



DRIFT studies on promotion mechanism of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ in selective catalytic reduction of NO with NH_3



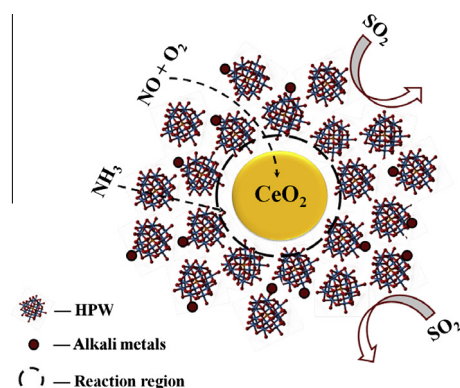
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GRAPHICAL ABSTRACT

The CeO_2 @HPW catalyst to relieve SO_2 and alkali metal poisonings.



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ABSTRACT

Heteropoly acids (HPAs) have been effectively utilized in selective catalytic reduction (SCR) of NO to improve the NH_3 absorption capacity and alkaline/alkali metal resistance for SCR catalysts. However, despite the promise on super-acidities, their other properties that would work on SCR process are still lack of exploration. In this study, a 12-tungstaphosphoric acid ($\text{H}_3\text{PW}_{12}\text{O}_{40}$, HPW) was selected to modify a well-reported CeO_2 catalyst. The resulted CeO_2 /HPW catalyst was subsequently utilized for SCR of NO with excess NH_3 , which revealed a significantly promoted performance in SCR reaction. DRIFT analyses showed that the unique NO_2 absorption capacity of HPW could prevent the NO_2 being further oxidized into nitrate species and the abundant Brønsted acid sites could effectively retain the NH_3 , avoiding them being over-oxidized at evaluated temperatures. The presence of NO_2 was demonstrated able to induce a so called “fast SCR” reaction over the CeO_2 /HPW catalyst, which effectively facilitated the SCR reaction. Furthermore, we have also constructed a CeO_2 @HPW catalyst, which showed an enhanced SO_2 poisoning resistance in SCR reaction.

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Abbreviations: SCR, selective catalytic reduction; HPW, 12-tungstaphosphoric acid, $\text{H}_3\text{PW}_{12}\text{O}_{40}$; CeO_2 /HPW, catalyst prepared via dry-mixing CeO_2 and $\text{H}_3\text{PW}_{12}\text{O}_{40}$ powders; CeO_2 @HPW, CeO_2 catalyst being “core-shell” protected by HPW; HPAs, heteropoly acids.

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1. Introduction

Selective catalytic reduction (SCR) of NO_x from coal-fired flue gas represents one of major applications of heterogeneous catalysts today. The SCR process is designed to selectively convert NO_x emission into relatively harmless products of N_2 and H_2O under a range of operation temperatures. Commercialized SCR catalysts (e.g. $\text{WO}_3\text{-V}_2\text{O}_5/\text{TiO}_2$ and $\text{MoO}_3\text{-V}_2\text{O}_5/\text{TiO}_2$) are designed to be operated under a comparably high operation temperatures (normally at 300–420 °C) [1], which leads them have to be located upstream of SO_2 and particulate control devices, hence susceptible to deactivation under high sulfur and dust conditions. Accordingly, there are great demands in current science on developments of more active SCR catalysts that could be placed downstream of the flue gas to avoid the SO_2 and dust poisonings.

Toward the developments of highly active SCR catalysts, numerous studies have been conducted in the past 10 years [2]. For example, Zhang et al. have reported a 5 wt% Cu-ZSM-5 catalyst, which showed more than 80% NO conversion in the temperature range of 198–470 °C [3]; Shan et al. have developed a Ce-W-Ti catalyst, which effectively performed 100% NO removal efficiency in the temperature range of 200–450 °C [4]. In fact, current works have effectively overcome the activity obstacle for SCR catalysts where numerous materials had been demonstrated able to fulfill the required SCR activity under less than 300 °C operation temperature [5]. However, the resistances of these materials against H_2O , SO_2 and alkali/alkaline metals are still not satisfied, which significantly hinders their industrial applications. In literature [6], an effective way to relieve SO_2 and alkali/alkaline metals poisonings is to utilize the supports that possess high-acidic or super-acidic properties. These supports could strongly interact with alkali/alkaline poisons or isolate the SO_2 absorption, hence preventing the active sites of SCR catalysts.

Heteropoly acids (HPAs) are well-known with their unique structure and extraordinarily strong acidity [7], which have been utilized as effective additive for SCR catalysts to improve their NH_3 absorption capacity and potassium metal resistances [7,8]. However, current works only focused on exploring the strong acidities of HPAs, which did not reveal any insights into their other properties, such as pseudo-liquid characteristic [9] and NO_x absorption capacity [10]. In fact, Yang and Chen [11] have reported that the small polar molecules (e.g. pyridine, alcohols, NO, NH_3 , etc.) can access into the body of HPAs. This would lead to that their reaction could occur not only over the HPAs surface but also inside the body. The absorptions of these polar molecules are mainly occurred via the replacement of structural H_2O present between the Keggin units of HPAs [12]. Belanger and Moffat [13] have further shown that the HPAs can effectively absorb NO and NO_2 at the flue gas temperatures [7], where the absorbed quantities of NO_2 followed the order of $\text{H}_3\text{PW}_{12}\text{O}_{40} > \text{H}_4\text{SiW}_{12}\text{O}_{40} > \text{H}_3\text{PMo}_{12}\text{O}_{40}$ within the temperature range of 150–300 °C. As such, despite the obvious promise of the strong acidities of HPAs, there are still other underlying properties need be extensively explored. These properties might be beneficial to SCR process, which would hence effectively promoted the performance of SCR catalysts.

