Removal of NO_x by Adsorption/Decomposition on H₃PW₁₂O₄₀·6H₂O Supported on Ceria

Hongjian Zhu, Shumei Song, Rui Wang*

School of Environmental Science and Engineering, Shandong University, Qingdao, 266237, China

ABSTRACT

We synthesized catalysts composed of CeO₂ and varying percentages of HPW and assessed their capacity to adsorb and decompose NO_x using XRD, FTIR spectroscopy, and BET analysis. The denitrification performance of the catalysts was evaluated by investigating the dynamic NO_x adsorption as well as other relevant factors. The IR spectra of the HPW revealed that the adsorbed NO_x entered the bulk phase of the HPW and replaced the crystallization water, combining with its protons to form NOH⁺. The HPW/CeO₂ composites displayed a maximum NO_x adsorption rate (85.6 mg-NO₂ g-HPW⁻¹) that far exceeded that of HPW alone (50.5 mg-NO₂ g-HPW⁻¹). GC-MS confirmed that temperature programming reduced the adsorbed NO_x to N₂.

Keywords: Polyoxometalates; NO_x; Adsorption and decomposition; H₃PW₁₂O₄₀·6H₂O/CeO₂.

INTRODUCTION

Nitrous oxides NO_x (NO + NO₂) abatement from stationary power sources and mobile sources has attracted great attention in recent years due to the caused environmental problems (acid rain, photochemical smog, and ozone layer depletion) and harm for human health (Huang *et al.*, 2019; Wang *et al.*, 2019; Shan *et al.*, 2020). To solve this serious environmental problem, many well-developed technologies have been employed for NO_x removal. Among these technologies, although selective catalytic reduction of NO_x with ammonia (NH₃-SCR) has been considered to be one of the most efficient techniques to resolve the NO_x issue (Imanaka and Masui, 2012), it has the disadvantages of high cost of NH₃ and secondary pollution caused by NH₃ leakage. The direct decomposition of NO_x is regarded as the most ideal and environmentally friendly technology for the removal of NO_x, in which NO_x can be direct decomposed into harmless N₂ and O₂ without reductant (Konsolakis *et al.*, 2015; Sun *et al.*, 2018). In general, the level of NO_x adsorption performance determines the alternative strategy for eliminating NO_x. Many different types of catalytic decomposition materials have been employed for NO_x removal (Sun *et al.*, 2018).

Polyoxometalates (POMs) have been extensively studied due to their excellent properties (pseudo-liquid phase, strong Brønsted acidity, and remarkable redox properties)

(Ren *et al.*, 2017a, b). As a new type of green environmental protection material, POMs has been used in a variety of catalytic fields (Wang and Yang, 2015; Wei *et al.*, 2018; Liu and Wang, 2019). Especially, the Keggin-type heteropolyacid (HPA) show attractive NO_x adsorption behavior (Heylen *et al.*, 2010). Yang and Chen reported that NO_x adsorbed on phosphotungstic acid (H₃PW₁₂O₄₀·6H₂O; HPW) was stimulated in the form of protonated NO (NOH⁺), which weakened the N-O band. The break of N-O generated in the rapid heating process, thus resulting in the yield of N₂ (Chen and Yang, 1995, Yang and Chen, 2004). Moffat *et al.* (1995) have further claimed that the adsorbed quantities of NO₂ followed the order of H₃PW₁₂O₄₀ > H₄SiW₁₂O₄₀ > H₃PMo₁₂O₄₀. However, pure HPA has a small specific surface area, low mechanical strength and is easily soluble in polar molecules. The high heating rate may easily cause the oven temperature to exceed the target temperature, leading to inactivation of HPA with inferior thermal stability, which makes it difficult to reuse in practical applications (Ma *et al.*, 2012; Zhang *et al.*, 2013). In order to increase the adsorption capacity, catalytic decomposition activity and catalyst stability, many heteropolyacid-based adsorbent materials have been developed. Zhang and Wang (2013) designed a new HPW-USY catalyst with a three-dimensional bottle-in-boat structure, which has high thermal stability and good NO_x decomposition performance. HPW/CNTs catalysts were prepared and the results show that the yield of N₂ by microwave heating is higher than that of rapid heating by resistance furnace (Zhang *et al.*, 2012). In representative lean-gas mixture conditions, the performance of NO_x storage and reduction over H₃PW₁₂O₄₀·6H₂O loaded on Ti-Zr and Ce-Zr were studied, which possess high nitrogen selectivity

* Corresponding author.

