

Adsorption and decomposition of NO_x on Rare Earth Phosphotungstates

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Abstract. To reduce NO_x emission, LnPW (Ln= La, Ce, Pr, Nd, Sm, Eu, Gd, Yb, Y; PW= PW₁₂O₄₀) were prepared and used for NO_x adsorption and decomposition. The adsorption results showed that NO_x adsorption capacity on LnPW were lower than phosphotungstic acid (HPW). After doping with HPW, the NO_x adsorption ability of LnPW/HPW was improved significantly. NO_x catalytic decomposition on LnPW/HPW was tested by rapid heating, the results showed that catalytic activity of LnPW/HPW was superior to HPW. The effects of doping ratio on NO_x adsorption and decomposition were studied on the catalyst of EuPW/HPW, and the results showed that HPW played the role of NO_x adsorbent, while EuPW was related to the NO_x conversion and N₂ selectivity.

Introduction

Nitrogen oxides (NO_x) are considered the primary atmospheric pollutants^[1-6]. In the last several decades extensive research have been carried out to reduce NO_x emission, and the NO_x catalytic decomposition was considered the best method for no reducing agents are consumed^[7-12]. Numerous experimental investigations have been carried out to look for the NO_x decomposition catalysts^[13]. Heteropoly acids (HPAs) attracted much attention due to their acidity, oxidation-reduction and pseudo-liquid phase model. Yang^[7] found that phosphotungstic acid (HPW) had the ability to decompose NO_x to N₂ by rapid heating, subsequently, Chen^[8], McCormick^[14], Zhang^[9] and the author^[12] reconfirmed the decomposition ability of HPW.

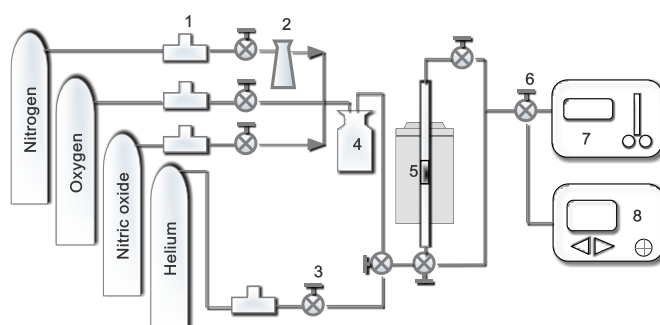
Rare earth has been widely used in catalysis research for its special catalytic performance, and cerium is one of the most used rare earth element in NO_x deduction, while the others rare earth elements are not investigated sufficiently^[15-21]. This paper presented the rare earth elements La, Ce, Pr, Nd, Sm, Eu, Gd, Yb and kin element Y, and then rare earth phosphotungstates LnPW (Ln= La, Ce, Pr, Nd, Sm, Eu, Gd, Yb, Y; PW= PW₁₂O₄₀) which were synthesized by rare earth and HPW were used to NO_x adsorption and catalytic decomposition.

Experimental

Catalyst synthesis. According to the literature^[22], LnPW (Ln= La, Ce, Pr, Nd, Sm, Eu, Gd, Yb, Y; PW= PW₁₂O₄₀) were prepared by the interaction of H₃PW₁₂O₄₀ with rare earth nitrate in aqueous solution. H₃PW₁₂O₄₀ (3.0 mmol) was dissolved in 20 ml 50% ethanol solution. To this solution 5 ml rare earth nitrate solution (3.0 mmol) was added dropwise. The mixed solution was gently evaporated to 10 ml in the water bath at 65 °C, and then the crystallization occurred. The crystal was filtrated and dried in vacua at 250 °C for 2 h. The LnPW were prepared for use.

Apparatus and gas composition. The schematic diagram of NO_x adsorption and decomposition reaction equipment was shown in Fig.1. The experiments were conducted in a quartz flow reactor (8 mm in diameter, with a fritted support) which was equipped with a thermocouple inserted in the catalyst bed. The catalyst was placed in the middle of the reactor between two quartz wool plugs. The feed gas contained 1000 ppm NO which was made by blending NO/N₂ premixed (1.0 vol. %) with N₂ carrier, and other gases such as O₂ (8%), H₂O (5%) were added also by blending. The blending was accomplished by using a D08-1D/ZM mass flow control blending system (Beijing Seven Star Co. Ltd. Beijing). Water vapor was added by using a heated gas wash bottle. NO/NO_x analyzer with a range of 0-2000 ppm (Nanjing Hepu technology Co., Ltd. China) was used to record the effluent NO_x concentration.

