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PERFORMANCE EVALUATION OF SEVERAL SOLID HETEROPOLY COMPOUNDS AS FUNCTIONAL TRAPS FOR NOX REMOVAL

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Abstract

Several Keggin heteropoly acids/salts were evaluated concerning their activities in adsorbing NO_x from gas stream. All experiments were conducted in a fixed-bed reactor. The candidate heteropoly acids/salts examined comprise $H_4PVMo_{11}O_{40}$, $H_5PV_2Mo_{10}O_{40}$, $H_6PV_3Mo_9O_{40}$, $(NH_4)_3PW_{12}O_{40}$, $(NH_4)_3PMo_{12}O_{40}$, $K_3PW_{12}O_{40}$, $K_2HPW_{12}O_{40}$, $KH_2PW_{12}O_{40}$. Results showed that substitution of coordination atom Mo in the $[PMo_{12}O_{40}]^{3-}$ anion by one or more V atoms leads to only slight change in NO_x adsorption activity; however, it is for the first time that nano $(NH_4)_3PW_{12}O_{40}$ was found to have an up to 10.6% enhancement in NO_x adsorption efficiency in comparison with the same catalyst of normal particle size; substitution of H^+ in $H_3PW_{12}O_{40}$ by metal cation tends to lower the adsorption activity, regardless of the metal cations introduced. By IR analysis, NO was found to be adsorbed via interaction with the proton of HPW structure.

Keywords: nitric oxides; heteropoly compound; catalyst; adsorption; decomposition.

1. Introduction

Being a harmful impurity in atmospheric environment, nitric oxides (NO_x) have been confirmed to contribute to the formation of acid rain and photochemical smog, damage of the ozone layer, and hence constitute a series of health and environmental problems. Creation of NO_x from human activities lies mainly in two sources — one is stationary discharge from industrial processes involving the incineration of fossil fuels, the other is automotive emission. In the past decade, the global need of treatment of NO_x pollution has become more and more stringent.

Among numerous deNO_x methods developed to date, direct catalytic decomposition of NO_x to N_2 and O_2 has been recognized as the most attractive one, since it does not require the addition of any reductant, avoids the production of secondary pollutant, and employs simple and economical process [1]. However, this method still has not met the requirement of practical application due to the unsatisfactory catalysts activities and/or their deactivation by hot water steam and SO_2 in the working atmosphere. In view of such status quo, the present authors developed new catalysts system employing heteropoly compounds with good NO_x adsorption-decomposition activity as well as agreeable tolerance to hot water steam and SO_2 [2]. Reported herein are the new results of the performance of some heteropoly compounds, focusing on their NO_x adsorption capabilities.

2. Experimental

2.1 Test rig

The test rig used for evaluating the catalyst performance during adsorption- decomposition of NO_x is illustrated in Fig.1. Operation procedure can be found in literature [2]. The experimental conditions for NO_x adsorption were set as follows: feed gas NO concentration, C_{NO}=500ppm; amount of heteropoly compound (abbr. to HPC) uesd, W_{HPC}=0.1mmol; adsorption temperature, T=150°C; rate of feed gas flow, G_f=0.4L/min; O_2 concentration in the feed gas, O_2=5%. It should be noted that, when the adsorption of NO_x was finished, the fixed-bed reactor containing solid heteropoly compound catalyst was swept by switching the feed gas to Argon flow at 100 ml/min for 1 hour then heated following a temperature-programmed desorption (TPD) procedure at a ramping rate of 150 °C/min accompanied by online examination of the outlet gas components by GC-MS.

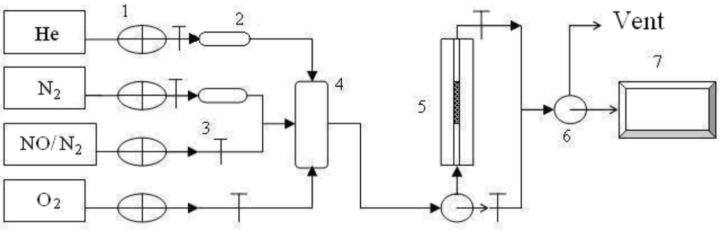

Figure 1. Test rig for the adsorption-decomposition of NO_x
1. mass flow controller; 2. moistener; 3. walve; 4. gas mixer; 5. fixed-bed reactor; 6. three-way valve; 7. NO_x analyzer

2.2 Chemicals

The Keggin heteropoly acids/salts used comprise $H_4PVMo_{11}O_{40}$, $H_5PV_2Mo_{10}O_{40}$, $H_6PV_3Mo_9O_{40}$, $(NH_4)_3PW_{12}O_{40}$, $(NH_4)_3PMo_{12}O_{40}$, $K_3PW_{12}O_{40}$, $K_2HPW_{12}O_{40}$, $KH_2PW_{12}O_{40}$. All these were prepared according to literature method [3].

