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Removal of volatile nitrosamines with copper modified zeolites†

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Copper oxide was used to modify zeolite NaY, NaZSM-5, NaA and mesoporous siliceous SBA-15, in order to strengthen their ability to remove volatile nitrosamines. Selective adsorption, temperature programmed surface reaction (TPSR) and FTIR along with TG-MS methods were employed to study the impact of copper modification on the ability of zeolite to adsorb and catalytically degrade nitrosamines. Due to the special interaction between the –N–N=O group of nitrosamines and the copper in the zeolite, nitrosamines can be very easily trapped by the copper modified zeolite, and this precedes or is the first step that leads to the catalytic reaction. Moreover, modification of copper oxide enabled the zeolite to degrade nitrosamines such as *N*-nitrosopyrrolidine (NPYR) at lower temperatures. It is practical to use the copper modified zeolites to treat mainstream smoke or add them to tobacco, reducing further the levels of nitrosamines in cigarette smoke compared with using the zeolite alone.

1. Introduction

The pollution caused by smoking cigarettes has become a global problem. Cigarette smoke contains various toxic species and among them nitrosamines are the most active carcinogenic compounds constituting a serious health risk, hence reducing the carcinogens in smoke becomes a challenge faced by chemists in the new century. Apart from the tobacco-specific nitrosamines (TSNA) presented in smoke, volatile nitrosamines (VNA) are also found in the vapor or semi-volatile phase of the mainstream inhaled by the smoker.[1] Nowadays most efforts have been directed towards the removal of TSNA, while the elimination of volatile nitrosamines in cigarette smoke is still ignored, although many volatile nitrosamine species such as *N*-nitrosodimethylamine (NDMA) and *N*-nitrosopyrrolidine (NPYR) are carcinogenic. On the other hand, volatile nitrosamines are difficult to remove from smoke owing to their volatility. NaY zeolite showed a higher capacity to adsorb volatile nitrosamines than NaZSM-5 and NaA,[2] due to its larger pore size and pore volume, but adding NaY catalysts at 4% (w/w) in the blend cigarette reduced *N*-nitrosodimethylamine (NDMA) in the mainstream by only 5–10% while 30–70% of tobacco-specific nitrosamines was eliminated.[3] With enormous pore apertures larger than 2 nm, ordered mesoporous materials like SBA-15 and MCM-48 were more active than zeolite NaY for degradation of the bulky *N′*-nitrosonornicotine (NNN), but their capacity for selectively adsorbing NPYR or NDMA was smaller.[4] Therefore, a novel material is sought to eliminate the volatile nitrosamines and another new strategy to change the pore structure should be adopted besides choosing the pore structure of the adsorbent. Monocyclic nitrosamines such as NPYR are known to adopt a planar structure because of the large rotational barriers around the N–NO bond,[5] and they may adsorb on zeolite by means of the –N–N=O groups inserting into the zeolite channels,[4] which is similar to the way in which NO*x* is adsorbed on to zeolite. Therefore, all of the methods helpful to adsorb nitrous oxide on zeolite should be beneficial for the adsorption of nitrosamines. Since incorporation of copper species in zeolite was helpful for adsorption and decomposition of nitrous oxide,[6–10] we designed and prepared some new functional materials to remove nitrosamines through a simple impregnation method, resulting in improved efficiency for selective adsorption of volatile nitrosamines.

Concerning smoking, two distinct types of burning take place with the cigarette:[1] puffing and natural smolder between puffs. During puffing the highest solid-phase temperature 1183 K occurs at the burning zone[11] and air is drawn into the cigarette through the burning zone to form the mainstream. In the interval between puffs the temperature at the burning zone cools from over 1183 K to 873 K within 1 second[11] while a natural convection flow of air around the burning zone sustains burning and forms sidestream smoke. Since pyro-synthetic formation of volatile nitrosamines occurs at the relatively low temperatures encountered during the interpuff smolder periods, sidestream smoke contains more volatile nitrosamines than mainstream,[1] but cigarette filters are inherently ineffective in removing harmful constituents in the sidestream. Consequently zeolite additives are developed: they are placed directly in the cigarette and activated when the hot zone in burning cigarette approaches them.[3] Zeolite can catalytically cleave the N–N=O functional groups of nitrosamines and destroys their carcinogenic ability, forming degradation fragments such as NO*x* and amines that are the common components of smoke.[12,13] This cigarette catalyst (we denote it as CatCig) is extraordinary, because its catalysis is one-off and after this the used zeolite will remain in the cigarette ash. A new problem arises from Virginia type cigarettes that contain less tobacco specific nitrosamines than blend cigarettes: the zeolite additive can remove 25–32% of them in smoke,[13] much less than that in blend cigarettes,[3] therefore the activity of CatCig needs to be enhanced. Zirconia and magnesia and zinc oxide had been coated on zeolite NaY,[14] enabling the composites to degrade more volatile nitrosamines like NPYR at lower temperatures.[15] However, adsorption of nitrosamines on the zeolite host was hindered at the same time, which limited the application of these composites. To overcome these shortcomings copper is selected to modify the zeolite because Cu is an essential element in enhancing the zeolite properties of chemisorption toward NO.[16] Besides, Cu-ZSM-5 represents, until now, the most promising catalyst for NO decomposition,[16] which is important for CatCig since cleavage of the N–N=O bond