NO (99.9%) and high purity grade N₂, He, O₂ were obtained from Xuzhou Huazhong Special Gas Co. Ltd. (Xuzhou, China).



1. Mass flow controller, 2. Water vapor generator, 3. Disconnecting valve, 4. Surge flask, 5. Heating equipment, 6. Three-way valve, 7. Chemiluminescent NO/NO₂ analyzer, 8. Gas chromatography.

Fig. 1 Schematic diagram of NO_x adsorption and decomposition reaction equipment

Test procedure. The test procedure comprised a stabilization period of 30 min in the bypass, for the complete gas mixture. The gas was then allowed to flow through the reactor containing adsorbent preheated to 50 °C and the temperature of oven was increased from 50 °C to 350 °C with a temperature ramp rate of 5 °C/min. The amount of NO_x trapped was estimated by an integration of the curve below the baseline (1000 ppm) for adsorption, and by expression as mg NO_x/g.

Decomposition stage: The sample placed in a quartz tube was washed with 20 ml/min helium for 1 h. Then temperature programmed decomposition was carried out on the catalyst adsorbed NO_x. The N₂ was detected by gas chromatography with 5A molecular sieve chromatography column.

Results and discussion

NO_x adsorption on LnPW. The LnPW were used as sorbents to adsorb 1000 ppm NO_x, and the results were shown in Fig.2. All of the rare earth phosphotungstates had the NO_x adsorption ability. Among LnPW, GdPW had the highest NO_x adsorption efficiency of 81.8%, PrPW was submitted to it with the efficiency of 76.6%, both SmPW and CePW had the efficiency of 72.2%, and the NO_x adsorption efficiency of LaPW was 71% a little higher than NdPW and EuPW, whose NO_x removal efficiencies were 63.2% and 56.8%. Heavy rare earth phosphotungstate YbPW and kin element phosphotungstate YPW had the NO_x adsorption efficiencies of 69.3% and 74.9%, which were similar to light rare earth phosphotungstates. In brief, the NO_x adsorption efficiencies of LnPW exhibited the following order: GdPW > PrPW > YPW > SmPW = CePW > LaPW > YbPW > NdPW > EuPW.

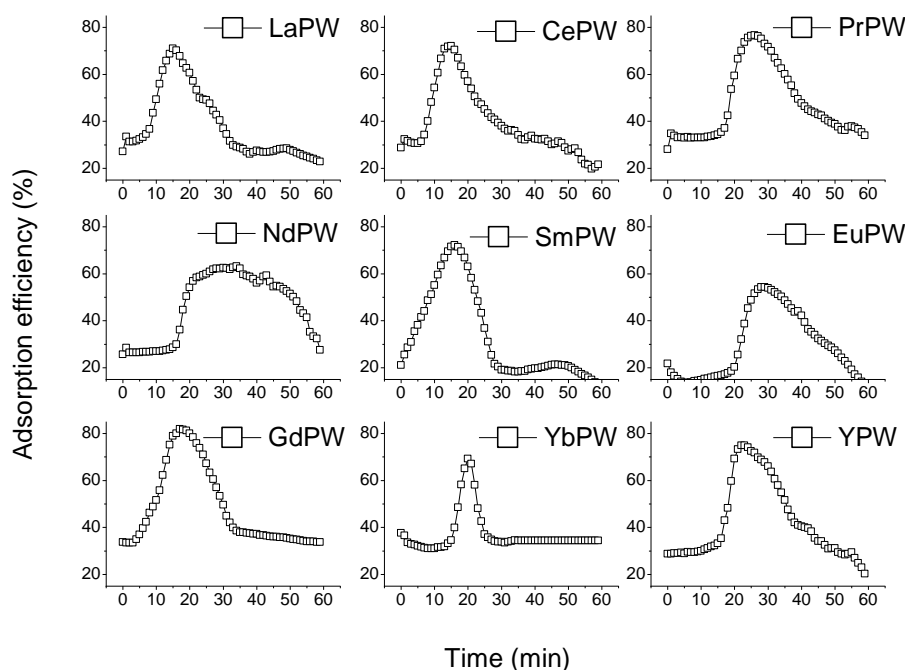


Fig. 2 NO_x adsorption efficiency on LnPW

The NO_x adsorption capacities on LnPW were calculated with integral curve, and the results were shown in table 1. The NO_x adsorption capacity on LnPW was lower, among them LaPW had the maximum NO_x adsorption capacity of 4.34 mg NO_x/g, while EuPW had the minimum NO_x adsorption capacity of 2.02 mg NO_x/g. The NO_x adsorption capacities on LnPW exhibited the following order: LaPW > GdPW > YPW > PrPW > CePW > NdPW > YbPW > SmPW > EuPW.

