = 1:1:4) followed by exposure to 1000 ppm NO and 5% O_2 at 200 °C for various times.

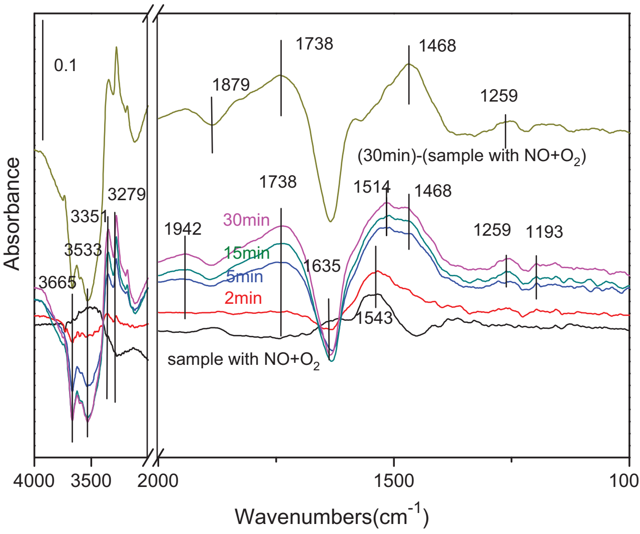

Fig. 8. DRIFT spectra of NO and O_2-adsorbed Fe–Ce–Mn/ZSM-5 catalyst (Fe:Ce:Mn = 1:1:4) followed by exposure to 1000 ppm NH_3 at 200 °C for various times.

to the surface O–H stretching [20]. The intensity of above the bands increased with time except the bands at 1879 and1621 cm^{-1}. After the sample was purged by Ar, the intensity of the band at 1621 cm^{-1} decreased, indicating that the adsorbed NO_2 was not very stable.

3.2.5. *Nitric oxide adsorption after NH_3*

Fe–Ce–Mn/ZSM-5 catalyst was first purged with NH_3 for 30 min followed by Ar purging at 200 °C. When NO and O_2 were introduced, the IR spectra were recorded as a function of time (Fig. 7). As noted above, coordinated NH_3 and $NH_4{}^+$species were detected. After NO and O_2 were passed over the sample for 15 min, the dominant bands attributed to $NH_4{}^+$ adspecies (1468 cm^{-1}), coordinated NH_3 (1259, 1177 and 1600–1570 cm^{-1}) and N_2O_4 (1740 cm^{-1}) decreased quickly and diappeared. The negative bands at 3665, 3508 and 1630 cm^{-1} also diappeared due to NH_3 species consumption. The bands at 3351, 3276, and 3188 cm^{-1} attributed to N–H stretching vibration could not be detected. At the same time, several new bands were detected at 1544 and 1437 cm^{-1} which could be attributed to nitrate species and nitro compounds, respectively. During this process, the bands around 3600 cm^{-1} and 1600 cm^{-1} attributed to H_2O could be observed.

3.2.6. *NH_3 adsorption after nitric oxide*

Fe–Ce–Mn/ZSM-5 catalyst was first treated with NO and O_2 for 30 min followed by Ar purging at 200 °C. NH_3 was then introduced into the cell and spectra were recorded as a function of time (Fig. 8). At first 2 min, the IR bands due to NO_2 (1621 cm^{-1}), NO (1879 cm^{-1}) and nitro compounds (1360 cm^{-1}) disappeared. The bands at 1259 and 1193 attributed to the coordinated NH_3 were observed. At the same time, the bands at 3351, 3279 and 3183 cm^{-1} attributed to N–H stretching vibration modes of coordinated NH_3 were formed and the negative bands at 3665, 3533 and 1635 cm^{-1} ascribed to O–H stretching vibration modes were detected. After the catalyst was purged with NH_3 for 5 min, the intensity of the bands at 1738 cm^{-1} due to N_2O_4 and at 1468 cm^{-1} due to $NH_4{}^+$ increased. Simultaneously, bands ranging from 1543 cm^{-1} to 1514 cm^{-1} due to amide species were formed [12,20]. The band at 1942 cm^{-1} most probably due to nitrosyl NO^- species was detected. The bands assigned to H_2O were difficult to observe because the water generated from the SCR reaction and the NH_3 species adsorbed on O–H group appeared in the same region.