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is crucial in nitrosamine degradation.[2,4] For elimination of nitrosamines in sidestream smoke, desorption of the carcinogen from the zeolite at high temperatures should be prevented,[17] which is also the aim of incorporating copper in the zeolite. To evaluate the impact of copper on the catalytic performance of the zeolite, degradation of NPYR is employed as a probe reaction and TG-MS used together with spectrophotometric method to analyze the products.

2. Experimental

NDMA, NPYR and *N*-nitrosohexamethyleneimine (NHMI) were purchased from Sigma and dissolved in methylene chloride at a volume ratio of 1 : 19.[17] Zeolite NaY, NaZSM-5 and NaA were commercially available powders; mesoporous silica SBA-15 was prepared in our laboratory according to recipes in the literature.[18] The properties of the materials are shown in Table 1.

Copper was incorporated into the porous support using 'drying impregnation':[19] 0.456 g $Cu(NO_3)_2{\cdot}3H_2O$ was dissolved in 40 ml H_2O and 5 g NaY added, the mixture was stirred vigorously and heated at 353 K (80 °C) for 30 min to drive off the solvent water to give a soft solid, 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 $Cu(NO_3)_2$ to copper oxide. The resulting sample contained 3% (w/w) CuO and is denoted as 3%CuO/NaY. Other samples were prepared in the same way and the concentration of aqueous solution controlled to get different loadings of copper cations. In order to survey the influence of the preparative method on the dispersion of copper species, the mixture of CuO and NaY zeolite was first ground, then calcined at 773 K to obtain the sample denoted as 3%CuO/NaY(cal), or irradiated in a microwave oven[20] to get the 3%CuO/NaY(mw) sample. XRD, BET[21] and XPS techniques[22] were employed to characterize the obtained sample. The purity of carrier gases N_2 and H_2 was 99.99%, and all agents used were of AR grade.

Adsorption of volatile nitrosamines was performed in a stainless steel micro-reactor, of 3 mm diameter and 150 mm length, of which one end was inserted deeply into the injector port of a Varian 3380 gas chromatograph (GC) and the other end connected with a separation column (10% Carbowax 20M + 5% KOH of 3 mm diameter and 3000 mm length) in the GC. A 5 mg powder sample was placed in the reactor and sealed with glass wool to fix the position where the temperature could be accurately controlled by the injector port of the GC. The sample was directly heated to the given temperature, without activation, in a flow of H_2 of 30 ml min^{-1}, and the nitrosamine standard solution was pulse injected with amounts of 2 μl each time. Gaseous effluent was analyzed by the TCD (thermal conductivity detector) of the gas chromatograph, and the decrement in the ratio of solute to solvent utilized to calculate the adsorbed amount.[4] IR tests were carried out in a Bruker 22 FT-IR spectrometer by use of an *in situ* cell;[23] typically the spectrometer operated at 4 cm^{-1} resolution collecting 40 scans in a single-beam mode. The sample disc (15 mg cm^{-2}) was activated in N_2 at 773 K for 2 h then brought into contact with NPYR at 453 K.

To evaluate the effect of zeolite for removing volatile nitrosamines in mainstream, 16 Virginia type cigarettes with a tar value of 15 mg per cigarette and a nicotine value of 1.2 mg per cigarette were conditioned at 295 K and 60% relative humidity for 48 h. They were machine-smoked under the standard ISO machine smoking regime of one 35 ml puff of 2 s duration taken every minute.[24] The mainstream smoke first passed through the adsorption column of 0.5 g zeolite, 20–40 mesh and inactivated, then passed through a citrate–phosphate buffer solution of pH 4.5 including 20 mM ascorbic acid to absorb the residual nitrosamines in the smoke. The amount of nitrosamines in the buffer was determined by the improved spectrophotometric method whose data reproducibility and analytical repeatability has been given previously.[17] The used zeolite adsorbent was put into action for successive TPD experiments, placed in a glass micro-reactor and purged with N_2, heated from room temperature to 773 K at a rate of 10 K min^{-1}. The desorbed nitrosamines were absorbed by the citrate–phosphate buffer solution and analyzed by spectrophotometric methods.[17]