Table 1. NO_x adsorption capacity on LnPW

Samples	LaPW	CePW	PrPW	NdPW	SmPW	EuPW	GdPW	YbPW	YPW
Adsorption Capacity (mg NO _x /g)	4.34	3.37	3.55	3.31	2.84	2.02	3.94	3.13	3.64

NO_x adsorption and decomposition on LnPW/HPW. Considering lower NO_x adsorption ability of pure LnPW, HPW was selected to mix with LnPW, then the doping LnPW/HPW was used as NO_x adsorbent to adsorb NO at first, then the adsorbed NO_x was catalytic decomposition on LnPW/HPW. The NO_x adsorption on LnPW/HPW was tested in the following conditions: NO_x 1000 ppm, O₂ 8%, water vapor 4.5%, space velocity 10000 h⁻¹ and temperature 200 °C. The adsorption results were shown in Fig.3. After doping with HPW, the NO_x adsorption on LnPW/HPW was increased obviously, and NO_x adsorption efficiencies on LnPW/HPW were different from each other. The NO_x adsorption capacities on LnPW/HPW were calculated with integral curve in 90 min, and the results were shown in table 2. The NO_x adsorption capacities on LnPW/HPW were higher than those on LnPW, which was because of HPW adsorbing abundant NO_x.

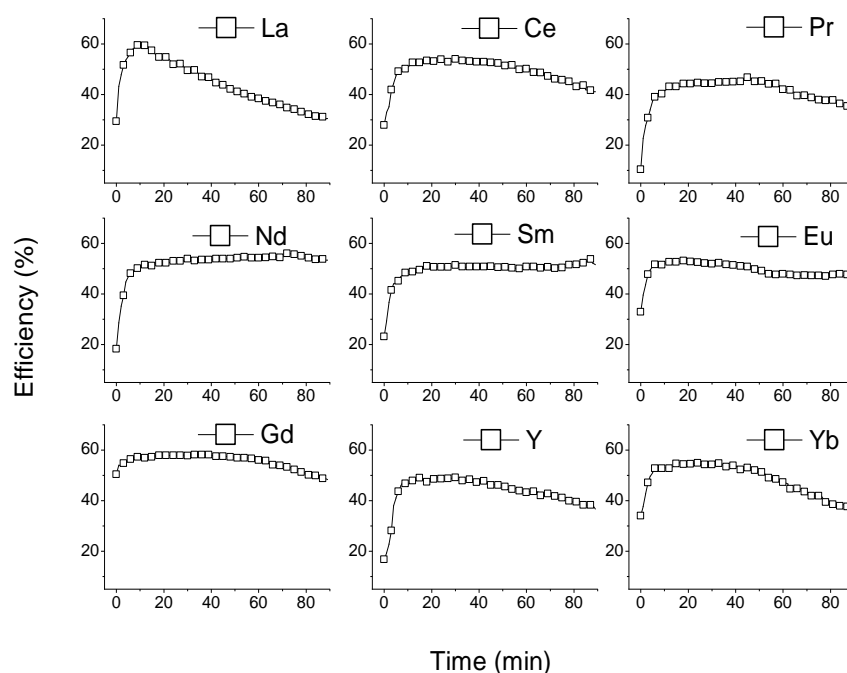


Fig. 3 NO_x adsorption on LnPW/HPW

Electric oven decomposition device was used to investigate the NO_x decomposition on LnPW/HPW adsorbed NO_x. The quartz tube reactor was placed in the oven preheated to 450 °C with catalyst part being outside, the catalyst part was moved into the oven quickly after washing with helium for 1 h. Sampling probe was used to capture the produced gas, and gas chromatography was used to calculate the N₂ production. NO_x decomposition and N₂ yield on LnPW/HPW were shown in table 2. The results showed that the catalytic decomposition of NO_x on LnPW/HPW were superior to that of HPW. The pure HPW had the NO_x decomposition efficiency of 4.17%. However, the catalyst of YPW/HPW had the highest N₂ yield of 18.07%, while NdPW/HPW had the lowest N₂ yield of 4.84%. In short, the N₂ yield decreased in the order of YPW/HPW > YbPW/HPW > PrPW/HPW > SmPW/HPW > EuPW/HPW > LaPW/HPW > CePW/HPW > GdPW/HPW > NdPW/HPW.

