

Characterization of W-Mn-Ce-Ti Oxides Catalysts Prepared by Different Methods for Selective Reduction of NO with NH₃

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Abstract

Aiming to develop low cost and environmentally friendly SCR catalysts, various transition metals and rare earth elements have been used and combined to prepare polymetallic oxide catalysts in recent years, which generally exhibit excellent SCR performance. Here four typical metal elements (Mn, Ce, W and Ti) have been selected to prepare polymetallic oxides (WMnCeTiO_x) catalysts, and the effects of preparation methods, such as coprecipitation (CP), sol-gel (SG), and deposition precipitation (DP), on the performance of selective catalytic reduction of NO with NH_3 at 160~360 °C have been investigated systematically. Some key techniques of XRD, BET, XPS, H_2 -TPR, NH_3 -TPD and in-situ DRIFTS were used to characterize the physicochemical properties of the prepared WMnCeTiO_x catalysts. The SCR activity measurement results showed that NH_3 -SCR activities of WMnCeTiO_x catalysts prepared through coprecipitation and deposition precipitation methods exhibited much better NO removal performance in the temperature range of 160~360 °C than that prepared via sol-gel method. More importantly, WMnCeTiO_x catalysts prepared through coprecipitation method exhibited superior SO_2 and H_2O tolerance compared with those prepared via deposition precipitation and sol-gel methods. It demonstrated that the preparation process imposed a crucial impact on the physicochemical properties of the prepared WMnCeTiO_x catalysts, thus influencing on their SCR performance. According to the characterization results, the better performance of $\text{WMnCeTiO}_x(\text{CP})$ catalyst could be ascribed to its higher concentrations of Mn^{4+} and Ce^{3+} , larger surface area and highly-dispersed active species on catalyst surface. In addition, compared with WMnCeTiO_x catalysts prepared by deposition precipitation and sol-gel methods, $\text{WMnCeTiO}_x(\text{CP})$ catalyst possessed much more surface acid sites, stronger reduction capacity and better adsorption capacity for NH_3 and NO, which might also play a key role in promoting its SCR performance.

Highlights

- WMnCeTiO_x catalysts were prepared by coprecipitation, deposition precipitation and sol-gel .
- The catalyst prepared by coprecipitation showed excellent NH_3 -SCR activity and much better SO_2 tolerance.
- The catalyst prepared by coprecipitation possessed much more surface acid sites, stronger reduction capacity and better adsorption capacity for NH_3 and NO.

1. Introduction

At present, nitrogen oxide (NO_x) emitted from stationary and mobile sources are still one of main pollutants to the atmosphere, which is related with a series of environmental problems, such as acid rain, photochemical smog, green-house effect, ozone depletion, haze and so on (Bosch. 1988; Castro et al. 2001). Selective catalytic reduction (SCR) with NH_3 is the most widely-used technology to control NO_x emission due to its high removal efficiency and low running cost (Park et al. 2013; Cimino et al. 2016). As the core of NH_3 -SCR system, the commercially available catalyst is usually $\text{V}_2\text{O}_5\text{-WO}_3(\text{MoO}_3)/\text{TiO}_2$ (Pei et

al. 2018; Wu et al. 2020). It exhibits desirable performance in eliminating NO_x with excellent thermal stability, but its narrow working temperature range (300 ~ 400°C), poor low temperature activity and toxicity of vanadium species are still critical challenges, which hinders their applications especially in low-temperature flue gas cases (Yan et al. 2017; Li et al. 2016). Thus, it is very imperative to develop novel vanadium-free NH_3 -SCR catalysts with a wide working temperature window.

It is known that manganese oxides (MnO_x) contain multivalent Mn species (Mn^{4+} , Mn^{3+} , Mn^{2+}) and abundant labile lattice oxygen. Since MnO_x catalyst exhibits good SCR low-temperature activity in NH_3 -SCR reaction, it is regarded as one of the promising alternatives for vanadium-based catalysts (Liu et al. 2016; Xin et al. 2018). But it is difficult for MnO_x catalysts to maintain high denitrification activities in a wide working temperature window, and its N_2 selectivity is also very poor especially with the increase of operating temperature (Chen et al. 2017). Up to now, several strategies, such as dispersion on a high-surface-area support (Li. 2013; Sang et al. 2012; Gang et al. 2013), modification by mixing with other metal oxides, and doping with other ions (Zhang et al. 2021; Zhang et al. 2020), have been employed to improve the de- NO_x activity of MnO_x catalysts. Moreover, rare-earth elements are often used as active catalyst components or catalyst promoters due to their incompletely occupied $4f$ and empty $5d$ orbitals (Yang et al. 2002). Among them, Ce has attracted increasing attentions due to its unique redox properties and high oxygen storage capacity, and it is of great potential to combine Ce with Mn to develop a novel SCR catalyst (Kwon et al. 2015). Boningari et al demonstrated that the introduction of ceria in MnO_x could improve the acid sites distribution and increase the concentration of acid sites (Boningari et al. 2015). Lin et al. prepared Mn-Ce oxide catalysts by sol-gel method yielded nearly 98% NO removal efficiency below 200 °C (Lin et al. 2019). TiO_2 is generally used as a support for commercial catalysts (Phil et al. 2008), but it can also play a crucial role in modifying the polyoxides catalysts to improve the comprehensive SCR performance such as N_2 selectivity and SO_2 resistance in NH_3 -SCR reactions (Zhang et al. 2019). As to WO_3 , it has been extensively used as stabilizer and promoter in the traditional V_2O_5 - WO_3/TiO_2 catalysts during the past decades, and it was found that WO_3 could greatly enhance the amount and strength of surface Bronsted acid sites and NO oxidation ability (Ma et al. 2015).

In recent years, more and more researchers around the world devoted to combine various metal oxides to develop a low cost and environmentally friendly SCR catalysts. Some previous work indicated that Ce-Mn-Ti ternary metallic oxides exhibited excellent catalytic performance and became a research hotspot for SCR application. Here W was selected to combine with Mn-Ce-Ti to prepare quaternary metal oxides catalysts aiming to further improve their SCR activity. Considered that, the catalytic activity of W-Mn-Ce-Ti oxides catalysts is also closely related to the dispersion and interaction of active components (Wang et al. 2019). And the catalyst preparation method is the key factor for determining the interaction and dispersion of active components, therefore, it is very meaningful to investigate the effects of preparation methods on the SCR activities of W-Mn-Ce-Ti oxides catalysts, and further explore the relation of structure and activity of WMnCeTiO_x catalysts.

In this work, W-Mn-Ce-Ti quaternary metal oxides catalysts have been prepared via three typical methods including coprecipitation (CP), sol-gel (SG), and deposition precipitation (DP). The results indicated that NH_3 -SCR activities of W-Mn-Ce-Ti catalysts prepared through coprecipitation and deposition precipitation methods exhibited much better NO removal performance in the temperature range of 160 ~ 360 °C than that prepared via sol-gel method. More importantly, W-Mn-Ce-Ti catalysts prepared through coprecipitation method exhibited superior SO_2 and H_2O tolerance compared with those prepared via deposition precipitation and sol-gel methods. XRD, BET, XPS, H_2 -TPR, NH_3 -TPD and in-situ DRIFTS were adopted to characterize the physicochemical properties of the prepared W-Mn-Ce-Ti catalysts, and the relevant influencing mechanism and the possible reaction pathways were discussed in detail.

2. Experimental

2.1 Catalyst preparation

The W-Mn-Ce-Ti catalysts were prepared using three different methods, namely CP, DP, and SG. $\text{TiO}(\text{SO}_4) \cdot x\text{H}_2\text{SO}_4 \cdot x\text{H}_2\text{O}$, TiO_2 , $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $(\text{NH}_4)_{10}\text{W}_{12}\text{O}_{41} \sim x\text{H}_2\text{O}$ were used as the precursors for Ti, Mn, Ce and W, respectively. Deionized water was used as solvent. NH_4OH (25-28%) and citric acid ($\text{C}_6\text{H}_8\text{O}_7$, 99.5%) were used as precipitator and complexing agent, respectively. The molar ratio of W, Mn, Ce, and Ti was set at 0.15:0.075:0.3:1.

