Selective catalytic reduction of NO_x with NH₃ over iron-cerium-tungsten mixed oxide catalyst prepared by different methods

Zhi-bo Xiong^{1,2,3*}, Jing Liu¹, Fei Zhou¹, Dun-yu Liu¹, Wei Lu¹, Jing Jin^{1,2}, Shi-fa Ding³

(1. School of Energy and Power Engineering, University of Shanghai for Science & Technology, Shanghai 200093, China; 2. Collaborative Innovation Research Institute, University of Shanghai for Science & Technology, Shanghai 200093, China; 3. Shanghai Power Equipment Research Institute, Shanghai 200240, China)

Abstract

A series of magnetic Fe_{0.85}Ce_{0.10}W_{0.05}O_z catalysts were synthesized by three different methods (Co-precipitation (Fe_{0.85}Ce_{0.10}W_{0.05}O_z-CP), Hydrothermal treatment assistant critic acid sol-gel method (Fe_{0.85}Ce_{0.10}W_{0.05}O_z-HT) and Microwave irradiation assistant critic acid sol-gel method (Fe_{0.85}Ce_{0.10}W_{0.05}O_z-MW)), and the catalytic activity was evaluated for selective catalytic reduction of NO with NH₃. The catalyst was characterized by XRD, N₂ adsorption-desorption, XPS, H₂-TPR and NH₃-TPD. Among the tested catalysts, Fe_{0.85}Ce_{0.10}W_{0.05}O_z-MW shows the highest NO_x conversion over per gram in unit time with NO_x conversion of 60.8% at 350 °C under a high gas hourly space velocity of 1,200,000 ml/(g · h). Different from Fe_{0.85}Ce_{0.10}W_{0.05}O_z-CP catalyst, there exists a large of iron oxide crystallite (γ-Fe₂O₃ and α-Fe₂O₃) scattered in Fe_{0.85}Ce_{0.10}W_{0.05}O_z catalysts prepared through hydrothermal treatment or microwave irradiation assistant critic acid sol-gel method, and higher iron atomic concentration on their surface. And Fe_{0.85}Ce_{0.10}W_{0.05}O_z-MW shows higher surface absorbed oxygen concentration and better dispersion compared with Fe_{0.85}Ce_{0.10}W_{0.05}O_z-HT catalyst. These features were favorable for the high catalytic performance of NO reduction with NH₃ over Fe_{0.85}Ce_{0.10}W_{0.05}O_z-MW catalyst.

* Corresponding author. Tel.: +86 21 55270508

Email addresses: xzb328@163.com (Zhi-bo Xiong)

Keywords: Selective catalytic reduction of NO_x, Iron-cerium-tungsten mixed oxide, Co-precipitation, Citric acid
Sol-gel, Hydrothermal treatment, Microwave irradiation

1. Introduction

Nitrogen oxides(NO, NO₂ and N₂O) emitted by the combustion of fossil fuels could result in a series of severe environmental problems [1-4]. Selective catalytic reduction of NO_x with NH₃(NH₃-SCR)is well known as the Best Available Control Technology(BACT) to control the nitrogen oxides emission from coal-fired power plants in terms of economics, removal efficiency and stability [5-8]. V₂O₅-WO₃(MoO₃)/TiO₂ catalysts with a relatively narrow temperature window of 300 ~ 400 °C have been commercialized for the past several decades [9-11]. Meanwhile, this type of catalyst still have many inevitable disadvantages in practical application: high cost, high conversion of SO₂ to SO₃ at high temperatures, the toxicity of vanadium pent-oxide to environment and human health [9-11]. Therefore, a lot of studies have been performed to develop new NH₃-SCR catalysts which probably to substitute the conventional V₂O₅-WO₃(MoO₃)/TiO₂ catalyst [12-23]. Among them, Iron-based catalysts(Molecular sieve catalyst and Mixed oxide catalyst) have attracted attention in NH₃-SCR of NO_x owing to high NH₃-SCR activity, low cost and lack of toxicity relative to vanadium pent-oxide. Meanwhile, the low-temperature NH₃-SCR activity of iron oxide is very poor because its surface area and surface acidity is relatively low [23,24]. Therefore, a series of iron-based mixed oxide catalysts mainly based on α-Fe₂O₃, such as Fe-Ce [25], Fe-Mn [26], Fe-Ti [13], Fe-W [27], Fe-W-Zr [28] and Fe-Ce-Ti [12], were developed by introducing a large number of auxiliaries into iron oxide to improve its low-temperature NH₃-SCR activity. Actually, γ-Fe₂O₃ showed better NH₃-SCR activity than α-Fe₂O₃ under the same reaction conditions [24]. However, its low-temperature NH₃-SCR activity is also poor similarity to α-Fe₂O₃. Therefore, the introduction of moderate and appropriate auxiliaries into γ-Fe₂O₃ might contribute to improve its low-temperature NH₃-SCR activity as the same optimized modification as α-Fe₂O₃ [29,30].

Due to be easily oxidized to α-Fe₂O₃ at relatively high temperature(>350 °C), γ-Fe₂O₃ is a meta-stable iron oxide, and it is difficult to obtain γ-Fe₂O₃ or γ-Fe₂O₃-based mixed oxide powder prepared through the traditional conventional co-precipitation method or directly decomposition of

iron nitrate usually used to prepare α -Fe₂O₃ and α -Fe₂O₃-based mixed oxide. At present, the preparation methods for γ -Fe₂O₃ and γ -Fe₂O₃-based mixed oxide usually includes Hydrogen reduction [31], Co-precipitation [32] and Critic acid sol-gel assisted by hydrothermal treatment [33]. For the hydrogen reduction method to prepare γ -Fe₂O₃, α -Fe₂O₃ is firstly obtained through precipitation, and then the abovementioned α -Fe₂O₃ is reduced to Fe₃O₄ by purging H₂ at relatively higher temperature. Finally, Fe₃O₄ is again oxidized to γ -Fe₂O₃ by purging the air at relatively lower temperature. According to the traditional hydrothermal treatment assistant critic acid sol-gel method to prepare γ -Fe₂O₃ and γ -Fe₂O₃-based mixed oxide, a mixture solution of nitrate precursors and critic acid needed to be treated in a water bath for about 20 h at 50~80 °C, a kind of iron-based wet sol is formed, and then this wet sol is dried at 80~110 °C for a long time to get a dry gel. Fe²⁺(FeSO₄·7H₂O and FeCl₂) and Fe³⁺(Fe(NO₃)₃·9H₂O and FeCl₃) are usually used as the iron precursors to prepare γ -Fe₂O₃ and γ -Fe₂O₃-based mixed oxide through the conventional co-precipitation method with NaOH or NH₄OH as the precipitant agent. However, the cakes obtained after co-precipitation need to be washed for a long time to remove the impurity ion in it, and then the filtrate cakes are dried at 80~110 °C for 12~14 h. In conclusion, the preparation of γ -Fe₂O₃ and γ -Fe₂O₃-based mixed oxide is high energy and time consumption through the traditional Hydrogen reduction, Co-precipitation and Hydrothermal treatment assistant critic acid sol-gel methods. Therefore, the development of an economical, simple and save-time method to prepare γ -Fe₂O₃ and γ -Fe₂O₃-based mixed oxide is very necessary.

