



Preparation and desulfurization activity of nano-CeO₂/γ-Al₂O₃ catalysts

Qi Yang, Hui Hu* , Shan-Shan Wang

Received: 15 July 2015 / Revised: 10 November 2015 / Accepted: 23 May 2016 / Published online: 21 June 2016
© The Nonferrous Metals Society of China and Springer-Verlag Berlin Heidelberg 2016

Abstract γ-Al₂O₃-supported CeO₂ catalysts were prepared by microemulsion and impregnation methods and characterized by X-ray diffraction (XRD) and scanning electron microscope (SEM) techniques. At the same time, the desulfurization activity of catalysts was investigated. The results show that nanoscale active substances and a high desulfurization effect are achieved by microemulsion, exhibiting a significant dominance compared with traditional impregnation method. The optimal preparation condition is temperature of 30 °C and ratio of [H₂O]/[surface active agent] of 7 with slow demulsification. The activated catalysts still keep high and stable desulfurization activity during a wide temperature range of 450–600 °C. Among a series of prepared catalysts, the desulfurization rate of 6CeO₂/γ-Al₂O₃ is the highest, reaching up to 80 % when temperature is higher than 550 °C. The catalytic reduction mechanism of SO₂ over nano-CeO₂/γ-Al₂O₃ follows redox mechanism.

Keywords Nano-CeO₂/γ-Al₂O₃; Microemulsion; Catalyst; Desulfurization

1 Introduction

Nanocatalysts have attracted wide attention because of their characteristics of more surface active site, high stability and large specific surface area. These characteristics exhibit excellent catalytic performance such as high activity and selectivity required in industrial production [1, 2]. The catalysts can be prepared by impregnation [3, 4], chemical deposition [5], sol–gel [6], chemical vapor deposition [7], hydrothermal synthesis [8], microemulsion [9], electrochemical method [10, 11], etc. Among these methods, microemulsion method, i.e., synthesis of particles with high sensitivity, well distributed, and no hard agglomeration [12], is recognized as an important way to prepare nanoparticles. Since Boutonnet [13] firstly synthesized nanometer noble metal, such as platinum, rhodium, palladium and iridium, etc., by microemulsion technique in the end of the 1980s, this technique has attracted a great deal of attention and has been widely used in environmental pollution treatment in recent years.

SO₂ pollution resulted from fire coal and fossil fuel has always been an international hot point [14]. The catalytic reduction dry technology for flue gas desulfurization was paid attention by domestic and international scholars since this technology can reduce SO₂ to elemental sulfur by CO with low investment and no secondary pollution [15, 16]. CeO₂ is a common rare earth metal oxide with special structure and properties [17, 18], exhibiting strong catalytic action in the reduction reaction of SO₂ by CO [19–22]. This oxide is also commonly used as a promoter to improve the catalytic performance of catalysts [23, 24]. Additionally, γ-Al₂O₃ is the most industrially used catalyst support because of its appropriate pore size distribution and large specific surface area. Currently, the research mainly focuses on

Q. Yang, H. Hu*
School of Environment Science and Engineering, Huazhong University of Science and Technology, Wuhan 430074, China
e-mail: hqh08@sina.com

Q. Yang
Department of Urban Construction, Wuchang Shouyi University, Wuhan 430064, China

S.-S. Wang
Wuhan Zuoling New Town Development and Investment Co., Ltd., Wuhan 430000, China

nanopowder catalysts [25–27]. This type of catalyst is not suitable for the treatment of SO₂ in flue gas because the tiny particle can be brought out of the flue system through gas flow before catalytic reaction.

In this study, a series of catalytic CeO₂ nanomaterials (nanocatalysts) supported on globular γ-Al₂O₃ were successfully prepared by microemulsion method and characterized by X-ray diffraction (XRD) and scanning electron microscope (SEM) techniques. Compared with traditional impregnation method, the optimal preparation conditions by microemulsion and the desulfurization activity of catalysts were investigated.

2 Experimental

2.1 Main materials

Ce(NO₃)₃·6H₂O (AR) was purchased from Hunan Rare Earth Metal Material Research Institute, China. Hexadecyltrimethylammonium bromide (CTAB, analytical reagent (AR)) was purchased from Shanghai Bio Science & Technology Co., Ltd, China. Globular γ-Al₂O₃ with size of 3–5 mm was purchased from Jiangsu Sanji Industrial Co., Ltd., China with Brunauer–Emmett–Teller (BET) surface area of $S_{\text{BET}} = 280 \text{ m}^2 \cdot \text{g}^{-1}$.

