

# New Development in Nanoporous Composites: Novel Functional Materials for Capturing Nitrosamines in Airstreams

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The latest progresses of the series of research on the trapper of nitrosamines are reported in this paper, involving the attempts to elevate the selective adsorption of zeolites through enhancing adsorbent-adsorbate interaction, in order to prepare the new functional nanoporous materials with high efficiency to eliminate the carcinogenic pollutants in environment and to protect public health. Incorporation of metal oxide such as copper oxide in NaY accelerated adsorption of volatile nitrosamines and anthracene, and moreover, coating zirconia onto the zeolite could dramatically suppress the release of nitrogen oxides in the decomposition of *N*-nitrosopyrrolidine (NPYR) during temperature-programmed surface reaction (TPSR) process.

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## 1. INTRODUCTION

Developing new processes for chemical production and controlling the environment pollution are two main challenges faced by the chemists of the 21st century, and these are also the new applications of nanoporous functional materials. Apart from a number of novel catalysts and adsorbents designed and synthesized for chemical industry, many efforts have been done for the protection of environment that connects the life of people much closer. Among these extensive efforts to be undertaken, one of the new developing areas of study is the application of nanoporous functional materials such as zeolites, because zeolite has excellent thermal and chemical stability along with the unique shape selectivity and sieving effect. These inherent features enable the nanoporous materials to recognize, discriminate, and organize molecules with precisions that can be less than 0.1 nm [1], and a noteworthy example is the zeolite additive in cigarette to remove carcinogenic agents like nitrosamines because smoking is a global problem causing health hazard [2–5]. Nitrosamines are known to be toxicant chemical not only to cause poisoning some times, but also to induce cancer and tumor in almost all organs of experimental animals [6]. They are important contributors to the total burden of carcinogens resulting from tobacco, especially the tobacco smoke, since

the nitrosamines in tobacco products and tobacco smoke can be directly deposited into the blood following inhalation through smoking. Moreover, environmental tobacco smoke is one of the major contaminants of indoor air leading to considerable exposure for the nonsmoker through passive smoking. Thus, removal of carcinogenic compounds from environment is important for environment protection. Zeolites are the potential trapper of nitrosamines owing to their unique function of selective adsorption, and about 50–70% of nitrosamines in smoke can be eliminated [2, 4]. In early literature this function of zeolite was attributed to its catalysis, but detailed researches reveal the crucial role played by the selective adsorption of zeolite [7–12]. The extraordinary interaction for the N–NO functional group of nitrosamines enables zeolite to capture the carcinogenic compounds in the smoke that contains more than 4000 components; even the zeolite A is able to adsorb the volatile nitrosamines through an especial inserting model of adsorption [13, 14], in which the carcinogens adsorb in zeolite by inserting the N–NO functional group into the narrow channel.

To meet the requirement of reducing the nitrosamines level in the aeration system of tower where the flow rate of airstreams is very large and the concentration of nitrosamines relatively lower [15], however, new functional nanoporous materials with higher efficiency are sought. These novel

candidates should have stronger capability to selectively adsorb nitrosamines and, if possible, other carcinogenic compounds in airstreams. Recently our group tried to incorporate copper oxide on NaY zeolite through impregnation method, and successfully enhanced its ability of trapping volatile nitrosamines, say, about one time higher, in the smoke of Chinese Virginia-type cigarette [16–19]. Nonetheless, suspicions still exist on the modified zeolites concerning whether they can adsorb the bulky polycyclic aromatic hydrocarbons (PAHs), that is, another carcinogens, in airstreams. Besides, further study is required to explore the possibility of replacing copper oxide by other metal oxides for lower cost and higher environmental benignity of the nanoporous functional materials.

In most cases, the degradation of nitrosamines, catalyzed by the modified zeolites or mesoporous silica, releases gaseous nitrogen oxides NO<sub>x</sub> due to the rupture of N–NO band in the carcinogenic molecule, which, however, is not environmental benign anyway. Therefore, seeking another modifier to replace copper oxide for these porous adsorbents is another aim of the present paper, and the candidate should be able to obviously reduce the release of NO<sub>x</sub> during the catalytic decomposition of nitrosamines. Based on our foregoing investigation [20, 21], zirconia is chosen because of its weak acidity and weak basicity. Nitrosamines possess both weak acidity and weak basicity, too; therefore establishing a suitable chemical environment in the nanoporous adsorbent should be beneficial to promote the decomposition of the worst carcinogenic compounds. Nonetheless the reason why the zirconia-coated zeolites can reduce the release of NO<sub>x</sub> in the catalytic degradation of nitrosamines is still not understood, which spurs us to critically examine the property-function relations of zirconia embedded in zeolite, not only for deep understanding of the selective removal of nitrosamines, but also for seeking the new concept for creating novel functional nanoporous materials.