Due to higher surface acidity, better thermal stability and better anti-SO₂ poison, W component have been usually introduced into vanadium-based, other transition metal-based and rare earth(CeO_x) catalysts to enhance their NH₃-SCR activities. Li et al. reported that the introduction of WO_x species improved the low-temperature NH₃-SCR activity of iron oxide through the enhancement of its surface acid sites stability and the adsorption of monodentate nitrite and NO₂ species adsorption of over it [27]. **Shan's research demonstrated that the cerium-tungsten mixed oxide catalyst prepared through the urea co-precipitation method showed excellent NH₃-SCR activity**, which was mainly attributed to a good synergistic effect between Ce and W species in cerium oxide after introducing tungsten oxide into it [34]. Currently, cerium oxide has

1 been confirmed to have elevated oxygen storage capacity and redox property through storing and
2 releasing oxygen via the redox shift between Ce^{4+} and Ce^{3+} under oxidizing and reducing
3 conditions, and the addition of cerium oxide might lead to smaller grain size and increases the
4 surface area of some transition metal oxides by inducing the creation of structure defect in the host
5 oxides, thereby improves their catalytic activity. Therefore, cerium oxide has been widely used as
6 support or active species in various industrial heterogeneous catalysts [35-37]. Our previous
7 research [12,25] indicated that the addition of cerium oxide enlarged the BET surface area and the
8 pore volume of iron oxide prepared through the co-precipitation method, made the formation of
9 amorphous phase iron oxide and also enhanced its oxidation activity of NO to NO_2 , thereby
10 improved its low-temperature NH_3 -SCR activity.

11 In this work, cerium oxide and tungsten oxide were used as the auxiliaries to enhance the
12 NH_3 -SCR activity of $\gamma\text{-Fe}_2\text{O}_3$. And $\gamma\text{-Fe}_2\text{O}_3$ -based iron-cerium-tungsten mixed oxide catalyst were
13 prepared through three different methods such as the conventional co-precipitation, the traditional
14 hydrothermal treatment assistant critic acid sol-gel and an new-style microwave irradiation
15 assistant critic acid sol-gel method, respectively. The NH_3 -SCR activity at the relatively high
16 space velocity of $60,000 \text{ h}^{-1}$ over these catalysts were investigated. Compared with the
17 conventional co-precipitation method and the traditional hydrothermal treatment assistant critic
18 acid sol-gel method, microwave irradiation assistant critic acid sol-gel was an new, simple,
19 economical and save-time method to prepare $\gamma\text{-Fe}_2\text{O}_3$ -based mixed oxide catalyst for NH_3 -SCR of
20 NO_x . And the $\gamma\text{-Fe}_2\text{O}_3$ -based iron-cerium-tungsten mixed oxide catalyst prepared through the
21 microwave irradiation assistant critic acid sol-gel method also showed the best NO_x conversion
22 over gram catalyst per unit time. The effects of different preparation methods on the structural and
23 chemical properties of the catalysts were studied using X-ray diffraction(XRD), N_2 adsorption-
24 desorption, X-ray photoelectron spectra(XPS), temperature programmed reduction of H_2 (H_2 -TPR)
25 and temperature programmed desorption of NH_3 (NH_3 -TPD).

26 2. Material and Methods

27 2.1 Catalysts Preparation and Activity Test

Three kinds of $\text{Fe}_{0.85}\text{Ce}_{0.10}\text{W}_{0.05}\text{O}_z$ catalysts were prepared through Co-precipitation method, Hydrothermal treatment assistant Critic acid sol-gel method and Microwave irradiation assistant Critic acid sol-gel method, respectively. $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and ammonium meta-tungsten are used as the precursors with critic acid as the complex agent for Hydrothermal treatment assistant Critic acid sol-gel method and Microwave irradiation assistant Critic acid sol-gel method. All the reagents used were of AR grade.

Co-precipitation: A certain amount of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and ammonium meta-tungsten were dissolved in the distilled water to get 250 ml mixed solution with the molar ratio of Fe/Ce/W kept at 85:5:10 and the total concentration of Fe, Ce and W being 0.2 mol/L. After being stirred for 1 h at ambient temperature to make sure the homogeneously mixing of the precursors, the mixed solution was slowly titrated into the ammonium hydroxide solution of 2 mol/L until its pH is between 9 and 10. And then the precipitate cake was firstly filtered and washed by distilled water for several times. This was followed by drying at 105 °C for 12 h and calcining at 500 °C with a heating rate of 5 °C/min for 5 h in air. The annealed samples were crushed and sieved to 40-60 mesh for NH_3 -SCR activity tests.

Hydrothermal treatment assistant Critic acid sol-gel: The same quality of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and ammonium meta-tungsten presented in the co-precipitation method were gradually dissolved in 10 ml distilled water, and then 5.894 g critic acid was added with the molar ratio of critic acid/(Fe+Ce+W) of 0.5. After being stirred for about 10 min, the mixture solution was placed in the thermostatic water-bath and treated by hydrothermal at 50 °C for 16 h to get wet sol. Finally, the wet sol was dried at 105 °C for 2 h, and then the subsequent treatment was the same as the co-precipitation method.

Microwave irradiation assistant Critic acid sol-gel: Different from the hydrothermal treatment assistant critic acid sol-gel method, the mixture solution of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, ammonium meta-tungsten and critic acid after being stirred for about 10 min was treated by microwave irradiation for 10 min with 36.4% power (microwave irradiation 8 s, 14 s suspended for a cycle with full power) using a household microwave ovens (EG8MEA6-NR, 2.45 GHz, 800 W), and one kind of pale red dry gel was obtained. The subsequent treatment was the

1 same as the co-precipitation method and the hydrothermal treatment assistant critic acid sol-gel
2 method.

3 These $\text{Fe}_{0.85}\text{Ce}_{0.10}\text{W}_{0.05}\text{O}_z$ catalysts prepared through the co-precipitation method, the
4 hydrothermal treatment assistant critic acid sol-gel method and the microwave irradiation assistant
5 critic acid sol-gel method in this work were denoted as $\text{Fe}_{0.85}\text{Ce}_{0.10}\text{W}_{0.05}\text{O}_z\text{-CP}$,
6 $\text{Fe}_{0.85}\text{Ce}_{0.10}\text{W}_{0.05}\text{O}_z\text{-HT}$ and $\text{Fe}_{0.85}\text{Ce}_{0.10}\text{W}_{0.05}\text{O}_z\text{-MW}$, respectively.