2.2 Catalyst preparation

2.2.1 Microemulsion

A certain volume of Ce(NO₃)₃·6H₂O (1 mol·L⁻¹, AR) was dropped into a certain proportion of cyclohexane/CTAB/butanol system to form colorless and transparent microemulsion. This microemulsion then gradually became canary yellow after adding NH₃·H₂O (AR) under constant temperature magnetic stirring for 15 min. Next, pretreated γ-Al₂O₃ supports were added into the well-prepared microemulsion under continuous stirring. 3 h later, γ-Al₂O₃-supported CeO₂ was obtained after demulsification for the above mixing solution by acetone (AR) and suction filtration. After being washed repeatedly by anhydrous alcohol and distilled water, dried at 70 °C for 24 h and calcinated at 500 °C for 4 h, the pale yellow product was obtained.

2.2.2 Impregnation

According to the different loads of CeO₂/γ-Al₂O₃ catalyst, the corresponding stoichiometric ratio of Ce(NO₃)₃·6H₂O was dissolved in distilled water. Thereafter, pretreated γ-Al₂O₃ supports were added into the above solution for impregnation at 25 °C for 24 h and 70 °C for 7 days.

Finally, the products were dried in an oven at 100 °C and calcinated in muffle furnace by temperature programming.

2.3 Catalyst characterization

XRD patterns were obtained by X'Pert Pro X diffractometer (PANalytical B.V. Co.) operated with Cu Kα radiation (40 mA and 40 kV) over 2θ range of 8°–90° with step size of 0.2 (°)·s⁻¹. SEM images were recorded using Quanta 200 electron microscope (FEI Co., Holland) with an accelerating voltage of 200 kV.

2.4 Catalyst activity evaluation

In the catalytic reduction reaction of SO₂ by CO (CO + SO₂ $\xrightarrow{\text{catalyst}}$ CO₂ + S), catalyst activity of CeO₂/γ-Al₂O₃ catalysts with different loads was investigated. The reaction device mainly consisted of temperature control system, fixed bed reactor, gas concentration detection system and mixed gas chamber. The temperature was controlled by thermocouple in the tubular furnace, the reactor was made of quartz material with height of 80 cm and diameter of 2.5 cm, and the analysis of the ingoing and outgoing stream was performed using non-dispersive infrared analyzer (SHIMADZU Co., Japan) with SOA-7000 for SO₂ detection and CGT-7000 for CO₂ and CO detection.

Before the experiment, nitrogen should be purged into the whole gas circuit for 30 min, and then reacted gases (10 vol% SO₂ + 25 vol% CO + 65 vol% N₂) with a flow rate at 1 L·min⁻¹ were passed in the reaction device. All the runs were performed using 15 g catalyst. The conversion (*X*) of SO₂ (*X* can also denote desulfurization efficiency of catalysts) was calculated by the following equation:

$$X(\text{SO}_2) = \left(\frac{[\text{SO}_2]_{\text{in}} - [\text{SO}_2]_{\text{out}}}{[\text{SO}_2]_{\text{in}}} \right) \times 100 \% \quad (1)$$

where [SO₂]_{in} is the inlet SO₂ concentration and [SO₂]_{out} is the outlet SO₂ concentration.

3 Results and discussion

3.1 Preparation condition of catalyst by microemulsion

3.1.1 Effect of reaction temperature

According to the method listed in Sect. 2.2.2, CeO₂ particles were prepared without adding γ-Al₂O₃ and acetone. Figure 1 shows SEM images of CeO₂ prepared at different reaction temperatures. CeO₂ particles prepared at 30 °C are tiny and well distributed (Fig. 1a). This is mainly because the growth and nucleation rate of nanoparticles are affected