In order to check the effect of copper modified zeolite on the elimination of nitrosamines in the smoldering smoke, the test cigarette samples containing 3% (w/w) of zeolite were hand-rolled, without filter tips, in the way reported by Meier and Siegmann.[3] 0.75 g finely cut tobacco was weighted in for each cigarette, both for the reference and the test cigarette containing the zeolite. 3% (w/w) of the copper modified zeolite powder, finer than 200 mesh, was added to the latter and mixed thoroughly with tobacco until the mix looked perfectly uniform. 4 cigarettes were naturally smoldered in the glass-made chamber designed by Caldwell,[25] while the rate of airflow was kept at 1 L min^{-1} and the smoke was collected to measure the mean content of nitrosamines. Each sample cigarette was smoldered within 20 minutes and the smoke was pulled through 60 ml citrate–phosphate buffer including 20 mM ascorbic acid to absorb nitrosamines.[13] The buffer solution was extracted with methylene chloride then the combined organic fractions were dried over a bed of anhydrous sodium sulfate and concentrated to a final volume of 25 mL; finally the mean amount of nitrosamines was determined as stated above.[17]

Temperature programmed surface reaction (TPSR) experiments were performed in the manner reported previously.[15] In catalytic reaction, 40 mg sample, of 20–40 mesh, was activated at 773 K in N_2 then cooled down to a given temperature. NPYR solution was pulse injected on to the sample with an amount of 10 μl each time. The formed NO*x* was detected and represented the amount of nitrosamines decomposed.[2] For the TG-MS test performed on a Netzsch STA449C instrument, the sample was first activated at 773 K, cooled and allowed to adsorb NPYR at 313 K. After being purged by a flow of He (99.999%), the sample was heated to 823 K at a rate of 20 K min^{-1}.

Table 1 Relevant parameters of the zeolites and molecular sieves

Sample	Si/Al	Pore size/ nm	Surface area/m^2 g^{-1}	Pore volume/ cm^3 g^{-1}
NaA	1.0	0.40	800	0.28
NaZSM-5	23.5	0.54 × 0.56	354	0.11
NaY	2.86	0.74	859	0.38
3%CuO/NaY	—	—	770	0.32
3%CuO/NaY(mw)	—	—	770	0.34
3%CuO/NaY(cal)	—	—	778	0.35
SBA-15	—	8.5	918	1.18
3%CuO/SBA-15	—	9.2	816	1.11
5%CuO/SBA-15	—	9.2	706	1.04

3. Results and discussion

Fig. 1 illustrates the XRD patterns of CuO/NaY samples with different loading levels. 1%CuO/NaY and 3%CuO/NaY samples showed identical XRD patterns with the parent zeolite on which no crystalline phase of CuO was found. Incorporation of copper on NaY lowered the surface area of the zeolite, accompanied by a decrease of micro-pore volume (Table 1), indicating that these moieties were located inside the channel of the zeolite. As the amount of CuO increased to 5 wt%, the XRD peak of the guest emerged near 2θ of 36° and 38°, and their intensity increased as the loading amount of CuO

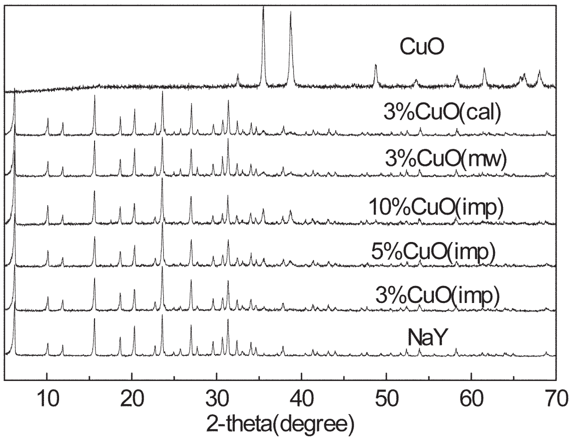

Fig. 1 XRD patterns of zeolite NaY incorporated with different amount of copper oxides.

was raised to 10 wt%. Meanwhile, the XRD peak intensity of NaY zeolite decreased slightly, meaning that most of the modifier was still located in the channels of the zeolite.[26] The efficiency of CuO dispersion on the NaY zeolite by three preparation methods is also compared in Fig. 1. All CuO/NaY samples prepared by the different methods possessed smaller surface areas and micropore volumes than NaY zeolite itself (Table 1). Although CuO of 3% (w/w) could be well dispersed on NaY by impregnation, fewer guests were dispersed on the host by microwave radiation or calcination, and the CuO peak of the residual phase could be distinguished in the XRD patterns of the composite (Fig. 1), though 3 wt% is usually a too small an amount to be checked using XRD techniques. For this difference in dispersion of copper, only the impregnated samples were used in following tests. To see if the high temperature can cause the sintering of copper on the Cu loaded zeolites, both the used 3%CuO/NaY and 5%CuO/NaY samples, after adsorption of cigarette smoke and heating at 773 K for 2 h, were detected by XRD, but no change was observed (the patterns are not shown), which excludes the possibility of time dependent sintering on the Cu loaded zeolites.

