SHORT COMMUNICATION

EFFECT OF HEATING METHOD ON NO$_x$ DECOMPOSITION ON H$_3$PW$_{12}$O$_{40}$·6H$_2$O

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ABSTRACT. The thermal decomposition of nitrogen oxides (NO$_x$) on phosphotungstic acid (H$_3$PW$_{12}$O$_{40}$·6H$_2$O or HPW) by two different heating methods is compared. Infra-red (IR) and X-ray diffraction (XRD) measurements are conducted to investigate the decomposition mechanism. Both heating methods, i.e. heating from 30 °C to 450 °C at a rate of 150 °C/min ("rapid heating") and heating at a constant temperature of 450 °C ("constant-temperature heating") lead to an actual, considerably high heating rate. Compared with rapid heating, however, constant-temperature heating results in enhanced N$_2$ conversion (21.8%). Furthermore, the catalyst can be reused after decomposition at constant-temperature heating, while its performance quickly degrades after decomposition via rapid heating.

KEY WORDS: Nitrogen oxides, Heteropoly acids, Decomposition, Heating

INTRODUCTION

Nitrogen oxides (NO$_x$) are considered as primary atmospheric pollutants because they not only cause environmental threats such as acid rain, photochemical smog, ozone layer depletion, and even global warming, but also have a detrimental effect on human health, provoking lung infections and respiratory allergies [1-4]. Over the latest decades, great efforts have been taken to reduce NO$_x$, and various technologies to control NO$_x$ emissions have been researched. These technologies can be classified into two major categories, based on whether reduction is employed or not: catalytic reduction and catalytic decomposition. The latter method has excellent prospects because it can decompose NO$_x$ into nitrogen and oxygen without using any reductant.

The most commonly studied catalysts for NO$_x$ catalytic decomposition include noble metals, metallic oxides, perovskites and perovskite-type oxides, ion-exchanged ZSM-5, heteropolyacids (HPAs), and hydrotalcites [5]. Among these catalysts, HPAs have attracted considerable attention owing to their acidity, redox properties, and pseudo-liquid phase [6]. HPAs, in particular H$_3$PW$_{12}$O$_{40}$·6H$_2$O (HPW), can adsorb large quantities of polar molecules such as NO$_x$ in the solid bulk [7, 8]. By rapid heating, the adsorbed NO$_x$ is then decomposed into nitrogen by the catalytic action of HPW [9-12], where it was found (by Yang [9]) that the heating rate is the single most important factor in determining the amount of N$_2$ produced, i.e. to increase the amount of N$_2$ released, a high heating rate is indispensable. Unfortunately, a high heating rate may readily lead the oven temperature to surpass the target temperature, resulting in degradation of the catalyst. It is therefore of key interest to develop a heating method that is based on a high heating rate yet does not surpass the target temperature.

In this study, to avoid degradation of the catalyst by exceeding the oven's target temperature (as associated with a high heating rate), we have explored a novel constant-temperature heating method and compared it with the traditional rapid-heating method for NO$_x$ decomposition. We

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found that constant-temperature heating is superior to the traditional heating method in terms of N_2 conversion and reusability of the HPW catalyst.

EXPERIMENTAL

Reactor set-up and gas composition. A schematic representation of the reactor is shown in Figure 1. Experiments were conducted in a quartz flow reactor (8 mm in diameter, containing 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 1,000 ppm NO and was obtained by blending premixed NO/N_2 (1.0% by vol.) with N_2 carrier gas. O_2 (8%) and H_2O (5%) were also introduced by this blending procedure. Blending was accomplished using a D08-1D/ZM mass-flow control blending system (Beijing Seven Star Co. Ltd., Beijing). Water vapor was introduced from a heated gas-wash bottle.
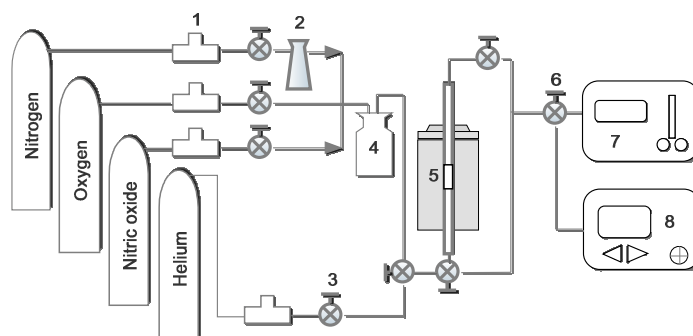

Figure 1. Schematic diagram of reactor. (1. Mass flow controller, 2. Water vapor generator, 3. Disconnecting valve, 4. Surge flask, 5. Heating equipment, 6. Three-way valve, 7. Chemiluminescent NO/NO_2 analyzer, 8. Gas chromatograph).