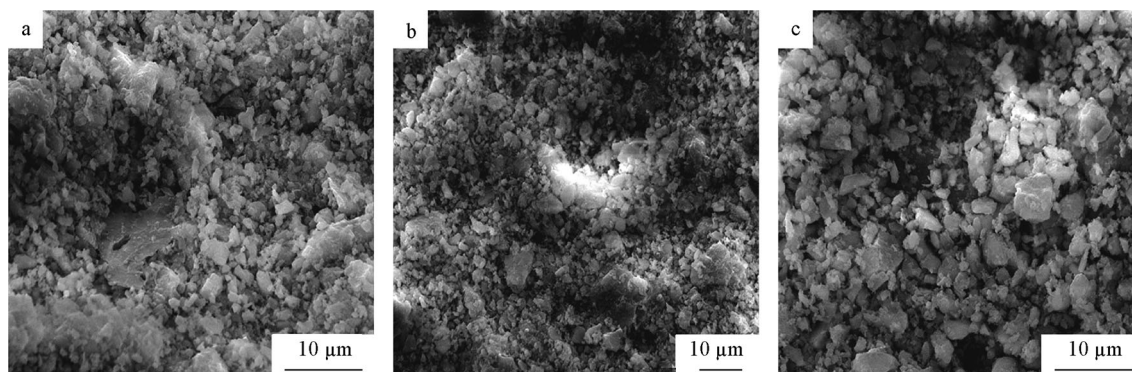


Fig. 1 SEM images of CeO₂ prepared at different temperatures: **a** 20 °C, **b** 30 °C, and **c** 40 °C

by reaction temperature [28]. On the one hand, movement of surface active agent and its encapsulated water droplets aggravate with temperature increasing. This not only destroys microemulsion structure but also leads to the increase in particle size and distribution [28]. On the other hand, the number of reactive crystal nucleus and velocity of molecular motion improve with temperature increasing. This causes the decrease in particle size because the nucleation rate is faster than the growth rate. Under a comprehensive consideration, the optimum synthetic temperature is 30 °C.

3.1.2 Effect of W value

W value is expressed as the ratio of [H₂O]/[surface active agent]. The particle size of CeO₂/γ-Al₂O₃ and radius of water droplets can be affected by W value. Figure 2 displays SEM

images of CeO₂/γ-Al₂O₃ under different W values. When W value is 3.5 or 7.0, the particle is fine with the average diameter of less than 100 nm. And the particle distribution shown in Fig. 2b ($W = 7.0$) is better than that in Fig. 2a ($W = 3.5$). Particle diameter increases when W value is 10.5 (Fig. 2c). As W value increases to 14.0, radius of water droplets increases and can be easily ruptured. This will result in uneven distribution as well as agglomeration phenomenon of particles (Fig. 2d). Therefore, the optimum W value for synthesis of CeO₂/γ-Al₂O₃ particle is 7.0.

3.1.3 Effect of demulsification method

The way of adding acetone (demulsifying agent) can affect the agglomeration degree of CeO₂/γ-Al₂O₃ particles. Figure 3 reveals SEM image of CeO₂/γ-Al₂O₃ prepared by different demulsification methods. The methods can be

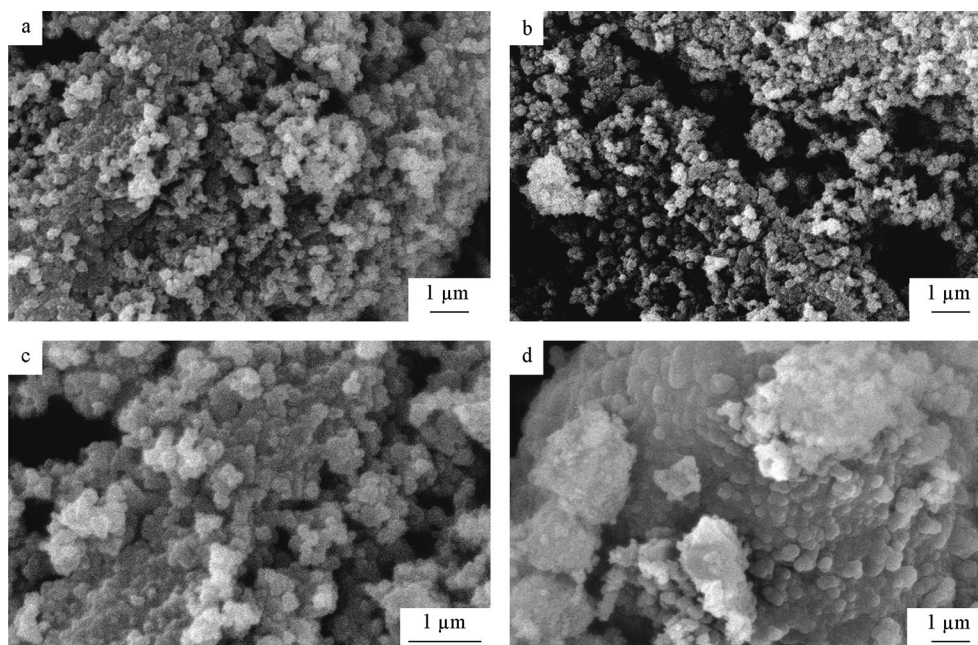


Fig. 2 SEM images of CeO₂/γ-Al₂O₃ prepared at different W values: **a** $W = 3.5$, **b** $W = 7.0$, **c** $W = 10.5$, and **d** $W = 14.0$