Tel.: +86-53-258630178

E-mail address: wangrui@sdu.cn

(Gómez-García *et al.*, 2005a, b). Ceria (CeO_2) as a catalyst promoter and catalyst has attracted considerable attention in the three-way catalyst (TWC) system owing to its excellent oxygen storage capacity (OSC), redox properties and ability to serve as a good support (Katta *et al.*, 2010; Zhu *et al.*, 2017). HPW-supported CeO_2 composites have been reported as the SCR catalysts (Song *et al.*, 2017; Weng *et al.*, 2016; Geng *et al.*, 2018), and the composites exhibit synergistic interaction due to their improved specific surface area and exposure of more acidic sites. As is well known, there are few reports on HPW-supported CeO_2 materials for adsorption and decomposition of NO_x . Detailed investigation of the key factors in the experimental process and reaction mechanisms are still need further research.

In this work, to improve the thermal stability and specific surface area of HPW, and to avoid inactivation of HPW due to exceeding the target temperature at high heating rate, a series of heteropolyacid-based adsorbent materials supported by CeO_2 were synthesized and used for vigorous removal of NO_x . The synthesized HPW/ CeO_2 were characterized by powder X-ray diffraction (XRD), Fourier-transform infrared (FTIR) spectroscopy and Brunauer-Emmett-Teller (BET) analysis. The denitrification performance of HPW/ CeO_2 was determined by the dynamic NO_x adsorption study, along with various relevant factors.

SYNTHESIS OF HPW-LOADED MATERIALS

The Transition Metal Doped Ceria-based Solid Solutions

CeO_2 support was prepared by precipitation method. $\text{NH}_3\cdot\text{H}_2\text{O}$ solution were added dropwise to the solution containing $\text{Ce}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ with continuous stirring until $\text{pH} = 10$. The precipitate was then filtered and washed three times with sufficient deionized water and absolute ethanol. The CeO_2 support was obtained after drying at 100°C for 12 h and calcination at 750°C for 4 h.

The HPW-doped CeO_2 supports was prepared by impregnation method. A certain mass ratio of the supports was immersed in a quantitative HPW solution for 24 h, and then dried in a 60°C water bath for 1 h to obtain the samples. The samples are denoted as $x\%\text{HPW}/\text{CeO}_2$ (x is the mass ratio of HPW/ CeO_2).

Catalyst Characterization

FTIR spectroscopy was performed on a Nicolet Avatar 370 and the spectral was recorded in the range of $400\text{--}4000\text{ cm}^{-1}$ with a 4 cm^{-1} resolution. The XRD patterns were recorded with a Rigaku D/MAX-RA powder X-ray diffractometer, using $\text{Cu K}\alpha$ monochromatized radiation at a scan speed of 5° min^{-1} . BET surface areas of the catalysts were measured by N_2 adsorption using a Micromeritics ASAP 2010 apparatus.

Activity Tests

Standard Test Procedure: Adsorption Stage

The test was conducted in a fixed-bed quartz tube reactor of 8 mm internal diameter. The amount of catalyst used is 0.2 g. The sample was first placed in the middle of the reactor between two quartz wool plugs and pretreated in a highly purified N_2 stream at 150°C for 1 h. During NO_x

adsorption, the feed gas containing NO , O_2 , H_2O and balance N_2 was passed through the bench blending reactor and partially converted to NO_2 ($2\text{NO} + \text{O}_2 = 2\text{NO}_2$), obtaining a mixture of NO and NO_2 . TH-990S NO and NO_2 analyzers were used to continually record the concentration of NO and NO_2 in the outlet.