2.1.1 Coprecipitation method

In a typical preparation process, 1.030 g $(\text{NH}_4)_{10}\text{W}_{12}\text{O}_{41} \sim x\text{H}_2\text{O}$, 0.505 g $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, 3.505 g $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, and 5.981 g $\text{TiO}(\text{SO}_4) \cdot x\text{H}_2\text{SO}_4 \cdot x\text{H}_2\text{O}$ were dissolved in 100 mL deionized water, followed by stirring thoroughly at 60 °C for 4 h. Then ammonia solution was added dropwise until solution pH reached at 10. After aging for 12 h, the synthetic precipitate was filtered. Then, the mixture solution was dried at 110 °C for 5 h and calcined at 500 °C for 3 h. The catalysts were crushed and sieved to 40-60 mesh for activity evaluation. The obtained catalyst was marked as WMCT(CP).

2.1.2 Deposition precipitation method

In a typical preparation process, 1.030 g $(\text{NH}_4)_{10}\text{W}_{12}\text{O}_{41} \sim x\text{H}_2\text{O}$, 0.505 g $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and 3.505 g $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were dissolved in 100 mL deionized water, followed by stirring thoroughly at 60 °C for 2 h. 2.5 g TiO_2 powder (Degussa P25) was added into the mixture solution, followed by stirring thoroughly at 60 °C for 2 h. Then ammonia solution was added dropwise until solution pH reached at 10. After aging for 12 h, the synthetic precipitate was filtered. Then, the mixture solution was dried at 110 °C for 5 h and calcined at 500 °C for 3 h. The catalysts were crushed and sieved to 40–60 mesh for activity evaluation. The obtained catalyst was marked as WMCT(DP).

2.1.3 Sol-gel method

In a typical preparation process, 1.030 g $(\text{NH}_4)_{10}\text{W}_{12}\text{O}_{41}\sim x\text{H}_2\text{O}$, 0.505 g $\text{Mn}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$ and 3.505 g $\text{Ce}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ were dissolved in 100 mL deionized water, followed by stirring thoroughly at 60 °C for 2 h. 7.810 g $\text{C}_6\text{H}_8\text{O}_7$ were dissolved in the mixture solution, followed by stirring for 0.5 h. The pH value of the resulting liquid mixture was maintained at 10, followed by stirring thoroughly at 80 °C for 4h form a transparent sol. After aging for 12 h, the sol was dried at 150 °C for 5 h to form a gel, followed by calcined at 500 °C for 3 h. The catalysts were crushed and sieved to 40–60 mesh for activity evaluation. The obtained catalyst was marked as WMCT(SG).

2.2. SCR activity test

The SCR performance of all prepared catalysts were evaluated in a fixed-bed, stainless steel reactor (inner diameter: 6 mm). A catalyst of 0.5 mL was used for catalytic assessment with a gas hourly space velocity (GHSV) of $30,000\text{ h}^{-1}$. The feed-gas mixture contained 500 ppm NO, 500 ppm NH_3 , 5% O_2 , 10% H_2O (if used), 100 ppm SO_2 (if used), and N_2 as the balance gas. The operating temperature window was 160~360 °C. The concentrations of out gas were monitored continuously by a FTIR spectrometer (iS50, Thermo Fisher Scientific) equipped with a heated low-volume multiple-path gas cell (2 m) and a MCT detector cooled by liquid nitrogen. The NO removal efficiency and N_2 selectivity were calculated as follows:

$$\text{NO removal efficiency (\%)} = \frac{[\text{NO}]_{\text{in}} - [\text{NO}]_{\text{out}}}{[\text{NO}]_{\text{in}}} \times 100\% \quad (1)$$

$$\text{N}_2 \text{ selevtivity (\%)} = \left(1 - \frac{[\text{NO}_2]_{\text{out}} + 2[\text{N}_2\text{O}]_{\text{out}}}{[\text{NO}]_{\text{in}} - [\text{NO}]_{\text{out}} + [\text{NH}_3]_{\text{in}} - [\text{NH}_3]_{\text{out}}}\right) \times 100\% \quad (2)$$

2.3. Catalyst characterization

The surface structure parameters of these catalysts were measured with a physisorption (ASAP 2020 PLUS, Micromeritics) by N_2 adsorption at 77 K, using the Brunauer-Emmet-Teller (BET) method to determine their specific surface area. The pore volumes and pore size distributions were calculated from the adsorption branch of the isotherm using the Barrett-Joyner-Halenda (BJH) algorithm. The sample was degassed for 4 h at 350 °C before each analysis.

Powder XRD patterns were performed on an X-ray diffraction meter (Empyrean, PANalytical) with Cu K α (40 kV, 30 mA) radiation. The diffractogram was recorded in the 2θ range of 10 to 80 ° with a scan rate of $0.02^\circ 2\theta\text{ s}^{-1}$.

H_2 -temperature programmed reduction (H_2 -TPR) and NH_3 -temperature programmed desorption (NH_3 -TPD) experiments were carried out on a chemisorption analyzer (Autochem II 2920, Micromeritics). Prior to each test, the samples were pretreated at 350 °C in a flow of high purified Helium (50 mL/min) for 1 h.

Then the catalysts were cooled down to 50 °C in a flow of Helium. Next, the samples were flushed at 100 °C for 2 h in pure He stream (50 mL/min) to remove physically absorbed NH₃. Finally, TPD profiles were obtained by heating the samples from 100 to 400 °C with a ramping rate of 10 °C/min in He stream (50 mL/min).

X-ray photoelectron spectroscopy (XPS) profiles were collected using a surface analysis photoelectron spectrometer (Kratos AXIS Supra, Shimadzu), with Al K α radiation.

The Fourier Transform InfraRed Spectrometer (FTIR) and the in-situ Diffuse Reflectance Infrared Fourier Transform spectra (DRIFTS) were collected using a Nicolet iS50 spectrometer to detect the functional group and the reaction behavior between adsorbed species, respectively. Prior to each test, the catalysts were pretreated in a flow of N₂ at 350 °C for 30 min and then cooled to room temperature. Then background spectra recorded in N₂ flow were automatically subtracted from the corresponding spectra. The spectral resolution was 4 cm⁻¹ with co-addition 64 scans.

3. Results And Discussion

3.1. NH₃-SCR performance

NO removal efficiencies of WMnCeTiO_x catalysts prepared by various methods were illustrated in Fig. 1(a). The figure showed that the WMnCeTiO_x catalysts prepared by the CP and DP methods yielded good catalytic activities over a broad temperature range, and nearly 97 % NO removal efficiencies was achieved in the temperature range 200 ~ 360 °C. By contrast, the WMCT(SG) catalyst could only achieve similar NO removal efficiency in the temperature range 280~360 °C. Interestingly, the N₂ selectivity of all these catalysts is extremely high (~99 %) in 160~360 °C (shown in Fig. 1(b)).

H₂O and SO₂ are main components of flue gas from stationary and mobile sources. Therefore, it is necessary for any low temperature SCR catalyst with application potential to be simultaneously resist to H₂O and SO₂ degradation and poison (Guo et al. 2009; Yezerets et al. 2016; Zhang et al. 2019).

The effects of 100 ppm SO₂ on NO removal efficiencies of the different WMnCeTiO_x catalysts at 250 °C were tested and the result was presented in Fig. 2(a). Compared with WMCT(SG) and WMCT(DP) catalysts, WMCT(CP) catalyst displayed much better SO₂ resistance performance. With the introduction of SO₂ in feed gas, NO removal efficiencies of WMCT(CP) catalyst had a slight drop, and it could still be maintained to 89 % after exposure to 100 ppm SO₂ for 5 h.

The resistance of H₂O and SO₂ over the different WMnCeTiO_x catalysts at 250 °C was presented in Fig. 2(b). At first 10 % H₂O was introduced into the flue gas, there was a decrease in NO removal efficiency. It indicated that H₂O had an inhibiting effect on SCR activity of WMnCeTiO_x at low temperature. Moreover, the catalytic activity was completely recovered after removal of water vapor, indicating that the inhibition was reversible. When 200 ppm of SO₂ was added to the reaction gas mixtures, a rapid decrease of NO

removal efficiencies was observed. When H₂O and SO₂ were removed from the reaction stream, the activity of WMCT(CP) and WMCT(DP) catalysts was restored. It can be observed that the resistance of H₂O and SO₂ over the different WMnCeTiO_x catalysts decrease in the following order: WMCT(CP) > WMCT(DP) > WMCT(SG).

