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Article

Mn/beta and Mn/ZSM-5 for the low-temperature selective catalytic reduction of NO with ammonia: Effect of manganese precursors

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ABSTRACT

Two series of Mn/beta and Mn/ZSM-5 catalysts were prepared to study the influence of how different Mn precursors, introduced to the respective parent zeolites by wet impregnation, affected the selective catalytic reduction (SCR) of NO by NH₃ across a low reaction temperature window of 50–350 °C. In this study, the catalysts were characterized using N₂ adsorption/desorption, X-ray diffraction, X-ray fluorescence, H₂ temperature-programmed reduction, NH₃ temperature-programmed desorption and X-ray photoelectron spectroscopy. As the manganese chloride precursor only partially decomposed this primarily resulted in the formation of MnCl₂ in addition to the presence of low levels of crystalline Mn₃O₄, which resulted in poor catalytic performance. However, the manganese nitrate precursor formed crystalline MnO₂ as the major phase in addition to a minor presence of unconverted Mn-nitrate. Furthermore, manganese acetate resulted principally in a mixture of amorphous Mn₂O₃ and MnO₂, and crystalline Mn₃O₄. From all the catalysts screened, the test performance data showed Mn/beta-Ac to exhibit the highest NO conversion (97.5%) at 240 °C, which remained >90% across a temperature window of 220–350 °C. The excellent catalytic performance was ascribed to the enrichment of highly dispersed MnO_x (Mn₂O₃ and MnO₂) species that act as the active phase in the NH₃-SCR process. Furthermore, together with a suitable amount of weakly acidic centers, higher concentration of surface manganese and a greater presence of surface labile oxygen groups, SCR performance was collectively enhanced at low temperature.

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1. Introduction

Nitrogen oxides (NO_x) are significant atmospheric pollutants that have significant impact on both air quality and human health and that result from the burning of fossil fuels such as refined crude oil products (petrol and diesel) or solid coal, from cars, ships and industrial processes [1–3]. Selective catalytic reduction (SCR) of NO_x is reported to be an already feasible and mature process, which is widely applied to flue gas denitrifica-

tion [4,5]. The SCR denitration catalyst is one of the key components in a SCR system, with typical commercial catalysts such as V₂O₅-WO₃/TiO₂ and V₂O₅-MoO₃/TiO₂ being employed as the active components in this system [6]. There are, however, some shortcomings related the aforementioned catalysts, for example, the narrow working temperature window (300–400 °C) and the toxic effect of V₂O₅. Hence, there has been a wealth of interdependent research focusing on developing new highly effective and environmentally friendly SCR catalysts

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[7,8].

Over the past few years, researchers have developed increasingly attractive and efficient SCR catalysts. Owing to the particular features, various transition metals (Cr, Mn, Fe, Cu and Ce) have been studied as the active components for SCR catalysts [9,10]. In particular, manganese-based catalysts are a current hot topic of interest because of the multiple valences, labile oxygen and diversiform oxidation states of manganese (Mn_3O_4 , Mn_2O_3 , MnO_2 , MnO) [11,12]. Mn-based supported catalysts have attracted significant attention with respect to the manganese precursor used. Hwang *et al.* [13] used manganese(II) nitrate, manganese(II) acetate and manganese(III) acetate to prepare $\text{MnO}_x/\text{TiO}_2$ catalysts through a sol-gel method, concluding that the catalysts synthesized with manganese acetate showed higher catalytic performance as a result of abundant MnO_2 species and strong acid sites. Fang *et al.* [14] claimed that catalysts prepared from manganese acetate and manganese carbonate, containing Mn_2O_3 and Mn_3O_4 , resulted in superior catalytic performance when compared with the corresponding catalysts prepared by manganese nitrate and manganese sulfate. However, Pena *et al.* [15] observed that catalysts prepared using manganese nitrate yielded MnO_2 and displayed enhanced catalytic performance than the corresponding catalyst prepared with manganese acetate. There remains on-going debate over how catalytic activity is influenced by the active phase of Mn-based catalysts prepared with different precursors. Therefore, to elucidate the influence of Mn precursors it is of interest to further investigate SCR performance and surface MnO_x species over Mn-based catalysts.