## 2. EXPERIMENTAL

Three volatile nitrosamines, the *N*-nitrosodimethylamine (NDMA), the *N*-nitrosopyrrolidine (NPYR), and the *N*-nitrosohexamethyleneimine (NHMI), were purchased from Sigma and dissolved in dichloromethane with volume ratio of 1 : 19, and stored at 273 K. Anthracene (Ant) was also obtained from Sigma and dissolved in cyclohexane with weight ratio of 0.18. Zeolite NaY, with Si/Al of 2.86 and a surface area of 766 m<sup>2</sup>·g<sup>-1</sup>, was purchased from Wenzhou catalyst factory (China). NaZSM-5 zeolite, with Si/Al ratio of 23, was provided by the catalysts factory of Nankai University (China). It possesses the surface area of 354 m<sup>2</sup>·g<sup>-1</sup> and the mean crystal size of 7 μm.

Copper was incorporated in the porous support using “drying impregnation”: 0.456 g Cu(NO<sub>3</sub>)<sub>2</sub> · 3H<sub>2</sub>O was dissolved in 40 ml H<sub>2</sub>O and 5 g NaY added; the mixture was stirred strongly and heated up to half dryness; then dried at 373 K overnight; finally the product was ground to

100 mesh and calcined at 773 K for 6 h in order to convert Cu(NO<sub>3</sub>)<sub>2</sub> to copper oxide. The resulting sample contained 3% (w/w) CuO and to be denoted as 3%CuO/NaY. Other samples were prepared in the same way and the concentration of aqueous solution was controlled to get different loadings of copper cations. Through similar process ZnO or Fe<sub>2</sub>O<sub>3</sub> was loaded on zeolites. The purity of carrier gases N<sub>2</sub> and H<sub>2</sub> was 99.99%, and all agents used were of AR grade. For the preparation of zirconia-modified zeolite, the guest oxide ZrO<sub>2</sub> (Toray Ltd., SA = 120 m<sup>2</sup>·g<sup>-1</sup>) was first ground along with NaY zeolite at a given weight ratio, then radiated in a microwave oven (2450 MHz, 850 W) for 20 minutes. The resulting materials were characterized by XRD, that carried out on an ARL XTRA diffractometer with Cu Kα radiation, and the XRD peak intensity ratio of ZrO<sub>2</sub> (111) to that of NaY (111) represented the proportion of the residual bulk zirconia in the sample. The static adsorption of *n*-hexane at 303 K was employed to characterize the pore volume of the nanoporous samples, in which the sample was evacuated at 673 K for 2 h then cooled to 303 K to contact with the adsorbate at the given pressure. XPS measurements on the VG ESCALab MK II instrument were performed using a 1253.6 eV Kα magnesium X-ray source, the energy scale of spectrometer was calibrated by setting the measured C1S binding energy to 284.6 eV. The concentration of each element was then calculated from the area of the corresponding peak, calibrated by using the relative sensitivity factor of Wagner.

Instantaneous adsorption of volatile nitrosamines is performed in a stainless steel microreactor whose one end inserts deeply into the injector port of Varian 3380 gas chromatograph (GC), while another end connects with the separation column in the GC. five mg samples, in 20–40 meshes, were filled in the reactor and sealed by glass wool to fix the position where the temperature could be accurately controlled by the injector port of GC. The sample was directly heated to the given temperature, without activation, in the flow of H<sub>2</sub> with a rate of 30 ml·min<sup>-1</sup>, and the nitrosamine solution was pulse injected with amounts of 2 μl each time. After being gasified in the injector, the nitrosamines were pushed by the carrier gas with a speed of 25 cm·s<sup>-1</sup> to pass through the zeolite bed layer then to the packed column, and the response at the column outlet was recorded by the GC with thermal conductivity detector. The rejection was repeated for several times over several hours to examine the capability of zeolite to capture the nitrosamines in gas stream. To avoid environment contamination, exhaust gas was treated by acid solution to destroy nitrosamines.

In the experiment of temperature-programmed surface reaction (TPSR), 20 mg sample was activated in N<sub>2</sub> at 773 K for 2 h. NPYR solution was injected in the sample at 423 K followed by purge of N<sub>2</sub> for 0.2 h, then the temperature of the sample was increased from 423 K to 773 K at the rate of 8 K·min<sup>-1</sup> and kept at 773 K for 0.5 h; the cracking products of nitrosamines were detected every 20 K by spectrophotometric method [5].

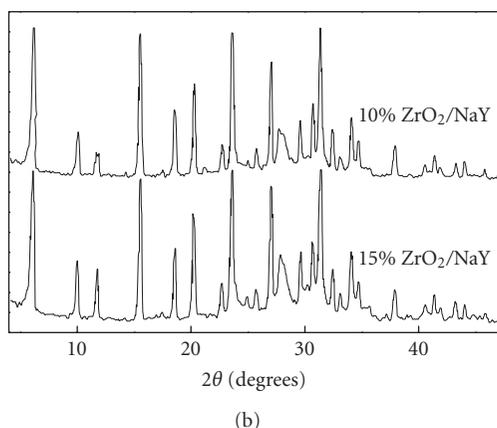
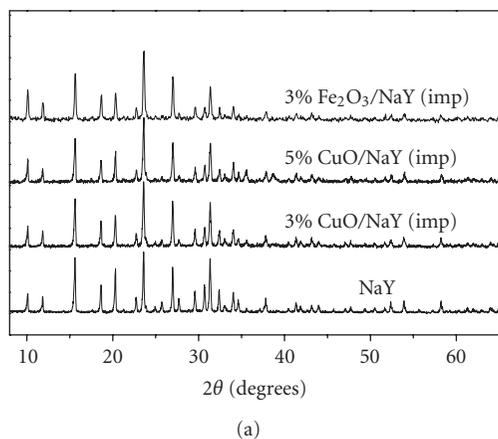


FIGURE 1: XRD patterns of transitional metal oxide-modified NaY samples.