[SO₂] = 100 ppm, 200 ppm, balance with N₂, and GHSV = 30,000 h⁻¹)

3.2.XRD

Fig. 3. Showed XRD patterns of the different catalysts. The diffraction peaks of 2θ at 25.3 °, 37.8 °, 48.0 °, 53.9 °, 55.1 °, 62.7 °, 68.8 °, 70.3 ° and 75.0 ° could be attributed to anatase TiO₂ characteristic peak (PDF#21-1272), and the diffraction peaks of 2θ at 28.6 °, 33.1 °, 47.5 and 56.3° could be attributed to CeO₂ characteristic peaks (PDF#34-0394). It could be seen that all catalysts exhibited the anatase TiO₂ diffraction peaks, and no obvious diffraction peaks of rutile TiO₂ were found. Anatase TiO₂ had more abundant active sites than rutile phase, which was beneficial to promote the catalytic performance of NH₃-SCR (Liu et al. 2008; Zhao et al. 2020). The diffraction peaks of CeO₂ in the WMCT(CP) and WMCT(SG) catalysts were not obvious. It suggested that WMnCeTiO_x catalysts prepared by CP and SG led to the amorphous structure or high dispersion of CeO₂, which was beneficial to enhance the catalytic. However, the activity of WMCT(DP) was better than WMCT (SG). Therefore, the high dispersion property of the active species was probably not the determining factor for the activity difference of WMnCeTiO_x catalysts.

3.3. N₂ adsorption/desorption

The N₂ adsorption-desorption isotherms of the catalysts were shown in Fig. 4. According to the classification of IUPAC, the absorption isotherms were type IV, indicating that the prepared catalysts belonged to mesoporous materials. The specific surface areas, total pore volumes, and average pore diameters of these three catalysts were summarized in Table 1. Compared with WMCT(DP) and WMCT(SG), WMCT(CP) has higher BET surface area (137.25 m²/g). It is generally believed that higher BET surface area could provide more available active sites on the catalyst surface for the reactants to participate in the reactions, Which may be one of the reasons for facilitating the de-NO_x activity of the catalyst (Yan et al. 2018; Chen et al. 2017).

Table1 The BET specific area (S_{BET}), total pore volume (V_{total}) and average pore diameter of all samples

Samples	S _{BET} (m ² /g)	V _{total} (cm ³ /g)	Average pore diameter(nm)
WMCT(CP)	137.25	0.25	6.92
WMCT(DP)	61.79	0.353	22.42
WMCT(SG)	37.99	0.091	9.09

WMCT (DP), WMCT(SG)

3.4. H₂-TPR

H₂-TPR was used to characterize the redox property of the prepared catalysts, and the results were shown in Fig. 5. All catalysts showed two reduction peaks between 400 to 800 °C, which could be assigned to the reduction of surface manganese, ceria and tungsten species (Aguilera et al. 2011; Fang et al. 2017; Putluru et al. 2015; Wu et al. 2010). In the low-temperature region, the peak at 432 °C in the profile attributed to the reduction of Mn₃O₄ to MnO (Aguilera et al. 2011; Fang et al. 2017), and the peak at 495 and 519 °C in the profile attributed to the reduction of Ce⁴⁺ to Ce³⁺ (Putluru et al. 2015). In the high temperature region, the peak at 700 to 800 °C in the profile attributed to the reduction of WO₃ to WO₂ (Wu et al. 2010). Compared with WMCT(SG), WMCT(CP) and WMCT(DP) had a better reducibility at lower temperature, which contributed to promoting the low temperature SCR reaction.

WMCT (DP), WMCT(SG)

3.5. NH₃-TPD

NH₃-TPD was frequently carried out to investigate the amount and strength of surface acid sites on the catalysts surface. Surface acid sites are crucial to the adsorption of NH₃ and the following SCR reaction (Fan et al. 2018). As illustrated in Fig. 6, all catalysts showed similar desorption curves and two desorption peaks: the NH₃ desorption peaks centered at low temperature (lower than 300 °C) assigned to weak acid sites, and the other NH₃ desorption peaks centered at high temperature (higher than 300 °C) originating from strong acid sites. It is well known that the area of desorption peak is proportional to the acid amount. The area of the WMCT(CP) was the largest, indicating that there are the largest amounts of weak adsorption sites on its surface. The more acid sites on the catalyst surface, the more adsorbed ammonia species available for surface reaction, which would be an obvious benefit to boost of de-NO_x efficiency.

WMCT (DP), WMCT(SG)

3.6. XPS

To investigate the surface element concentrations and elementary oxidation states of the prepared catalysts, Ce, Mn, W, O and Ti elements over the three catalysts were measured by XPS (Table 2 and Figure 7). As displayed in Table 2, Surface atomic ratios of Mn 2p, Ce 3d and O 1s of the prepared catalysts were obviously different, which is mainly due to the different preparation methods.

As shown in Fig. 7(a), the binding energies of Mn 2p_{3/2} and Mn 2p_{1/2} peaks were located at 641.7 and 653.5 eV, corresponding to Mn⁴⁺ and Mn³⁺, respectively (Lei et al. 2014). It is well known that Mn⁴⁺ is more active than Mn³⁺ species in redox reaction, so that a high relative proportion of Mn⁴⁺ / (Mn³⁺ +

Mn⁴⁺) is beneficial to the low-temperature NH₃-SCR activity (Chen et al. 2014; Liu et al. 2017; Leng et al. 2018). It can be seen from Table 2 that the values of Mn⁴⁺ / (Mn³⁺ + Mn⁴⁺) decrease in the following order: WMCT(CP) > WMCT(DP) > WMCT(SG). This order was consistent with that of the low-temperature activity. It demonstrated that Mn⁴⁺ played a key role in determining the low-temperature activity of the WMnCeTiO_x catalysts.

The significant differentials of Ce valence state had a great influence on redox reaction (Yao et al. 2016). Fig. 7(b) showed the XPS spectra of Ce 3*d* for the different catalysts. Two sets of multiplets related to Ce 3*d*_{5/2} and Ce 3*d*_{3/2} were labelled as *u* and *v*, respectively. The band labeled *u'* and *v'* can be ascribed to Ce³⁺, while the peaks labeled *u*, *u''*, *u'''*, *v*, *v''*, *v'''* can be assigned to Ce⁴⁺ (Romeo et al. 1993; Si et al. 2010). According to literatures (Yao et al. 2014; Zheng et al. 2003), Ce³⁺ contributes to generate oxygen vacancies and leads to charge imbalance. The highly enriched oxygen vacancies would bring the rising of surface chemisorbed oxygen by supplying gaseous oxygen, which would increase the activity of the catalyst (Liu et al. 2009; Gu et al. 2010). Moreover, the Ce³⁺ / (Ce³⁺ + Ce⁴⁺) ratio of WMnCeTiO_x catalysts decreased according to the sequence: WMCT(DP) < WMCT(CP) < WMCT(SG), which was inconsistent with catalytic activity. It suggested that the Ce³⁺ / (Ce³⁺ + Ce⁴⁺) ratio may not be the determinant factor for SCR performance of the prepared for WMnCeTiO_x catalysts.

Fig. 7(c) exhibited the O1*s* spectra of WMnCeTiO_x catalysts, which can be fitted into three peaks, lattice oxygen (O_α, 528.6~530.0 eV), surface chemisorbed oxygen species (O_β, 531.4–532.0 eV), and oxygen containing surface groups (O_γ, 532.6~533.5 eV) like the defect oxide and hydroxyl species (Schindler et al. 2009; Wang et al. 2015). Some previous studies had pointed out that surface chemisorbed labile oxygen (O_β) was a key factor affecting the SCR reaction of the catalysts because it was of high mobility and played a critical role in oxidation reaction (Wang et al. 2016; Du et al. 2020). The order of O_β / (O_α + O_β) is WMCT(CP) > WMCT(DP) > WMCT(SG),

which is consistent with the low-temperature SCR performance, indicating that a higher ratio of O_β / (O_α + O_β) was conducive to improve the NO removal efficiency.

