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Rare earth salt of 12-tungstophosphoric acid supported on iron oxide as a catalyst for selective catalytic reduction of NO_x

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ABSTRACT

A series of rare earth Keggin-type tungstophosphorate doped iron oxide catalysts were prepared by physical mixing method. The effects of type and the content of rare earth element over NH_3-SCR activity were investigated and the catalysts were characterized by FT-IR, XRD, SEM, EDS, XPS, BET, TGA, ICP-AES, H_2-TPR and NH_3-TPD. It is indicated that the addition of rare earth Keggin-type tungstophosphorate could increase the NH_3-SCR activity of the iron oxide catalysts, while the effect of rare earth species on SCR activity over Fe_yO_x is not obvious. Effects of O_2 concentration, SO_2 and SO_2 + H_2O on NH_3-SCR activity over NdPW/$Fe_yO_{x(25)}$ and the control experiments were also investigated, the results of which illustrates that O_2 exerts a significant promotion effect on the SCR reaction and the impact of SO_2 (470 ppm) on catalytic activity is almost negligible. NdPW/$Fe_yO_{x(25)}$ presents appealing properties of hydrothermal stability and SO_2-tolerance, and exhibits a great potential in practical applications.

1. Introduction

It has been well recognized that nitrogen oxides (NO_x) emitted from mobile and stationary sources remain a major source of air pollution, such as photochemical smog, ozone depletion and acid rain [1, 2], which could make a great threat to human health. Nowadays, selective catalytic reduction (SCR) of NO with NH_3 has been widely utilized as an efficient and economic technique for abatement of NO_x. It is observed from the previous studies that numerous catalysts have shown high activity in NH_3-SCR system, most of which mainly fasten on transition metal oxides [3–12], and metal exchanged zeolites [13–21]. And the commercial catalyst commonly used is V_2O_5/TiO_2 promoted by WO_3 and/or MoO_3, exhibiting a good catalytic activity, however, it still has some practical problems, such as the toxicity of vanadium pentoxide and the high reaction temperature [22–24], which restricted its further application. Hence, the environment-friendly properties and the excellent catalytic performance of SCR catalysts have become the focus of research.

A number of researchers have paid great attentions to Fe-based catalysts, including Fe_yO_x [3–8], Fe/ZSM-5 [13–17], Fe/BEA [19, 20], Fe/SBA-15 [21], iron titanate [25, 26], Fe^{3+}-exchanged TiO_2-pillared clay [27–29], Fe_2O_3-WO_3/ZrO_2 [30], Fe_2O_3/TiO_2 [31–33] and Fe-Mn [5, 34–39]. Recently, WO_3 was used to modify Fe_2O_3 catalyst, which exhibited high NH_3-SCR activity in a wide range of temperature, a great resistance to H_2O and SO_2 and a well thermal stability [3, 30]. Li et al. [10] also combined the tungsten species and iron species, he firstly synthesized the novel FeW catalyst with a high NO conversion and good H_2O/SO_2 durability. Vanadium is another kind of species usually used in deNO_x process. He et al. [4] prepared iron vanadate ($FeVO_4$), and showed high activity and N_2 selectivity as an NH_3-SCR catalyst for the first time. Besides, Mn species is also commonly used to modify Fe-based catalysts, He et al. [25] investigated the catalytic activity of Mn substituted iron titanate catalyst over NH_3-SCR reaction, Fehrmann et al. [36] prepared Mn/TiO_2 and Mn-Fe/TiO_2 catalysts showing superior low-temperature SCR activity, and Lin et al. [35] indicated that the addition of hexadecyl trimethyl ammonium bromide (CTAB) to FeMnTiO_x could not only increase the Lewis acid sites but also extended the active phase. In addition, Fe exchanged zeolites have attracted many researchers, Tronconi et al. [15] investigated the effect of phase separation in Fe-ZSM-5 + BaO/Al_2O_3 system and showed the relevance of gas-phase intermediates over zeolites. Shwan et al. [19] reported a kinetic model which could predicted well over deactivation of Fe-BEA catalyst. The previous work has proved that Fe-based catalysts was widely used and had high activity in NH_3-SCR reaction with a great poisoning resistance over NO_x conversion.