Table 2. NO_x adsorption and decomposition on LnPW/HPW

Catalyst	NO _x adsorption (ml)	N ₂ formation (ml)	N ₂ yield ^a (%)
LaPW/HPW	3.99	0.145	7.26
CePW/HPW	4.43	0.152	6.86
PrPW/HPW	3.70	0.248	13.4
NdPW/HPW	4.72	0.114	4.84
SmPW/HPW	4.57	0.206	9.02
EuPW/HPW	5.03	0.188	7.41
GdPW/HPW	5.01	0.169	6.74
YbPW/HPW	4.37	0.294	13.5
YPW/HPW	3.94	0.356	18.1
HPW	5.42	0.113	4.17

^a N₂ yield = 2 × N₂ formation / NO_x adsorption

Effect of doping ratio on NO_x adsorption and decomposition. EuPW/HPW was prepared by mechanical grinding methods, and the mass ratio between EuPW and HPW were 1:9, 1:1 and 9:1. The effect of EuPW/HPW doping ratio on adsorbing NO_x was studied in the following conditions: NO_x 1000 ppm, O₂ 8%, water vapor 4.5% and temperature 150 °C. NO_x adsorption results on EuPW/HPW were shown in Fig.4. The effect of doping ratio on maximum NO_x adsorption efficiency was unobvious, and all of the three maximum efficiencies were about 55%. However, the NO_x adsorption capacity of EuPW/HPW increased with the improving proportion of HPW, which can be assigned to the possibility that the HPW play the role of NO_x sorbent in the catalyst of EuPW/HPW. Thus more HPW in EuPW/HPW would result in more NO_x being adsorbed.

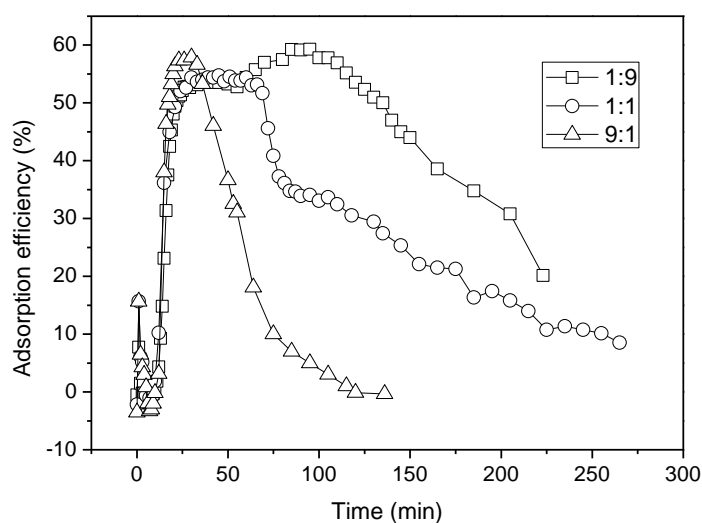


Fig. 4 NO_x adsorption on EuPW/HPW with mass doping ratio of EuPW: HPW = 1:9, 1:1 and 9:1

To investigate the effect of doping ratio on NO_x catalytic decomposition, EuPW/HPW with different doping ratio was selected as catalyst. 20 ml/min helium was used to wash out the N₂ and O₂ adsorbed in the catalyst for 1 h, then the EuPW/HPW saturated with NO_x was rapid heating from 30 °C to 450 °C with a temperature ramp rate of 150 °C/min by electric oven. N₂ produced in the NO_x decomposition was detected by Gas chromatograph. The result of doping ratio on NO_x decomposition was shown in table 3. N₂ yield was 3.9% when EuPW:HPW = 1:9, while the yield was 24.6 % when the ratio increased to 9:1. Thus more EuPW in the catalyst would improve the decomposition of NO_x and the N₂ yield, and the active ingredient of EuPW/HPW was rare earth phosphotungstate EuPW.

Table 3. NO_x adsorption and decomposition on EuPW/HPW with different doping ratio

EuPW/HPW	Weight(g)	Adsorbed NO _x (mg)	Production of N ₂ (ml)	N ₂ yield(%)
1:9	1.2	16.3	0.40	3.9
1:1	1.0	12.6	0.80	10.0
9:1	1.3	4.7	0.73	24.6

Conclusions

The following specific conclusions can be drawn from the experimental results. First, the rare earth phosphotungstates had the excellent ability to catalyze decomposition NO_x into N₂. Second, increasing the rare earth phosphotungstates amount on the LnPW/HPW catalyst improved the catalytic performance and N₂ formation significantly.

Acknowledgements

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