Table 2 Surface atomic ratios of Mn 2*p*, Ce 3*d* and O1*s* of the different catalysts

Catalyst	Surface atomic ratio (%)		
	Mn ⁴⁺ / (Mn ⁴⁺ + Mn ³⁺)	Ce ³⁺ / (Ce ³⁺ + Ce ⁴⁺)	O _β / (O _β + O _α)
WMCT(CP)	40.0	42.4	92.5
WMCT(DP)	31.7	28.4	92.1
WMCT(SG)	18.1	65.1	69.4

3.7 In-situ DRIFTS

In order to investigate the mechanism and the effect of SO_2 in the SCR reaction with WMnCeTiO_x catalysts prepared by different methods, we conducted in-situ DRIFTS experiments. Fig. 8 and 9 showed the in-situ DRIFTS spectra of the WMnCeTiO_x catalysts prepared by different methods at 250 °C, and spectra from the reactions of the adsorbed NH_3 with $\text{NO} + \text{O}_2$ and the adsorbed $\text{NO} + \text{O}_2$ with NH_3 as well as the reaction under an atmosphere containing SO_2 after the SCR are included.

Fig. 8 (a), (c), (e) showed the in-situ DRIFTS spectra of the reaction between the NH_3 species and $\text{NO} + \text{O}_2$ at 250 °C on the prepared catalysts. After the catalysts absorbed NH_3 for 30 min, several bands were observed in the ranges of 1000-1750 and 3000-4000 cm^{-1} on WMnCeTiO_x catalysts. The bands (1201, 1435, 3355, 3260 and 3160 cm^{-1}) were assigned to coordinate NH_3 on Lewis acid sites, and the band (1675 cm^{-1}) was assigned to NH_4^+ species on Brønsted acid sites (Chen et al. 2017; Wu et al. 2007; Zhang et al. 2015; Mu et al. 2018; Zhang et al. 2020). After $\text{NO} + \text{O}_2$ was introduced, we found that the intensity of the bands corresponding to the NH_3 groups on the Lewis acid sites decreased obviously, and the intensity of the bands assigned to NH_4^+ groups on the Brønsted acid sites changed a little. This result indicated that the NH_3 groups adsorbed on the Lewis acid sites were more active than the NH_4^+ groups on the Brønsted acid sites. As compared to WMCT(DP) and WMCT(SG) catalysts, WMCT(CP) catalyst had more NH_3 groups on the Lewis acid sites, which was beneficial to the activity in the SCR reaction. As the reaction progressed, the band at 1590 cm^{-1} was overridden by the bands assigned to bidentate nitrate (1574 cm^{-1}) (Li et al. 2017). It can be observed that new bands ascribed to bidentate nitrate (1559 cm^{-1}), free nitrate ions (1379, 1362 cm^{-1}), monodentate nitrate (1374 cm^{-1}) appeared on the catalysts surface and they were enhanced with the proceeding of reaction (Gao et al. 2018; Zeng et al. 2017; Yang et al. 2020). It implied that the NH_3 -SCR reaction over the WMnCeTiO_x catalysts followed an Eley-Rideal (E-R) mechanism.

Fig. 8 (b), (d), (f) showed the in-situ DRIFTS spectra of the reaction between the NO species and NH_3 at 250 °C on the prepared catalysts. After the catalysts absorbed $\text{NO} + \text{O}_2$ for 30 min, bands located at 1362, 1370, 1380, 1559 and 1580 cm^{-1} were detected, which were ascribed to bidentate nitrate (1559, 1580 cm^{-1}), free nitrate ions (1380, 1362 cm^{-1}), monodentate nitrate (1370 cm^{-1}). With the introduction of NH_3 , the bands assigned to bidentate nitrate (1580 cm^{-1}), free nitrate ions (1380 cm^{-1}) on WMnCeTiO_x catalysts exhibited an obvious decrease in intensity. We concluded that bidentate nitrate and free nitrate ions were active compounds and were involved in the reaction. WMCT(CP) and WMCT(DP) catalysts had more bidentate nitrate and free nitrate ions, which was beneficial to the activity in the SCR reaction. As the reaction progressed, while coordinate NH_3 species on Lewis acid sites (1201, 3156, 3267 and 3356 cm^{-1}) and NH_4^+ species (1721, 1675 and 1430 cm^{-1}) on Brønsted acid sites began to appear.

The NH_3 -SCR reaction over the WMnCeTiO_x catalysts followed an Langmuir-Hinshelwood (L-H) mechanism.

To elucidate the mechanism of sulfur poisoning on the SCR reaction, we conducted the reaction under an atmosphere containing 100 ppm SO_2 after conducting the SCR under standard conditions at 250 °C. Fig. 9 (a), (c), (e) showed the in-situ DRIFTS spectra of the reaction between the NH_3 species and SO_2 at 250 °C on the prepared catalyst. All catalysts were then exposed to both NH_3 and SO_2 for 30 min. Compared with only NH_3 exposure, the intensity of bands corresponding to NH_3 on Lewis sites (3355, 3260 and 3160 cm^{-1}) and Brønsted sites (1675 cm^{-1}) slightly decreased, suggesting that SO_2 caused the number of acid sites to decrease. However, there was less reduction in the acid sites on WMCT(CP) catalyst. The band at 1590 cm^{-1} corresponds to NH_3 species on Lewis acid sites shifted to 1580 and 1542 cm^{-1} . The bands at 1340 and 1374 cm^{-1} which ascribed to sulfates appeared, and they also enhanced with the increase of SO_2 injection (Chen et al. 2010; Yan et al. 2018).

Fig. 9 (b), (d), (f) showed the in-situ DRIFTS spectra of the reaction between the NO species and SO_2 at 250 °C on the prepared catalysts. All catalysts were then exposed to both $\text{NO}+\text{O}_2$ and SO_2 for 30 min. When SO_2 was introduced, a new band (1351 cm^{-1}) ascribed to sulfates appeared and the bands corresponding to bidentate nitrate (1557, 1545 cm^{-1}), monodentate nitrate (1370 cm^{-1}) were decreased in intensity. It indicated that SO_2 could restrain the adsorption between NO_x species on WMnCeTiO_x catalysts which inhibited the SCR reaction under L-H mechanism, which might be the main reason for the low NO removal efficiency in the presence of SO_2 . However, the bands assigned to bidentate nitrate (1545 cm^{-1}) on WMCT(CP) catalyst exhibited a slowly decrease in intensity. This data demonstrated that the WMCT(CP) catalyst has better resistance to SO_2 than WMCT(DP) and WMCT(SG) catalysts.

In this paper, WMnCeTiO_x catalysts were prepared by CP, DP and SG methods. Different preparation methods lead to different surface structural characteristics, dispersion of active components, chemical states of the surface species. More importantly, the reduction capacity and the number of acid sites of WMnCeTiO_x catalysts varied with the preparation process, which also would impose a great impact on the absorption and activation of NO and NH_3 on the surface of WMnCeTiO_x catalysts. These factors made WMnCeTiO_x catalysts show an obvious difference in catalytic activity.

The result indicated that the catalysts prepared by the CP method had better SCR activity and SO_2 resistance than that prepared by the DP and SG methods. The WMnCeTiO_x catalyst prepared by CP method has the largest specific surface area and highly-dispersed active species. From the result of in-situ DRIFTS, WMCT(CP) catalyst had more NH_3 groups on the Lewis acid sites and bidentate nitrate and free nitrate ions, which was beneficial to the activity in the SCR reaction. It was revealed that the NH_3 -SCR reaction over the prepared WMCT(CP), WMCT(DP) and WMCT(SG) obeyed both L-H and E-R mechanisms.

Declarations

Ethics approval and consent to participate

Not applicable

Consent for publication

Not applicable

Authors' contributions

Xiaodi Li: Conceptualization, Investigation, Writing - Original draft. Zhitao Han: Conceptualization, Validation, Supervision, Project administration, Writing - Review & Editing. Qingdong Shi: Formal analysis. Xitian Wu, Yu gao: Methodology. Chenglong Li, gang liu: Data curation.

Availability of data and materials

Not applicable

Competing interests

The authors declare that they have no competing interest.

