Fuel 219 (2018) 248–258

Contents lists available at ScienceDirect

Fuel

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

Full Length Article

Influence of calcination temperature on $Fe_{0.8}Mg_{0.2}O_z$ catalyst for selective catalytic reduction of NO_x with NH_3

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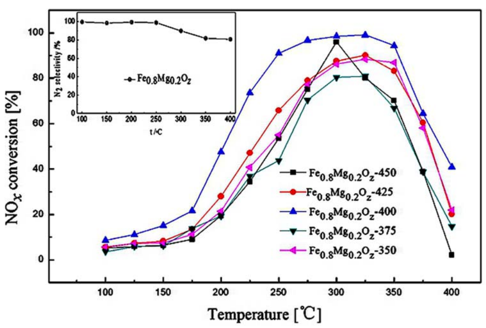
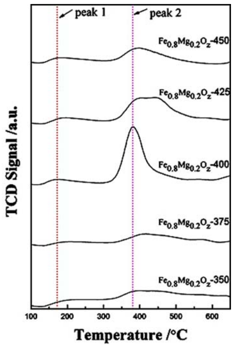
GRAPHICAL ABSTRACT

$Fe_{0.8}Mg_{0.2}O_z$ catalyst calcined at 400 °C showed the best catalytic performance and excellent N_2 selectivity. More than 90% NO_x conversion could be achieved in a wide temperature range of 250–350 °C. Calcination temperature significantly affected the total amount of the surface acidity. The surface acidity (mainly Brönsted acid sites in $Fe_{0.8}Mg_{0.2}O_z$-400 catalyst) played an important role in SCR reaction.





ARTICLE INFO

Keywords:
Selective catalytic reduction (SCR)
Catalyst
Calcination temperature
NO_x conversion

ABSTRACT

A series of $Fe_{0.8}Mg_{0.2}O_z$ catalysts for selective catalytic reduction (SCR) of NO*x* with NH_3 were prepared via co-precipitation method with microwave thermal assistant at different calcination temperature. The influence of calcination temperature on the catalytic performance, microstructure properties, surface elements and acidity over $Fe_{0.8}Mg_{0.2}O_z$-T catalysts was investigated by various characterization methods. $Fe_{0.8}Mg_{0.2}O_z$ catalyst calcined at 400 °C showed the highest NO_x conversion and excellent N_2 selectivity. More than 90% NO_x conversion could be achieved in a wide temperature range of 250–350 °C. $Fe_{0.8}Mg_{0.2}O_z$-400 with large surface area and pore volume obtained a high purity γ-Fe_2O_3 crystalline phase with the calcination temperature of 400 °C. Meanwhile, Magnesium had strong interaction with γ-Fe_2O_3 and existed in either highly dispersed or amorphous phase. Surface oxygen concentration and acidity (mainly Brönsted acid sites in $Fe_{0.8}Mg_{0.2}O_z$-T catalysts) played an important role in SCR reaction. The results implied that the higher surface area, pore volume, strong interaction, superior surface acidity and redox ability contributed to the excellent SCR catalytic performance of $Fe_{0.8}Mg_{0.2}O_z$ catalyst calcined at 400 °C.

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https://doi.org/10.1016/j.fuel.2018.01.083
Received 14 August 2017; Received in revised form 20 January 2018; Accepted 22 January 2018