Loading 3 wt% CuO on NaZSM-5 and NaA zeolite did not change their XRD patterns. This means that the spontaneous dispersion threshold of CuO on zeolite is above 3 wt%.[27]. Table 1 also shows the influence of CuO loading on the textural properties of mesoporous silica. As the amount of CuO increased, the surface area and the pore volume of the host progressively decreased. Only the pore size slightly increased, consistent with that reported by Konya *et al.*[28] The color of the zeolite changed from white to brown by incorporation of copper, and after calcination it occasionally turned to gray, which was beneficial for the application as cigarette additives because the color was close to that of Flue-cured tobacco.

3.1 Trapping volatile nitrosamines by copper modified zeolites

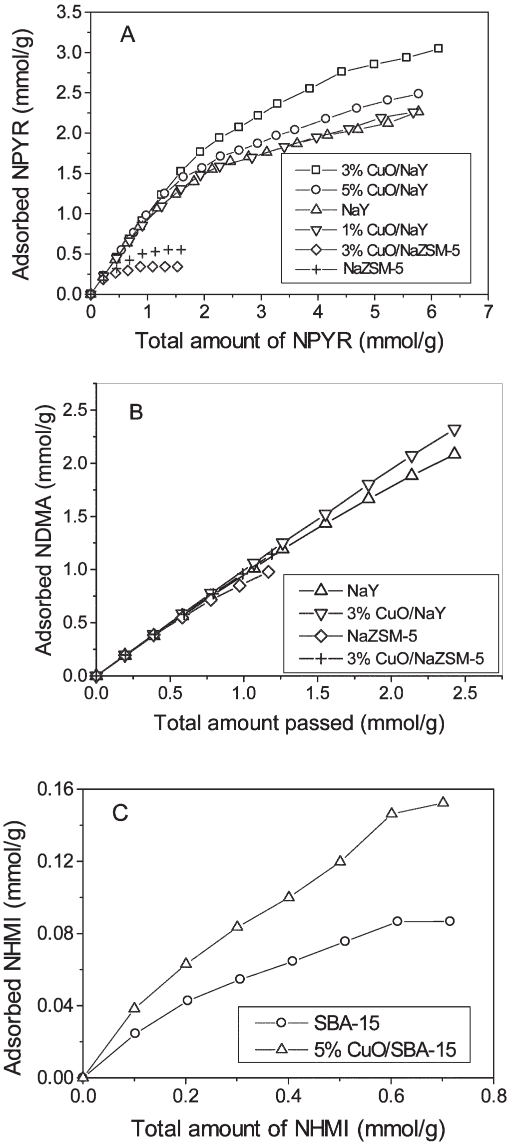

Fig. 2 Influence of loading copper on the selective adsorption of NPYR (upper) and NDMA (middle) over zeolite NaY and NaZSM-5, and NHMI (lower) on SBA-15 at 453 K.

Fig. 2A shows the influence of loading CuO on the capacity of zeolite NaY for selective adsorption of NPYR; 3 wt% was proven to be the best amount of loading. More NPYR can be selectively adsorbed on the 3%CuO/NaY sample without interference from organic solvents in comparison with the parent zeolite, though the surface area of the former was smaller than the latter. When the total amount of NPYR passed reached 3.0 mmol g^{-1}, 75.0% of the carcinogenic compound could be adsorbed by 3%CuO/NaY while 56.8% adsorbed on NaY. When 5.60 mmoles of NPYR passed through the adsorbents, about half was adsorbed on the former whereas two-fifths were adsorbed by the latter. Further increase of the amount of CuO loaded on zeolite NaY caused no further increase in the adsorption of NPYR, because it partly blocks the channel. Promotion by copper was also observed in the selective adsorption of NDMA, the typical volatile nitrosamine with the smallest molecular size. Zeolite NaZSM-5 is known to adsorb less NDMA than NaY under the same conditions,[2,17,29] due to the smaller pore volume and pore size as well as the smaller surface area (Table 1), as discussed previously in detail.[17,29] However, loading 3 wt% of CuO on NaZSM-5 made this difference disappear (Fig. 2B), indicating a new way to promote the adsorption of zeolite for volatile nitrosamines through chemical modification. As further proof of this inference, 3%CuO/NaY sample adsorbs more NDMA than NaY zeolite (Fig. 2B); moreover, a 5%CuO/SBA-15 sample adsorbed more NHMI than SBA-15 under the same conditions as illustrated in Fig. 2C. For instance, a quarter of the adsorbates were adsorbed on the former at a total amount of 0.40 mmol g^{-1} while 15.7% adsorbs on the latter. The difference increases as the total amount of NHMI reaches 0.70 mmol g^{-1}: 21.7% of it can be adsorbed on the former but only 12.1% adsorbs on the latter. Under the same conditions only trace amounts of nitrosamines were adsorbed on bulk CuO, for example 0.03 mmol g^{-1} at a total amount of 0.9 mmol NPYR, less than one-thirtieth of zeolite NaY. When the pore size of adsorbent is a close match to that of the adsorbate, however, modification of zeolite with copper cannot increase, and sometimes decreases, the adsorption of nitrosamines, because the copper species partially blocks the channel and hinders the adsorption. For instance, the molecular diameter of NPYR (0.56 nm)[2] is critical to the pore size of zeolite NaZSM-5, so loading CuO on NaZSM-5 decreased its selective adsorption capacity for NPYR (Fig. 2A).