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Figures

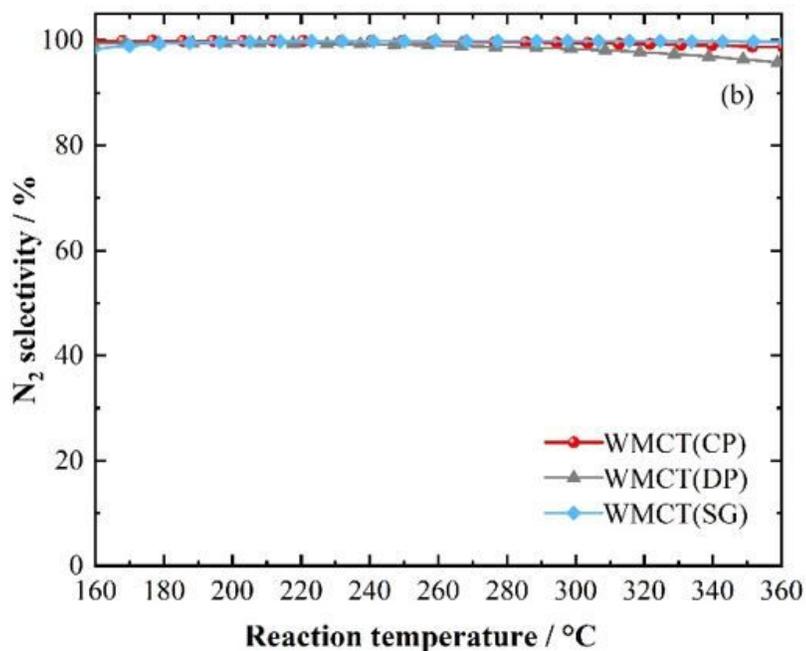
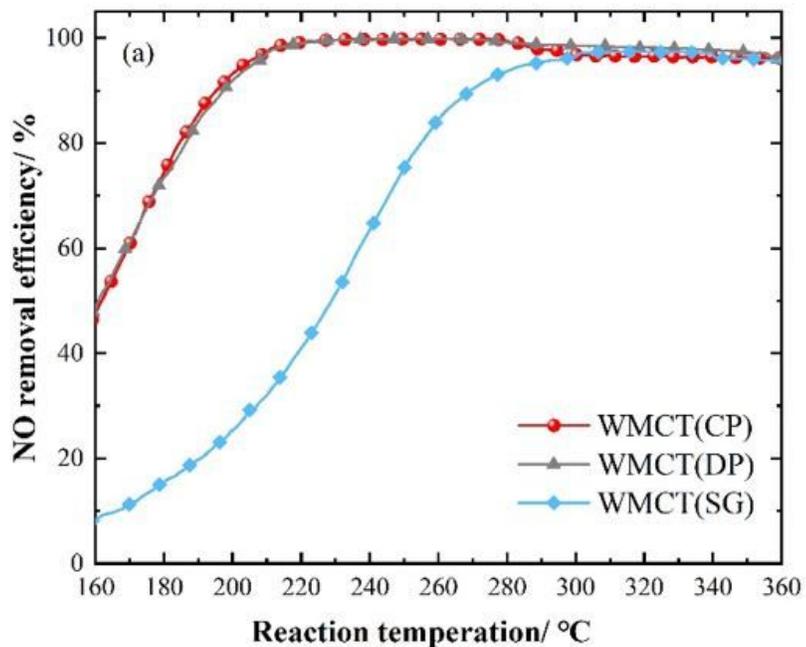


Figure 1

(a) NO removal efficiency, (b) N₂ selectivity in the NH₃-SCR reaction, (Reaction conditions: 0.5 mL catalyst, [NO] = [NH₃] = 500 ppm, [O₂] = 5 vol.%, balanced with N₂, GSHV = 30,000 h⁻¹). H₂O and SO₂ are main components of flue gas from stationary and mobile sources. Therefore, it is necessary for any low temperature SCR catalyst with application potential to be simultaneously resist to H₂O and SO₂ degradation and poison (Guo et al. 2009; Yezerets et al. 2016; Zhang et al. 2019).

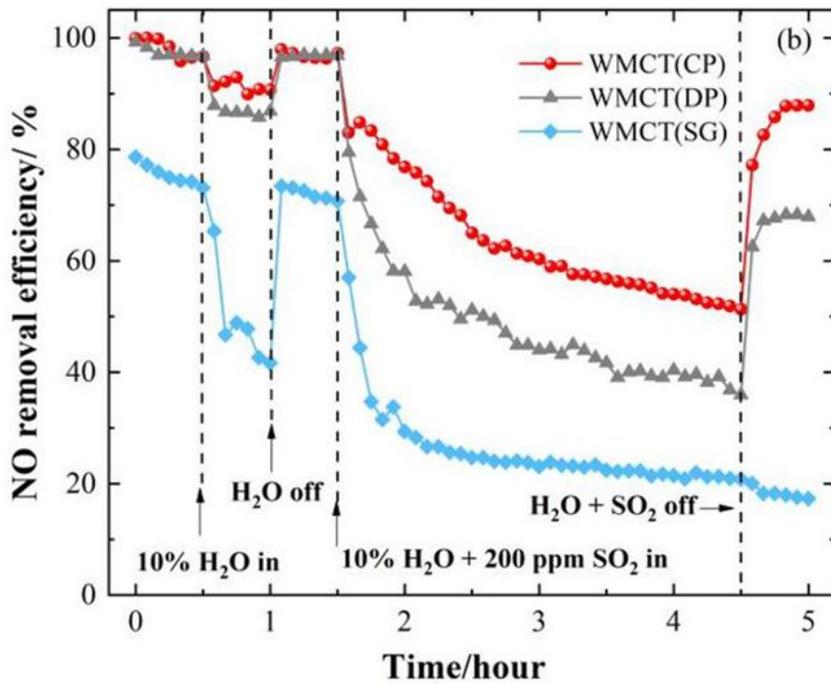
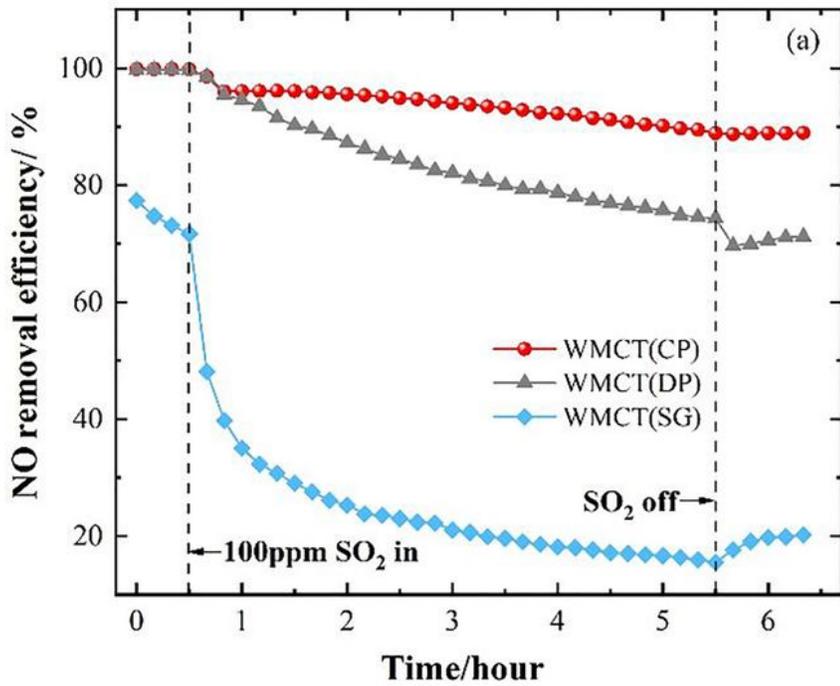


Figure 2

(a) resistance to sulfur poisoning test, (b) resistance to water vapor and sulfur poisoning test. (Reaction conditions: $[NO] = [NH_3] = 500$ ppm, $[O_2] = 5$ vol.%, $[H_2O] = 10$ vol.%, $[SO_2] = 100$ ppm, 200 ppm, balance with N_2 , and GHSV = 30,000 h⁻¹)