NO_x adsorption and decomposition experiments were carried out by placing the experimental setup in an oven. During the adsorption stage, the composition of the inlet gas was N_2, O_2, and NO, and the process temperature was 150 °C. A chemiluminescent NO/NO_x analyzer with a range of 0 to 2000 ppm (Wuhan Tianhong Intelligent Instrument Co. Ltd., China) was used to monitor the effluent NO_x concentration. After NO_x adsorption, the inlet gas was changed to helium, while the outlet gas flowed to a GC system. We used three-way valve to shift from the adsorption setup to the decomposition setup. In the decomposition stage, the experiment temperature was either increased from 30 °C to 450 °C at a heating rate of 150 °C/min, or isothermal conditions (450 °C) were employed. The outlet gas detector was a SP-6890 gas chromatograph (GC; Shandong Lunan Ruihong Chemical Apparatus Co. Ltd, China), which was used to detect the N_2 gas formed during the decomposition stage.

NO (99.9%), N_2 (high-purity grade), O_2 (99.5%), and He (high-purity grade) were obtained from Jinan Deyang Special Gas Co. Ltd. (Jinan, China). Analytical-grade phosphotungstic acid ($H_3PW_{12}O_{40}\cdot xH_2O$) was purchased from the National Drug and Chemical Group Co., Ltd. and dried at 80 °C for 6 h to obtain $H_3PW_{12}O_{40}\cdot 6H_2O$ (HPW). A measured amount of 0.5 g of HPW was used in the experiments.

Standard test procedure: adsorption stage. The test procedure comprised a stabilization period of 30 min, to completely flush the system with the gas mixture. The gas was then allowed to flow through the reactor containing the adsorbent, which was preheated at 150 °C. During NO_x adsorption, the feed gas was composed of NO, O_2, and N_2, which, after blending in the tube, was partially converted to NO_2 ($2NO + O_2 = 2NO_2$), obtaining a mixture of NO and NO_2, i.e. NO_x, where $_x$ = 1 or 2.

The amount of adsorbed NO_x was estimated by integration of the curve below the baseline (1000 ppm) and presented in mg NO_x/g HPW. Since both signals of NO and NO_2 are recorded, this is an exact value.

Standard test procedure: decomposition stage. After NO_x adsorption, the inlet gas was changed to helium. A He flow of 5 mL/min was used to purge the reactor containing the catalyst for 1 h. Decomposition was carried out under the same flow by either of the following two methods. The first method (rapid heating) involved rapid heating from 30 °C to 450 °C at a heating rate of 150 °C/min. In the second method (constant-temperature heating), the reactor was placed in an oven, which was preheated at 450 °C, and after washing for 1 h with He, the catalyst was rapidly transferred to the oven and decomposition was carried out. Both decomposition processes were conducted for 10 min. The decomposition product was sampled to the GC through a gas valve, separated over a column containing 5 Å molecular sieves, and analyzed using a thermal conductivity detector. To obtain the exact peak concentration of N_2, we calculated the N_2 sampling time by taking into account the N_2 production time and the residence time of N_2 in the tubing connecting the reactor and the GC sampling valve. These experiments were repeated to correct for the N_2 sampling time. Based on the above procedure, we could accurately measure the exact N_2 concentration.

NO conversion was then calculated by: N_2 yield = $2N_{2\ formation}/NO_{x\ adsorbed}$, where $NO_{x\ adsorbed}$ stands for the amount of NO_x adsorbed by HPW and $N_{2\ formation}$ stands for the amount of N_2 generated during NO_x decomposition.