3. Results and Discussion

The effects of NO_x adsorption by $H_4PVMo_{11}O_{40}$(HPVMo), $H_5PV_2Mo_{10}O_{40}$(HPV_2Mo) and $H_6PV_3Mo_9O_{40}$(HPV_3Mo) are shown in Fig. 1. Although adsorption efficiencies of 28%, 24% and 29% were observed for HPVMo, HPV_2Mo and HPV_3Mo respectively, however, it can be concluded in general that subjecting to substitution of V for Mo in $H_3PMo_{12}O_{40}$ structure no marked change is brought in NO_x adsorption activity.

Shown in Table 1 are the NO_x adsorption efficiencies obtained using $K_xH_{3-x}PW_{12}O_{40}$. Apparently, the efficiency of NO_x adsorption decreases with the increase of the substituted number of K^+, i.e. $K_1H_2PW_{12}O_{40}>K_2H_1PW_{12}O_{40}>K_3PW_{12}O_{40}$. This result indicates the principal contribution of Brønsted acid in the adsorption of NO_x.

Contrary to $K_xH_{3-x}PW_{12}O_{40}$, $(NH_4)_3PW_{12}O_{40}$ has much higher activity in NO_x adsorption than $H_3PW_{12}O_{40}$, the parent compound. Apparently, this is due to the substitution of NH_4^+ for H^+ in the HPW structure. The role of NH_4^+ lies in its reduction property which enables the direct conversion of NO_x to N_2 in one step. The replacement of H^+ by K^+ reduces the number of Brønsted acid sites, and hence decreases the coordination adsorption of NO_x. Furthermore, following the foregoing substitution with any cation from Ag^+, Pb^{2+} or Fe^{3+} for H^+ in the HPW structure, we found similar results. This implies that the number of Brønsted acid sites do play an important role in NO_x adsorption activity.

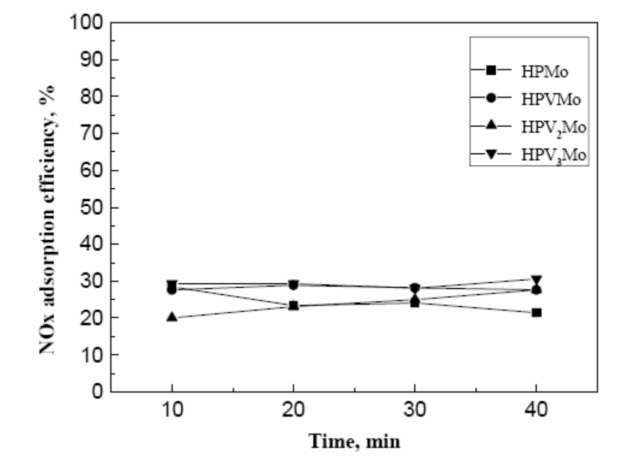

Figure 2. NO_x adsorption by vanadium addenda of $H_3PMo_{12}O_{40}$

Table 1. NO_x adsorption efficiencies on $K_xH_{3-x}PW_{12}O_{40}$ and $(NH_4)_3PW_{12}O_{40}$

Cat. Time/min	KH_2PW	K_2HPW	K_3PW	NH_4PW
10	60	45	44	79
30	72	50	41	79
45	72	51	41	76

The nano-effect of P-W heteropoly compound was observed for the first time, where $(NH_4)_3PW_{12}O_{40}$ in solid particles with a nano size of 40-80 nm was found to have NO_x adsorption efficiencies being up to 10.6% higher than that of normal size (Fig.3). Furthermore, the NO_x adsorption activity of $(NH_4)_3PMo_{12}O_{40}$ is superior to $(NH_4)_3PW_{12}O_{40}$.