### 3. RESULTS AND DISCUSSION

#### 3.1. Characterization of the zeolite modified with metal oxide

Figure 1(a) depicts the dispersion of metal oxides on zeolite NaY, and all of three samples incorporated copper oxide or ferric oxide show the identical XRD patterns to that of parent zeolite NaY. No extra phase is observed in the case of loading 3 wt.-% of copper oxide or ferric oxide on NaY, and increasing the loading amount of copper oxide to 5 wt.-% cannot create the crystal phase of the guest on the patterns of the composite, either. It appears that the impregnation process can well disperse the metal oxide-like copper oxide or ferric oxide in zeolite NaY provided the loading amount is about 3 wt.-%.

Well-dispersion of zirconia in zeolite NaY was also observed. Microwave radiation did not damage the pore structure of NaY zeolite under the experimental conditions we used here [22, 23]. After the mixture of NaY and zirconia was microwave-radiated, no characteristic XRD peak of zirconia emerged in the patterns with the  $2\theta$  value of  $28.1^\circ$ , and the composite exhibited the same XRD pat-

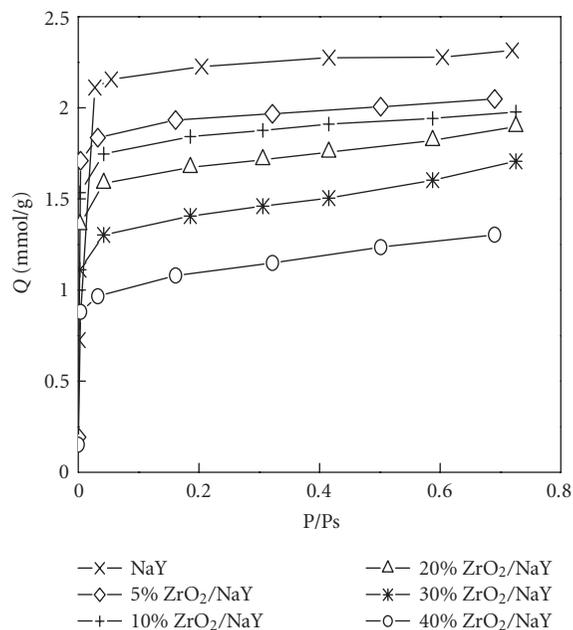


FIGURE 2: The isotherm of *n*-hexane adsorbed in zirconia-modified zeolite NaY at 303 K.

TABLE 1: Impact of loading zirconia on the adsorption of *n*-hexane in zeolite NaY ( $P/P_s = 0.7$ , at 303 K).

Loading amount (wt.-%)	0	5	10	20	30	40
Adsorption (mmol/g)	2.3	2.1	2.0	1.9	1.7	1.3
Decrease (%)	—	8.9	13.0	17.4	26.1	43.5

terns as that of zeolite NaY, even the loading amount reached 15 wt.-% (Figure 1(b)), since the spontaneous dispersion threshold of zirconia in the zeolite was 15 wt.-% [21]. However, adsorptive isotherm of *n*-hexane revealed the variation of the pore volume of the resulting composites. As is evident from Figure 2 and Table 1, the pore volume of zeolite NaY host, represented by the adsorption amount of *n*-hexane at 303 K, is gradually lowered owing to the occupation of the channel of zeolite by the guest oxide. Besides, the isotherm of 20%ZrO<sub>2</sub>/NaY sample became turned up as the  $P/P_s$  exceeded 0.4, and such trend was observed on the sample of 30%ZrO<sub>2</sub>/NaY and 40%ZrO<sub>2</sub>/NaY. Nonetheless, the adsorption isotherm of *n*-hexane on ZrO<sub>2</sub>/NaY sample still kept its original Langmuir type as that on zeolite NaY (Figure 2). This phenomenon demonstrates the existence of the uniform channel in the ZrO<sub>2</sub>/NaY composites, that is, the characteristic of zeolite and very important for selective adsorption or catalysis. In general the reduced pore volume of zeolites goes against their adsorption of nitrosamines [12, 14], consequently the sample loaded with the zirconia of more than 20 wt.-% will not be used for further experiments.