Fig. 3A illustrates the difference spectra of NPYR adsorbed on zeolite NaY and CuO/NaY. This is the first reported IR spectrum of nitrosamines adsorbed on zeolite. 1458, 1371 and 1306 cm^{-1} bands were observed on the spectrum of NPYR adsorbed on zeolite NaY, similar to that of $\nu_3(NO_2)$ (ν_3 = 1470–1450 cm^{-1}), nitro species[30] and C–N vibration reported in the standard spectrum of NDMA. However, different IR bands appeared in the spectra of NPYR adsorbed on CuO/NaY. The band at 2212 cm^{-1} could be assigned to the isolated nitrosonium ion. However, in salts the frequency would be shift to around 2165 cm^{-1}. The 2134 cm^{-1}band might result from NO_2^+ species located on copper ions or NO_2 adsorbed on Cu^{2+} ion.[31] As the loading amount of CuO increased to 5 wt%, the band centered at 1616 cm^{-1} which originates from the adsorbed NO_2^- reached its maximum.[32] Besides the N=O vibration band around 1454 cm^{-1}, a 1422 cm^{-1} band originating from a nitrito complex[33] was also observed, accompanied by weak bands at 1383 cm^{-1}, which is one of the characteristic bands of pyrrolidine (PYR), and 1322 cm^{-1}, whose assignment is not clear yet. Through the comparison of spectrum *d* with *a*–*c* it is clear that NPYR adsorbed on the CuO/NaY samples in fact has undergone a different interaction with the adsorbent and therefore probably degraded at 453 K to form the fragments including nitrogen oxides and PYR. To confirm this assumption, PYR was also adsorbed on both zeolite NaY and 3%CuO/NaY under the same conditions. However, the spectra obtained were almost the same as those demonstrated in Fig. 3A. Both NPYR and PYR molecules contain a five-membered ring, and the only difference is that the former has a –N–N=O functional group while the latter has a –N–H group. That means, the –N–N=O functional group of nitrosamines has a strong interaction with the copper species dispersed on zeolite NaY so that the carcinogenic compounds can be very easily selectively adsorbed and decomposed on the CuO/NaY sample. Thus, modifying the zeolites with metal species like copper oxides will elevate the efficiency for trapping nitrosamines, especial for removal of volatile nitrosamines in cigarette smoke.

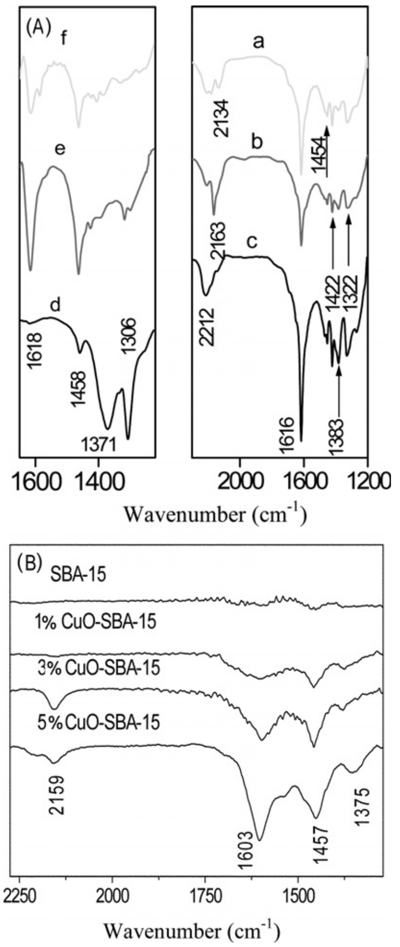

Fig. 3 (A) FT-IR spectra of NPYR adsorbed on (a) 1%CuO/NaY, (b) 3%CuO/NaY, (c) 5%CuO/NaY and (d) NaY zeolite, and PYR adsorbed on (e) NaY zeolite and (f) 3%CuO/NaY sample at 453 K. (B) Influence of loading copper on the adsorption of NHMI on SBA-15 samples at 493 K.

Fig. 3B shows the difference spectra of NHMI adsorbed on ordered mesoporous material SBA-15 and CuO/SBA-15. Only a few nitrosamines were adsorbed on SBA-15 at 493 K, resulting in a weak band near 1457 cm^{-1} assigned to the N=O vibration. Incorporation of copper strengthens the adsorption of NHMI on SBA-15 and the intensity of the 1457 cm^{-1} band obviously increased as the loading amount of CuO increased from 1% to 5%. In addition, the nitro species band at 1375 cm^{-1},[30] the 1603 cm^{-1} band from adsorbed NO_2^-[32] and the 2159 cm^{-1} band assigned to the isolated nitrosonium ion appeared in the spectra, and their intensities kept increasing as the amount of the copper guest increased. Clearly incorporation of copper was helpful for adsorption of nitrosamines on SBA-15.