In this research, a 12-tungstaphosphoric acid ($\text{H}_3\text{PW}_{12}\text{O}_{40}$, hereafter referred as HPW) was selected for studying its underlying properties. The material was physically mixed with a well-reported CeO_2 catalyst for SCR of NO with excess NH_3 . A series of *in situ* DRIFT analyses were conducted to evaluate how the extraordinary properties of HPW affect the CeO_2 performance and SCR reaction pathway. Furthermore, since the SO_2 was reported not able to substitute H_2O linkages in the secondary structure of HPW as NO did [11], it was speculated that the HPW might be capable to act as a protected shell for CeO_2 catalyst to relieve the

SO_2 poisoning, where additional works were hence conducted with an aim to validate this assumption.

2. Materials and methods

CeO_2 particles were prepared via a calcination of cerium nitrate hexahydrate at 450 °C for 2 h in static air. 12-Tungstaphosphoric acids (HPW) were provided from Aladdin Industrial Corporation, which was utilized as obtained. CeO_2/HPW catalyst was prepared by simply dry-mixing the CeO_2 and HPW powders in a ball miller (XQM-2, Nanjing Ke Xi Experimental Instrument Institute) with the rotation speed at 180 r/min for 10 h. The weight ratio of CeO_2 and HPW was set at 1:2. Afterwards, the resulted solids were crushed and sieved to 40–60 meshes. The core-shelled $\text{CeO}_2@/\text{HPW}$ catalyst was prepared via a two-step process. Firstly, a CeO_2 sol was fabricated by mixing the CeO_2 particles with a certain of concentrated HNO_3 and H_2O_2 . The mixture was then stirred until it turned to gel. Afterwards, NH_3 was added to adjust the pH of gel to 1–2, which was subsequently mixed with DBS. Secondly, the HPW solution was added into the gel and the resulted mixture was slowly dried at 70 °C with continuously stirring, followed by a calcination at 350 °C for 2 h in static air.

BET surface areas (BET) were determined using N_2 physisorption at 77 K with a Micromeritics ASSP 2020 equipment. Sample degassing pre-treatment was conducted at 80 °C for 2 h under vacuum.

NH_3 -SCR was carried out in a fixed-bed reactor with 2.3 mL of catalyst (40–60 mesh). The experiments were performed under an atmospheric pressure at 140–300 °C. A water bubbler was utilized to provide ca. 5 vol% H_2O for the reactions. The gas mixture consisted of 600 ppm NO, 600 ppm NH_3 , 3 vol% O_2 , 5 vol% H_2O (with or without according to the case) and a N_2 balance. The total gas hourly space velocity (GHSV) was at ca. 40,000 h^{-1} . The concentration of NO, NO_2 and O_2 were monitored by a flue gas analyzer (Testo 335, Testo Inc., USA). The concentration of N_2O was detected by a FT-IR gas analyzer (Madur Photon Portable IR Gas Analyzers, Madur Ltd., Austria). NO conversion was calculated according to the following equation:

$$\text{NO conversion\%} = ([\text{NO}]_{\text{in}} - [\text{NO}]_{\text{out}}) / [\text{NO}]_{\text{in}} \times 100\%$$

where the subscripts in and out indicated the inlet and outlet concentration of NO at steady state, respectively.

FT-IR spectra were acquired using an *in situ* DRIFT cell equipped with a gas flow system. The DRIFT measurements were performed with ZnSe windows coupled to Nicolet 6700 FTIR spectrometers at 4 cm^{-1} resolution with 64 co-added scans. In the DRIFT cell, catalysts were pretreated at 350 °C in a He environment for 2 h, and then cooled to required temperature in a flow of He. The background spectrum was recorded with flowing He and was subtracted from the catalyst spectrum.

3. Results and discussion

3.1. NH_3 -SCR measurements

The catalytic performances of CeO_2 and CeO_2/HPW catalysts at elevated temperatures are shown in Fig. 1. It can be seen that the CeO_2/HPW catalyst revealed a much higher SCR activity than the CeO_2 catalyst. With the assistance of HPW, the NO conversion over the CeO_2/HPW catalyst had reached ca. 90% at the temperature of 220 °C and showed no signs of decline until 300 °C. No obvious N_2O production was detected over the catalyst, revealing a satisfied N_2 selectivity for the catalyst. In contrast, the CeO_2 catalyst yielded only about 40% NO conversion within the investigated temperature

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