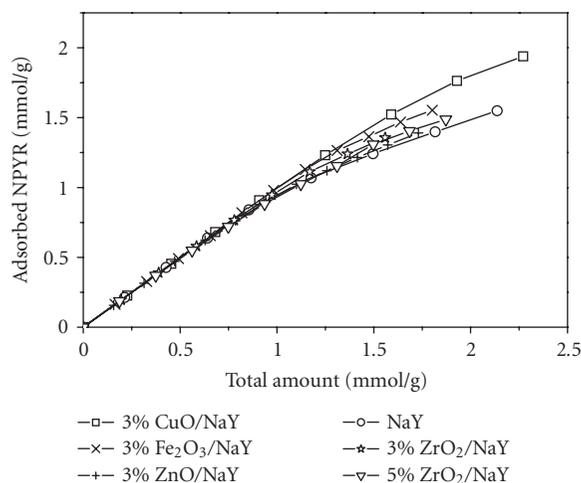


FIGURE 3: Adsorption of NPYR in zeolite NaY and metal oxide-modified NaY at 453 K.

### 3.2. The promoted adsorption capacity of zeolite for trapping nitrosamines in stream

Figure 3 illustrates the impact of loading 3 wt.-% transitional metal oxide on the capacity of zeolite NaY for instantaneous adsorbing NPYR at 453 K. It should be pointed out that the contact time between the adsorbent and the nitrosamines is very short in these tests, say, less than 0.1 second, which is similar to that in actual application of zeolites in aeration system. Both copper oxide and ferric oxide show an obvious promotion on zeolite NaY while a faint effect is found in the modification with zinc oxide. When the accumulated amount of NPYR reached  $1.00 \text{ mmol}\cdot\text{g}^{-1}$ , CuO/NaY or  $\text{Fe}_2\text{O}_3/\text{NaY}$  could adsorb 99.2% of the carcinogenic compound while ZnO/NaY or NaY adsorbed 93.8%. As the accumulated amount of NPYR increased to  $1.70 \text{ mmol}\cdot\text{g}^{-1}$ , ZnO/NaY exhibited a little larger adsorption capacity (81.0%) than the parent zeolite (78.5%). Promoted adsorption of nitrosamines in stream by zeolite is also observed on the samples of 3%ZrO<sub>2</sub>/NaY and 5%ZrO<sub>2</sub>/NaY, and they exhibit an enhanced adsorptive capacity slightly higher than both parent zeolite and zinc-modified NaY as demonstrated in Figure 3. Nitrosamines adsorbed in zeolite through the manner of inserting the N–NO group into the channel [9, 10, 12], which is accelerated by the strong interaction with the metal ions in the zeolite. Among the metal oxides used here, CuO appears to be the best one, however ferric oxide-modified sample possesses an excellent promotion function on the adsorptive ability of zeolite NaY, much close to that of copper-modified sample (Figure 3), which implies the possibility of replacing copper modifier by ferric oxide to promote the adsorptive capability of zeolite.

Figure 4 shows the promotion of CuO on the adsorption of NPYR in different zeolites. As the accumulated amount of NPYR rose from 0.5 to  $1.5 \text{ mmol}\cdot\text{g}^{-1}$ , CuO/NaY ad-

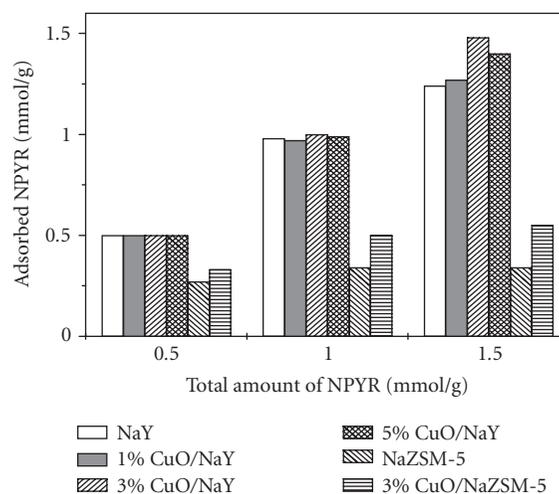
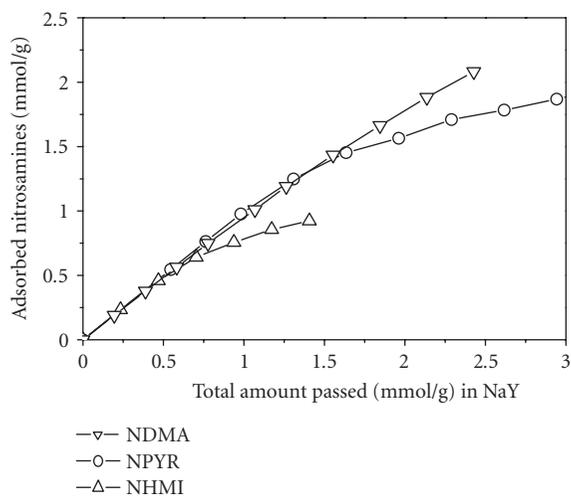