7 The activities for selective catalytic reduction of NO_x with NH_3 over $\text{Fe}_{0.85}\text{Ce}_{0.10}\text{W}_{0.05}\text{O}_z\text{-CP}$,
8 $\text{Fe}_{0.85}\text{Ce}_{0.10}\text{W}_{0.05}\text{O}_z\text{-HT}$ and $\text{Fe}_{0.85}\text{Ce}_{0.10}\text{W}_{0.05}\text{O}_z\text{-MW}$ were carried out in a fixed-bed quartz reactor
9 at atmospheric pressure. The concentrations of gaseous reactants were controlled as follows: 1000
10 ppm NO , 1000 ppm NH_3 , 3 vol.% O_2 and N_2 as the balance. The total flow rate was 2000 ml, and
11 catalyst used in experiment was 2 ml(2.4622 g of $\text{Fe}_{0.85}\text{Ce}_{0.10}\text{W}_{0.05}\text{O}_z\text{-CP}$, 1.3244 g of
12 $\text{Fe}_{0.85}\text{Ce}_{0.10}\text{W}_{0.05}\text{O}_z\text{-HT}$ and 1.049 g of $\text{Fe}_{0.85}\text{Ce}_{0.10}\text{W}_{0.05}\text{O}_z\text{-MW}$) or 0.1 g for these three catalysts
13 yielding a gas hourly space velocity(GHSV) of 60,000 /h or 1,200,000 ml/(g · h). The effluent gas
14 including NO and NO_2 at the inlet and outlet of the reactor were analyzed by a Flue Gas Analyzer
15 (Model 60i, ThermoFisher Scientific Co. Ltd, USA). NO conversion(X_{NO_x}) was calculated as
16 follows: $X_{\text{NO}_x} = (1 - [\text{NO}_x]_{\text{out}} / [\text{NO}_x]_{\text{in}}) \times 100\%$ with $[\text{NO}_x] = [\text{NO}] + [\text{NO}_2]$.

17 2.2 Catalyst characterization

18 The powder X-ray diffraction(XRD) measurement between 10° and 80° at a step rate of 2
19 $^\circ/\text{min}$ was measured on the 6100 X-ray diffraction Analyzer (Japan, Shimadzu, Cu K_α as radiation
20 resource, $\lambda = 1.54 \text{ \AA}$) to determine the crystal structure. N_2 adsorption-desorption isotherms
21 measurements were measured using Micromeritics ASAP2450 Surface Area and Porosity
22 Analyzer at -196°C . The results of X-ray photoelectron spectroscopy (XPS) experiments were
23 obtained on a Scanning X-ray Photoelectron Spectroscopy(ESCALAB-250, ThermoFisher
24 Scientific, USA) using Al K_α radiation(1486.7 eV). The Binding energy was calibrated using C 1s
25 peak(BE=284.8 eV) as standard. The $\text{H}_2\text{-TPR}$ (Temperature programmed reduction) experiments
26 were carried out on AutoChem II with TCD detection(Micromeritics, USA) with 0.1 g catalyst in
27 a H_2 (10 vol.%)/Ar(40 ml/min) at $10^\circ\text{C}/\text{min}$ raised linearly to 900°C . The $\text{NH}_3\text{-TPD}$ (Temperature

programmed desorption) experiments were also carried out on AutoChem II with TCD detection with 0.1 g catalyst. Prior to NH₃-TPD experiment, the sample was pretreated at 500 °C under He atmosphere (99.999%, 30 ml/min) for 1 h, and then cooled down to 100 °C. The sample was exposed to a flow of NH₃ (20 vol.%) / He (120 ml/min) at 100 °C, and followed by He (99.999%, 30 ml/min) purge for another 1 h. Finally, the temperature was raised linearly to 600 °C at the rate of 10 °C/min in He flow.

3. Results and discussion

3.1 NH₃-SCR activity

Fig.1(A) shows the NO_x conversions as a function of reaction temperature in the NH₃-SCR over three kinds of Fe_{0.85}Ce_{0.10}W_{0.05}O_z catalysts prepared through the conventional co-precipitation method, the traditional hydrothermal treatment assistant citric acid sol-gel method and the new microwave irradiation assistant citric acid sol-gel method. From the results it can be seen that under the GHSV of 60,000 /h, Fe_{0.85}Ce_{0.10}W_{0.05}O_z-CP showed higher NH₃-SCR activity than Fe_{0.85}Ce_{0.10}W_{0.05}O_z-HT and Fe_{0.85}Ce_{0.10}W_{0.05}O_z-MW at the low-temperature range of 125~150 °C and at the high-temperature range of 400 ~ 500 °C. However, among those Fe_{0.85}Ce_{0.10}W_{0.05}O_z catalysts prepared through different methods, Fe_{0.85}Ce_{0.10}W_{0.05}O_z-MW showed the best NH₃-SCR activity at the medium-temperature of 200~275 °C under the same reaction conditions. It should be concerned Fe_{0.85}Ce_{0.10}W_{0.05}O_z-HT or Fe_{0.85}Ce_{0.10}W_{0.05}O_z-MW is very fluffy compared with the Fe_{0.85}Ce_{0.10}W_{0.05}O_z-CP, and the mass of Fe_{0.85}Ce_{0.10}W_{0.05}O_z-CP, Fe_{0.85}Ce_{0.10}W_{0.05}O_z-HT or Fe_{0.85}Ce_{0.10}W_{0.05}O_z-MW for 2 mL were 2.4622 g, 1.3244 g and 1.049 g, respectively. Therefore, the amount of NO_x conversion over per gram at 150~250 °C for these catalysts in one hour were also calculated and the results are also shown in Fig.1(A). Compared with other two Fe_{0.85}Ce_{0.10}W_{0.05}O_z catalysts, the amount of NO_x conversion over per gram of Fe_{0.85}Ce_{0.10}W_{0.05}O_z-MW was the largest in one hour at the low-temperature range of 150~250 °C. Because the NO_x conversion was 100% in a wide temperature range (250~400 °C) for these three iron-cerium-tungsten mixed oxide catalysts prepared by different methods, therefore the NO_x

conversions at the temperature range of 250~500°C for these three kinds of $\text{Fe}_{0.85}\text{Ce}_{0.10}\text{W}_{0.05}\text{O}_z$ catalysts were also investigated under the GHSV of 1,200,000 ml/(g·h) and the results are shown in Fig.1(B). It can be found that $\text{Fe}_{0.85}\text{Ce}_{0.10}\text{W}_{0.05}\text{O}_z$ -MW also showed the highest NO_x conversion over per gram catalyst at 250~425 °C compared with $\text{Fe}_{0.85}\text{Ce}_{0.10}\text{W}_{0.05}\text{O}_z$ -CP and $\text{Fe}_{0.85}\text{Ce}_{0.10}\text{W}_{0.05}\text{O}_z$ -HT. During the preparation process for these three kinds of $\text{Fe}_{0.85}\text{Ce}_{0.10}\text{W}_{0.05}\text{O}_z$ catalysts, the time used to prepare $\text{Fe}_{0.85}\text{Ce}_{0.10}\text{W}_{0.05}\text{O}_z$ through the new microwave irradiation assistant critic acid sol-gel method was about 30 min, and it was very less than the times for the conventional co-precipitation method (about 1200 min) or the traditional hydrothermal treatment assistant critic acid sol-gel method (about 1100 min). Therefore, the microwave irradiation assistant critic acid sol-gel method used to prepare iron-cerium-tungsten mixed oxide catalyst is time-saving and economic. In conclusion, compared with the conventional co-precipitation method and the traditional hydrothermal treatment assistant critic acid sol-gel method, critic acid sol-gel assisted by microwave irradiation is a simple, time-saving and cost-effective method to prepare iron-cerium-tungsten mixed oxide catalyst with high NO_x conversion at low-temperature NH_3 -SCR reaction.