The NO_x adsorption amount is calculated by integrating the curve below the baseline (1000 ppm) and expressed in $\text{mg-NO}_2\text{ g-HPW}^{-1}$. The calculation formula is shown below:

$$M = \frac{\int_0^t C dt}{m} \quad (1)$$

where m : mass of adsorbent (g), Q : total gas flow ($\text{m}^3\text{ min}^{-1}$), C : NO_x removal concentration (mg m^{-3}), t : adsorption time (min).

Decomposition Stage

After NO_x adsorption saturation, the reactor containing catalyst was purge with He flow (5 mL min^{-1}) for 1 h. Then reactor placed in an oven was rapid heated from 30°C to 450°C at a heating rate of $150^\circ\text{C min}^{-1}$. The decomposition product was detected by GC-MS analyzer.

NO conversion was then calculated by: $\text{N}_2\text{ yield} = 2\text{N}_2\text{ formation}/\text{NO}_x\text{ adsorbed}$, where $\text{NO}_x\text{ adsorbed}$ represents the NO_x adsorbed amount of HPW and $\text{N}_2\text{ formation}$ represents the generated N_2 amount during NO_x decomposition.

RESULTS AND DISCUSSION

Characterizations

Figs. 1 and 2 are XRD and FTIR spectra of HPW and HPW/ CeO_2 with different loadings, respectively. It could be seen that XRD patterns of CeO_2 correspond to that of a mixture of cubic fluorite structure (PDF: 43-1022). The crystalline-phase HPW diffraction peak appears when the HPW loading is 40%. With the increase of the HPW loading, the diffraction peaks attributed to the HPW crystal phase and its peaks intensity gradually increases. It can be seen from Fig. 2, pure CeO_2 has only a strong peak assigned to symmetrical stretching mode of Ce-O at about 450 cm^{-1} . For HPW, several distinct characteristic peaks can be observed. According to the previous studies (Yang *et al.*, 2005; Cheng and Wang, 2013), the peaks at 1083 and 988 cm^{-1} can be ascribed to the stretching vibration of P-O_a and W-O_d , and the stretching of $\text{W-O}_c\text{-W}$ between edge-sharing octahedra and vibration of $\text{W-O}_b\text{-W}$ between vertex-sharing W_3O_{13} octahedra appeared approximately at about 802 and 891 cm^{-1} , respectively, which is an accepted way to identify Keggin structure of HPA. In addition, the band at 1640 cm^{-1} are characteristic peak of lattice water in HPA. When the HPW loading is 70%, the characteristic peaks of the Keggin structure appear at $700\text{--}1100\text{ cm}^{-1}$, indicating that the basic Keggin structure does not change after the HPW loaded on CeO_2 . The results of BET analysis showed that the specific surface area of HPW is only $3.2\text{ m}^2\text{ g}^{-1}$. When HPW was supported on CeO_2 , its specific surface area is as high as

$13.8 \text{ m}^2 \text{ g}^{-1}$ (70%HPW/CeO₂), which also indicates that HPW was effectively loaded on the CeO₂ support.

Effect of HPW Loading on NO_x Adsorption

The effect of HPW loading on NO_x adsorption was investigated over CeO₂ as support. As can be seen from Fig. 3, the adsorption rate of NO_x of the mixture was higher than pure oxide. After the loading of HPW is increased to 50%, the adsorption rate of the system rapidly increases to 74.6%, and the best removal rate, i.e., 75.3%, is obtained over 70%HPW/CeO₂. Combined with the XRD and IR characterization results of the HPW/CeO₂ system, it can be seen that when the HPW loading is 70%, the crystal phase of HPW on the support surface is almost identical to the pure HPW. Although HPW is the active component of the system, the adsorption rate of NO_x of the mixture increased by nearly 10% compared to HPW (66.3%). This indicates that CeO₂ is an excellent carrier, and there is a synergistic effect between CeO₂ and HPW. Considering this fact,

Fig. 1. XRD spectra of HPW/CeO₂ with different loading capacities: (a) 0%, (b) 40%, (c) 50%, (d) 70%, and (e) HPW.