Furthermore, TiO_2 exhibits poor specific surface areas, which is thought to hinder the performance of Mn-based supported catalysts [16]. However, other supports that include transition metal oxides [17], carbon materials [18] and zeolites [19] have been widely used for the preparation of Mn-containing catalysts. Zeolites possess several advantageous characteristics such as large specific surface areas, unique pore structures and abundant acid sites, and are reported to be excellent catalyst supports [2,20]. Recent trends in zeolite-based catalysts have led to a proliferation of studies, such as $\text{MnO}_x/\text{ZSM-5}$ [21], MnO_x/beta [22], MnO_x/USY [23] and $\text{MnO}_x/\text{SAPO-34}$ [24]. Among these catalysts, the ZSM-5 series of catalysts [25,26] have attracted significant attention as alternative SCR catalysts. Additionally, there is significant research focus on metal-modified beta zeolite because of the superior hydrothermal stability reported in recent years. For example, Frey *et al.* [27] demonstrated that Fe/beta exhibited higher activity than Fe/ZSM-5 and Fe/ZSM-12 across a broad temperature window. Additionally, Corma *et al.* [28] reported a stable Cu-beta catalyst having SCR activity as high as that of Cu/ZSM-5. These studies suggest that beta zeolite has been regarded as a promising SCR catalyst support. Hitherto, significant efforts have focused on Mn/ZSM-5 in terms of preparation methods, calcination temperature and catalytic behavior [16,29]. Nevertheless, there are few reports offering insight into the SCR performance and physicochemical properties of Mn/beta; while, in addition, the influence of manganese precursors on NH_3 -SCR performance of Mn/ZSM-5 and Mn/beta remains unclear. Ac-

cordingly, further studies are required to conduct systematic research on manganese-modified beta zeolite.

In this paper, different Mn precursors such as manganese nitrate, manganese acetate and manganese chloride were employed to prepare Mn/ZSM-5 and Mn/beta catalysts *via* wet impregnation, and the catalytic performance compared at 50–350 °C. Characterization methods including N_2 adsorption/desorption, X-ray diffraction (XRD), X-ray fluorescence (XRF), H_2 temperature-programmed reduction (H_2 -TPR), NH_3 temperature-programmed desorption (NH_3 -TPD) and X-ray photoelectron spectroscopy (XPS) were used to identify the surface active MnO_x species over the catalysts and to investigate the influence of the manganese precursors on SCR performance.

2. Experimental

2.1. Catalyst preparation

Commercial H/beta and H/ZSM-5 (Si/Al = 25, Nankai University, China) served as the supports, and different Mn precursors such as manganese nitrate ($\text{Mn}(\text{NO}_3)_2$, 50% solution, Aladdin, China), manganese acetate ($\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, Aladdin, China) and manganese chloride ($\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, Aladdin, China) were employed as the source of Mn to fabricate Mn/beta and Mn/ZSM-5 catalysts *via* wet impregnation. A desired quantity of manganese precursors and 50 mL distilled water formed the required solution to which 10 g of zeolite support (H/beta or H/ZSM-5) was added. The mixtures were constantly stirred at 30 °C for 5 h, before heating in a water bath at 80 °C to remove the excessive moisture. Thereafter, the samples were dried at 100 °C overnight and then calcined at 400 °C for 5 h in air. The obtained catalyst powders were ground to 100–200 mesh, pressed to form tablets using a tableting press, and crushed to 20–40 mesh. The catalysts were denoted as Mn/beta-*x* or Mn/Z-*x*, where *x* represents Ac (manganese acetate), NO_3 (manganese nitrate) and Cl (manganese chloride). For example, Mn/beta-Ac or Mn/Z-Ac corresponds to Mn/beta or Mn/ZSM-5, respectively, prepared from the manganese acetate precursor. In this study, Mn loading was fixed at 20 wt% (based on the support) for all catalysts.

2.2. Catalyst activity test

For all prepared catalysts, SCR performance was evaluated using a fixed-bed quartz reactor (inner diameter 13 mm) at a reaction temperature of 50–350 °C under atmospheric pressure. The reactor was equipped with a temperature-programming controller. Catalyst (1.5 cm^3) was used for the catalytic assessment with a gas hourly space velocity (GHSV) of 50000 h^{-1} , with the simulated flue gas (total flow rate of 1250 mL/min) comprising 0.1% NO, 0.11% NH_3 , 5% O_2 , and N_2 as the balance gas. An online flue gas analyzer (Gasboard 3000) was employed to record the concentration of NO.

NO conversion was determined by the following equation:

$$X_{\text{ON}} \% = \frac{[\text{NO}]_{\text{inlet}} - [\text{NO}]_{\text{outlet}}}{[\text{NO}]_{\text{inlet}}} \times 100$$

where $[\text{NO}]_{\text{inlet}}$ and $[\text{NO}]_{\text{outlet}}$ correspond to the NO concentration at the inlet and outlet steady state, respectively.

2.3. Catalyst characterization

For all samples, the textural properties (specific surface area, total pore volume, average pore diameter) were measured at $-196\text{ }^{\circ}\text{C}$ (liquid N_2 temperature) using a Tristar 3020 (Micromeritics, Shanghai) nitrogen adsorption analyzer following a static-volumetric method. To remove adsorbed gases, the catalysts (100 mg) were subjected to a degassing step by heating to $200\text{ }^{\circ}\text{C}$ under vacuum for 4 h prior to any testing. Specific surface areas were measured via the Brunauer-Emmett-Teller (BET) model from the adsorption data.

XRD data were collected using an X-ray diffractometer (RU-200B, Rigaku, Japan) using $\text{Cu K}\alpha$ as the source of radiation at 40 kV and 30 mA. 2θ was scanned over a range of 10° – 70° at a step size of 0.02° .