3.2 Structural properties

To investigate the reason for the improvement on NH_3 -SCR activity, characterization of the catalysis is necessary [12]. Therefore, micro-pore structure properties and the crystallite of these $\text{Fe}_{0.85}\text{Ce}_{0.10}\text{W}_{0.05}\text{O}_z$ catalysts prepared through different methods were analyzed. Powder XRD patterns of $\text{Fe}_{0.85}\text{Ce}_{0.10}\text{W}_{0.05}\text{O}_z$ -CP, $\text{Fe}_{0.85}\text{Ce}_{0.10}\text{W}_{0.05}\text{O}_z$ -HT and $\text{Fe}_{0.85}\text{Ce}_{0.10}\text{W}_{0.05}\text{O}_z$ -MW are shown in Fig. 2. No diffraction peaks attributed to iron oxide, cerium oxide and tungsten oxide was found in $\text{Fe}_{0.85}\text{Ce}_{0.10}\text{W}_{0.05}\text{O}_z$ -CP with only a peak package in the range from 20 to 40 °, indicated there exist a highly dispersive state of iron, cerium and tungsten element within $\text{Fe}_{0.85}\text{Ce}_{0.10}\text{W}_{0.05}\text{O}_z$ -CP, rather than forming iron oxides, cerium oxides or tungsten oxides particles. Meanwhile, $\text{Fe}_{0.85}\text{Ce}_{0.10}\text{W}_{0.05}\text{O}_z$ catalysts prepared through the critic acid sol-gel method assisted by hydrothermal treatment or microwave irradiation showed the diffraction peaks attributed to $\alpha\text{-Fe}_2\text{O}_3$ and $\gamma\text{-Fe}_2\text{O}_3$ according to #33-0664 and #39-1346 in Joint Committee of Powder Diffraction Standards (JCPDS), respectively. And the intensity of those diffraction peaks in

1 $\text{Fe}_{0.85}\text{Ce}_{0.10}\text{W}_{0.05}\text{O}_z$ -MW was stronger. Therefore, it can be deduced that the formation of $\alpha\text{-Fe}_2\text{O}_3$
2 and $\gamma\text{-Fe}_2\text{O}_3$ in iron-cerium-tungsten composite catalyst might contribute to enhance its low-
3 temperature NH_3 -SCR activity over per gram catalyst.

4 Fig.3 and Table 1 shows the effect of different preparation methods on the pore structure
5 properties of magnetic $\text{Fe}_{0.85}\text{Ce}_{0.10}\text{W}_{0.05}\text{O}_z$ catalyst. From the results it can be found that there
6 existed a large portion of meso-porous structure within magnetic $\text{Fe}_{0.85}\text{Ce}_{0.10}\text{W}_{0.05}\text{O}_z$ catalysts
7 prepared through the conventional co-precipitation method, the traditional hydrothermal treatment
8 assistant critic acid sol-gel method and the microwave irradiation assistant critic acid sol-gel
9 method. And, $\text{Fe}_{0.85}\text{Ce}_{0.10}\text{W}_{0.05}\text{O}_z$ -CP had a large of meso-porous structure more than those of
10 $\text{Fe}_{0.85}\text{Ce}_{0.10}\text{W}_{0.05}\text{O}_z$ -HT and $\text{Fe}_{0.85}\text{Ce}_{0.10}\text{W}_{0.05}\text{O}_z$ -MW. Meanwhile, the peak position of the pore
11 size distribution curve for $\text{Fe}_{0.85}\text{Ce}_{0.10}\text{W}_{0.05}\text{O}_z$ -HT or $\text{Fe}_{0.85}\text{Ce}_{0.10}\text{W}_{0.05}\text{O}_z$ -MW was left than that for
12 $\text{Fe}_{0.85}\text{Ce}_{0.10}\text{W}_{0.05}\text{O}_z$ -CP, and there existed a large of pore structure with its pore size less than 5 nm
13 for $\text{Fe}_{0.85}\text{Ce}_{0.10}\text{W}_{0.05}\text{O}_z$ prepared through critic acid sol-gel assisted by the traditional hydrothermal
14 treatment or microwave irradiation with 5~10 nm pore size for $\text{Fe}_{0.85}\text{Ce}_{0.10}\text{W}_{0.05}\text{O}_z$ -CP(As shown
15 in Fig. 3(B)). Therefore, the BET surface areas and the pore volumes for $\text{Fe}_{0.85}\text{Ce}_{0.10}\text{W}_{0.05}\text{O}_z$ -HT
16 or $\text{Fe}_{0.85}\text{Ce}_{0.10}\text{W}_{0.05}\text{O}_z$ -MW were less than those for $\text{Fe}_{0.85}\text{Ce}_{0.10}\text{W}_{0.05}\text{O}_z$ -CP(As shown in Table 1).
17 In order to better comparison of the NH_3 -SCR activities over per BET surface area for
18 $\text{Fe}_{0.85}\text{Ce}_{0.10}\text{W}_{0.05}\text{O}_z$ -CP, $\text{Fe}_{0.85}\text{Ce}_{0.10}\text{W}_{0.05}\text{O}_z$ -HT and $\text{Fe}_{0.85}\text{Ce}_{0.10}\text{W}_{0.05}\text{O}_z$ -MW, the NO_x conversion
19 in one hour on per BET surface area of these catalysts at 150 °C, 200 °C and 250 °C were
20 calculated and the results were also shown in Table 1. It can be found $\text{Fe}_{0.85}\text{Ce}_{0.10}\text{W}_{0.05}\text{O}_z$ -MW
21 showed the best NO_x conversion on per BET surface area in one hour compared with
22 $\text{Fe}_{0.85}\text{Ce}_{0.10}\text{W}_{0.05}\text{O}_z$ -CP and $\text{Fe}_{0.85}\text{Ce}_{0.10}\text{W}_{0.05}\text{O}_z$ -HT catalysts.

23 3.3 Redox properties

24 XPS is a widely used technique to investigate the redox properties of catalysts. Fig.4 show
25 the XPS results of the $\text{Fe}_{0.85}\text{Ce}_{0.10}\text{W}_{0.05}\text{O}_z$ catalysts prepared through the co-precipitation method,
26 the traditional hydrothermal treatment assistant critic acid sol-gel method and critic acid sol-gel
27 assisted by microwave irradiation. And the surface atomic concentrations and valence states of Fe,
28 O, Ce and W elements of these catalysts are also calculated and are summarized in Table 2.