Fig. 2. FTIR spectra of (a) CeO₂, (b) 70%HPW/CeO₂, and (c) HPW.

Fig. 3. Effect of HPW loading on NO_x adsorption efficiency. Reaction conditions: 800 ppm NO, 8% O₂, 4.2% H₂O, T = 150°C, space velocity (SV) = 5298 h⁻¹.

70%HPW/CeO₂ is used as the representative material to further explore the effect of different experimental factors on NO_x adsorption performance in the following section.

Effect of Oxygen Content on NO_x Adsorption

The oxygen content is an important factor for affecting the NO_x adsorption performance. NO_x adsorption experiments were carried out at different oxygen content over 70%HPW/CeO₂ and the results were shown in Fig. 4. It can be seen that under oxygen-free conditions, the adsorption rate of the system is low at only about 20%. As the oxygen content increases, the adsorption rate of the system gradually increases. When the oxygen content reaches 8%, the maximum adsorption rate is obtained, and the adsorption rate remains stable even with further increase of oxygen content. Therefore, the suitable oxygen content for NO_x adsorption by HPW/CeO₂ system is 8%.

Effect of Water Vapor Content on NO_x Adsorption

Fig. 5 shows the adsorption performance of 70%HPW/CeO₂ at different water vapor content. It can be clearly seen that the adsorption rate shows a volcanic curve with the increasing water vapor content. When the water vapor content is less than 4.2%, the adsorption rate increases with the water vapor content. However, when the water vapor content is higher than 4.2%, the adsorption rate is gradually decreasing. The suitable water vapor content for NO_x adsorption in HPW/CeO₂ system is about 4.2%.

Effect of Reaction Temperature on NO_x Adsorption

Temperature is a key factor for chemical reactions, especially for adsorption experiments. Fig. 6 shows the effect of temperature on the NO_x adsorption performance of HPW/CeO₂ system. In the temperature range of 125–250°C, NO_x adsorption rate is maintained above 60%. When the reaction temperature is 170°C, the adsorption rate can reach to 76.3%. After the temperature rises to 300°C, the adsorption rate drops sharply to less than 50%. The experimental results

show that HPW has better thermal stability when supported on CeO_2 , and the suitable temperature for HPW/ CeO_2 is 170°C .

Fig. 4. The effect of oxygen content on the NO_x adsorption over 70%HPW/ CeO_2 . Reaction conditions: 800 ppm NO , 8% O_2 , 4.2% H_2O , $\text{SV} = 5298 \text{ h}^{-1}$.

Fig. 5. The effect of water vapor content on the NO_x adsorption performance. Reaction conditions: 800 ppm NO , 8% O_2 , $T = 150^\circ\text{C}$, $\text{SV} = 5298 \text{ h}^{-1}$.

Fig. 6. NO_x adsorption curves of 70%HPW/ CeO_2 at different temperatures. Reaction conditions: 800 ppm NO , 8% O_2 , 4.2% H_2O , $\text{SV} = 5298 \text{ h}^{-1}$.

The Effect of Space Velocity on NO_x Adsorption

The space velocity (SV) of reaction gas could be also a factor for its removal in the process due to the residence time of the gas in the reactor can be actually affected by the change of space velocity. Therefore, the effect of space velocity of NO_x on NO_x adsorption performance of HPW/ CeO_2 at 150°C was studied (Fig. 7). It should be noted that the adsorption rate of the system decreases as the space velocity increases, indicating that free diffusion of gas has little effect on the adsorption surface reaction. The experimental results are mainly due to the reduction of the residence time of gas in the reactor by the changing space velocity. Considering the space velocity is in the range of $2649\text{--}5298 \text{ h}^{-1}$, the adsorption rate of NO_x is relatively stable, and its decrease sharply due to the increasing space velocity. Therefore, the suitable space velocity for the adsorption of NO_x by the HPW/ CeO_2 system is $2649\text{--}5298 \text{ h}^{-1}$.

Effect of Initial NO Concentration

Fig. 8 shows the effect of initial NO concentration on the NO_x adsorption performance of the system. With the

Fig. 7. NO_x adsorption performance under different space velocity. Reaction conditions: 800 ppm 8% O_2 , 4.2% H_2O , $T = 150^\circ\text{C}$.