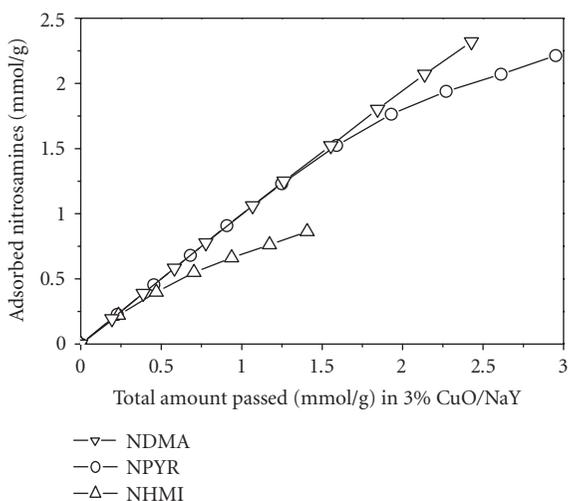
FIGURE 4: Amount of NPYR adsorbed on zeolites Y and ZSM-5 before and after loading copper oxide at 453 K.

sorbed more NPYR than NaY ( $1.24 \text{ mmol}\cdot\text{g}^{-1}$ ), and the highest capacity was observed on 3%CuO/NaY sample ( $1.48 \text{ mmol}\cdot\text{g}^{-1}$ ). Promotion of CuO became more obvious on NaZSM-5 zeolite, and the 3%CuO/NaZSM-5 adsorbed more NPYR ( $0.33 \text{ mmol}\cdot\text{g}^{-1}$ ) than the parent zeolite ( $0.27 \text{ mmol}\cdot\text{g}^{-1}$ ) even at the low accumulated amount of NPYR ( $0.5 \text{ mmol}\cdot\text{g}^{-1}$ ). This difference became larger when the accumulated amount of NPYR reached  $1.5 \text{ mmol}\cdot\text{g}^{-1}$ : the former adsorbed  $0.55 \text{ mmol}\cdot\text{g}^{-1}$  while the latter adsorbed  $0.34 \text{ mmol}\cdot\text{g}^{-1}$ . The adsorptive capability of NaZSM-5 is elevated about 60%.

Figure 5 depicts the impact of the molecular size on the adsorption of nitrosamines in the copper modification NaY zeolite. NDMA, NPYR, and NHMI have the molecular diameter of 0.45, 0.56, and 0.59 nm, respectively [12, 24], so that the adsorbed amount of three nitrosamines is diverse. For NaY when the accumulated amount of nitrosamines arrived  $1.25 \text{ mmol}\cdot\text{g}^{-1}$ , 70.5% of NHMI, 94.6% of NDMA, or NPYR could be adsorbed. In case  $2.40 \text{ mmol}\cdot\text{g}^{-1}$  of nitrosamines passed through the adsorbents, about 85.7% of NDMA and 72.0% of NPYR were adsorbed. No doubt the NDMA with the smallest molecular volume can be adsorbed in zeolite much more easily due to its fast diffusion inside the channel of adsorbent [7]. Same tendency was found on 3%CuO/NaY. When the accumulated amount reached  $1.25 \text{ mmol}\cdot\text{g}^{-1}$ , 64.1% of NHMI, 97.9% of NDMA, or NPYR could be adsorbed; while the amount rose to  $2.40 \text{ mmol}\cdot\text{g}^{-1}$ , 95.1% of NDMA and 82.9% of NPYR were adsorbed. It is conclusive that the difference between the adsorption of three volatile nitrosamines is magnified on the copper-modified zeolite: more NDMA or NPYR but less NHMI adsorbed on the sample of 3%CuO/NaY. That is to say, incorporation of copper oxide delicately modifies the channel of zeolite and made the shape selectivity increased which may be beneficial for the separation in environment protection.



(a)



(b)

FIGURE 5: Different nitrosamines adsorbed on (a) NaY and (b) 3%CuO/NaY at 453 K.

Figure 6 shows the adsorption of anthracene (Ant), one of polycyclic aromatic hydrocarbons that exists widely in environment such as smoke [25], on zeolite NaY. In case that the accumulated amount of Ant was  $30.0 \text{ mg} \cdot \text{g}^{-1}$ , 70.4% of the adsorbate could be trapped by NaY. For 3%CuO/NaY, the corresponding value was 94%, one third higher than that of the parent zeolite. As is evidenced from Figure 6, the sample of 3%CuO/NaY can capture more anthracene molecules than NaY zeolite in the instantaneous adsorption in which the contact time is less than 0.1 second. This result replies a new application of the copper-modified nanoporous adsorbent in protection of environment, and this functional material may be used to trap the polycyclic aromatic hydrocarbons (PAH) in aeration system of tower. It is the first time to find the promotion of CuO modification on the instantaneous adsorption of both nitrosamines and PAH in zeolite

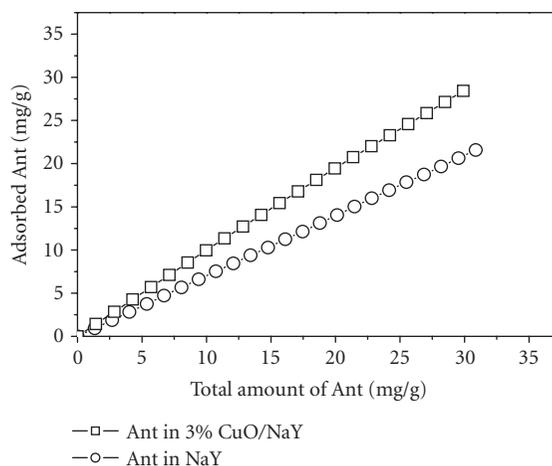


FIGURE 6: Anthracene (Ant) adsorbed on NaY and 3%CuO/NaY at 503 K.