According to Fig.4(A), the O1s peaks could be separated into two peaks by the same fitting deconvolution technique, and the sub-bands at low binding energy(529.2 eV) and at high binding energy(531.1 eV) attribute to the lattice oxygen(O^{2-} , denoted as O_{β}) and the absorbed oxygen(O^{-} and O^{2-} , denoted as O_{α}), respectively. Due to the higher mobility, the absorbed oxygen(O_{α}) is often thought to more reactive in oxidation reactions, and higher $O_{\alpha}/(O_{\alpha}+O_{\beta})$ ratio is beneficial for the NO oxidation to NO_2 in the NH_3 -SCR reaction at low temperatures and thereafter facilitates the "fast SCR" reaction [38-40]. In contrast, higher $O_{\beta}/(O_{\alpha}+O_{\beta})$ ratio is harmful to the NH_3 -SCR activity at high temperature through promoting the catalytic activity of oxidizing NH_3 to NO_x [40]. Interesting, $Fe_{0.85}Ce_{0.10}W_{0.05}O_z$ -CP had the greatest amount of the absorbed oxygen(O_{α}) and the total oxygen($O_{total}, O_{\alpha}+O_{\beta}$) followed by $Fe_{0.85}Ce_{0.10}W_{0.05}O_z$ -MW, and the lattice oxygen concentration of $Fe_{0.85}Ce_{0.10}W_{0.05}O_z$ -MW was the most(As shown in Fig.4(A) and Table 2). Consequently, Based on the influence of the absorbed oxygen and the lattice oxygen the catalytic activity for NO_x reduction, $Fe_{0.85}Ce_{0.10}W_{0.05}O_z$ -MW should show higher low-temperature NO_x conversion with its high-temperature NH_3 -SCR being the worst. Meanwhile, the NO_x conversion over per gram of $Fe_{0.85}Ce_{0.10}W_{0.05}O_z$ -MW at low-temperature was great more than that over per gram of $Fe_{0.85}Ce_{0.10}W_{0.05}O_z$ -CP. This means that the concentrations of the surface absorbed oxygen might not play a primary role on improving the NH_3 -SCR activity of $Fe_{0.85}Ce_{0.10}W_{0.05}O_z$ catalysts. For iron oxide in Fig.4(B), the binding energies of Fe 2p_{3/2}(710 eV) and Fe 2p_{1/2}(724 eV) together with the Fe 2p_{3/2} satellite peak(717.9~718.1 eV) corresponded mainly with Fe^{3+} [13]. As listed in Table 2, compared with $Fe_{0.85}Ce_{0.10}W_{0.05}O_z$ -CP, $Fe_{0.85}Ce_{0.10}W_{0.05}O_z$ -HT shows higher iron atomic concentration and less cerium/tungsten atomic concentrations. This implied that the electron cloud for all elements in $Fe_{0.85}Ce_{0.10}W_{0.05}O_z$ -HT were different from those in $Fe_{0.85}Ce_{0.10}W_{0.05}O_z$ -CP. And hydrothermal treatment assistant critic acid sol-gel might depress the reaction of iron with cerium and tungsten in $Fe_{0.85}Ce_{0.10}W_{0.05}O_z$ catalyst, leading to an inhibition in oxidation ability. Meanwhile, microwave irradiation introduced to assist the critic acid sol-gel preparation of $Fe_{0.85}Ce_{0.10}W_{0.05}O_z$ catalyst could enhance the reaction of iron with cerium and tungsten in it, which improved the dispersion of cerium/iron on the surface of $Fe_{0.85}Ce_{0.10}W_{0.05}O_z$ catalyst and enhanced its oxidation ability. The XPS spectra of W_{4f} were also obtained for $Fe_{0.85}Ce_{0.10}W_{0.05}O_z$ -CP, $Fe_{0.85}Ce_{0.10}W_{0.05}O_z$ -HT and $Fe_{0.85}Ce_{0.10}W_{0.05}O_z$ -MW, and no significant

change in the peak positions was observed among this three catalysts (Fig. 4(C)). This indicated the surface binding energies of W_{4f} were not almost affected by preparation method. While the surface concentration of W^{6+} cation was different in $Fe_{0.85}Ce_{0.10}W_{0.05}O_z$ catalysts prepared through different methods. The XPS spectra peaks of Ce 3d over $Fe_{0.85}Ce_{0.10}W_{0.05}O_z$ -CP, $Fe_{0.85}Ce_{0.10}W_{0.05}O_z$ -HT and $Fe_{0.85}Ce_{0.10}W_{0.05}O_z$ -MW could be fitted into eight peaks with being labeled as u(u, u', u'', u''') and v(v, v', v'', v''') which attributed to Ce 3d_{5/2} and Ce 3d_{3/2}(Fig.4(D)), respectively. According to literatures [40], u(about 882.3 eV) belonged to the characteristic peak of Ce^{4+} with u'(about 885.1 eV) attributed to the characteristic peak of Ce^{3+} , indicating the coexistence of both Ce^{3+} and Ce^{4+} oxidation states in $Fe_{0.85}Ce_{0.10}W_{0.05}O_z$ prepared through different method. However, the $Ce^{3+}/(Ce^{3+}+Ce^{4+})$ ratio slightly decreased according to the sequence: $Fe_{0.85}Ce_{0.10}W_{0.05}O_z$ -HT < $Fe_{0.85}Ce_{0.10}W_{0.05}O_z$ -MW < $Fe_{0.85}Ce_{0.10}W_{0.05}O_z$ -CP.

To further investigate the reducibility of $Fe_{0.85}Ce_{0.10}W_{0.05}O_z$ -CP, $Fe_{0.85}Ce_{0.10}W_{0.05}O_z$ -HT and $Fe_{0.85}Ce_{0.10}W_{0.05}O_z$ -MW catalysts, the H_2 -TPR experiments were conducted and the results are exhibited in Fig.5. Previous researches indicated that Fe_2O_3 usually showed two reduction peaks with one peak in the range of 300~400 °C and another large broad peak in the range of 400~900 °C, attributed to the reduction from Fe_2O_3 to Fe_3O_4 , and the further reduction from Fe_3O_4 to FeO and partial Fe^0 , respectively[27]. Fig. 5 shows that there existed about three bigger H_2 consumption peaks for $Fe_{0.85}Ce_{0.10}W_{0.05}O_z$ -CP in the temperature range of 200 ~ 1000 °C. In view of the weaker reducibility of WO_x species and the H_2 consumption peaks of iron oxide [26], the introduction of cerium oxide and tungsten oxide through the co-precipitation method might enhance the H_2 reduction temperature(the low-temperature peak position located at 489 °C) for iron oxide in catalyst, and there existed a high-temperature H_2 reduction peak in the temperature range of 800 ~ 1000 °C for cerium oxide in catalyst. Meanwhile, different the H_2 -TPR spectra of $Fe_{0.85}Ce_{0.10}W_{0.05}O_z$ -CP, $Fe_{0.85}Ce_{0.10}W_{0.05}O_z$ -HT and $Fe_{0.85}Ce_{0.10}W_{0.05}O_z$ -MW shows four obvious reduction peaks in the temperature range of 200~1000 °C with a sharp peak located at 700~800 °C, not a sharp peak located at about 480 °C similar to $Fe_{0.85}Ce_{0.10}W_{0.05}O_z$ -CP with peak position located at 368 °C. This indicated that the crystal of iron oxide formed in $Fe_{0.85}Ce_{0.10}W_{0.05}O_z$ -CP

was less than that of $\text{Fe}_{0.85}\text{Ce}_{0.10}\text{W}_{0.05}\text{O}_z$ prepared through the critic acid sol-gel methods, and there existed a large of amorphous iron oxide in $\text{Fe}_{0.85}\text{Ce}_{0.10}\text{W}_{0.05}\text{O}_z\text{-CP}$ which was in accordance with the results of XRD in Fig.2. Compared with the traditional hydrothermal treatment, microwave irradiation used to assist the critic acid sol-gel method to prepare $\text{Fe}_{0.85}\text{Ce}_{0.10}\text{W}_{0.05}\text{O}_z$ enhance the reducibility of catalyst and made the H_2 consumption peak shifted to the left. The reduction peaks of $\text{Fe}_{0.85}\text{Ce}_{0.10}\text{W}_{0.05}\text{O}_z\text{-CP}$, $\text{Fe}_{0.85}\text{Ce}_{0.10}\text{W}_{0.05}\text{O}_z\text{-HT}$ and $\text{Fe}_{0.85}\text{Ce}_{0.10}\text{W}_{0.05}\text{O}_z\text{-MW}$ catalysts were deconvoluted into twelve sub-bands for the optimum combination of Guassian bands with the correlation coefficients(r^2) above 0.998. And these five sub-bands on the left are attributed to the reduction of surface adsorbed oxygen and lattice oxygen during the process from Fe^{3+} to Fe^{2+} [28,29]. From Fig.5(B), it can also be found the critic acid sol-gel method might decrease the H_2 reduction temperature of $\text{Fe}_{0.85}\text{Ce}_{0.10}\text{W}_{0.05}\text{O}_z$ on the left compared with the co-precipitation method, which attributed to the reduction of surface adsorbed oxygen during the process from Fe^{3+} to Fe^{2+} . And the XPS results also demonstrated that there existed more reducible Fe^{3+} cation in $\text{Fe}_{0.85}\text{Ce}_{0.10}\text{W}_{0.05}\text{O}_z\text{-HT}$ and $\text{Fe}_{0.85}\text{Ce}_{0.10}\text{W}_{0.05}\text{O}_z\text{-MW}$ than that of $\text{Fe}_{0.85}\text{Ce}_{0.10}\text{W}_{0.05}\text{O}_z\text{-CP}$.