Fig. 8. The effect of initial NO concentration on the NO_x adsorption performance. Reaction conditions: 8% O_2 , 4.2% H_2O , $T = 150^\circ\text{C}$, $\text{SV} = 5298 \text{ h}^{-1}$.

increase of the NO concentration of intake gas, the adsorption rate of the system gradually decreases. It should be noted that a linear relationship is exhibited between the NO_x adsorption rate and the initial NO concentration. When the initial concentration of NO is 387 ppm, the adsorption rate of the system is up to 79.3%.

Adsorption Mechanism

Under optimized experimental conditions (800 ppm NO, 8% O₂, 4.2% H₂O, T = 150°C, SV = 5298 h⁻¹), the saturated adsorption capacity was calculated. The saturation adsorption capacity of the system is significantly increased after the HPW was supported on CeO₂, and the saturation adsorption time became shorter. Based on experimental data, the saturated adsorption of NO_x by HPW catalyst is 50.5 mg-NO₂ g-HPW⁻¹. In addition, as shown in Table 1, the saturated adsorption of NO_x by 70%HPW/CeO₂ catalyst is up to 85.6 mg-NO₂ g-HPW⁻¹, which is higher than that of Ti-Zr (28 mg-NO₂ g-HPW⁻¹) and TiO₂ (46 mg-NO₂ g-HPW⁻¹) as support reported in previous literature (Hodjati *et al.*, 2001b; Gómez-García *et al.*, 2005a). Combined with the results of BET analysis, when HPW is loaded on CeO₂ support (70%HPW/CeO₂), its specific surface area is as high as 13.8 m² g⁻¹, which is much higher than the specific surface area of HPW (3.2 m² g⁻¹). That indicates that HPW could be highly dispersed on the CeO₂, leading to more available adsorption sites were used for NO_x adsorption.

The IR spectra of HPW before and after adsorption saturation are shown in Fig. 9. In the range of 700–1100 cm⁻¹, four characteristic peaks of Keggin structure for 70%HPW/CeO₂ after adsorption saturation still exist, indicating that the Keggin structure of HPW has not changed. In addition, a new characteristic peak appears at 2266 cm⁻¹ and the characteristic peak of H₂O (in secondary structure of HPW) at 1617 cm⁻¹ become weaker.

According to previous reports, there are two different viewpoints on the characteristic peak at 2266 cm⁻¹. Bélanger and Moffat (1995) reported that the characteristic peak at 2266 cm⁻¹ is caused by HNO₂⁺ vibration. The interaction of NO₂ and HPW is not only appeared on the surface. NO₂ can also enter the secondary structure of HPW and combine with protons in the secondary structure to form HNO₂⁺. Chen and Yang (1995) and Yang and Chen (2004) carried out NO_x adsorption tests over HPW, and considered that the characteristic peak at 2266 cm⁻¹ was caused by NOH⁺ vibration. In the presence of oxygen, NO can pass through the surface of HPW into its bulk to replace H₅O₂⁺ in the secondary structure, and finally NOH⁺ is formed. Thermogravimetric analysis (TGA) and calculation of mass conservation principle

of nitrogen proved that the bond with HPW is NO instead of NO₂. Herring *et al.* (1998) used KPW as an adsorbent to perform NO₂ adsorption experiments, and the DRIFTS results showed that the ion of NO₂ is only adsorbed on the surface of KPW (KPW does not contain crystal water). Besides the other characteristic peaks of NO⁺, NO₂⁺ and NO_x^{y-} are detected on the surface of KPW after adsorption saturation. This result supported the view of Yang and Chen (2004), and the mechanism of NOH⁺ formation was proposed.