Residual chloride concentration in Mn/Z-Cl and Mn/beta-Cl was determined by XRF using a Panalytical Axios advanced instrument (Netherlands).

H_2 -TPR profiles were obtained using an AutoChem TPDRO1100 chemisorption analyzer (Thermo Fisher, Italy). Catalysts (50 mg) were pretreated by flowing He (50 mL/min) at $120\text{ }^{\circ}\text{C}$ for 2 h before testing. After cooling to $30\text{ }^{\circ}\text{C}$, a feed stream of 5% H_2 in He was fed to the catalyst at a flow rate of 50 mL/min, prior to increasing the temperature from $30\text{ }^{\circ}\text{C}$ to $700\text{ }^{\circ}\text{C}$ (ramp rate of $10\text{ }^{\circ}\text{C}/\text{min}$). A thermal conductivity detector was applied to record H_2 consumption.

NH_3 -TPD experiments were conducted using a Tianjin XQ TP-5080 multifunctional chemisorption analyzer. Catalysts (100 mg) were pretreated by flowing He (50 mL/min) at $150\text{ }^{\circ}\text{C}$ for 1 h. Thereafter, the catalysts were saturated with 10% NH_3 at $100\text{ }^{\circ}\text{C}$ for 1 h, followed by purging with pure He for 1 h to remove physically absorbed NH_3 . Finally, TPD profiles were obtained under a He atmosphere (50 mL/min) from 100 to $500\text{ }^{\circ}\text{C}$ (ramp rate of $10\text{ }^{\circ}\text{C}/\text{min}$).

XPS profiles were collected using a surface analysis photoelectron spectrometer (ESCALAB 250Xi, USA), with $\text{Al K}\alpha$ as the source of radiation at 300 W. For the purpose of eliminating sample charging effects, the binding energy (BE) values were corrected by the C 1s line (284.6 eV), and an approximated error of 0.1 eV was considered across all measurements. XPSPEAK 4.1 was used to deconvolute the Mn 2p and O 1s spectra.

3. Results and discussion

3.1. SCR activity

Fig. 1 compares NO conversion performance of the Mn/beta and Mn/ZSM-5 catalysts across the temperature window of 50 – $350\text{ }^{\circ}\text{C}$. It can be observed that both the precursor and support type influence SCR performance. At low temperatures, there are distinct differences in NO conversion. The Mn/beta-Cl and Mn/Z-Cl catalysts only converted approximately 50% NO at $350\text{ }^{\circ}\text{C}$, showing significantly less activity at low tempera-

Fig. 1. Mn precursor influence on NH_3 -SCR activity of Mn/beta and Mn/ZSM-5 catalysts. Reaction conditions: 1.5 cm^3 catalyst, 0.1% NO, 0.11% NH_3 , 5% O_2 , N_2 balance, GHSV = 50000 h^{-1} .

tures, possibly correlated to a lower degree of MnCl_2 decomposition [30]. For the corresponding catalysts prepared using the manganese nitrate and manganese acetate precursors, all of which exhibited good catalytic activity, NO conversion remained high at $>80\%$ from 220 – $350\text{ }^{\circ}\text{C}$, albeit with a slight decline in activity at higher reaction temperatures owing to the non-selective oxidation of NH_3 by oxygen [16,26]. From all the catalysts, Mn/beta-Ac exhibited the highest NO conversion (97.5% at $240\text{ }^{\circ}\text{C}$), which remained over 90% across a temperature window of 220 – $350\text{ }^{\circ}\text{C}$. For the Mn/Z-Ac, Mn/beta- NO_3 and Mn/Z- NO_3 catalysts, NO conversion at $240\text{ }^{\circ}\text{C}$ was 92.5%, 91.1% and 87.6%, respectively, and to maintain a NO conversion above 90%, an operating temperature range of 240 – $350\text{ }^{\circ}\text{C}$, 240 – $330\text{ }^{\circ}\text{C}$, 280 – $330\text{ }^{\circ}\text{C}$ was needed, respectively. Hence, the activity test data shows Mn/beta-Ac and Mn/Z-Ac to perform considerably better than the corresponding Mn/beta- NO_3 and Mn/Z- NO_3 catalysts. Furthermore, Mn/beta-Ac displayed the maximum NO conversion across the largest active temperature range, indicating the excellent catalytic performance.

3.2. N_2 adsorption/desorption

N_2 adsorption/desorption isotherms for the parent H/beta and H/ZSM-5 zeolites, and the Mn/beta and Mn/ZSM-5 catalysts are shown in Fig. 2. The isotherms can be classified as type I, which is characteristic of microporous structures [20,31]. Table 1 summarizes the textural properties for all samples. Significant changes to the textural properties are observed after the introduction of Mn when compared with the parent H/beta and H/ZSM-5 supports, with both specific surface area and total pore volume decreasing. Conversely, for all catalysts, the average pore diameters increased after loading manganese, which is attributed to MnO_x species occluding the zeolite pores and channels, and larger MnO_x species being deposited over the catalyst surface resulting in the formation of new pores [32]. Specific surface areas of Mn/beta- NO_3 , Mn/beta-Ac and Mn/beta-Cl are 324, 363 and $296\text{ m}^2/\text{g}$, respectively, while Mn/Z- NO_3 , Mn/Z-Ac, Mn/Z-Cl present specific surface areas of

Fig. 2. N₂ adsorption/desorption isotherms of (a) H/beta, Mn/beta catalysts and (b) H/ZSM-5, Mn/ZSM-5 catalysts.