3.4 NH_3 absorption abilities

Fig.6 shows the desorption spectra of NH_3 on $\text{Fe}_{0.85}\text{Ce}_{0.10}\text{W}_{0.05}\text{O}_z\text{-CP}$, $\text{Fe}_{0.85}\text{Ce}_{0.10}\text{W}_{0.05}\text{O}_z\text{-HT}$ and $\text{Fe}_{0.85}\text{Ce}_{0.10}\text{W}_{0.05}\text{O}_z\text{-MW}$ catalysts in the temperature range of $100\sim 500\text{ }^\circ\text{C}$. From Fig.6(A), it can be seen that all the catalyst display a big desorption peak for NH_3 reductive agent in the temperature range, but the intensity of NH_3 desorption for $\text{Fe}_{0.85}\text{Ce}_{0.10}\text{W}_{0.05}\text{O}_z\text{-MW}$ is the worst. This desorption peak of NH_3 could be fitted into five peaks based on the intensity of acid site(As show in Fig.6(B)), and these peaks according to the temperature the NH_3 desorption peak located at are attributed to the weak acid sites(weakly bonded NH_3), the medium acid site and the strong acid sites from the low-temperature to the high-temperature [27], respectively. $\text{Fe}_{0.85}\text{Ce}_{0.10}\text{W}_{0.05}\text{O}_z\text{-CP}$ showed more weak acid sites, medium acid site and strong acid sites than $\text{Fe}_{0.85}\text{Ce}_{0.10}\text{W}_{0.05}\text{O}_z\text{-HT}$ and $\text{Fe}_{0.85}\text{Ce}_{0.10}\text{W}_{0.05}\text{O}_z\text{-MW}$, which are usually thought a key factor in the $\text{NH}_3\text{-SCR}$ reaction. Meanwhile, the NO_x conversions over per gram in unit time for these catalysts decreased as follows: $\text{Fe}_{0.85}\text{Ce}_{0.10}\text{W}_{0.05}\text{O}_z\text{-MW} > \text{Fe}_{0.85}\text{Ce}_{0.10}\text{W}_{0.05}\text{O}_z\text{-CP} > \text{Fe}_{0.85}\text{Ce}_{0.10}\text{W}_{0.05}\text{O}_z\text{-HT}$. Therefore,

the absorption of NH_3 reductive agent on $\text{Fe}_{0.85}\text{Ce}_{0.10}\text{W}_{0.05}\text{O}_z$ might be not a key factor in its NH_3 -SCR reaction.

4. Conclusions

Three methods were used to prepare magnetic iron-cerium-tungsten mixed oxide catalyst. Compared with the conventional co-precipitation method and the traditional citric acid sol-gel method, the citric acid sol-gel assisted by microwave irradiation is a simple, time-saving and economic technology to prepare magnetic iron-cerium-tungsten mixed oxide NH_3 -SCR catalyst. Although the BET surface area, the pore volume and the surface absorbed oxygen concentration of $\text{Fe}_{0.85}\text{Ce}_{0.10}\text{W}_{0.05}\text{O}_z$ -MW is less than $\text{Fe}_{0.85}\text{Ce}_{0.10}\text{W}_{0.05}\text{O}_z$ -CP, it shows the highest NO_x conversion over per gram of catalyst in unit time compared with those over $\text{Fe}_{0.85}\text{Ce}_{0.10}\text{W}_{0.05}\text{O}_z$ -CP and $\text{Fe}_{0.85}\text{Ce}_{0.10}\text{W}_{0.05}\text{O}_z$ -HT catalysts. This is mainly attributed to the formation of $\gamma\text{-Fe}_2\text{O}_3$ crystallite which disperses well in the $\text{Fe}_{0.85}\text{Ce}_{0.10}\text{W}_{0.05}\text{O}_z$ -MW. And compared with the traditional hydrothermal treatment assisted citric acid sol-gel, microwave irradiation used to assist the preparation of $\text{Fe}_{0.85}\text{Ce}_{0.10}\text{W}_{0.05}\text{O}_z$ through the citric acid sol-gel method improved the intensity of $\gamma\text{-Fe}_2\text{O}_3$ crystallite and the surface absorbed oxygen concentration in/on it, and optimized the dispersion of iron/cerium elements on the surface of $\text{Fe}_{0.85}\text{Ce}_{0.10}\text{W}_{0.05}\text{O}_z$ catalyst.

Acknowledgment

This work was supported by the National Science Foundation of China (No. 51406118), Shanghai Basic Research Foundation (Key Program, No. 14JC1404800), Program of Special Appointment (Eastern Scholar) at Shanghai Institutions of Higher Learning (No. QD2015017), Key Laboratory of Flow Control and Simulation (No. D15013).

References

- [1] K. Zhao, W.L. Han, G.X. Lu, J.Y. Lu, Z.C. Tang, X.P. Zhen. Promotion of redox and stability features of doped Ce-W-Ti for NH_3 -SCR reaction over a wide temperature range. *Appl. Surf. Sci.* 379(2016)316-322.
- [2] Q.L. Zhang, L.S. Xu, P. Ning, J.J. Gu, Q.Q. Guan. Surface characterization studies of $\text{CuO-CeO}_2\text{-ZrO}_2$ catalysts for selective catalytic reduction of NO with NH_3 . *Appl. Surf. Sci.* 317(2014)955-961.