Based on the above analysis, we believe that the characteristic peak at 2266 cm⁻¹ is caused by the NOH⁺ vibration entering the HPW secondary structure for 70%HPW/CeO₂. There is an antisymmetric stretching vibration peak near 2300 cm⁻¹ for NO⁺, which is only 34 cm⁻¹ different from the vibration peak at 2266 cm⁻¹ detected by this experiment. The stretching vibration peak of NO₂⁺ mainly exist in 2350–2375 cm⁻¹. The minimum difference between stretching vibration peak of NO₂⁺ and the peak at 2266 cm⁻¹ detected by the experiment is 84 cm⁻¹. On the other hand, the characteristic peaks of bending vibration of NO₂⁺ and the characteristic peaks of N₂O₃ on the surface of 70%HPW/CeO₂ were not detected. Furthermore, the weakening characteristic peak of H₂O at 1617 cm⁻¹ is mainly caused by the partial crystal water in the HPW secondary structure being replaced by NOH⁺. This experimental result is consistent with the conclusion of Herring *et al.* (1998). The heteropolyacid used in this work is H₃PW₁₂O₄₀·6H₂O. At most, six crystal water molecules can be replaced in one HPW molecule and there is competitive adsorption between H₂O and NO_x. Therefore, a conclusion can be draw for HPW/CeO₂ system, namely, NO_x is adsorbed on the surface of HPW in the form of NOH⁺, and NOH⁺ enters its bulk phase by replacing part of the crystal water in the secondary structure of HPW.

Catalytic Decomposition of Adsorbed NO_x

GC-MS was used to detect the decomposition products, and N₂ was found in the products. The results are shown in Fig. 10. The decomposition characteristics of adsorbed NO_x on HPW and HPW/CeO₂ catalytic systems are similar. The detected N₂ reaches a peak at about 10 min, and the decomposition is basically completed at about 20 min. The results of this experiment show that for NO in an oxygen-enriched atmosphere, HPW/CeO₂ catalytic systems can achieve a better decomposition and conversion effect due to the interaction between two components. Therefore, a new heteropoly compound catalysis system has been design for NO_x elimination by adsorption/decomposition and the catalytic conversion of NO_x to N₂ can be achieved without

Table 1. NO_x adsorption capacity of different catalyst systems.

Catalyst	NO _x adsorption capacity (mg-NO ₂ g-HPW ⁻¹)	Ref.
HPW	38	Hodjati <i>et al.</i> (2001a)
HPW/Ti-Zr	28	Gómez-García <i>et al.</i> (2005a)
HPW/TiO ₂	46	Hodjati <i>et al.</i> (2001b)
HPW/SiO ₂	17	
HPW/NaY	2.38	Zhang and Wang (2013)
HPW/CeO ₂	85.6	This work

Fig. 9. FTIR spectra of 70%HPW/CeO₂ before and after adsorption saturation.

Fig. 10. Catalytic decomposition of adsorbed NO_x over HPW and 70%HPW/CeO₂.

reducing agents. The used catalyst can be placed in humid air (5% water vapor), and HPW can replenish the lattice water replaced by NO_x by adsorbing water molecules, thereby regenerating the catalyst. Detailed decomposition mechanism and process of the conversion of the adsorbed intermediate product (NOH⁺) into N₂ by the temperature programming process need to be further investigated.

CONCLUSIONS

In this study, we synthesized catalysts composed of CeO₂ and varying percentages of HPW and assessed their capacity to adsorb and decompose NO_x. The adsorption performance of the most efficient catalyst, 70%HPW/CeO₂, was approximately linearly proportional to the initial NO concentration. The optimal conditions for adsorption were an environment containing 8% O₂ and 4.2% H₂O, a reaction temperature of 170°C, and a space velocity of 2649–5298 h⁻¹. The IR spectra of the HPW revealed similar adsorption mechanisms for

HPW/CeO₂ and HPW catalysts: The adsorbed NO_x entered the bulk phase of the HPW and replaced the crystallization water, combining with its protons to form NOH⁺. However, the maximum adsorption rate of the HPW/CeO₂ catalysts (85.6 mg-NO₂ g-HPW⁻¹) greatly exceeded that of pure HPW (50.5 mg-NO₂ g-HPW⁻¹). GC-MS confirmed that temperature programming reduced the adsorbed NO_x to N₂.

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