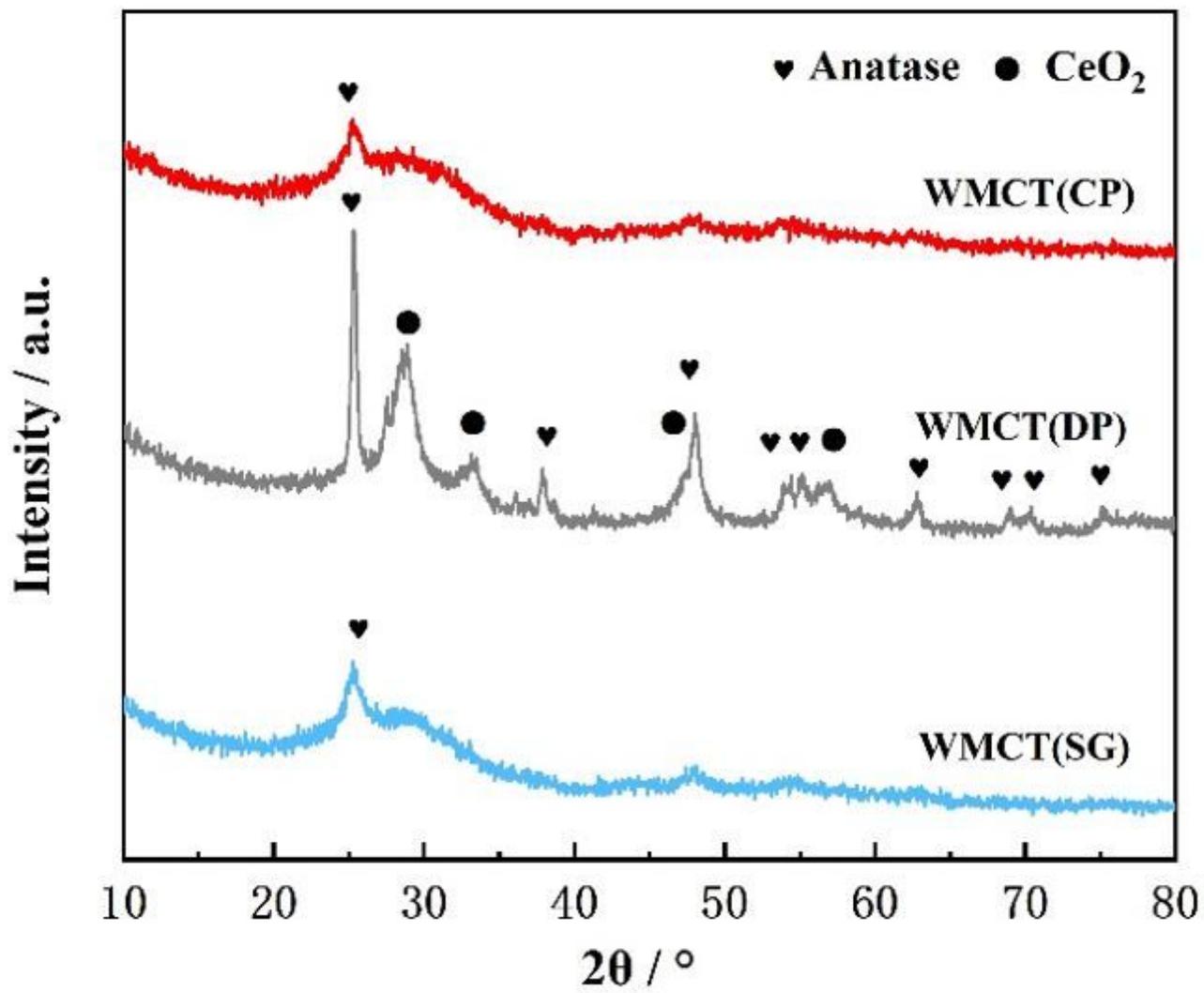


Figure 3

XRD patterns of the prepared catalysts

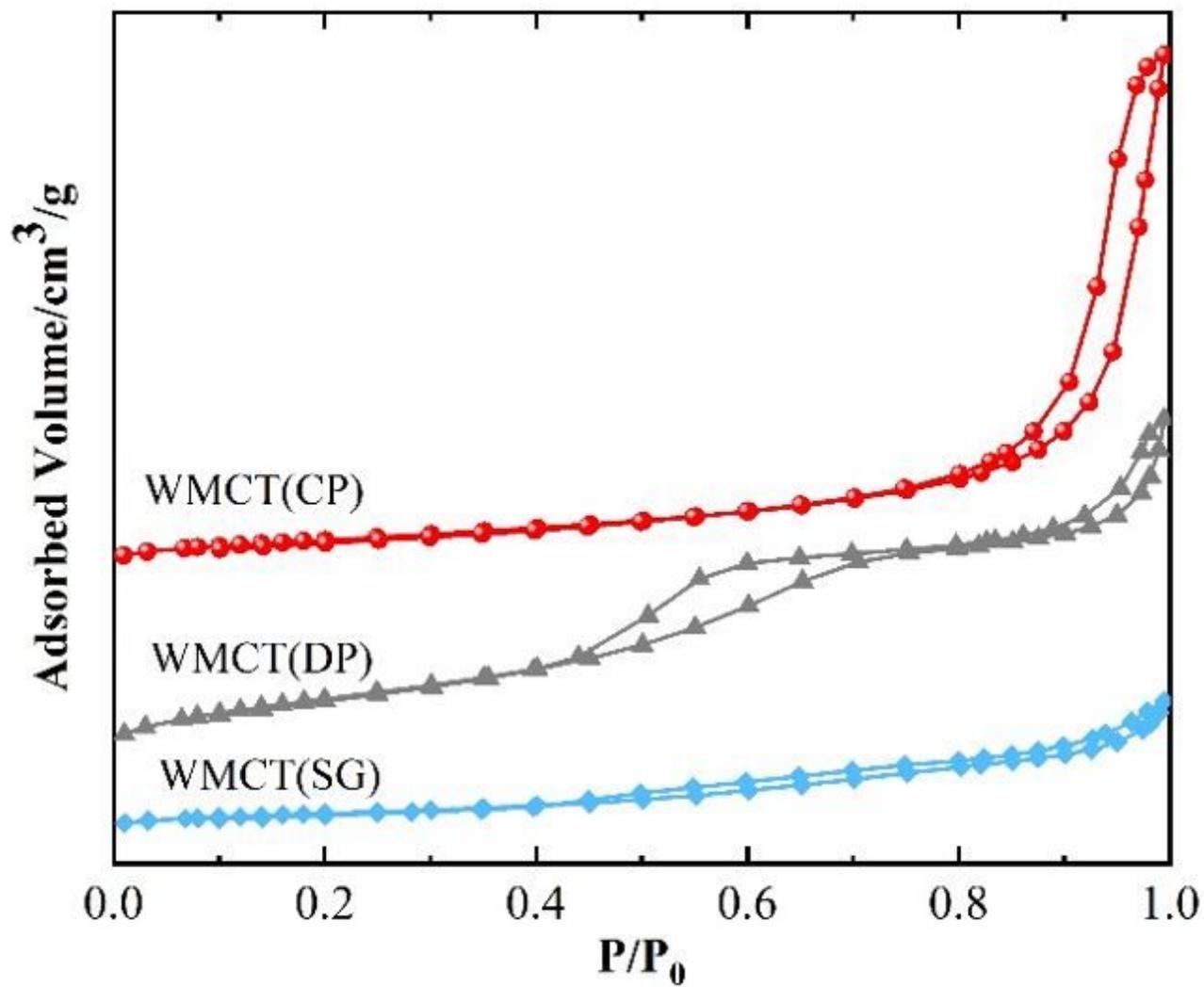


Figure 4

N₂ adsorption-desorption isotherms of WMCT(CP), WMCT (DP), WMCT(SG)