Fig. 4 illustrates the treatment downstream of the cigarette, representing removal of nitrosamines in the cigarette mainstream, by use of zeolite NaY. Although the mainstream smoke passes through the cigarette filter and the Cambridge pad of the smoking machine, there still is a considerable amount of nitrosamines, 2.36 nmol per cigarette, in the smoke though the absolute quantity depends on the type and brand of the cigarette. Adsorption by the zeolite eliminated about half of the nitrosamines and the residual content was lowered to 1.24 nmol per cigarette. Modification with copper obviously increased the efficiency of NaY for removing volatile nitrosamines as seen in Fig. 4. The residual nitrosamines in the citrate–phosphate buffer solution decreased to 1.04, 0.72 and 0.85 nmol per cigarette, as the mainstream smoke passed through the sample of 1%CuO/NaY, 3%CuO/NaY and 5%CuO/NaY respectively. This means that about 56%, 69% and 64% of nitrosamines are removed. To confirm the existence of the nitrosamines trapped in the composite, the used 3%CuO/NaY adsorbent was examined by XPS

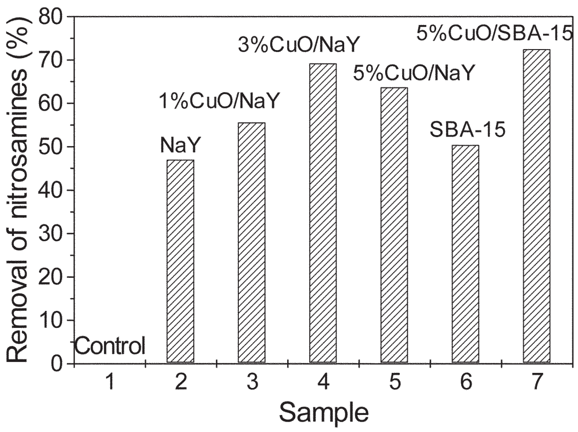

Fig. 4 Removal of nitrosamines in mainstream cigarette smoke by use of zeolite modified with CuO.

spectroscopy[22,34] and about 2.65% N-containing species were detected on the surface whereas no N1s signal is observed on fresh sample. Besides, more than 100 nmol g^{-1} of nitrosamines are released from the sample in a TPD process from 373 K to 773 K, providing further proof of the adsorption.

Concerning the nitrosamines detected in the TPD process, the strange thing is that its amount usually approaches, sometimes exceeds, the trapped volatile nitrosamines. One reason is, as we suggested, the trapped amount of nitrosamines (that calculated from the absorbed concentration in buffer solution) differs from that actually adsorbed by the zeolite. Another possible reason is the thermal synthesis of nitrosamines by the amines and nitrogen oxides co-adsorbed in the zeolite, though the zeolite did show any prominent catalytic activity in such a reaction.[17] Since it is impossible to determine whether the released nitrosamines are the original ones desorbed from the trapper or new ones thermally synthesized on the zeolite, the available data do not allow a discussion of their possible source and further study is desirable. At present time, two conclusions can be safely made. The first is that this does not affect the application of zeolite in cigarette filters as an adsorbent, because desorption of nitrosamines on zeolite usually occurs above 425 K[17] whereas the temperature of the filter is below 373 K, and consequently no such desorption happens on the filter containing zeolite. The second is that incorporation of copper on zeolite suppresses nitrosamine desorption from the used adsorbent. 1%CuO/NaY and 3%CuO/NaY filtered more volatile nitrosamines than zeolite NaY in mainstream cigarette smoke (Fig. 4), but a similar amount of, if not less, nitrosamines desorbed in the subsequent TPD process.

Incorporating copper oxide also makes the siliceous SBA-15 much more efficient in adsorbing nitrosamines. 72% of the nitrosamines in mainstream smoke could be removed by the sample of 5%CuO/SBA-15 whereas about half is eliminated by SBA-15. Since the pore size of SBA-15 is enormous in comparison with volatile nitrosamines, the copper species incorporated cannot significantly reduce the pore size of the adsorbent to create optimized adsorbate–adsorbent interaction as is often observed in zeolites. The enhanced ability in selective adsorption of volatile nitrosamines can only result from some effect between the nitrosamines and copper. That means that some materials located in the zeolite will attract the –N–N=O functional group of nitrosamines so that the adsorption can thus be accelerated, though the mechanism still needs to be explored in detail.

Selective adsorption of carcinogenic compounds is a key step for removing pollutants from the environment, which precedes or is the first step that leads to the catalytic reaction. Thus, increasing the selectivity of adsorbent materials is highly desirable. Compared with adjusting pore structures of adsorbents, it is low-cost and timesaving to change the surface properties of zeolites and mesoporous materials by using chemical modification, in order to increase the adsorbate–adsorbent interaction resulting in novel trapper materials for protecting public health and life.