NaY, but the mechanisms of the promotion may be different. Copper oxide attracts the N–NO group, through the interaction similar to that with NO<sub>x</sub> [26], to accelerate adsorption of nitrosamines in NaY. Anthracene consists of only C and H without N and O as well as N–NO group, so the copper nanoparticles embedded in NaY cannot induce it into the channel as that happens in the case of nitrosamines. Decoration of channel of the adsorbent may result in this promotion, since the copper oxide dispersed into the channel of NaY should reduce the actual pore size, even a little. Anthracene has a molecular size of 0.49 nm, smaller than the pore size of NaY (0.76 nm), so the delicately reducing of the pore size and/or the curvature of channel in the adsorbent will be helpful for anthracene because the confinement of channel is elevated and thus forms a stronger adsorbate-adsorbent interaction with the adsorbate. Judged on these results, it seems feasible to promote adsorption of both nitrosamines and PAH in airstreams by nanoporous materials like zeolite, through tailoring the pore structure and surface state by coating metal oxide on the porous host.

### 3.3. Suppressing the release of nitric oxygen in decomposition of nitrosamines on zeolite NaY

Figure 7 depicts the degradation of NPYR on zeolite NaY in the temperature-programmed surface reaction (TPSR) process. NPYR is a volatile nitrosamines consisting of five-membered ring and its degradation starts from the rupture of N–NO bond to release nitric oxygen product [27, 28]. Consequently, the detected nitric oxide and other nitrogen oxides, that result from the further reactions of the primary nitric oxide, represent the amount of nitrosamines to be degraded [5, 8]. The NPYR adsorbed in ZrO<sub>2</sub>/NaY began to degrade and liberate NO<sub>x</sub> at 473 K when nitrogen was used as the carrier gas, giving rise to a maximum concentration of NO<sub>x</sub> near 593 K on the sample of 5%ZrO<sub>2</sub>/NaY

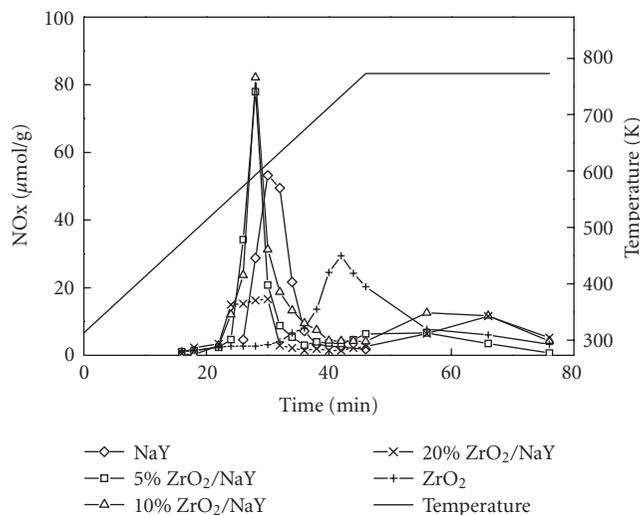


FIGURE 7: Impact of loading zirconia in zeolite NaY on the decomposition of NPYR.

and 10%ZrO<sub>2</sub>/NaY with the amount of 78 and 82  $\mu\text{mol}\cdot\text{g}^{-1}$ , respectively. When the reaction temperature was held at 773 K for 0.5 h, another unobvious desorption of nitrogen oxides appeared on 5%ZrO<sub>2</sub>/NaY with a relative low concentration of about 6.6  $\mu\text{mol}\cdot\text{g}^{-1}$ . This phenomenon became obvious in the sample of 10%ZrO<sub>2</sub>/NaY and the corresponding value increased to 11.8  $\mu\text{mol}\cdot\text{g}^{-1}$ . As a comparison, the maximum value of 53  $\mu\text{mol}\cdot\text{g}^{-1}$  emerged on parent zeolite NaY at 613 K, and no further desorption of NO<sub>x</sub> was detected during which the sample was held at 773 K (Figure 7). The unsupported zirconia itself could adsorb a considerable amount of nitrosamines and most of them seemed to be decomposed at around 733 K, giving rise to a maximum concentration of 29  $\mu\text{mol}\cdot\text{g}^{-1}$ . These nitrogen oxides continuously desorbed when the sample was held at 773 K, similar to that observed on those ZrO<sub>2</sub>/NaY composites. On the basis of these results, it is very likely that desorption of NO<sub>x</sub> from the zirconia-modified zeolite NaY at 773 K in the TPSR process of NPYR originates from the inherent feature of zirconia. The unsupported zirconia is a porous material with a pore volume of 0.23  $\text{ml}\cdot\text{g}^{-1}$  and an average pore size of 6.66 nm [29]. Under the test conditions used here, the detected total amount of NO<sub>x</sub> in the decomposition of NPYR over zirconia (0.164  $\text{mmol}\cdot\text{g}^{-1}$ ) is smaller than that over zeolite NaY (0.179  $\text{mmol}\cdot\text{g}^{-1}$ ). However, the surface area of zirconia (120  $\text{m}^2\cdot\text{g}^{-1}$ ) is one sixth of that of NaY (766  $\text{m}^2\cdot\text{g}^{-1}$ ), so that the oxide probably possesses a comparable capability to NaY for trapping the volatile nitrosamine if judged on the efficiency per square meter surface area of the sample. Thus, coating zirconia on zeolite NaY through microwave-radiation considerably enhanced the efficiency for catalytic degradation of NPYR, and more NPYR were degraded at lower temperature than that on the parent zeolite. Moreover, desorption of NO<sub>x</sub> at high temperature in TPSR process appeared on these nanoporous composites as the characteristic