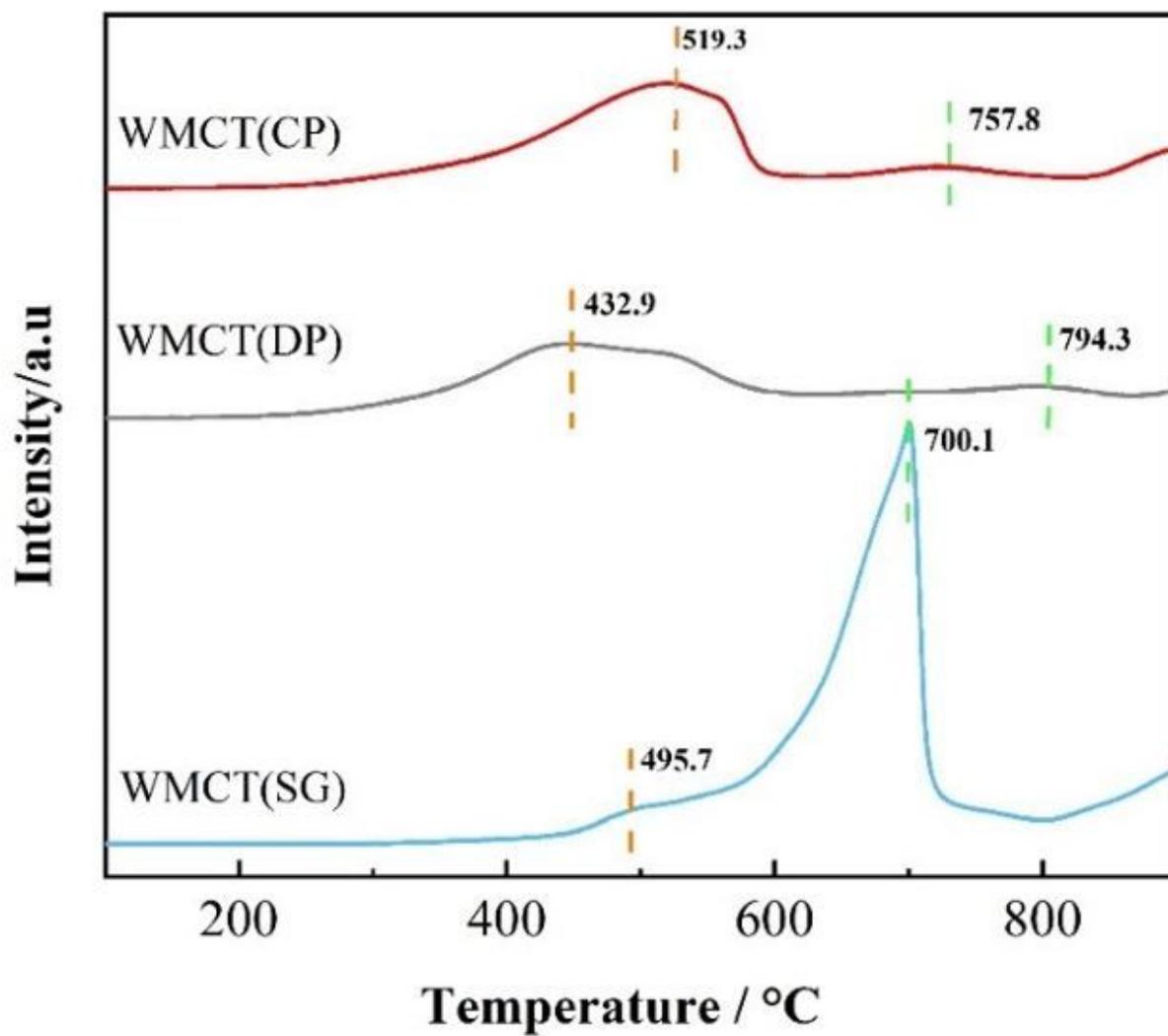


Figure 5

H₂-TPR profiles of the prepared WMCT(CP), WMCT (DP), WMCT(SG)

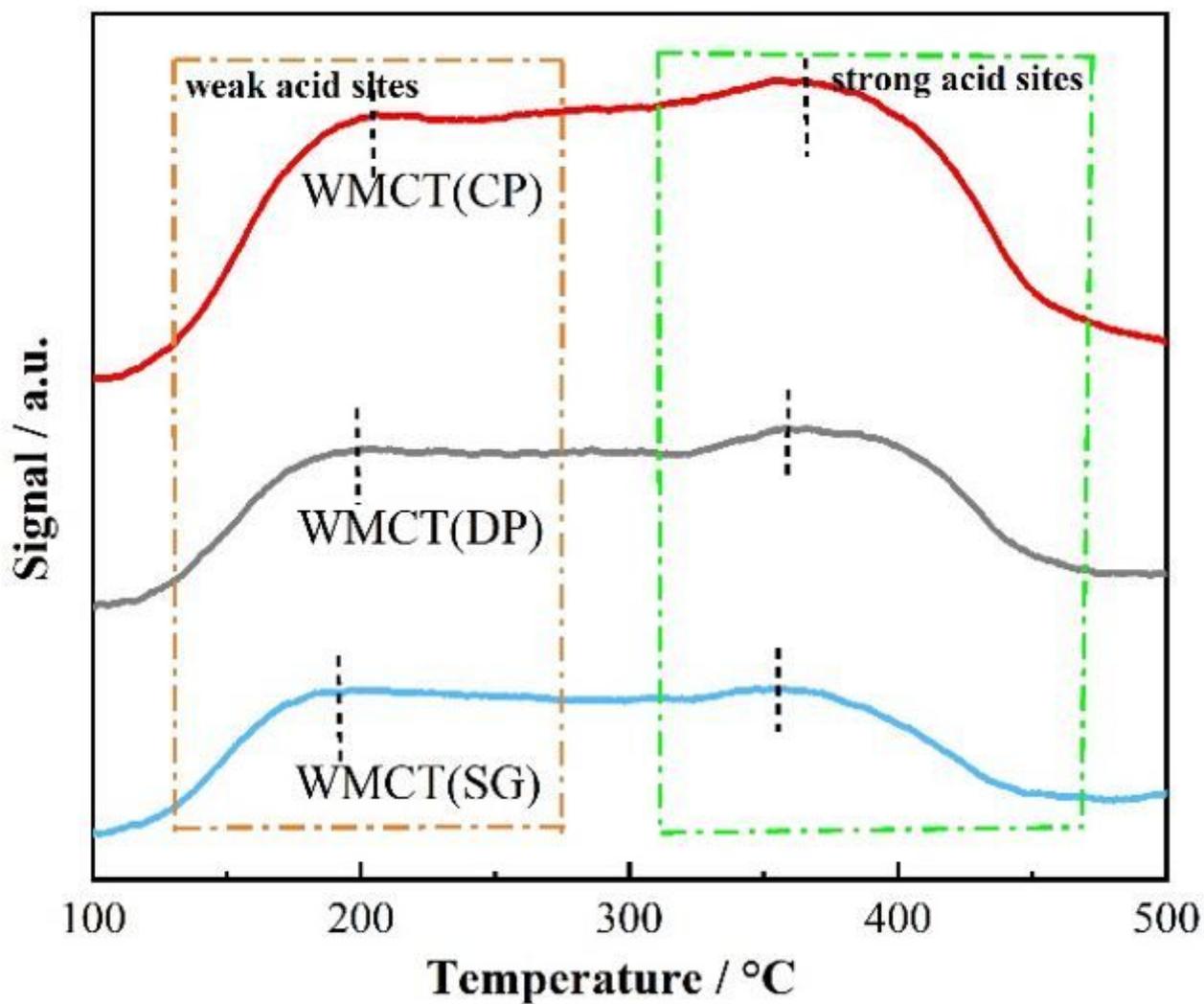


Figure 6

NH₃-TPD profile of the prepared WMCT(CP), WMCT (DP), WMCT(SG)

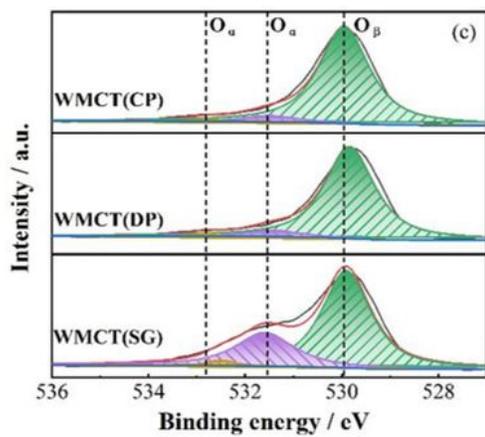
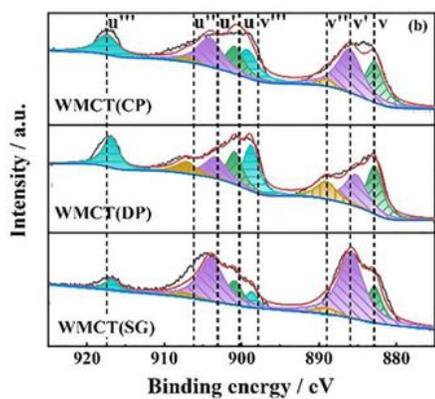
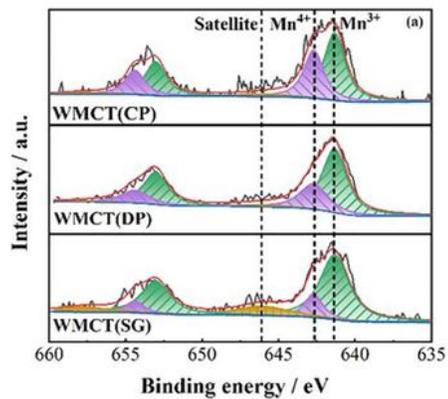