3.2 Degradation of nitrosamines on copper modified zeolite

Table 2 demonstrates the impact of incorporating copper on the catalytic degradation of NPYR over zeolites in a temperature programmed surface reaction (TPSR). TPSR is a common method for assessing the activity of catalysts, whose principle is similar to TPD: NPYR molecules are adsorbed on the surface of the zeolite at ambient temperature, then catalytically degraded at elevated temperatures characterized by desorption of nitrogen oxide fragments. The more active the site is, the lower the temperature at which degradation would occur. The total amount of NOx product reflects the number of active centers in the zeolite while the $T_{\max}$, a temperature at which the maximum concentration of NOx appeared, indicates the activity of the active centers.[2,4] NaY zeolite could degrade 308.27 μmol g^{-1} of NPYR with a $T_{\max}$ around 573 K. Introducing 1 wt% CuO indeed enhanced the catalytic activity to about 8% while loading 3 wt% made the activity further increase to about 12%. In the latter case the $T_{\max}$ was decreased to 553 K, implying more NPYR was decomposed at lower temperature. 5%CuO/NaY exhibited the best performance: it degraded 33% of the NPYR which exceeded that on the parent zeolite. Further loading more copper did not create a higher activity on the zeolite; on the contrary the NOx detected on 10%CuO/NaY was lower than that on 5%CuO/NaY.

Table 2 TPSR results of NPYR on copper modified zeolite

Sample	NOx/μmol g^{-1}	$T_{\max}$ for NO desorption/K
NaY	308.27	573
1%CuO/NaY	334.21	573
3%CuO/NaY	344.28	553
5%CuO/NaY	410.82	553
10%CuO/NaY	378.12	553
NaZSM-5	30.56	633
3%CuO/NaZSM-5	91.96	633
NaA	1.90	593
3%CuO/NaA	7.57	593

There was less NOx detected on zeolite NaZSM-5 or NaA (Table 2), because of the lack of metal ions[17] or the limitations of small pore size.[2] However, loading CuO on these zeolites dramatically enhanced their catalytic activity. The amount of NOx detected on 3%CuO/NaZSM-5 was three times that on NaZSM-5 while four times as much NOx formed on 3%CuO/NaA compared with NaA zeolite alone. However, their $T_{\max}$ was unchanged which differs from CuO/NaY catalysts. In our opinion, this difference originates from the different function of the CuO guest location in different types of zeolite. All guests were highly dispersed in these zeolites loaded with 3 wt% of CuO, no matter whether they were located inside or outside the channel, as proven by XRD results. NaY zeolite possesses a large pore size relative to the NPYR molecular diameter, and occupation of these ultra-fine particles (often referred to as nanoparticles) in the channel did not reduce the pore size to an amount too constrictive for the adsorption of NPYR. Therefore the adsorbate could enter the channel as usual and undergo interaction with copper species in the special geometric space provided by the zeolite. Because of the affinity of copper for the –N–N=O group of nitrosamines and the zeolite catalysis, the NPYR molecule can thus be decomposed at lower temperatures, although the details of the catalytic mechanism cannot be deduced yet. Those copper species located outside the channel should make a contribution to the TPSR of NPYR, but it is minor because the external surface is too small compared with the large surface of the zeolite and most of the guest is located inside the channels. For zeolites NaZSM-5 and NaA, the situation is totally different. Loading CuO made the ZSM-5 channels too narrow for NPYR to enter so its adsorption was hence suppressed and most of the nitrosamine might participate in the degradation on the external surface, probably in the entrance of the pores. Of course the copper species located outside the channels catalyze this. Thus, although more NPYR molecules could be catalytically degraded and form gaseous NOx as detected in the TPSR experiments, the $T_{\max}$ in the desorption of NOx was kept unchanged probably due to the lack of zeolite catalysis. Based on these results, it is very likely that incorporated copper species cannot have their optimal catalysis until they are located in a suitable microenvironment provided by the zeolite host, especially the right geometric space for adsorbate–adsorbent optimal interactions.