Catalyst characterization. To characterize HPW by Fourier-transform IR (FTIR), fresh catalyst, as well as catalyst withdrawn from the reactor after decomposition by either heating method was diluted into KBr and pressed into a pellet (diameter: 13 mm). FTIR spectra between 400 and 4000 cm^{-1} were recorded using an Avatar 370 FTIR system at 2 cm^{-1} resolution.
XRD experiments were performed with a Siemens D-5000 diffractometer using Cu Kα radiation, under continuous acquisition between 5 ° and 45 ° and a step width of 0.02 ° at 1 s per step.

RESULTS AND DISCUSSION

Rapid heating and constant-temperature heating. The temperature change during both decomposition processes (rapid heating or constant-temperature heating) was simulated by inserting a thermocouple into the center of the catalyst bed, and the temperature variation was recorded. As shown in Figure 2 and Table 1, the traditional rapid heating method resulted in a high heating rate of approximately 150 °C/min after 3 min. The temperature of the oven exceeded the target temperature, however, because of the response time of the oven. The highest measured temperature was 558 °C, exceeding the target temperature by 108 °C. According to thermal stability studies on HPAs conducted by Moffat, who employed differential thermal analysis, thermogravimetric analysis, and XRD analysis, the structure of HPW is destroyed at 525 °C [6]. The rapid heating method is thus expected to damage the catalyst, which was confirmed by FTIR.

By heating at a constant temperature, a high heating rate (as high as 150 °C/min in the first 2 min) was obtained, where it should be noted that by virtue of the design, this heating method will never cause the oven temperature to surpass target temperature, thus avoiding decomposition of the catalyst at high temperature. Based on these two advantages, constant-temperature heating is expected to ensure the efficient decomposition of NO_x on the HPW catalyst.
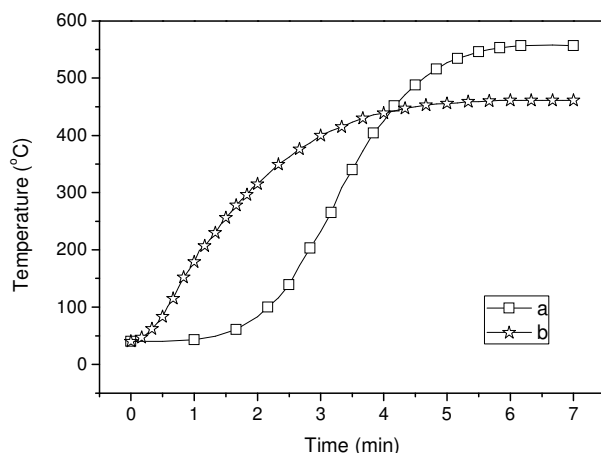

Figure 2. Temperature of sample in the decomposition stage: (a) decomposition by rapid heating from 30 °C to 450 °C with a heating rate of 150 °C/min; (b) decomposition by constant temperature heating at 450 °C.

Table 1. Heating rate of rapid heating and constant temperature heating.

Method of heating	Heating rate (°C/min)						
	0-1 min	1-2 min	2-3 min	3-4 min	4-5 min	5-6 min	6-7 min
Rapid heating	3	40	149	193	102	28	2
Constant temperature heating	149	136	85	39	17	5	0

Adsorption and decomposition. A two-stage NO_x adsorption/decomposition approach was adopted during this study, where HPW was used both as the sorbent and as the catalyst. During the first stage, HPW acted as a sorbent, adsorbing NO_x in the fixed-bed reactor at 150 °C. The adsorption results are shown in Table 2. The inlet gas was then changed to helium, leading to HPW-catalyzed decomposition of the adsorbed NO_x by either rapid heating or constant-temperature heating, and the outlet gas was directed to a GC system. The experiments were repeated three times. The results (including mean value and standard deviation) are displayed in Figure 3.The catalyst was reused after decomposition to compare its reusability after application of the different heating methods.