Table 1

Catalyst textural properties.

Sample	$A_{\text{BET}}/(\text{m}^2/\text{g})$	$V_{\text{p}}/(\text{cm}^3/\text{g})$	d_{a}/nm
H/beta	507.79	0.49	3.87
Mn/beta-NO ₃	325.70	0.36	4.09
Mn/beta-Ac	365.38	0.37	4.52
Mn/beta-Cl	281.26	0.31	4.43
H/ZSM-5	343.89	0.19	2.24
Mn/Z-NO ₃	183.27	0.11	2.38
Mn/Z-Ac	219.81	0.15	2.71
Mn/Z-Cl	152.79	0.09	2.43

219, 183 and 152 m²/g, respectively. This indicates that when H/beta zeolite and H/ZSM-5 zeolite are employed as supports for Mn-based catalysts prepared with the same precursor, the

Mn/beta catalysts possessed higher specific surface areas. Additionally, for both Mn/beta catalysts and Mn/ZSM-5 catalysts, the catalysts prepared employing the manganese acetate precursor retained specific surface areas closer to the respective parent zeolite, which is likely to be attributed to MnO_x species being highly dispersed over the catalyst. The catalysts prepared using the manganese chloride precursors exhibited the greatest loss of specific surface area relative to the parent zeolite. It is interesting to observe that the changes to textural properties correlate to SCR performance. Hence, to a degree, the textural properties of the catalysts may influence catalytic activity. However, although some influence can be attributed to changes in textural properties, this is not a key factor, as the main factors to influence SCR activity are the zeolite structure and the catalyst active metal phase [18].

3.3. XRD

Fig. 3 presents the XRD patterns of Mn/beta and Mn/ZSM-5 catalysts together with the diffractograms of the parent supports (H/beta and H/ZSM-5). The Mn-loaded catalysts exhibit typical diffraction peaks of the respective parent zeolite indicating that structural integrity was retained. The diffractogram of Mn/beta-NO₃ exhibited several strong characteristic peak reflections at 28.6°, 37.3°, 42.7°, 56.6°, 59.3°, 64.9° corresponding to pyrolusite (MnO₂, PDF #24-735) [14,16]. Additionally, strong MnO₂ diffraction peaks were also observed in the Mn/Z-NO₃ catalyst. The results are consistent with Li *et al.* [33] who reported that the manganese nitrate precursor formed principally MnO₂. For Mn/beta-Ac and Mn/Z-Ac, the distinctive diffraction peaks observed at 32.4°, 36.0° and 59.9° were assigned to crystalline Mn₃O₄ (PDF #18-0803) [24]. However, the intensities of the Mn₃O₄ diffraction peaks were observed to be stronger for Mn/Z-Ac than for Mn/beta-Ac. This phenomenon may be explained by either the high dispersion of Mn₃O₄ in the Mn/Z-Ac catalyst or low Mn₃O₄ loading levels in the Mn/beta-Ac catalyst. Furthermore, although a small amount of crystalline Mn₂O₃ was previously reported on the surface of MnO_x/TiO₂ [9,14], no distinct peaks ascribed to Mn₂O₃ were detected in Mn/beta-Ac and Mn/Z-Ac. Therefore, Mn₂O₃ can be

Fig. 3. XRD patterns for (a) H/beta and Mn/beta catalysts and (b) H/ZSM-5 and Mn/ZSM-5 catalysts.

inferred to be either highly dispersed or in an amorphous state. However, with regard to the XRD patterns of Mn/beta-Cl and Mn/Z-Cl, both Mn_3O_4 and MnCl_2 species were detected, the latter assigned by the weak diffraction peaks at 15.1° , 49.1° and 50.3° (PDF #22-0720). Previous reports related to MnCl_2 -modified zeolites show that MnCl_2 is only partially decomposed when subjected to calcination temperatures of $310\text{--}600^\circ\text{C}$ [34,35]. Further increasing the calcination temperature above 600°C results in the facile transformation to Mn oxides. Additionally, XRF results showed residual chloride content in Mn/Z-Cl and Mn/beta-Cl to be 13.41 wt.% and 10.52 wt.% (based on the catalyst), respectively. The results indicate limited manganese chloride decomposition during the preparation of the catalysts prepared using the manganese chloride precursor, which compromises catalytic performance.