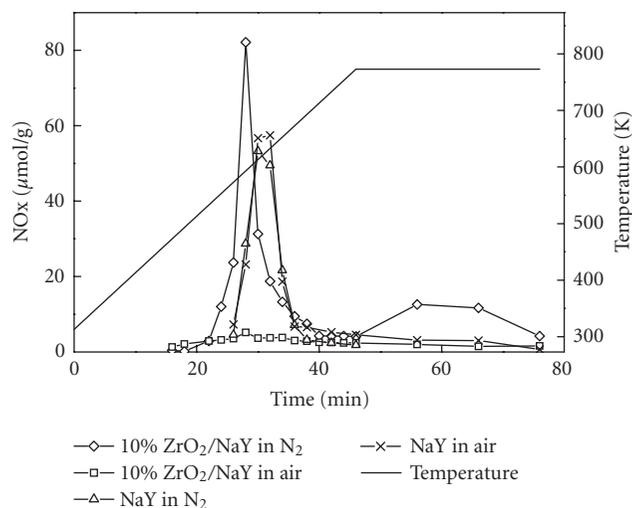


FIGURE 8: TPSR of NPYR over zeolite NaY in different carrier gases.

of zirconia. Incorporation of more zirconia in NaY did not cause further promotion on the catalytic activity of the composite, the detected amount of NO<sub>x</sub> from the sample of 20%ZrO<sub>2</sub>/NaY dramatically declined, as demonstrated in Figure 7, at the same time the desorption of NO<sub>x</sub> at 773 K was still obvious.

When the carrier gas in TPSR process was changed from nitrogen to air, however, the maximum concentration of NO<sub>x</sub> released from the sample of 10%ZrO<sub>2</sub>/NaY was abruptly decreased to below 10  $\mu\text{mol}/\text{g}$  under the same conditions (Figure 8). Similar phenomenon was also observed on 5%ZrO<sub>2</sub>/NaY sample, and these results were confirmed by several repeated experiments. In contrary, only slightly variation was found on the desorption of NO<sub>x</sub> on NaY zeolite alone, and the concentration of NO<sub>x</sub> at 633 K increased from 49.4 to 54.5  $\mu\text{mol}\cdot\text{g}^{-1}$  instead, as demonstrated in Figure 8. One may argue that these differences result from the different amounts of NPYR adsorbed on 10%ZrO<sub>2</sub>/NaY in the different carrier gases, this argument however, is not justified by experiments. Two samples adsorbed NPYR in nitrogen or air prior to the TG-DTA tests, and the similar weight loss (about 8%) emerged accompanied by the same exothermic peak of NPYR decomposition that appeared around 473 K and continued to 873 K [21], indicating the similar amount of NPYR adsorbed on ZrO<sub>2</sub>/NaY regardless of the kind of carrier gas. To check if the most of adsorbed NPYR escaped from the nanoporous material, the nitrosamine content of the exhaust gas was analyzed. However, only less than 1% of the adsorbed NPYR was found to desorb from 10%ZrO<sub>2</sub>/NaY sample during the TPSR process, which confirms that most of the nitrosamines are degraded. This is rationalized by proposing that the products distribution of NPYR degradation is changed in the sample of 10%ZrO<sub>2</sub>/NaY when the carrier gas becomes air. That is to say, the release of nitrogen oxides is suppressed though the reason is not known yet.

TABLE 2: XPS analysis of 10%ZrO<sub>2</sub>/NaY sample.