4. Discussion

Mn and Fe based catalysts have been studied extensively for the SCR reaction in the past [19,22,31]. MnO_x was considered as very active for low temperature SCR of NO [10,32]. Liu et al. [23] studied on the effect of manganese substitution on the structure and activity of iron titanate catalyst. They found that the low temperature SCR activity was greatly enhanced when partial Fe was substituted by Mn. In their *in situ* DRIFTS study of NH_3 adsorption, they found that the intensities of the negative bands at 3732 and 3676 cm^{-1} ascribed to O–H stretching vibration modes due to the interaction of surface hydroxyls with NH_3 became larger during this Mn substitution process. They proposed that the introduction of Mn resulted in more Bronsted acid sites on the catalyst surface, which was favorable for the promotion of SCR activity. From our *in situ* DRIFTS spectra of NH_3 adsorption on Fe–Ce–Mn/ZSM-5 catalyst, with increasing time, the intensities of the negative bands at 3665, 3508 and 1630 cm^{-1} became very strong. Combined with Fig. 1a, with increasing manganese content, SCR activities of Fe–Ce–Mn/ZSM-5 catalysts were significantly improved below 300 °C, although the activities decreased at higher temperature probably due to the over-oxidation of NH_3 to NO, as shown in Fig. 2b. Based on above the results, the addition of Mn was considered to contribute to the formation of strong negative bands and provide more Bronsted acid sites on the catalyst surface which was beneficial for the adsorption of NH_3. Lin et al. [22] investigated a series of catalysts of Mn/USY and Mn–Fe/USY. They found that addition of Fe into Mn/USY promoted NO oxidation which could contribute to high SCR activity. Ceria has been studied extensively for its oxygen storage and redox properties [12,18]. After addition of cerium into MnO_x, ceria acts as the oxygen storage promoter, which could enhances the oxidation of Mn_2O_3 to MnO_2 in the presence of O_2. The co-existence of MnO_2–Mn_2O_3 might enhance oxidation of ammonia [12,33,34] and NO oxidation to NO_2 [18,35]. In present study, the catalytic activity of SCR of NO by NH_3 Fe–Ce–Mn/ZSM-5 catalysts increased with increasing temperature below 300 °C and NO conversion decreased at higher temperature. From NO oxidation reactions over Mn/ZSM-5, Fe–Mn/ZSM-5 and Fe–Ce–Mn/ZSM-5 catalysts, the addition of both Fe and Ce into Mn/ZSM-5 could obviously increase the conversion of NO to NO_2 at the lower temperature below 300 °C which could contribute to high SCR activity. For NH_3 oxidation reactions, introduction of Fe into

Mn/ZSM-5 increased the oxidation of NH_3 slightly and the addition of Ce increased the oxidation of NH_3 significantly. Additionally, from Fig. 1b, SCR activity of Fe–Ce–Mn/ZSM-5 catalyst was significantly higher than that of the other catalysts (viz., Fe–Mn/ZSM-5, Fe/ZSM-5, Ce/ZSM-5, Mn/ZSM-5) at lower temperature. Based on above the analysis, it may be concluded that the combination of manganese, iron and cerium could significantly enhance the low temperature SCR activity.

From the DRIFT study, it was evident that NH_3 could be adsorbed on Fe–Ce–Mn/ZSM-5 catalysts, resulting in coordinated NH_3 and NH_4^+. When NO and O_2 was passed over the sample pretreated by NH_3 at 200 °C, the bands corresponding to coordinated NH_3 and NH_4^+ decreased quickly and disappeared, indicating that all the bands formed during the NH_3 adsorption were active in the SCR reaction. In NO and O_2 flowing process over the sample, NO_2 was detected. After NH_3 was introduced to the catalyst preadsorbed with NO and O_2, nitrate species deceased and quickly vanished. The bands due to coordinated NH_3 and NH_4^+ were detected. The amide species which was considered as the intermediate of the SCR reaction were formed. Therefore, it could be concluded that SCR reaction could also take place in another way.