3.4. H_2 -TPR

H_2 -TPR curves of the prepared catalysts are shown in Fig. 4. Table 2 lists reduction peak information (low-temperature

peak denoted as peak-1 and high-temperature peak denoted as peak-2) of all the catalysts, which shows that catalysts prepared with different precursors present distinct hydrogen consumption differences. For Mn/beta- NO_3 and Mn/Z- NO_3 , the catalysts exhibit similar patterns, and both are characterized by two reduction peaks at $362, 440^\circ\text{C}$ and $372, 480^\circ\text{C}$, respectively. It is widely accepted that a sequential reduction process of bulk MnO_x proceeds and is often described as follows: $\text{MnO}_2 \rightarrow \text{Mn}_2\text{O}_3 \rightarrow \text{Mn}_3\text{O}_4 \rightarrow \text{MnO}$ [36]. Furthermore, Qi *et al.* [9] introduced an equation (1) based on theoretical oxygen loss of MnO_x during each reduction step to determine the MnO_x species.

The peak-1 area to peak-2 area ratios of Mn/beta- NO_3 and Mn/Z- NO_3 approach 2. Therefore, combining the H_2 consumption data with the XRD results, the two reduction peaks of the catalysts correspond to a stepwise reduction of MnO_2 to Mn_2O_3 , Mn_3O_4 and finally to MnO , which is complementary to the results reported by Fang *et al.* [14]. The two reduction peaks of

Fig. 4. H_2 -TPR profiles of (a) Mn/beta catalysts and (b) Mn/ZSM-5 catalysts.

Table 2

Catalyst hydrogen consumption as a function of temperature.

Sample	Peak temperature ($^\circ\text{C}$)		Peak area (a.u.)		Ratio Peak-1/Peak-2	Total area
	Peak-1	Peak-2	Peak-1	Peak-2		
Mn/beta- NO_3	362	440	82000	43000	1.9	125000
Mn/beta-Ac	334	462	27000	21000	1.3	48000
Mn/beta-Cl	—	580	—	11000	—	11000
Mn/Z- NO_3	372	480	75000	39000	1.9	114000
Mn/Z-Ac	340	484	19000	27000	0.7	46000
Mn/Z-Cl	—	585	—	8000	—	8000

Mn/beta-Ac and Mn/Z-Ac are located at 334, 462 °C and 340, 484 °C, respectively. For Mn/beta-Ac, the peak-1 area to peak-2 area ratio is 1.3, however, this ratio lowers to 0.7 for Mn/Z-Ac. Based on the equation (1), it can be concluded that MnO₂ content is higher than that of Mn₂O₃ in Mn/beta-Ac, while Mn/Z-Ac showed the opposite result. Hence, the catalyst low-temperature peaks are attributed to the reduction of MnO₂ and Mn₂O₃ to Mn₃O₄, while the high-temperature peaks correlate to the reduction of Mn₃O₄ to MnO. Additionally, analysis of the XRD data showed only the presence of Mn₃O₄ in the catalysts. Hence, we propose that Mn₂O₃ and MnO₂ were highly dispersed in the catalysts, similar to that previously reported [9,13]. Furthermore, H₂ consumption (peak-1) for Mn/beta-Ac was greater than that of Mn/Z-Ac, suggesting a higher abundance of active oxygen species in Mn/beta-Ac, which enhanced SCR performance at low temperatures [37]. Conversely, when compared with Mn/Z-NO₃ and Mn/Z-Ac, Mn/beta-NO₃ and Mn/beta-Ac displayed lower peak-1 temperatures, respectively, indicating the higher reducibility of the MnO_x species, which favored the low-temperature catalytic performance [19].

However, for Mn/beta-Cl and Mn/Z-Cl, only high-temperature peaks were displayed in the H₂-TPR profiles, with reduction temperatures of ~580 and ~585 °C, respectively. The broad redox peak for each catalyst was assigned to the reduction of Mn₃O₄ to MnO [38], which is in agreement with previous XRD results that presented the Mn₃O₄ phase. Additionally, H₂ consumption of the catalysts prepared in the presence of the manganese chloride precursor was appreciably lower than the other catalysts, suggesting very low content of the active MnO_x species in the catalysts. Combining the XRD and XRF results, this phenomena can be explained by the low level of MnCl₂ decomposition under the preparation conditions employed, which also complements the lowest *A*_{BET} (Table 1) observed among the Mn/beta and Mn/ZSM-5 catalysts. Accordingly, these results demonstrated that the catalysts prepared using the manganese chloride precursor were inactive for the NH₃-SCR process.