As listed in Table 2, the catalyst exhibited similar adsorption capacities of 13.10 mg NO_x/g HPW and 12.44 mg NO_x/g HPW for rapid heating and constant-temperature heating, respectively. However, N_2 conversion by constant-temperature heating was more than twice that produced via rapid heating (21.8% vs. 9.97%), presumably because HPW does not disintegrate by constant-temperature heating at 450 °C. Rapid heating, on the other hand, suffers from the disadvantage that the actual temperature surpasses the target temperature, thus destroying the HPW structure. As a result, the material loses the ability to catalytically decompose NO_x into N_2. The experiment could not be run with the reused catalyst because less than 0.1 mg NO_x was

adsorbed. As shown in Figure 3, decomposition by constant-temperature heating already produced N_2 in the first 2 min, while decomposition occurred with a delay of 2 min for the rapid heating method. This is because constant-temperature heating displayed an increased temperature ramp rate as compared to rapid heating during the initial stages.

The results of the recycling tests are shown in Table 2. The catalyst could not be reused after rapid-heating decomposition, while the catalyst was reusable following constant-temperature heating. Here, adsorption capacity and N_2 conversion of the reused catalyst were reduced by 6.4% and 2.8%, respectively.
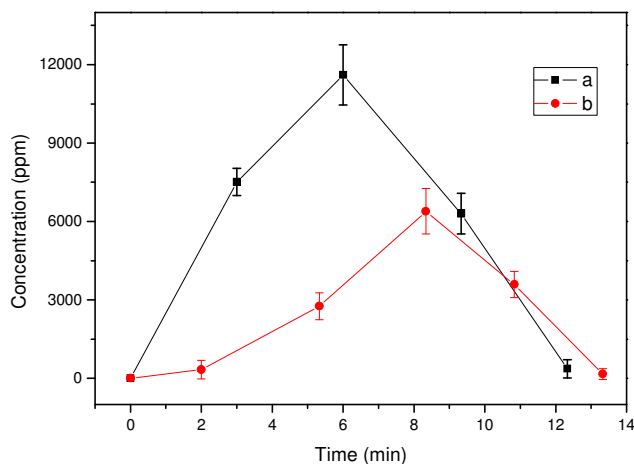

Figure 3. Formation of N_2 by decomposition of absorbed NOx on HPW: (a) decomposition by constant temperature heating at 450 °C; (b) decomposition by rapid heating from 30 °C to 450 °C with a heating rate of 150 °C/min.

Table 2. Reusability of catalyst after rapid heating and constant temperature heating decomposition.

Parameter	Rapid heating		Constant temperature heating	
	First time	Reuse[*]	First time	Reuse
HPW (g)	0.5	0.5	0.5	0.5
NOx adsorption (mg NOx/g HPW)	13.10	-	12.44	11.64
N_2 production (mL)	0.19	-	0.40	0.34
N_2 yield (%)	9.97	-	21.8	19.0

[*]Can not be reused. Less than 0.1 mg NO_x was adsorbed.

Mechanism. FTIR spectra of the HPW fresh sample, HPW after decomposition by rapid heating and HPW after constant-temperature heating, are shown in Figure 4. As shown in Figure 4a, the FTIR spectrum of fresh HPW shows strong vibrational bands at 793, 889, 984, and 1079 cm^{-1}. As reported previously [13], bands in the 700–1100 cm^{-1} region are characteristic of the Keggin structure. The intense band at 1079 cm^{-1} is assigned to the stretching mode of the P-O species, while the band at 984 cm^{-1} corresponds to W=O (terminal bonds). Furthermore, the vibrations at 889 cm^{-1} and 793 cm^{-1} corresponds to "inter" and "intra" W-O-W bridges. As shown in Figure 4b, the four vibrations characteristic of the Keggin structure disappears after rapid heating decomposition, indicating that the Keggin structure of HPW has disintegrated. Figure 4c shows the IR spectrum of HPW after constant-temperature heating decomposition, with the vibrations at 1080 cm^{-1} (P-O), 983 cm^{-1} (W=O), 887 cm^{-1} (W-Ob-W), and 799 cm^{-1} (W-Oc-W) being