Sample	Before activation		After activation in nitrogen	
	Atom %	Binding energy (eV)	Atom %	Binding energy (eV)
O1s	66.74	531.61	63.0	531.72
Zr3d	3.20	181.65	3.66	181.54
Na1s	7.65	1072.15	8.68	1072.15
Si2p	16.80	102.35	18.68	102.45
Al2p	5.59	73.95	5.97	74.25

Figure 9 shows the degradation of NPYR on the unsupported zirconia in different carrier gases. Unlike the sample activated and tested in nitrogen on which a lot of nitrogen oxides formed as aforementioned, only a few the gaseous NO<sub>x</sub> products were detected on the bare oxide when the sample was activated and tested in air, and the total amount of NO<sub>x</sub> lowered to 0.009 mmol·g<sup>-1</sup>, about 5% of that on the former (0.164 mmol·g<sup>-1</sup>). If the zirconia was directly used in the TPSR test in air without activation, the analyzed amount of nitrogen oxides (0.133 mmol·g<sup>-1</sup>) was still smaller than that in nitrogen (0.164 mmol·g<sup>-1</sup>), however dramatically higher than that activated in air (0.009 mmol·g<sup>-1</sup>). Accordingly, activation of zirconia in nitrogen seems to elevate its ability to catalyze the formation of nitrogen oxides in decomposition of NPYR. Table 2 lists the XPS analysis results of the zirconia-modified zeolite NaY before and after activation in nitrogen, and both samples possess the same value of binding energy within the experimental error. This excludes the possibility that activation changes the electrovalent state of zirconium in the composite. Although the surface composition of the sample is slightly changed, say, the concentration of sodium cation increases from 7.65% to 8.68%, which cannot be used to account for the different catalytic properties of the composite activated in different carrier gases.

Figure 10 illustrates the XRD patterns of bare zirconia activated in air or nitrogen. Two crystal phases monoclinic baddeleyite and tetragonal form exist in the zirconia, and the former has intensity weaker than the latter. The peaks at 2θ of 30.2°, 50.2°, and 60.2° in the XRD patterns are the characteristic of tetragonal form [30]. After the sample was activated at 773 K in air, the XRD peak of monoclinic baddeleyite with 2θ value of 28.3° [29] became stronger but the tetragonal form was still the main phase. By contrary, activation at 773 K in nitrogen made the monoclinic baddeleyite to be the primary phase while the peak with 2θ value of 31.3° grew dramatically along with that of 28.3°. Drawing on these results, the impact of carrier gas in activation is further proposed. Tetragonal crystal in zirconia is metastable phase [29, 31], and activation in nitrogen seems to promote its conversion. Nonetheless, the available data do not allow a discussion of the possible mechanism involved, and further study is thus required to explore the relationship between the phase conversion extent of zirconia and the suppression of nitrogen oxides in TPSR test.

Although the reason why the zirconia-modified zeolite NaY can strangely suppress the release of NO<sub>x</sub> during the decomposition of nitrosamines is still enigmatic; discovery

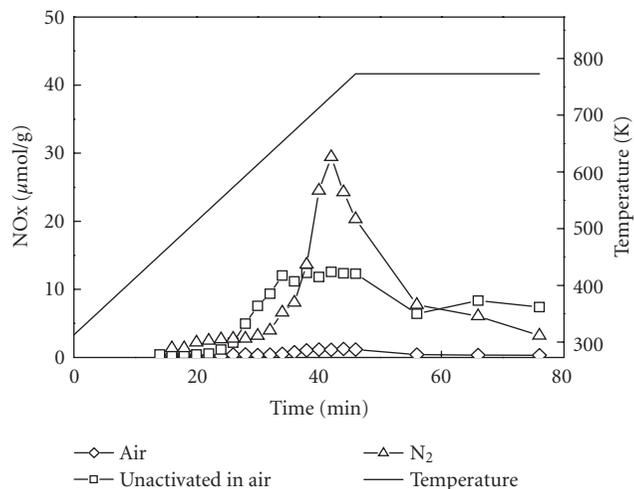


FIGURE 9: Decomposition of NPYR on the unsupported zirconia in different carrier gases.

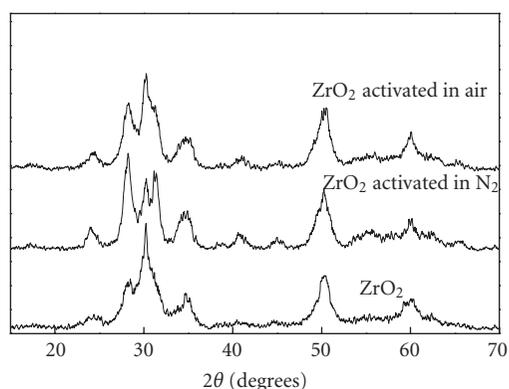


FIGURE 10: XRD patterns of zirconia activated in different atmospheres.

of this unwanted feature of the nanoporous adsorbent gives a clue for design and synthesis of novel functional materials that can act as killer traps for the carcinogenic pollutants in environment, for which choosing suitable guest components and incorporating them inside the pore of nanoporous host will be crucial.

#### 4. CONCLUSION

Incorporation of transitional metal oxide such as copper oxide in zeolite can efficiently elevate the capability of the host to selectively trap the volatile nitrosamines in airstreams, opening the new application of the nanoporous materials into the aeration system of tower.

Ferric oxide-modified zeolite NaY exhibits a high ability of adsorbing volatile nitrosamines in stream, too, proving the possibility to replace copper oxide for modification of zeolites.

Coating zirconia on NaY through microwave-radiation can enhance the capability of the zeolite to capture nitrosamines in stream, too, and more importantly it dramatically suppress the release of nitrogen oxides when the decomposition of nitrosamine is performed in air, which may relate with the crystal phase of the guest but further investigation is needed.

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