The mechanism of the SCR reaction had been studied extensively elsewhere [12,19,20,32] and different hypotheses had been proposed. The formation of NH_2 was the key step in the mechanism of NO reduction. Kijlstra et al. [36] proposed that the SCR reaction started with the transformation of coordinated NH_3 to NH_2 species. The NH_2 would then react with gas phase NO (the E–R mechanism) and nitrite intermediates on the surface (the L–H hypothesis). Long and Yang [19] suggested a possible reaction mechanism for NO reduction involving NO_2 and $NO_2(NH_4^+)_2$ as intermediates. In our investigation of NO adsorption on the catalyst preadsorbed with NH_3, the NH_4^+ on Bronsted acid sites was consumed rapidly after NO and O_2 was introduced, and the bands assigned to H_2O were observed. In NO and O_2 flowing process over the sample, NO_2 was detected. It mean that NO_2 could react with NH_4^+ to form $NO_2(NH_4^+)_2$. Therefore, the SCR reaction of NO by NH_3 on the Fe–Ce–Mn/ZSM-5 catalysts could take place as shown:

$$NH_3(g) \rightarrow NH_3(a) \quad (6)$$

$$NH_3(a) + H^+ \rightarrow NH_4^+(a) \quad (7)$$

$$NO(g) + (1/2)O_2(g) \rightarrow NO_2(a) \quad (8)$$

$$NO_2(a) + 2NH_4^+(a) \rightarrow NO_2(NH_4^+)_2(a) \quad (9)$$

$$NO_2(NH_4^+)_2(a) + NO(g) \rightarrow \ldots \rightarrow 2N_2(g) + 3H_2O + 2H^+ \quad (10)$$

When NH_3 was introduced to Fe–Ce–Mn/ZSM-5 catalysts pretreated with NO and O_2, nitrate species, weak adsorbed NO and NO_2 deceased and quickly disappeared. Coordinated NH_3 and NH_4^+ appeared. The amide species were formed and nitrosyl NO^- species was detected. NO could be abated and the SCR reaction would also proceed between the coordinated NH_3 and NO in another way according to the following step as proposed by Qi et al. [12]:

$$O_2 \rightarrow 2O(a) \quad (11)$$

$$NH_3(g) \rightarrow NH_3(a) \quad (12)$$

$$NH_3(a) + O(a) \rightarrow NH_2(a) + OH(a) \quad (13)$$

$$NO(g) + (1/2)O_2(g) \rightarrow NO_2(a) \quad (14)$$

$$NO_2(a) + OH(a) \rightarrow O(a) + HNO_2(a) \quad (15)$$

$$NH_2(a) + NO(g) \rightarrow NH_2NO(a) \rightarrow N_2(g) + H_2O \quad (16)$$

$$NH_3(a) + HNO_2(a) \rightarrow NH_4NO_2(a) \rightarrow NH_2NO(a) + H_2O \rightarrow N_2(g) + 2H_2O \quad (17)$$

In this way, NH_3 was adsorbed on the Fe–Ce–Mn/ZSM-5 catalysts and was activated through H abstraction to form NH_2, which then reacted with the gas-phase NO to form a nitrosamide (NH_2NO) species. The nitrous acid was produced by reoxidation reaction or disproportionation of $2NO_2$ with H_2O [12,37]. The nitrous acid reacted with ammonia and then produced ammonium nitrite. Both ammonium nitrite and nitrosamine were unstable and would decompose into N_2 and H_2O.

5. Conclusions

Fe–Ce–Mn/ZSM-5 catalysts were of high SCR activity in the range of 200–400 °C. Over 95% of NO conversion was obtained at 200 °C and 300 °C on Fe–Ce–Mn/ZSM-5 catalyst of 1:1:4 molar ratio of Fe:Ce:Mn. The addition of Mn in Fe–Ce–Mn/ZSM-5 catalysts was considered to contribute to provide more Bronsted acid sites which was beneficial for the adsorption of NH_3. The addition of both Fe and Ce could obviously increase the conversion of NO to NO_2. Introduction of Fe increased the oxidation of NH_3 slightly and the addition of Ce increased the oxidation of NH_3 significantly. The combination of manganese, iron and cerium could significantly enhance the low temperature SCR activity. DRIFT studies found that nitrosyl NO^- species were formed when catalysts were treated in flow of NH_3 and O_2 at high temperature. NH_3 over-oxidation reduced the SCR activity above 300 °C. Two possible reaction pathways were proposed. One was that NO_2 could react with NH_4^+ on Bronsted acid sites and the formed $NO_2[NH_4^+]_2$ would react with NO, producing N_2 and H_2O. Another way was that NH_3 was adsorbed and then reacted with NO or HNO_2. Possible intermediate NH_4NO_2 and NH_2NO were unstable and would decompose into N_2 and H_2O.

Acknowledgment

This work was supported by the National Natural Science Foundation of China (20977034).

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