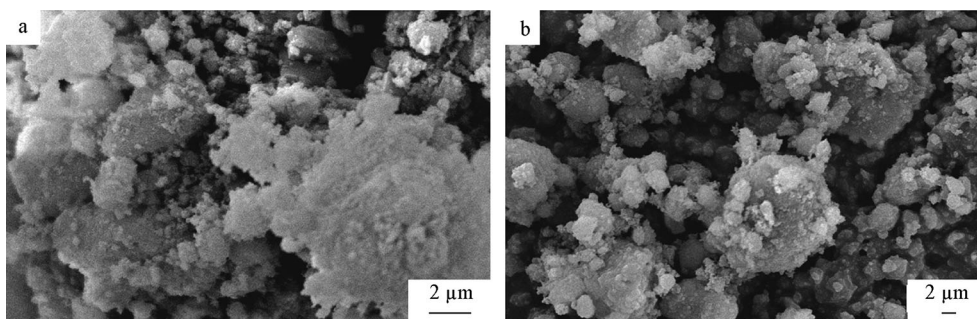


Fig. 3 SEM images of CeO₂/γ-Al₂O₃ prepared by different demulsification methods: **a** rapid demulsification and **b** slow demulsification

classified into two types: adding acetone slowly by burette (demulsification slowly, Fig. 3b) and adding acetone for only once (demulsification rapidly, as shown in Fig. 3a). Particles prepared by the former are better dispersed and less agglomerated than the ones by the latter. The main reason is that by the latter way, CeO₂ particle can detach from the encapsulation of CTAB rapidly and then agglomerate together before being absorbed onto γ-Al₂O₃. Thus, the optimum demulsification method is adding acetone slowly.

3.2 Catalyst characterizations

Based on the analysis of Sect. 3.1, the optimal condition for synthesizing CeO₂/γ-Al₂O₃ catalyst by microemulsion is temperature of 30 °C, *W* value of 7.0, and slow demulsification. A series of nano-CeO₂/γ-Al₂O₃ catalysts prepared under this optimal conditions were named as 2CeO₂/γ-Al₂O₃, 4CeO₂/γ-Al₂O₃, 6CeO₂/γ-Al₂O₃, 8CeO₂/γ-Al₂O₃, and 10CeO₂/γ-Al₂O₃ (the numbers before CeO₂ denote the mass ratios in the nanoparticles).

3.2.1 XRD

XRD patterns of nano-CeO₂/γ-Al₂O₃ catalysts are portrayed in Fig. 4. The catalysts with different proportions of CeO₂ exhibit similar XRD patterns. In addition, the crystal peaks in Fig. 4 match with (111), (200), (220), and (311) crystal planes of CeO₂ (JCPDS No. 03-065-5923) besides the characteristic peak of Al₂O₃ (JCPDS No. 00-004-0880). The results suggest that CeO₂ crystal phase is contained in the prepared catalysts.

The grain size was calculated by Debye–Scherrer formula:

$$D = K\lambda/\beta\cos\theta \quad (2)$$

where *D* is grain size, *K* is shape factor, λ is wavelength, β is full width at half maximum (FWHM), and θ is diffraction angle. The results are summarized in Table 1,

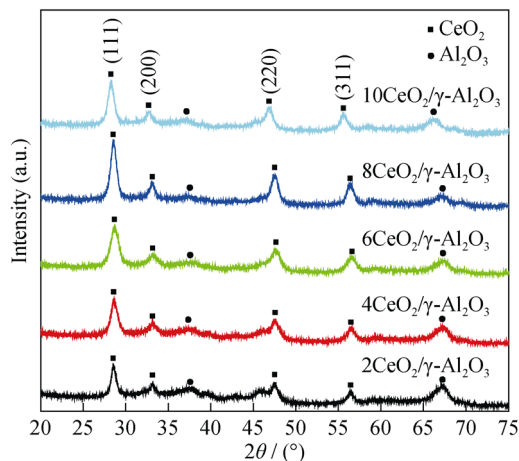


Fig. 4 XRD patterns of different catalysts

Table 1 Calculated results of grain size

Catalyst	<i>K</i>	λ /nm	β^a /rad	θ (°)	<i>D</i> /nm
2CeO ₂ /γ-Al ₂ O ₃	0.89	0.154	0.0052525	14.2684	26.9
4CeO ₂ /γ-Al ₂ O ₃	0.89	0.154	0.0064700	14.2669	21.9
6CeO ₂ /γ-Al ₂ O ₃	0.89	0.154	0.0064196	14.2737	22.0
8CeO ₂ /γ-Al ₂ O ₃	0.89	0.154	0.0020427	14.2382	69.2
10CeO ₂ /γ-Al ₂ O ₃	0.89	0.154	0.0070031	14.2812	20.2

^a (111) crystal plane

indicating that the catalysts prepared by microemulsion can be controlled in nanosize.