In 1994, Yang et al. [40] firstly used the $H_3PW_{12}O_{40}$ to decompose the nitric oxide, and from then on, heteropoly compounds (HPCs) have been widely utilized as NO_x absorbent and catalyst in NO_x selective

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catalytic reduction due to its special structure, strong BrØnsted acid, outstanding redox nature and pseudo liquid phase behavior. Belanger et al. [41] found that the ammonium 12-tungstophosphate ($(NH_4)_3PW_{12}O_{40}$) of microspores structure was able to reduce NO_2 to N_2 at low temperature. Vaezzadeh et al. [42] investigated the NO_x sorption and reduction capacities of 12-tungstophosphoric hexahydrate ($H_3PW_{12}O_{40}·6H_2O$) and found the NO_x sorption was large in lean exhaust-gas mixture. And now the most studies of HPCs are on Keggin-type acid (HPW) [43–51], Wu et al. [46] utilized 12-tungstophosphoric acid ($H_3PW_{12}O_{40}$) to modify the CeO_2 catalyst and found the $H_3PW_{12}O_{40}$ could significantly enhance the catalytic activity of SCR reaction. The previous study has shown the introduction of rare earth elements as cations counter into HPCs would significantly influence its catalytic activity and its thermal stability. Now, many researchers have focused on the rare earth salts of heteropoly acid, and most of which are widely used in oil product desulfurization, catalyzing biodiesel, catalyzing the oxidation of alcohol and etc. [52–54]. Yet, rare studies have applied the rare earth salts of heteropoly acid as NH_3-SCR catalyst.

In this work, iron oxide was used as catalytic active component, and it also played a role of the carrier with supported rare earth salts of 12-tungstophosphoric acid (LnPW; Ln = Nd,Gd,Eu) acting as the accelerant. Iron oxide was prepared by precipitation method, and then LnPW/Fe_yO_x was synthesized by physical mixing method and characterized by Fourier transform infrared spectroscopy (FT-IR), powder X-ray diffraction (XRD), scanning electron microscope (SEM), energy dispersive spectroscopy (EDS), the X-ray photoelectron spectroscopy (XPS) analysis, specific surface areas (BET), thermo gravimetric analysis, (TGA), inductively coupled plasma element analysis (ICP-OES), temperature programmed reduction of hydrogen (H_2-TPR) and temperature programmed desorption of ammonia (NH_3-TPD). In addition, the effects of LnPW species and NdPW doping amounts on NH_3-SCR activity over Fe_yO_x, and the impacts resulted from variation of O_2 concentration, introduction of SO_2 and $H_2O + SO_2$ over the optimal catalyst were also investigated.

2. Materials and method

2.1. Materials

All reagents and solvents were available commercially and used without further purification. $Nd(NO_3)_3·6H_2O$, $Eu(NO_3)_3·6H_2O$ and $Gd(NO_3)_3·6H_2O$, all A.R. Grade, were purchased from Baotou rare-earth institute. $H_3PW_{12}O_{40}·xH_2O$ (HPW) and $Fe(NO_3)_3·9H_2O$, all A.R. Grade, were consumed from the Kermel Reagent Co. Ltd. $NH_3·H_2O$ (A.R Grade) was supplied by Laiyang Kangde Chemical Co. Ltd. Ethanol (A.R Grade) was produced by Tianjin Fuyu Fine Chemical Co. Ltd.

2.2. Catalyst preparation

2.2.1. Preparation of 12-tungstophosphoric acid (LnPW)

LnPW was synthesized by a recrystallization method according to the following procedure [55, 56]: 8.964 g of HPW (3 mmol) was dissolved in 30 mL 1:1 ethanol solution in a beaker, then lanthanide nitrate crystallization hydrate (3.3 mmol) was added into it successively under vigorous magnetic stirring at 75 °C. The resultant mixture was kept stirring for about 45 min with atmospheric distillation until the volume of mixture was reduced to 1/4 of original. After the mixture was naturally cooled to room temperature, filtration was conducted, then used small amount of deionized water to wet the crystals and collected the products by suction filtration over three times to wash them. Subsequently, the precipitate was dried at 120 °C for 12 h and then calcined at 300 °C for 3 h. After that, the final product was obtained and denoted as $LnPW_{12}O_{40}$ (LnPW).