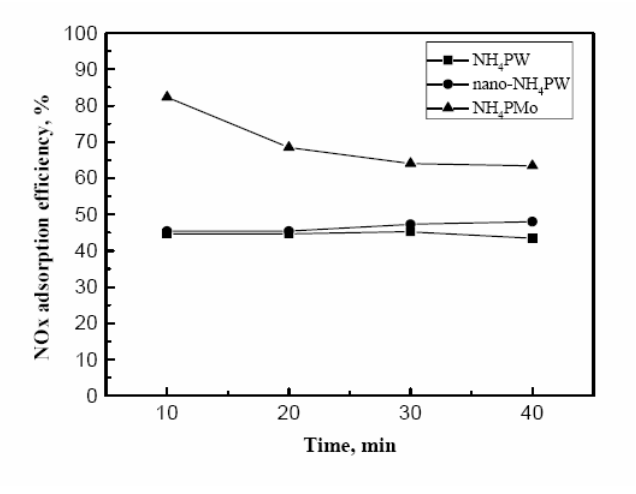

Fig. 3. NO_x adsorption by $(NH_4)_3PW_{12}O_{40}$ and $(NH_4)_3PMo_{12}O_{40}$

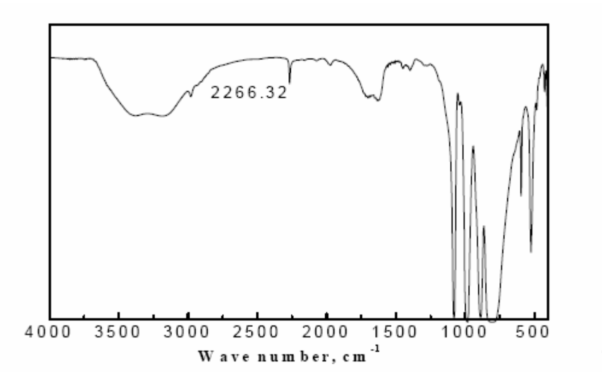

Fig. 4. IR spectrum of HPW after adsorbing NO_x

Under same conditions, we used the potassium salts of phosphotungstic acid and nano potassium phosphomolybdate for same purpose and found that the NO_x adsorption capability of them follows the order of $KH_2PW_{12}O_{40}$>$K_2HPW_{12}O_{40}$>$K_3PW_{12}O_{40}$>nano $K_3PMo_{12}O_{40}$. Among them, $KH_2PW_{12}O_{40}$ gives the highest NO_x adsorption efficiency of 72%; then comes $K_2HPW_{12}O_{40}$, with the corresponding value of 51%; and $K_3PW_{12}O_{40}$, 41%; nano $K_3PMo_{12}O_{40}$ shows its value of only 30%. These NO_x adsorption efficiency values all correspond to the asymptotic stages of the adsorption curves. Apparently, the adsorption performance of these heteropoly compounds increases with the number of proton they have, or, in another word, is proportional to their acidity. Nano effect doesn't contribute so much to NO_x adsorption in the case of $K_3PMo_{12}O_{40}$ as to make it surpass $K_3PW_{12}O_{40}$, owing to the lower acidity of phosphomolybdic acid in comparison with phosphotungstic acid. Furthermore, we examined the NO_x adsorption efficiency of $Pb_3PW_{12}O_{40}$, $Ag_3PW_{12}O_{40}$ and $FePW_{12}O_{40}$, and also proved the same rationale. In our results, we found that, any of these salts gives low adsorption efficiency. The corresponding data are: 43% for $Pb_3PW_{12}O_{40}$, 33% for $Ag_3PW_{12}O_{40}$, and 27% for $Ag_3PW_{12}O_{40}$.

The used $H_3PW_{12}O_{40}$ after NO_x adsorption were characterized by IR. A new bands can be found at 2266 cm^{-1} which can be assigned to the interaction of NO with the proton of the HPW structure (ca. 2266 cm^{-1}) [4].

Adsorption temperature has marked effect on NO_x adsorption on HPW, and the optimal adsorption temperature is around 200^oC (Fig. 4).

Subsequent to the process of NO_x adsorption in the foregoing reactor, decomposition of the adsorbed NO_x was conducted accompanied by online GC-MS detection using Helium as carrier gas. From the results, it can be estimated that about 30%~70% of the adsorbed NO_x decomposed into N_2 upon rapid heating at a ramping rate of 150^oC/min.

4. Conclusion

Substitution of coordination atom Mo in the $[PMo_{12}O_{40}]^{3-}$ anion by one or more V atoms leads to only slight change in NO_x adsorption activity; however, it is for the first time that nano $(NH_4)_3PW_{12}O_{40}$ was found to have an up to 10.6% enhancement in NO_x adsorption efficiency in comparison with the same catalyst of normal particle size; substitution of H^+ in $H_3PW_{12}O_{40}$ by metal cation tends to lower the adsorption activity, regardless of the metal cations introduced. By IR analysis, NO was found to be adsorbed via interaction with the proton of HPW structure. With the aid of GC-MS analysis, the process effectiveness for NO_x decomposition into N_2 was confirmed.

Acknowledgements

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