- [3] W. Tian, H.S. Yang, X.Y. Fan, X.B. Zhang. Catalytic reduction of NO_x with NH₃ over different-shaped MnO₂ at low temperature. *J. Hazard. Mater.* 188(2011)105-109.
- [4] B.Q. Jiang, Y. Liu, Z.B. Wu. Low-temperature selective catalytic reduction of NO on MnO_x/TiO₂ prepared by different methods. *J. Hazard. Mater.* 162(2009)1249-1254.
- [5] R.T. Guo, Q.S. Wang, W.G. Pan, W.L. Zhen, Q.L. Chen, H.L. Ding, N.Z. Yang, C.Z. Lu. The poisoning effect of Na and K on Mn/TiO₂ catalyst for selective catalytic reduction of NO with NH₃: A comparative study. *Appl. Surf. Sci.* 317(2014)111-116.
- [6] P. Ning, Z.X. Song, H. Li, Q.L. Zhang, X. Liu, J.H. Zhang, X.S. Tang, Z.Z. Huang. Selective catalytic reduction of NO with NH₃ over CeO₂-ZrO₂-WO₃ catalysts prepared by different methods. *Appl. Surf. Sci.* 332(2015)130-137.
- [7] X. Gao, S.J. Liu, Y. Zhang, Z.Y. Luo, K.F. Cen. Physicochemical properties of metal-doped activated carbons and relationship with their performance in the removal of SO₂ and NO. *J. Hazard. Mater.* 188(2011)58-66.
- [8] D.H. Shang, Q. Zhong, W. Cai. High performance of NO oxidation over Ce-Co-Ti catalyst: The interaction between Ce and Co. *Appl. Surf. Sci.* 325(2015)211-216.
- [9] Y.T. Li, Q. Zhong. The characterization and activity of F-doped vanadia/titania for the selective catalytic reduction of NO with NH₃ at low temperatures. *J. Hazard. Mater.* 172(2009)635-640.
- [10] T. Cheng, H. Lin, B. Guan, X.Y. Gong, K. Li, Z. Huang. Promoting the low temperature activity of Ti-V-O catalysts by premixed flame synthesis. *Chem. Eng. J.* 296(2016)45-55.
- [11] Y. Jiang, X. Gao, Y.X. Zhang, W.H. Wu, H. Song, Z.Y. Luo, K.F. Cen. Effects of PbCl₂ on selective catalytic reduction of NO with NH₃ over vanadia-based catalysts. *J. Hazard. Mater.* 274(2014)270-278.
- [12] Z.B. Xiong, Q. Hu, D.Y. Liu, C. Wu, F. Zhou, Y.Z. Wang, J. Jin, C.M. Lu. Influence of partial substitution of iron oxide by titanium oxide on the structure and activity of iron-cerium mixed oxide catalyst for selective catalytic reduction of NO_x with NH₃. *Fuel* 165 (2016)432-439.
- [13] F.D. Liu, H. He, C.B. Zhang, Z.C. Feng, L.R. Zheng, Y.N. Xie, T.D. Hu. Selective catalytic reduction of NO with NH₃ over iron titanate catalyst: Catalytic performance and characterization. *Appl. Catal. B-Environ.* 96(2010)408-420.
- [14] Z.B. Xiong, C. Wu, Q. Hu, Y.Z. Wang, J. Jin, C.M. Lu, D.X. Guo. Promotional effect of microwave hydrothermal treatment on the low-temperature NH₃-SCR activity over iron-based catalyst. *Chem. Eng. J.* 286 (2016)459-466.
- [15] L.L. Zhou, C.T. Li, L.K. Zhao, G.M. Zeng, L. Gao, Y. Wang, M. Yu. The poisoning effect of PbO on Mn-Ce/TiO₂ catalyst for selective catalytic reduction of NO with NH₃ at low temperature. *Appl. Surf. Sci.* 389(2016)532-539.

- [16] T. Zhang, J. Shi, J. Liu, D.X. Wang, Z. Zhao, K. Cheng, J.M. Li. Enhanced hydrothermal stability of Cu-ZSM-5 catalyst via surface modification in the selective catalytic reduction of NO with NH₃. *Appl. Surf. Sci.* 375(2016)186-195.
- [17] F.A. Deorsola, S. Andreoli, M. Armandi, B. Bonelli, R. Pirone. Unsupported nanostructured Mn oxides obtained by Solution Combustion Synthesis: Textural and surface properties, and catalytic performance in NO_x SCR at low temperature. *Appl. Catal. A-Gen.* 522(2016)120-129.
- [18] X. Li, X.S. Li, J.H. Li, J.M. Hao. Identification of the arsenic resistance on MoO₃ doped CeO₂/TiO₂ catalyst for selective catalytic reduction of NO_x with ammonia. *J. Hazard. Mater.* 318(2016)615-622.
- [19] X. Gao, Y. Jiang, Y. Zhong, Z.Y. Luo, K.F. Cen. The activity and characterization of CeO₂-TiO₂ catalysts prepared by the sol-gel method for selective catalytic reduction of NO with NH₃. *J. Hazard. Mater.* 174(2010)734-739.
- [20] B. Yang, Y.S. Shen, Y.W. Zeng, B. Ling, S.B. Shen, S.M. Zhu. Effects of tin doping level on structure, acidity and catalytic performance of Ti-Ce-O-x catalyst for selective catalytic reduction of NO by ammonia. *J. Mol. Catal. A-Chem.* 418(2016)138-145.
- [21] W.W. Yang, F.D. Liu, L.J. Xie, Z.H. Lan, H. He. Effect of V₂O₅ Additive on the SO₂ Resistance of a Fe₂O₃/AC Catalyst for NH₃-SCR of NO_x at Low Temperatures. *Ind. Eng. Chem. Res.* 55(2016)2677-2685.
- [22] S.X. Cai, H. Hu, L.Y. Shi, D.S. Zhang. Design of multi-shell Fe₂O₃@MnO_x@CNTs for the selective catalytic reduction of NO with NH₃: improvement of catalytic activity and SO₂ tolerance. *Nanoscale* 8(2016)35288-3598.
- [23] S.H. Zhan, Q. Shi, Y. Zhang, Y. Li, Y. Tang. Preparation of novel CeMo(x) hollow microspheres for low-temperature SCR removal of NO_x with NH₃. *Rsc Adv.* 6(2016)59185-59194.
- [23] G.H. Yao, F. Wang, X.B. Wang, K.T. Gui. Magnetic field effects on selective catalytic reduction of NO by NH₃ over Fe₂O₃ catalyst in a magnetically fluidized bed. *Energy* 35(2010) 2295-300.
- [24] Z.B. Xiong, C.M. Lu, D.X. Guo, X.L. Zhang, K.H. Han. Selective catalytic reduction of NO_x with NH₃ over iron-cerium mixed oxide catalyst: catalytic performance and characterization. *J. Chem. Technol. Biot.* 88(2013)1258-65.
- [25] H.X. Jiang, L. Zhang, J. Zhao, Y.H. Li, M.H. Zhang. Study on MnO_x-FeO_y composite oxide catalysts prepared by supercritical antisolvent process for low-temperature selective catalytic reduction of NO_x. *J. Mater. Res.* 31(2016)702-712.
- [26] X. Li, J.H. Li, Y. Peng, T. Zhang, S. Liu, J.M. Hao. Selective catalytic reduction of NO with NH₃ over novel iron-tungsten mixed oxide catalyst in a broad temperature range. *Catal. Sci. Technol.* 5(2015)4556-4564.
- [27] R. Foo, T. Vazhnova, D.B. Lukyanov, P. Millington, J. Collier, R. Rajaram, S. Golunski. Formation of reactive Lewis acid sites on Fe/WO₃-ZrO₂ catalysts for higher temperature SCR applications. *Appl. Catal. B-Environ.* 162(2015)174-179.