2.2.2. Preparation of iron oxide (Fe_yO_x)

Iron oxide (Fe_yO_x) was prepared by precipitation approach [57]. First, $Fe(NO_3)_3·9H_2O$ was dissolved in deionized water to get a solution in which the concentration of Fe^{3+} was 0.2 mol/L, and then the pH of the solution was adjusted to 8.5–9.5 using dilute aqueous ammonia with vigorous stirring. The formed slurry was filtered and washed several times to remove anion impurities. After that, the obtained precipitate was dried at 105 °C for 12 h and then calcined at 400 °C for 5 h in a muffle furnace. The final product was respectively marked as Fe_yO_x.

The LnPW/Fe_yO_x was synthesized by physical mixing method and the mixture obtained was labeled as LnPW/$Fe_yO_{x(m)}$, where m refers to the mass fraction of LnPW. The sample was crushed and sieved to 40–60 mesh to test.

2.3. Catalyst characterization

Fourier transform infrared (FT-IR) spectra were recorded on a 5DXC IR spectrometer instrument with the wave number region between 4000 and 400 cm^{-1} at a 2 cm^{-1} resolution, and samples were diluted into KBr and pressed into the form of pellet.

Powder X-ray diffraction (XRD) measurements were performed using a Bruker D8 Advanced in the range of $2θ = 5$ and 50^o at a scanning rate of 2^o per minute, and a position-sensitive detector with a nickel filter was used.

The morphology of the catalysts was observed by scanning electron microscope (SEM) (SU 8010), and energy dispersive spectroscopy (EDS) was carried out in the same facility.

The Thermo Fisher Scientific ESCALAB 250 spectrometer was used for the analysis of X-ray photoelectron spectroscopy (XPS), and correction of binding energy shift was conducted regarding C 1s line at 284.6 eV from adventitious hydrocarbon contamination as an internal criterion. Then, the spectra of the Fe 2p and O 1 s were recorded.

Surface areas analysis (BET) was conducted on Micromeritics Tri StarII 3020 Surface Area and Porosity Analyzer (77 K, N_2 as the adsorbent). Prior to N_2 physisorption, the catalysts were degassed at 150 °C for 2 h. The specific surface areas were calculated with the multipoint Brunauer-Emmett-Teller (BET) approach.

The Inductively Coupled Plasma element analysis (ICP-AES) was conducted on IRIS INTREPID II XSP to analyze the ratio of Ln to $PW_{12}O_{40}$.

Temperature programmed reduction of hydrogen (H_2-TPR) using 100 mg of each samples was performed to investigate their redox characteristic. The catalysts were heated to 450 °C with a ramp rate of 10 °C/min. After cooling to the ambient temperature, the samples were heated up to 800 °C with a ramp rate of 8 °C with a flow of H_2.

Temperature programmed desorption of ammonia (NH_3-TPD) using 100 mg of each samples was carried out to investigate their NH_3 adsorption ability. The samples were heated to 450 °C with a ramp rate of 10 °C/min under N_2 (50 mL/min) to remove the adsorbed species. After cooling to the ambient temperature, the catalysts were exposed to a flow of NH_3 (500 ppm, 50 mL/min) for 1 h, then the physically absorbed NH_3 was removed by N_2 purging for 0.5 h, subsequently, the temperature was raised to 500 °C at a ramp rate of 8 °C/min with a flow of He. The H_2-TPR and NH_3-TPD results were recorded using an on-line gas chromatograph with a thermal conductivity detector (TCD).

2.4. SCR activity

Catalytic measurements for the SCR of NO_x were carried out in a continuous stream fixed-bed reactor, consisting a quartz glass tube with the inner diameter of 8 mm placed in the center of a tubular furnace. The reaction temperature was regulated by a microcomputer controller which was accurate and reliable. The catalyst (0.5 g; particle size, 180–250 μm) corresponding to bulk volume of 0.4 cm^3 was fixed between two layers of inert quartz wool. The typical reaction conditions were adopted as follows: 1050 ppm NO_x ($NO + NO_2$), 1150 ppm NH_3, 6% O_2 and balance N_2. The total flow rate was controlled at 100 mL/