3.2.2 SEM

SEM images of 2CeO₂/γ-Al₂O₃ catalysts prepared by impregnation and microemulsion are presented in Fig. 5. According to Fig. 5a, particles prepared by traditional impregnation method exhibit uneven distribution and serious agglomeration which can easily plug the pore of support. This significantly affects the performance of CeO₂/γ-Al₂O₃ catalyst. Compared with those by impregnation method, the CeO₂/γ-Al₂O₃ particles synthesized by

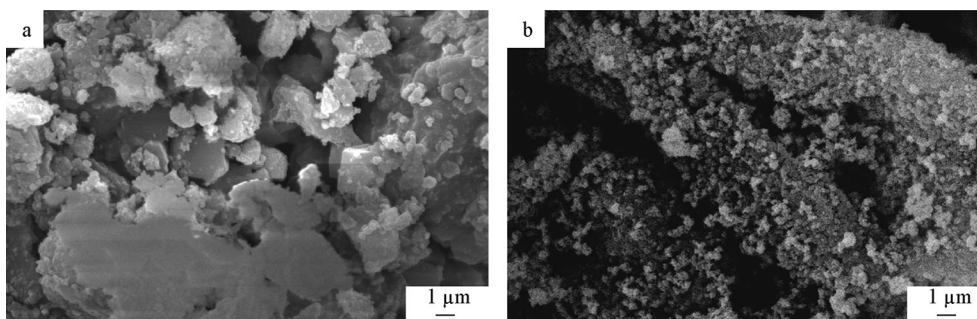


Fig. 5 SEM images of $2\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$ catalysts prepared by different methods: **a** impregnation and **b** microemulsion

microemulsion under the optimum condition are well distributed with less agglomeration (Fig. 5b). Additionally, the average diameter of particles occurred in Fig. 5a is obviously larger than that in Fig. 5b. The former cannot reach nanoscale, and the latter is less than 100 nm. The above difference reveals that the diameter of active substances can be effectively controlled by microemulsion method.

3.3 Catalyst desulfurization activity

3.3.1 Activation temperature

To determine the optimum activation temperature, reaction temperature was controlled at 350, 450, 550, and 600 °C by gradually temperature-programmed of tubular furnace. Figure 6 shows desulfurization activation curves of $2\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$. This can be divided into four stages. (1) When temperature is below 400 °C, SO_2 concentration decreases rapidly because of the early absorption of catalyst. CO_2 has not been detected in the outlet. (2) Low concentration CO_2 can be detected in the outlet as the temperature is enhanced to 450 °C. At the same time, SO_2 concentration begins to increase due to desorption on the catalyst. (3) SO_2 concentration decreases continually as a result of chemical adsorption effect of catalyst when temperature increases from 450 to 500 °C. (4) When temperature is up to 600 °C, elemental sulfur generates and adheres to the tube wall. Moreover, conversion rate of SO_2 is steadily maintained around 68 %. This suggests that catalytic reaction has been entered into the activation stage (this stage denotes that active materials on $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$ react with CO and SO_2). Therefore, the optimum activation temperature is 600 °C.

3.3.2 Average desulfurization rate

After nano- $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$ was activated at 600 °C for 2 h, operation of decreasing temperature to room temperature and then increasing temperature again were implemented. From the two stages of decreasing and increasing

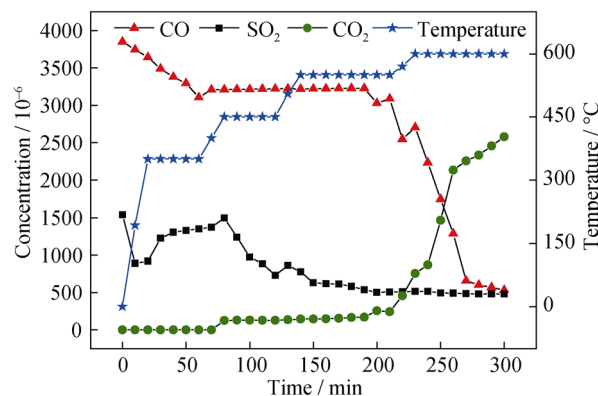


Fig. 6 Desulfurization activation curves of $2\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$