3.5. NH₃-TPD

There is scientific agreement on the importance of acid sites to the NH₃-SCR reaction because NH₃ adsorbs onto the acid sites and activates the reductant [27]. Additionally, according to a previous report, weak acid sites favor low-temperature catalytic performance, while strong acid sites influence the NH₃-SCR reaction at high temperatures [19]. Therefore, for the purpose of further analyzing the surface properties of the Mn/beta and Mn/ZSM-5 catalysts, the surface acidity properties of these samples were quantitatively investigated by NH₃-TPD. Catalyst NH₃-TPD profiles are presented in Fig. 5. As can be observed from the NH₃-TPD data, the catalysts prepared using the manganese acetate and manganese nitrate precursors present two desorption peaks, whereas, the catalysts prepared employing the manganese chloride precursor displayed only low-temperature desorption peaks. Previous studies have identified the desorption peaks of weak acid sites being presented at low temperatures (150–250 °C), and have attributed

Fig. 5. NH₃-TPD profiles of (a) Mn/beta catalysts and (b) Mn/ZSM-5 catalysts.

the desorption peaks centered at high temperatures (350–500 °C) to strong acid sites [10,24]. Weak acid concentrations of the catalysts were obtained by integrating the desorption peak area with the results for Mn/beta-Cl, Mn/Z-Cl, Mn/beta-Ac, Mn/Z-Ac, Mn/beta-NO₃ and Mn/Z-NO₃ as 4000, 1800, 1650, 1350, 1050 and 950, respectively. Mn/beta-Cl and Mn/Z-Cl are observed to retain the highest quantity of weakly acidic centers compared with the other catalysts. However, these catalysts exhibited poor SCR performance because of the extremely low presence of active MnO_x species. Hence, it is inferred that the concentration of weak acid sites is not the determinant factor for SCR performance [19,27]. Conversely, with respect to the catalysts prepared employing the manganese acetate and manganese nitrate precursors, all of which displayed an abundance of the active phase, catalytic performance was enhanced. Mn/beta-NO₃ and Mn/beta-Ac possessed higher concentrations of weak acid sites than the corresponding Mn/Z-NO₃ and Mn/Z-Ac catalysts. Additionally, from either the Mn/beta or Mn/ZSM-5 catalysts, employing the manganese acetate precursor resulted in the presence of significantly more weak acid sites than the corresponding catalysts prepared using the manganese nitrate precursor. These observations are in good agreement with the SCR activity results. Therefore, for low-temperature SCR performance, it is proposed that an appropriate amount of weakly acidic centers may be advantageous.

3.6. XPS

XPS analysis was performed to further explore the chemical species and surface atomic composition of the catalysts pre-

Fig. 6. XPS spectra of Mn/beta-NO₃, Mn/beta-Ac, Mn/Z-NO₃ and Mn/Z-Ac. (a) Mn 2p; (b) O 1s.

pared using the manganese nitrate and manganese acetate precursors. Fig. 6 displays the Mn 2p and O 1s spectra of the catalysts. Surface atomic concentrations of Mn, detected by XPS, are listed in Table 3. Mn/beta-Ac showed the maximum surface manganese concentration, suggesting a high dispersion of manganese in this catalyst, which enhanced catalytic performance [16]. For all samples, the Mn 2p spectra (Fig. 6(a)) displays two broad peaks located at ~642 eV and 653 eV ascribed to Mn 2p_{3/2} and Mn 2p_{1/2}, respectively [39]. For catalysts prepared using the manganese nitrate precursor, the Mn 2p_{3/2} spectra was deconvoluted and fitted with three components: Mn₂O₃ (641.2 eV), MnO₂ (642 eV) [13,15] and an obvious peak at 644.2 ± 0.4 eV corresponding to Mn-nitrate [40,41]. This result proved that manganese nitrate decomposed incompletely when subjected to a low sintering temperature of 400 °C. With regard to the catalysts employing the manganese acetate precursor, Mn 2p_{3/2} can be deconvoluted into three peaks located at 641.3, 641.8 and 643.8 eV correlating to Mn₃O₄, Mn₂O₃ and MnO₂, respectively [16,42,43], suggesting the coexistence of Mn₃O₄, Mn₂O₃ and MnO₂ at the surface of Mn/beta-Ac and Mn/Z-Ac. XPS data reveals that surface MnO₂ is the main MnO_x species present in Mn/beta-NO₃ and Mn/Z-NO₃, while a large percentage of MnO₂ and Mn₂O₃ were observed in

Mn/beta-Ac and Mn/Z-Ac. These results are also in agreement with the H₂-TPR studies. Previous reports have observed that the coexistence of MnO₂-Mn₂O₃ could not only promote the oxidation of NH₃, but also the oxidation of NO to NO₂, which improved the SCR performance at low temperature [1,4,44]. Additionally, in this study, considering that the catalysts prepared using the manganese acetate precursor showed superior catalytic performance, it is proposed that the presence of MnO₂ and Mn₂O₃ may play a key role in the SCR process. As expected, Mn/beta-Ac can be observed (Table 3) to possess a greater presence of active MnO_x (MnO₂ and Mn₂O₃) species than the other catalysts, resulting in excellent catalytic performance. The Mn 2p_{3/2} BEs of Mn₂O₃ and MnO₂ for the catalysts prepared employing the manganese acetate precursor are nearly 0.6–1.8 eV higher than the corresponding catalysts prepared using the manganese nitrate precursor, showing that the manganese acetate precursor may have induced the high dispersion of the MnO_x species, which resulted in a stronger electrostatic field [1]. Again, the results are in agreement with the observations from XRD and H₂-TPR data.