1. Introduction

Nitrogen oxides (NO_x, mainly NO and NO_2) are one of the most primary pollutants that have caused nitric acid rain, photochemical smog, ozonosphere hole, etc., and seriously impact on human health [1,2]. The removal of NO_x has become an important environmental issue due to the severe air pollution and the more and more rigorous emission standards. NO_x are mainly from the emission of fossil-fuel power station and automotive exhaust [3,4]. NH_3-SCR [5] has been proved to be the most efficient mature technology with acceptable cost [6] reliably applied in coal-power station to limit the emission of NO_x [7]. The selection of catalyst is vital for the operation of denitrification system. Although vanadium-titanium catalysts [8–11] with a temperature window of 300–400 °C [12] have been widely used as the common commercial catalysts in eliminating NO_x, several inevitable disadvantages such as the toxicity of vanadium pentoxide, the low selectivity at high temperature and the high conversion of SO_2 to SO_3 with increasing vanadium loadings have restricted the further application of these catalysts [13,14]. Nowadays, the increasingly stringent regulations of NO_x emission and vanadium-titanium as hazardous waste make iron-based catalysts comprehensively concerned by the researchers. It is of great significance to study on iron-based catalysts with advantages such as low manufacturing cost, wide material sources, favorable SCR activity and N_2 selectivity, etc. [15–17]. Recently, it is reported that iron-based catalysts, such as Ce-Fe/WMH [18], Mn-Fe/TiO_2 [19], WO_3/Fe_2O_3 [20], Fe/WO_3-ZrO_2 [21], Fe-Ti [22,23], Fe/TiO_2 [24], Fe/Ce-Ti [25,26], Fe-Ce-W [27,28], etc., show excellent SCR activity and N_2 selectivity. In these researches, γ-Fe_2O_3 exhibited potential low-temperature de-NO_x SCR performance [29]. Maghemite (γ-Fe_2O_3) widely used for the production of catalysts [30] is reported to be in a metastable state with a lower activation energy than α-Fe_2O_3, which makes the Lewis acid sites on the surface easily react with H atoms in NH_3. Casanova [31] found that SCR activity correlated directly with the Fe loading of the catalyst at medium and low temperature. Cao [32] reported that the increase of surface area and pore volume of the catalyst due to the addition of Fe and strengthening of the Brönsted and Lewis acid sites were responsible for the increase of SCR activity. Specifically, the presence of Fe could significantly improve the SO_2 resistance of the sorbent [33]. Schill [34] found that the presence of Fe in V/TiO_2 catalyst could increase the surface area and surface acid sites. Liu [35] studied on Co-Ce-Ti catalyst with the excellent low-temperature activity and broadened temperature window, which could be attributed to the improvement of the physic-chemical properties and acceleration of the reactions in L-H and E-R mechanisms. The characterization results by Zhu [36] manifested that Co-Fe/TiO_2 owned more adsorption capacity of the reactants and Cu-Fe/TiO_2 had better redox ability. Further researches proved that the calcination temperature had an important influence on the valence state of species, as well as the dispersion extent of active phase and the crystal phase structure of support [37]. The appropriate calcination temperature was important for the DeNO_x activity of the catalysts [38]. The SCR activities in different temperature range over various catalysts were influenced by the calcination temperature in varying degree. CeO_2-ZrO_2-WO_3 [39] catalyst calcinated at 600 °C showed the best NO_x conversion and excellent N_2 selectivity with a wide temperature window from 250 to 500 °C. Nearly 100% NO conversion of Sm-Mn-0.1 catalyst was obtained at 65–200 °C after calcinating at 450 °C [40]. Generally speaking, agglomeration caused by high calcination temperature would lead to the decrease in activity of the catalysts. Obvious decreases were observed for CeO_2-ZrO_2-WO_3 catalyst [39] calcinated above 600 °C and Sm-Mn-0.1 catalyst [40] calcinated at 450 °C. $CeMoO_x$ catalyst calcinated at 600 °C and 700 °C led to drops of NO_x conversion [41]. But not all the activities were decreased with increasing calcination temperature. For example, high DeNO_x activity to N_2 of Ag(2) catalyst was attained with a high calcination temperature [42]. Recently, research showed that $Fe_{0.8}Mg_{0.2}O_z$ catalyst exhibited potential in converting NO_x to N_2 with NH_3, but there are few researches about the influence of calcination temperature on $Fe_{0.8}Mg_{0.2}O_z$ catalyst [43]. Therefore, the objective of this paper is to investigate the SCR activities of $Fe_{0.8}Mg_{0.2}O_z$ catalysts calcinated at different temperatures and reveal the effect of calcination temperature on the physical and chemical properties of the catalysts such as crystalline phase, BET surface area, pore diameter distribution, micro-morphology, chemical states of the elements and surface acidity etc. by XRD, N_2-adsorption–desorption, SEM, EDS, XPS and NH_3-TPD.