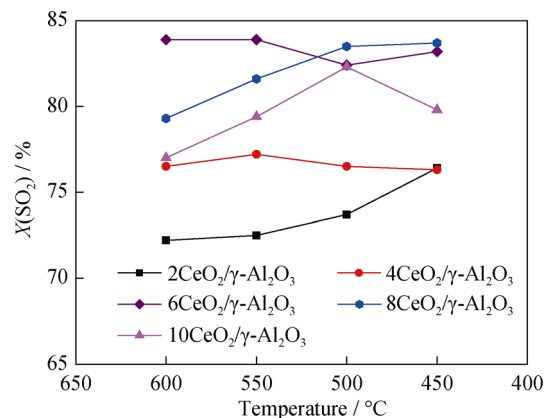


Fig. 7 Conversion of SO_2 with temperature decreasing

temperature, catalytic reduction action of nano- $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$ on SO_2 was researched.

Figure 7 displays the conversion (X) of SO_2 with temperature decreasing. Desulfurization rates of the activated $2\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$, $4\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$, $6\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$, $8\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$, and $10\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$ catalysts do not decrease rapidly with temperature decreasing, and basically keep in the range of $\pm 4\%$, indicating that the activity of prepared catalysts maintains stable in a certain temperature range.

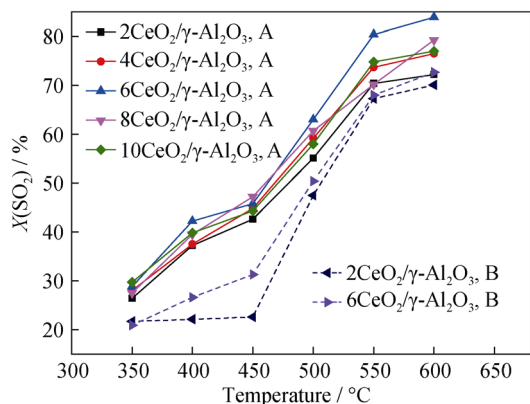


Fig. 8 Conversion of SO₂ with temperature increasing by microemulsion method (A) and impregnation method (B)

The conversion (X) of SO₂ with temperature increasing is shown in Fig. 8. Firstly, catalytic reduction action of 6CeO₂/γ-Al₂O₃ catalyst prepared by microemulsion on SO₂ is the best. The conversion rate can reach up to 80 % when temperature is higher than 550 °C. Moreover, in the load range from 2 % to 6 %, desulfurization efficiency of catalysts prepared by microemulsion improves with the increase in load amount at corresponding temperature. However, while the load amount increases to 8 %, desulfurization efficiency decreases because the increase in active materials amount on the catalyst causes the uneven distribution as well as agglomeration phenomenon of active constituents.

Secondly, at the same temperature, desulfurization efficiency of catalysts with the same load prepared by microemulsion is obviously higher than that by the traditional impregnation method. This further demonstrates the effect of the microemulsion method.

3.3.3 Mechanism analysis

There are generally two kinds of mechanism models, i.e., (1) redox mechanism [29]: reduction of SO₂ by CO to elemental sulfur and CO₂ can be completed over oxygen vacancies on the surface of catalyst, which is promoted by oxygen transfer; (2) intermediate product mechanism [30]: metal active substance of catalyst can be activated to metal sulfides (active phase) and then react with CO to form COS with better reducibility, which finally reduces SO₂ to elemental sulfur.

Figure 9 shows XRD patterns of 6CeO₂/γ-Al₂O₃ prepared by microemulsion. By comparing the wave peaks of 6CeO₂/γ-Al₂O₃ before and after desulfurization reaction in Fig. 9, it can be seen that only CeO₂ instead of sulfide is observed before and after reaction. Furthermore, abundant lattice oxygen is considered to be contained in the structure of CeO₂ [29]. Therefore, catalytic reduction mechanism of

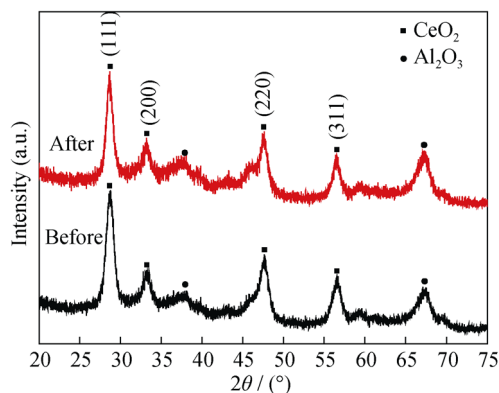


Fig. 9 XRD patterns of 6CeO₂/γ-Al₂O₃ before desulfurization reaction and after desulfurization reaction

SO₂ over nano-CeO₂/γ-Al₂O₃ follows redox mechanism. These reactions are inferred as follows:



where * and ** are active adsorption sites of CO and SO₂ in CeO₂, respectively, O is lattice oxygen, and \Box is vacancy of lattice oxygen.