Fig. 6 presents the deconvoluted O 1s spectra of the catalysts. Three distinct peaks are observed, located at 528.7–530.0, 530.9–531.0 and 532.0–532.2 eV, and are attributed to

Table 3

Surface atomic concentration, binding energies (BE) and the percent of different manganese species determined from deconvoluted XPS spectra.

Sample	Surface concentration (at %)			Percent of manganese species (%) (BE, eV)				
	Mn	O	Others ^a	Mn ₃ O ₄	Mn ₂ O ₃	MnO ₂	Mn-nitrate	Mn ₂ O ₃ +MnO ₂
Mn/beta-NO ₃	4.27	61.91	33.82	—	13.3(641.2)	66.7(642.0)	20.0(643.8)	80.0
Mn/beta-Ac	8.73	62.34	28.93	14.2(641.3)	40.2(641.8)	45.6(643.8)	—	85.8
Mn/Z-NO ₃	3.12	59.43	37.45	—	15.9(641.2)	61.9(642.0)	22.2(644.0)	77.8
Mn/Z-Ac	5.54	61.52	32.94	17.1(641.3)	55.6(641.8)	27.3(643.8)	—	82.9

^a Other elements include Si, Al, C.**Table 4**BE and O_β/(O_β+O_α) ratios.

Sample	BE (eV)			O _β /(O _β +O _α) ^a
	O _α	O _β	O _γ	
Mn/beta-NO ₃	528.7	531.0	532.0	0.74
Mn/beta-Ac	530.0	531.0	532.0	0.77
Mn/Z-NO ₃	528.9	530.9	532.2	0.68
Mn/Z-Ac	529.7	531.0	532.2	0.71

^a O_β/(O_β+O_α) = A_{Oβ}/(A_{Oβ}+A_{Oα}).

lattice oxygen O²⁻ (labeled as O_α), surface labile oxygen such as O⁻ or OH⁻ belonging to defect-oxide or hydroxyl-like groups (designated as O_β), and other absorbed oxygen species (labeled as O_γ), respectively [27,37,45]. Furthermore, to reduce error, the peak at 533–534 eV was assigned as a satellite peak. Table 4 lists the quantitative data of O_β/(O_β+O_α) ratios of the catalysts calculated by the relative peaks areas. Previous studies have noted the importance of surface chemisorbed labile oxygen (O_β) in the SCR process at low temperatures, which is considered to be the most active oxygen because of its high mobility and that it plays a vital role in the oxidation reaction [37]. Accordingly, the high ratio of O_β/(O_β+O_α) was conducive to NO oxidation to NO₂, which enhanced the low-temperature catalytic performance by a “Fast-SCR” route [46,47]. In our present study, the O_β/(O_β+O_α) ratios of Mn/beta-Ac and Mn/beta-NO₃ were significantly higher than those of Mn/Z-Ac and Mn/Z-NO₃, respectively. Conversely, from the Mn/beta catalysts, Mn/beta-Ac possessed more surface labile oxygen than Mn/beta-NO₃, and similar results were observed for the Mn/ZSM-5 catalysts. The results are also in good agreement with the SCR performance.

4. Conclusion

We compared the NH₃-SCR performance and physicochemical properties between Mn/beta and Mn/ZSM-5 catalysts, which were prepared using manganese nitrate, manganese acetate and manganese chloride precursors. From the Mn/beta and Mn/ZSM-5 catalysts, Mn/beta-Cl and Mn/Z-Cl displayed extremely low NO conversion (~50% at 350 °C), while Mn/beta-Ac showed excellent catalytic performance, displaying the highest NO conversion of 97.5% at 240 °C while maintaining >90% conversion across the widest active temperature range of 220–350 °C. BET results revealed that the textural properties may influence SCR performance, to a degree. XRD, XRF and H₂-TPR results show that the catalysts prepared employing the manganese chloride precursor present poor catalytic activity because of low MnCl₂ decomposition yielding only

a small quantity of crystalline Mn₃O₄. XPS analyses revealed that samples prepared using the manganese nitrate precursor resulted in crystalline MnO₂ with a small presence of Mn nitrate, and employing the manganese acetate precursor resulted primarily in a mixture of highly dispersed Mn₂O₃ and MnO₂, and crystalline Mn₃O₄. Additionally, combining the SCR activity data with the physicochemical properties suggests that the enhancement of catalytic performance can be attributed to the coexistence of amorphous MnO_x (Mn₂O₃ and MnO₂) species. Conversely, systematical analysis revealed that the superior catalytic activity of Mn/beta-Ac correlates to the increased amorphous Mn₂O₃ and MnO₂ content, higher concentration of surface manganese and surface labile oxygen. Furthermore, NH₃-TPD results indicated that manganese-modified beta zeolite possessed an appropriate number of weakly acidic centers, which may favor the catalytic performance at low temperatures. Therefore, Mn/beta-Ac can be considered as a promising material for the preparation of manganese-supported SCR denitration catalysts in future applications.