Figure 7

XPS spectra of Mn 2p (a), Ce 3d (b) and O 1s (c) of prepared catalysts

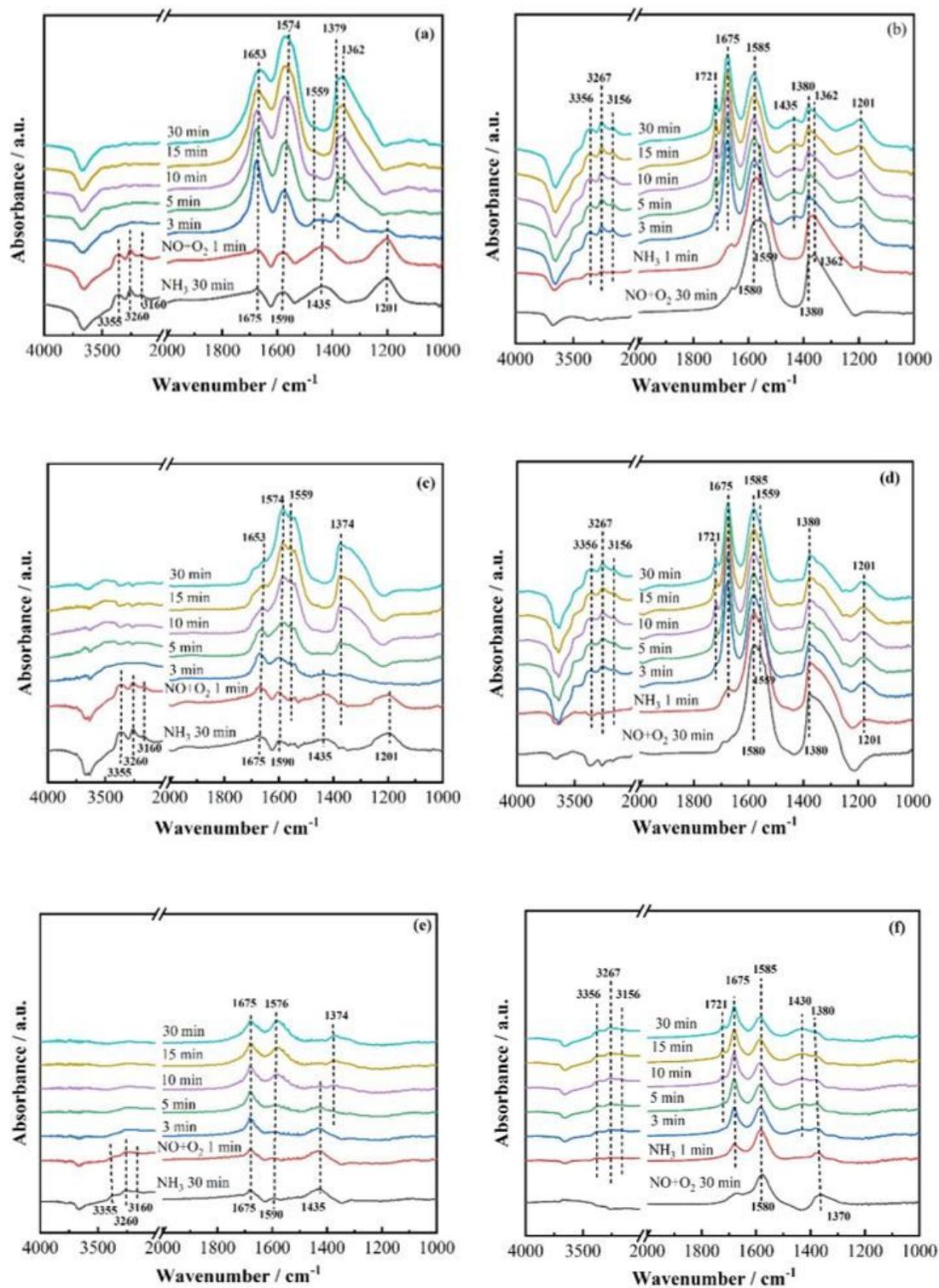


Figure 8

In-situ DRIFTS spectra of NH_3 -SCR reaction over WMCT(CP) (a, b), WMCT(DP) (c, d) and WMCT(SG) (e, f) catalysts at 250°C

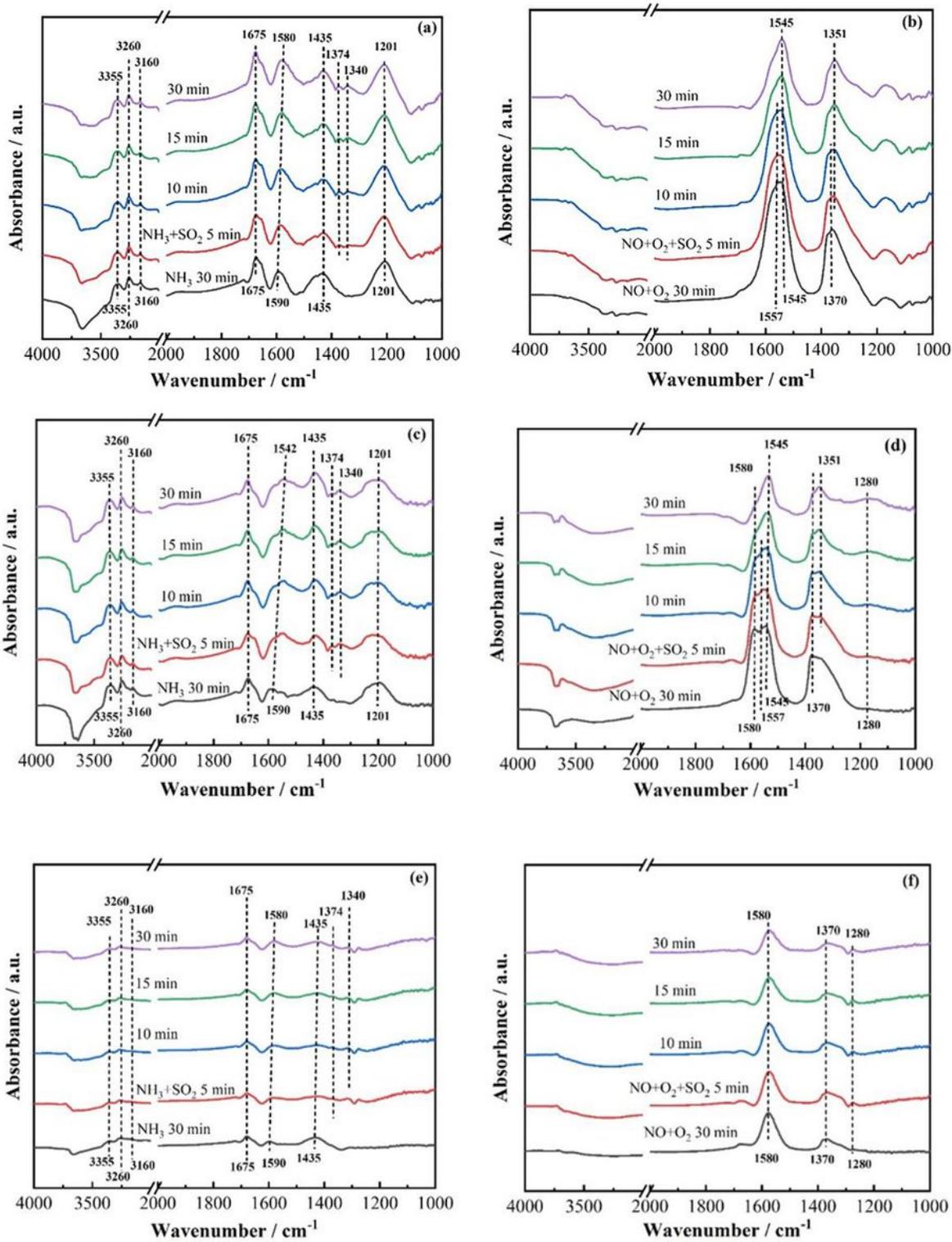


Figure 9

In-situ DRIFTS spectra of SO₂ poisoning over WMCT(CP) (a, b), WMCT(DP) (c, d) and WMCT(SG) (e, f) catalysts at 250 °C

Supplementary Files

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