4 Conclusion

A series of γ-Al₂O₃-supported CeO₂ nanocatalysts were successfully prepared by microemulsion method, employed for the removal of SO₂ and exhibiting high activity in the reaction compared with traditional impregnation method. The desulfurization rate of these nanocatalysts maintains stable with the temperature decreasing from 600 to 450 °C. Moreover, with the temperature increasing from 350 to 600 °C, the desulfurization rate of 6CeO₂/γ-Al₂O₃ catalyst is the best, reaching up to 80 % when temperature is higher than 550 °C. The catalytic reduction mechanism of SO₂ over nano-CeO₂/γ-Al₂O₃ follows redox mechanism. From the facts mentioned above, these nano-CeO₂/γ-Al₂O₃ catalysts prepared by microemulsion method may find potential applications in the catalytic reduction of SO₂.

Acknowledgments This study was financially supported by the Natural Science Foundation of Hubei Province, China (No. 2009CDB246) and the Applied Basic Research Project of Wuhan City (No. 2015060101010068).

References

- [1] Sudarsanam P, Malleshram B, Reddy PS, Großmann D, Grünert W, Reddy BM. Nano-Au/CeO₂ catalysts for CO oxidation: Influence of dopants (Fe, La and Zr) on the physicochemical properties and catalytic activity. *Appl Catal B Environ.* 2014; 144(1):900.
- [2] Monjezi BH, Yazdani ME, Mokfi M, Ghiaci M. Liquid phase oxidation of diphenylmethane to benzophenone with molecular oxygen over nano-sized Co-Mn catalyst supported on calcined cow bone. *J Mol Catal A Chem.* 2014;383–384(3):58.
- [3] Wang P, Tang XL, Yi HH, Li K, Wang JG, Xiang Y, Xu XM. Preparation of core-shell structure catalysts and catalytic property for catalytic oxidation of NO at low temperatures. *J Cent South Univ T (Nat Sci).* 2014;45(1):328.
- [4] Liu LC, Zi XH, Dai HX, Zhao Z, Wang XP, He H. Preparation and characterization of Rh-Au/ γ -Al₂O₃ three-way nanocatalysts. *Chin J Catal.* 2010;31(7):781.
- [5] Lee DS, Chen YW. Nano Ag/TiO₂ catalyst prepared by chemical deposition and its photocatalytic activity. *J Taiwan Inst Chem E.* 2014;45(2):705.
- [6] Rakmak N, Wiyaratn W, Bunyakan C, Chungsiriporn J. Synthesis of Fe/MgO nano-crystal catalysis by sol-gel method for hydrogen sulfide removal. *Chem Eng J.* 2010;162(1):84.
- [7] Mohamed MS, Mohamed NM. Stack growth of aligned multi-walled carbon nanotubes using floating catalyst chemical vapor deposition technique. *Chem Phys Lett.* 2015;625(4):53.
- [8] Yang GK, Ding KQ. Preparation of Pt-Pd/MWCNTs and Pd/MWCNTs catalysts by hydrothermal synthesis in room temperature ionic liquids. *Chem J Chinese U.* 2010;31(5):994.
- [9] Tavasoli A, Taghavi S. Performance enhancement of bimetallic Co-Ru/CNTs nano catalysts using micro-emulsion technique. *J Energy Chem.* 2013;22(5):747.
- [10] Lu JL, Wang L, Li JD, Wang YY, Li SL, Cui XQ. Pd-Au nano-catalysts synthesized by electrodeposition and its catalytic performance for methanol. *Chin J Rare Met.* 2015;39(6):493.
- [11] Yousefi T, Torab-Mostaedi M, Ghasemi M, Ghadirifar A. Synthesis of Gd₂O₃ nanoparticles: using bulk Gd₂O₃ powders as precursor. *Rare Met.* 2015;34(8):540.
- [12] Zolfaghari Z, Tavasoli A, Tabyar S, Pour AN. Enhancement of bimetallic Fe-Mn/CNTs nano catalyst activity and product selectivity using microemulsion technique. *J Energy Chem.* 2014;23(1):57.