similar to those observed for the fresh sample. The IR measurements thus confirm that the Keggin structure was preserved after constant-temperature heating decomposition.
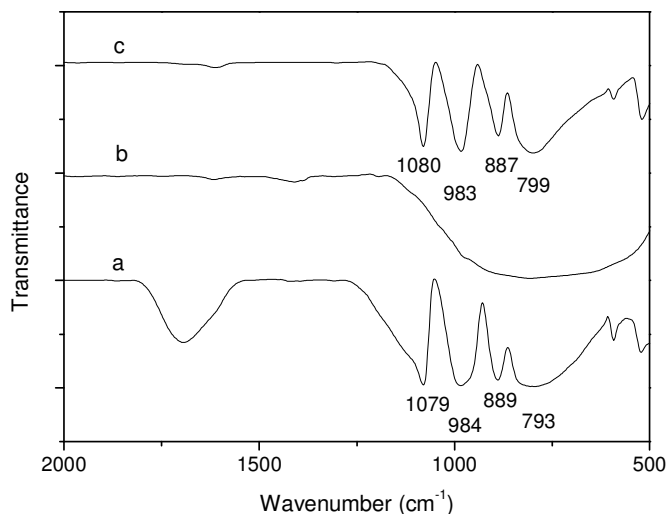

Figure 4. IR spectra of HPW: (a) fresh HPW; (b) after decomposition by rapid heating from 30 °C to 450 °C with a heating rate of 150 °C/min; (c) after decomposition by constant temperature heating at 450 °C.
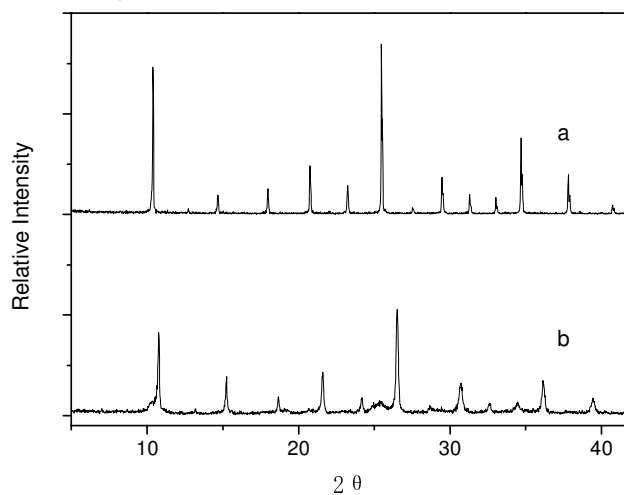

Figure 5. XRD diagrams of HPW: (a) fresh HPW; (b) after constant temperature heating decomposition at 450 °C.

The powder XRD patterns of HPW, before and after constant-temperature heating decomposition, shows the crystal structure of the sample has been preserved after decomposition (Figure 5). Compared with the fresh sample, the peak of the sample after decomposition shifts to higher diffraction angles, which was also observed by Yang [9] and

Belanger [14]. According to Bragg's law, lattice spacing is inversely proportional to θ, and the increase in 2θ indicates the lattice spacing of HPW after decomposition is reduced. The reduction in the lattice constant might be caused by substitution of the six coordinated water molecules in the Keggin unit by three NO molecules during adsorption, and the resultant loss of NO during subsequent decomposition. The results indicate that while the secondary structure of HPW is retained after constant-temperature heating decomposition, the lattice constant for the secondary structure is reduced due to the loss of crystal water.

CONCLUSIONS

To decompose NO_x on the polyacid HPW ($H_3PW_{12}O_{40}\cdot6H_2O$), two heating processes were employed, i.e. rapid heating from 30 °C to 450 °C at a rate of 150 °C/min, or constant-temperature heating at 450 °C. The following conclusions drawn from the experimental results demonstrate that constant-temperature heating is more effective for the decomposition of NO_x on HPW: (i) both rapid heating and constant-temperature heating can provide the high heating rate required for the NO_x decomposition process, with the highest heating rates approaching 150 °C/min; (ii) compared with rapid heating, constant-temperature heating results in an increased NO_x decomposition rate, mainly because it preserves the catalytic activity of HPW, with the N_2 conversion efficiency reaching 21.8%, which is more than twice that in the case of the rapid heating method; (iii) rapid heating causes the oven temperature to surpass the target temperature, hence destroying the structure of HPW and preventing reuse of the catalyst. Constant-temperature heating, however, overcomes these drawbacks, allowing effective reuse of the catalyst.

ACKNOWLEDGEMENTS

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