- [28] S.J. Yang, J.H. Li, C.Z. Wang, J.H. Chen, L. Ma, H.Z. Chang, L. Chen, Y. Peng, N.Q. Yan. Fe-Ti spinel for the selective catalytic reduction of NO with NH₃: Mechanism and structure-activity relationship. *Appl. Catal. B-Environ.* 117-118(2012)73-80.
- [29] S.C. Xiong, Y. Liao, X. Xiao, H. Dang, S.J. Yang. The mechanism of the effect of H₂O on the low temperature selective catalytic reduction of NO with NH₃ over Mn-Fe spinel. *Catal. Sci. Technol.* 5(2015)2132-2140.
- [30] J. Zielinski, L. Zglinicka, L. Znak, Z. Kaszkur. Reduction of Fe₂O₃ with hydrogen. *Appl. Catal. A-Gen.* 381(2010)191-196.
- [31] B. Abasht, A. Beitollahi, S.M. Mirkazemi. Processing, structure and magnetic properties correlation in co-precipitated Ca-ferrite. *J. Magn. Magn. Mater.* 420(2016)263-268.
- [32] K. Cao, X.Q. Shen, J.Y. Shen, M.X. Jing. Preparation of Fine Fibers of the FeNiCo Ternary Alloy by the Organic Gel-Thermal Reduction Process. *Rare Metal Mater. Eng.* 37(2008)56-59.
- [33] W.P. Shan, Y. Geng, X.L. Chen, N. Huang, F.D. Liu, S.J. Yang. A highly efficient CeWO_x catalyst for the selective catalytic reduction of NO_x with NH₃. *Catal. Sci. Technol.* 6(2016)1195-1200.
- [34] Y. Peng, K.Z. Li, J.H. Li. Identification of the active sites on CeO₂-WO₃ catalysts for SCR of NO_x with NH₃: An in situ IR and Raman spectroscopy study. *Appl. Catal. B-Environ.* 140-141(2013)483-492.
- [35] L. Chen, D. Weng, Z.C. Si, X.D. Wu. Synergistic effect between ceria and tungsten oxide on WO₃-CeO₂-TiO₂ catalysts for NH₃-SCR reaction. *Prog. Nat. Sci. Mater. Intern.* 22(2012)265-272.
- [36] C.X. Liu, L. Chen, H.Z. Chang, L. Ma, Y. Peng, H. Arandiyana, J.H. Li. Characterization of CeO₂-WO₃ catalysts prepared by different methods for selective catalytic reduction of NO_x with NH₃. *Catal. Commun.* 40(2013)145-148.
- [37] K.Z. Li, H. Wang, Y.G. Wei, D.X. Yan. Syngas production from methane and air via a redox process using Ce-Fe mixed oxides as oxygen carriers. *Appl. Catal. B-Environ.* 97 (2010)361-372.
- [38] F. He, Y.G. Wei, H.B. Li, H. Wang. Synthesis Gas Generation by Chemical-Looping Reforming using Ce-Based Oxygen Carriers Modified with Fe, Cu, and Mn oxides. *Energy Fuel* 23(2009)2095-2102.
- [39] R.A. Satyanarayana, C.Y. Chen, C.C. Chen, S.H. Chien, C.J. Lin, K.H. Lin, C.L. Chen, S.C. Chang. Synthesis and characterization of Fe/CeO₂ catalysts: Epoxidation of cyclohexene. *J. Mol. Catal. A: Chem.* 318(2010)60-67.
- [40] H. He, H.X. Dai, C.T. Au. Defective structure, oxygen mobility, oxygen storage capacity, and redox properties of RE-based (RE=Ce, Pr) solid solutions. *Catal. Today* 90(2004) 245-254.

Fig.1 The NH_3 -SCR activity of iron-tungsten mixed oxide catalysts prepared through different methods. Reaction conditions: $[\text{NO}] = [\text{NH}_3] = 1000$ ppm, $[\text{O}_2] = 3.0$ vol.% and 2000 ml/min of total flow rate((A) 2 ml of catalyst with gas hourly space velocity(GHSV)=60,000 /h, (B) 0.1 g of catalyst with gas hourly space velocity(GHSV)=1,200,000 ml/(g · h))

Fig.2 XRD spectra of magnetic $\text{Fe}_{0.85}\text{Ce}_{0.10}\text{W}_{0.05}\text{O}_z$ catalysts prepared through Co-precipitation (a), Hydrothermal treatment assistant critic acid sol-gel (b) and Microwave irradiation assistant critic acid sol-gel(c)(▼ $\alpha\text{-Fe}_2\text{O}_3$ (#33-0664), ★ $\gamma\text{-Fe}_2\text{O}_3$ (#39-1346)).

Fig.3 N_2 adsorption-desorption of magnetic $\text{Fe}_{0.85}\text{Ce}_{0.10}\text{W}_{0.05}\text{O}_z$ catalysts prepared through different methods ((A) N_2 adsorption-desorption isotherms, (B) Pore size distributions).

Fig.4 XPS spectra of magnetic $\text{Fe}_{0.85}\text{Ce}_{0.10}\text{W}_{0.05}\text{O}_z$ catalysts prepared through Co-precipitation (a), Hydrothermal treatment assistant critic acid sol-gel (b) and Microwave irradiation assistant critic acid sol-gel(c) ((A) O 1s, (B) Fe 2p, (C) W 4f, (D) Ce 3d)

Fig. 5 H_2 -TPR spectra of magnetic $\text{Fe}_{0.85}\text{Ce}_{0.10}\text{W}_{0.05}\text{O}_z$ catalysts prepared through different methods

Fig.6 NH_3 -TPD spectra of magnetic $\text{Fe}_{0.85}\text{Ce}_{0.10}\text{W}_{0.05}\text{O}_z$ catalysts prepared through different methods

1

2

1

2

1

2

1

2

1

2

1

2

1

2

1

2

1

2

1

2

1

2

1

2

1

2

1 Table1. N₂ adsorption-desorption of magnetic Fe_{0.85}Ce_{0.10}W_{0.05}O_z catalysts prepared through different
2 methods

Sample	S _{BET} ^a (m ² /g)	Pore volume ^b (cm ³ /g)	Pore diameter ^c (nm)	The NO _x conversion over per surface area of catalysts in one hour(mg/(m ² ·h))		
				150 °C	200 °C	250 °C
Fe _{0.85} Ce _{0.10} W _{0.05} O _z -CP	98.44	0.231	6.8	0.14	0.21	0.30
Fe _{0.85} Ce _{0.10} W _{0.05} O _z -HT	52.66	0.076	4.3	0.43	0.97	2.08
Fe _{0.85} Ce _{0.10} W _{0.05} O _z - MW	53.34	0.086	4.5	0.62	2.27	2.87

3 ^a BET surface area, ^b BJH desorption pore volume, ^c BJH desorption pore diameter.

4

1

Table 2 XPS results of $\text{Fe}_{0.85}\text{Ce}_{0.10}\text{W}_{0.05}\text{O}_z$ catalysts prepared through different methods

Samples	Surface atomic concentration(%)					
	Fe	Ce	W	O_α	O_β	O_{total}
$\text{Fe}_{0.85}\text{Ce}_{0.10}\text{W}_{0.05}\text{O}_z\text{-CP}$	16.64	6.85	1.82	41.75	32.93	74.68
$\text{Fe}_{0.85}\text{Ce}_{0.10}\text{W}_{0.05}\text{O}_z\text{-HT}$	20.9	6.66	1.20	34.96	36.28	71.24
$\text{Fe}_{0.85}\text{Ce}_{0.10}\text{W}_{0.05}\text{O}_z\text{-MW}$	18.53	5.96	1.33	36.78	37.4	74.18

2

3