- [13] Boutonnet M, Kizling J, Stenius P, Maire G. The preparation of monodisperse colloidal metal particles from microemulsions. *Colloids Surf.* 1982;5(3):209.
- [14] Zhang GJ, Du YN, Zhang YF, Xu Y. Desulfurization reaction model and experimental analysis of high sulfur coal under hydrogen atmosphere. *J Ind Eng Chem.* 2014;20(2):487.
- [15] Han GB, Park NK, Lee TJ. Effect of O₂ on SO₂ reduction with CO or H₂ over SnO₂-ZrO₂ catalyst. *Ind Eng Chem Res.* 2009; 48(23):10307.
- [16] Hu H, Wang SX, Zhang XL, Zhao QZ, Li J. Study on simultaneous catalytic reduction of sulfur dioxide and nitric oxide on rare earth mixed compounds. *J Rare Earth.* 2006;24(6):695.
- [17] Nemade KR, Waghuley SA. Synthesis of CeO₂ nanoparticles using flame-assisted spray pyrolysis and solid state diffusion routes. *Rare Met.* 2015;34(1):6.
- [18] Chen J, Meng DQ, Zhang GK, Li SQ, Chen QY. Thickness and optical properties of nanocrystalline CeO₂ thin film. *Chin J Rare Met.* 2014;38(1):28.
- [19] Hu H, Wang SX, Zhao QZ, Zhang XL, He ZH, Li J. The function of γ -Al₂O₃ in catalytic reduction of SO₂ to elemental sulfur over CeO₂-La₂O₃ catalysts. *Ind Catal.* 2006;14(9):59.
- [20] Hu H, Li SL, Zhang SX, Li J. Studies on reaction mechanism of SO₂ reduction catalyzed by CeO₂-La₂O₃/ γ -Al₂O₃. *Chin J Catal.* 2004;25(2):115.
- [21] Zhou JH, He ZH, Yu FS, Li J, Hu H, Zhao QZ, Wang SX. La₂O₃-CeO₂/ γ -Al₂O₃ catalysts for CO reduction of SO₂ in the presence of oxygen. *Environ Pollut Control.* 2007;29(2):99.
- [22] Zhang JL, Hu H, Wang WC, Wu GM, Wang ZP, Zeng ZW. Catalytic desulfurization and denitration over activated alumina with different sizes supported CeO₂-Fe₂O₃. *Environ Eng.* 2014; 32(10):94.
- [23] Sang XL, Li KZ, Wang H, Wei YG. Selective oxidation of methane and carbon deposition over Fe₂O₃/Ce_{1-x}Zr_xO₂ oxides. *Rare Met.* 2014;33(2):230.
- [24] Yu CL, Hu JB, Yang K, Liu XY, Fan QZ. Preparation of Ni/M_xO_y/CeO₂-ZrO₂ (M = Cu, Ba, Al) composite catalysts and their catalytic performance in methane partial oxidation. *Chin J Rare Met.* 2014;38(1):60.
- [25] Wu X, Tayal J, Basu S, Scott K. Nano-crystalline Ru_xSn_{1-x}O₂ powder catalysts for oxygen evolution reaction in proton exchange membrane water electrolyzers. *Int J Hydrogen Energy.* 2011;36(22):14796.
- [26] Mosaddegh E. Ultrasonic-assisted preparation of nano eggshell powder: a novel catalyst in green and high efficient synthesis of 2-aminochromenes. *Ultrason Sonochem.* 2013;20(6):1436.
- [27] Machocki A, Denis A, Grzegorzczak W, Gac W. Nano- and micro-powder of zirconia and ceria-supported cobalt catalysts for the steam reforming of bio-ethanol. *Appl Surf Sci.* 2010; 256(7):5551.
- [28] Capek I. Preparation of metal nanoparticles in water-in-oil(w/o) microemulsions. *Adv Colloid Interface Sci.* 2004;110(4):49.
- [29] Liu W, Saromfim AF, Stephanopoulos MF. Reduction of sulfur dioxide by carbon monoxide to elemental sulfur over composite oxide catalysts. *Appl Catal B.* 1994;4(2–3):167.
- [30] Lau NT, Fang M, Chan CK. The role of SO₂ in the reduction of NO by CO on La₂O₂S. *J Catal.* 2007;245(2):301.