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Graphical Abstract

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Mn/beta and Mn/ZSM-5 for the low-temperature selective catalytic reduction of NO with ammonia: Effect of manganese precursors

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Mn/beta-Ac showed excellent low-temperature NH₃-SCR performance attributed to a combination of enriching the amorphous MnO_x (MnO₂ and Mn₂O₃) content, higher surface manganese concentration and labile oxygen groups, and a suitable number of weakly acidic centers.

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Mn/beta与Mn/ZSM-5催化剂对氨选择性催化还原NO的低温催化活性比较：锰前驱体的影响

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摘要: 氮氧化物(NO_x)作为主要的大气污染物之一, 给环境和人类带来一定危害, 其主要源于汽车、轮船以及工厂中液态(汽油和柴油)或固态(煤)化石原料的燃烧。目前, 选择性催化还原法(SCR)因技术相对成熟且经济有效, 被广泛应用于氮氧化物脱除。催化剂是该技术的关键, 而典型的商业钒系催化剂(V₂O₅-WO₃/TiO₂和V₂O₅-MoO₃/TiO₂)存在工作窗口温度窄(300–400 °C)、V₂O₅的生物毒性以及较高的SO₂氧化性能等缺点, 因此开展高效且环境友好催化剂的研究工作迫在眉睫。

近年来, 锰基催化剂因其丰富的价态变化以及氧化形态而受到科研工作者的广泛关注。研究者已经对锰前驱体做了大量研究, 但是关于不同锰前驱体制备得到的催化剂的活性物种组成以及催化活性往往存在着不同观点。因此进一步开展对锰前驱体研究仍有必要。同时, 二氧化钛载体比表面积较小, 并不是制备锰基催化剂的理想载体。分子筛载体因其比表面积大、特殊的孔道结构以及丰富的酸位等特点引起了研究者的关注。用于制备锰基催化剂的分子筛载体主要有ZSM-5, Beta, USY和SAPO等, 其中ZSM-5系列催化剂是研究热点。另一方面, 研究发现Beta分子筛具有良好的水热稳定性, 被认为是理想的NH₃-SCR催化剂载体。研究者对比了不同金属负载的Beta分子筛与ZSM-5分子筛的催化活性, 结果表明, Fe/beta的催化活性高于Fe/ZSM-5和Fe/ZSM-11; Cu/beta的催化活性与Cu/ZSM-5相当, 均表现出较高的活性。而关于Mn/ZSM-5的研究已有大量文献报道, 但关于Mn/beta的研究相对较少。另外, 关于不同锰前驱体在Beta以及ZSM-5分子筛载体表面的物化性质差异也少有报道。

本文以H/beta和H/ZSM-5分子筛作为载体, 采用硝酸锰、乙酸锰和氯化锰三种前驱体, 通过湿法浸渍制备了Mn/beta和Mn/ZSM-5两类NH₃-SCR催化剂, 并在固定床管式反应器中对比评价了两类催化剂的催化活性。凭借氮气等温吸附/脱附(BET)、X射线衍射(XRD)、X射线荧光(XRF)、氢气程序升温还原(H₂-TPR)、氨气程序升温脱附(NH₃-TPD)以及X射线光电谱(XPS)等技术对催化剂进行了表征, 系统分析了不同前驱体在两种载体表面形成的活性组分以及理化性质对催化性能的影响。

催化剂活性评价结果表明, 对于Mn/beta和Mn/ZSM-5催化剂, 在220–350 °C反应温度区间内, 乙酸锰和硝酸锰制备的催化剂NO脱除率均在80%以上。其中Mn/beta-Ac在240 °C时达到最高的NO脱除率97.5%, 并且在220–350 °C温度区间内保持着90%以上的活性, 具有最宽的活性温度窗口。同时, 在两系列锰基催化剂中, 乙酸锰制备的催化剂均表现出最佳的催化活性, 且对于同一种前驱体制备的催化剂, Mn/beta催化剂的NH₃-SCR活性优于Mn/ZSM-5。BET数据显示, 负载锰物种之后, 催化剂的比表面积和孔体积均明显减小, 但相对于Mn/ZSM-5催化剂, Mn/beta催化剂仍保持着优良的织构性质。XRD、XRF及H₂-TPR结果表明, 氯化锰前驱体主要产生少量的结晶Mn₃O₄并且大部分保持以MnCl₂的形式存在, 这也是此类催化剂表现出较差的低温催化活性的原因。结合XPS表征分析了催化剂的表面性质。结果表明, 硝酸锰前驱体主要产生结晶MnO₂和少量未分解的硝酸锰, 乙酸锰前驱体主要产生高度分散的无定形MnO₂和Mn₂O₃混合物以及结晶Mn₃O₄。进一步结合NH₃-TPD分析结果以及活性评价结果可以得出: 丰富的无定形MnO_x (MnO₂和Mn₂O₃)物种、较高的表面锰含量和表面活性氧基团以及适当含量的弱酸位有利于提升催化剂的低温NH₃-SCR催化活性。

关键词: Mn/beta; Mn/ZSM-5; 低温; 催化性能; 选择性催化还原; 锰前驱体

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