2. Experimental

2.1. Preparation of catalyst

The iron-magnesium mixed oxide catalysts were prepared via the co-precipitation method with microwave thermal treatment. $FeSO_4·7H_2O$ and $Mg(NO_3)_2·6H_2O$ (analytically pure, provided by Tianjin Kermel Chemical Reagent Co., Ltd) were used as the precursors. 2 mol/L $NH_3·H_2O$ solution was used as a precipitator. A certain amount of $FeSO_4·7H_2O$ and $Mg(NO_3)_2·6H_2O$ were dissolved in deionized water and stirred for 1 h at room temperature to get a fully dissolved solution. The solution was slowly titrated into $NH_3·H_2O$ solution under stirring until pH of the synthesis solution became 9–10. The precipitate was filtered and washed by deionized water until pH of filter liquor was about 7 to remove foreign ions. Then the solid product was impregnated with 1 mol/L Na_2CO_3 solution and disposed by microwave thermal treatment. The intermediate was washed by deionized water and then dried at 105 °C, which was followed by calcination at 350–450 °C for 5 h in air atmosphere. The samples were crushed and sieved into 40–60 mesh (0.28–0.45 mm) for test. The catalysts prepared were denoted as $Fe_{0.8}Mg_{0.2}O_z$-T, where 0.2 was the molar ratio of Mg/(Mg + Fe) in the catalysts, and T was the calcination temperature, which equaled to 350, 375, 400, 425, 450 °C, respectively.

2.2. Catalytic activity test

The catalytic performances of $Fe_{0.8}Mg_{0.2}O_z$-T catalysts for selective catalytic reduction with ammonia were investigated in a quartz fixed-bed reactor at ambient pressure. 4 mL catalyst (about 2.5 g) was used and the reactant gas was simulated as 0.1 vol.% NO, 0.1 vol.% NH_3, 3.5 vol.% O_2 and balanced N_2. The total gas flow rate was 2 L/min and the gas hourly space velocity (GHSV) was about 30,000 h^{-1}. The concentrations of NO and NO_2 in the inlet and outlet were analyzed by MGA5 Flue Gas Analyzer (York Instrument, MRU, Germany), and the concentration of N_2O and NH_3 was monitored by Finland FTIR flue gas analyzer GASMET DX400. To avoid the impact of ammonia on the analyzer, phosphoric acid solution was installed before the analyzer to absorb the ammonia. Data were collected from 100 °C to 400 °C with an increment of 25 °C. NO_x conversion and N_2 selectivity were calculated according to Eqs. (1) and (2) respectively.

$$\eta = \frac{C(NO_x)_{in} - C(NO_x)_{out}}{C(NO_x)_{in}} \times 100\% \qquad (1)$$

$$S_{N_2} = \frac{C(NO_x)_{in} + C(NH_3)_{in} - 2C(N_2O)_{out}}{C(NO_x)_{in} + C(NH_3)_{in}} \times 100\% \qquad (2)$$

where $C(NO_x)_{in}$ and $C(NO_x)_{out}$ were denoted as the concentrations of NO_x in the inlet and outlet of the reactor, while $C(NH_3)_{in}$ and $C(N_2O)_{out}$ meant the concentrations of NH_3 in the inlet and N_2O in the outlet, μL/L. NO_x represented the sum of NO and NO_2.

2.3. Catalyst characterization

The X-ray Diffraction was performed on a Rigaku D/max 2500 PC diffractometer with Cu Kα radiation, 50 kV × 150 mA. The data of the 2θ from 10° to 90° were collected at 4 °/min with the step size 0.1°. N_2-