Fig. 5A shows the desorption profile of NO*x* released from the NaY sample loaded with different amounts of CuO. NPYR began to decompose near 453 K on all of the CuO/NaY samples, whereas it was around 523 K on the parent zeolite NaY,[22] which indicates the acceleration by copper of the degradation of nitrosamines in zeolite. Similar acceleration has been observed on acidic HZSM-5 zeolite where NDMA began to degrade at 513 K, but at 553 K on NaZSM-5,[15,17] and this has been attributed to the function of protons to form hydrogen bonds with the N atoms of amino-groups in nitrosamines.[35] Judged on the profile of NO*x* desorption, it is conclusive that loading amounts of CuO between 3 wt% and 5 wt% are suitable for zeolite NaY to enhance degradation of NPYR, and 3 wt% will be preferable considering the cost of catalysts. The products of nitrosamine degradation on zeolites are very complicated: several nitrogen oxides such as NO_2, NO and N_2O exist along with the analogous amines and their pyrolytic fragments.[12] One of the reasons is that nitrosamines can produce NO through homolytic cleavage of the N–NO bond or form NO^+ through heterolytic cleavage of the relevant bond.[35] Most of the nitrogen oxide products can be divided into two groups according to the valence of the nitrogen element and NO_2 can be directly determined by use of spectrophotometric methods.[17] Fig. 5B illustrates the impact of loading CuO on the formation of NO_2 over NaY zeolite. NO_2 was released from zeolite NaY above 513 K and became the predominant product in the TPSR of NPYR with a maximum around 573 K, whereas it was detected on modified zeolite near 473 K, indicating the promotion by copper of formation of NO_2 on zeolite. The detected NO_2 remained constant on CuO/NaY composites as the loading of CuO was raised from 1% to 5% (w/w), but the T_{max} of NO_2 desorption shifted from 573 K to 553 K. Nitrosamines were considered to be a stable pool of NO[36] because of their degradation manner on zeolite through a cleavage of the N–NO bond, yet the released NO could be converted to NO_2 by the zeolite catalyst immediately.[33] Incorporation of copper in zeolite can accelerate the conversion, since Cu enhances the chemisorption of NO on zeolite, and the adsorption capacity of NO on CuZSM-5 is 40% more than that of the parent material.[16] Cu loaded ZSM-5 was intrinsically much more reactive than H- or NaH forms of ZSM-5, in which oxygen rapidly consumes Cu adsorbed NO to produce adsorbed NO_2 and nitrites and nitrates.[32] However, further addition of CuO on NaY made NO_2 desorption decline remarkably in the TPSR process, and two reasons could be tentatively used to explain this phenomenon. One is the dispersion state of the copper guest in the zeolite which must change as the loading amount increases to 10 wt% because a CuO phase emerged in the XRD test. Aggregation of CuO particles could not preserve the catalytic properties of ultrafine ones. As seen in Fig. 5B, only trace amounts of NO_2 were produced on the unsupported CuO. Another reason is the obstruction of the copper guest in the channels of the zeolite, which may hinder the formation of NO_2. Although the mechanism of NO_2 formation in degradation of nitrosamines on zeolites is not clear yet, this reaction seems to occur preferentially in wider channels and/or bigger cavities of the zeolite. 7 μmol g^{-1} of NO_2 was detected on NaZSM-5 in the TPSR process of NPYR, and loading 3% (w/w) of CuO suppressed two-thirds of the product (Fig. 6B). Only trace amounts of NO_2 formed on NaA and incorporation of copper did not increase its production, either. In contrast, much more NO_2 was formed on zeolite NaX itself under the same reaction conditions. Such close relation between NO_2 formation and space demand limits the loading amount of copper in zeolite NaY for removal of nitrosamines, because the reactants need to adsorb in the zeolite prior to degradation and moreover, aggregation of copper species unavoidably block the channels of the host. On zeolites with small pore size, nitrosamines may still adsorb by inserting the –N–N=O groups in the channels,[4] but the efficiency is

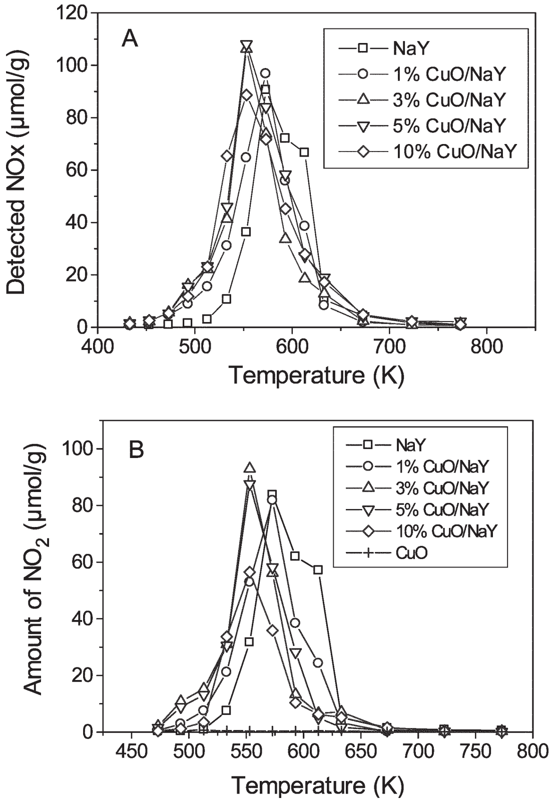

Fig. 5 Profile of NO*x* (upper) and NO_2 (lower) released in the TPSR process of NPYR on zeolite NaY loaded with different amounts of CuO.

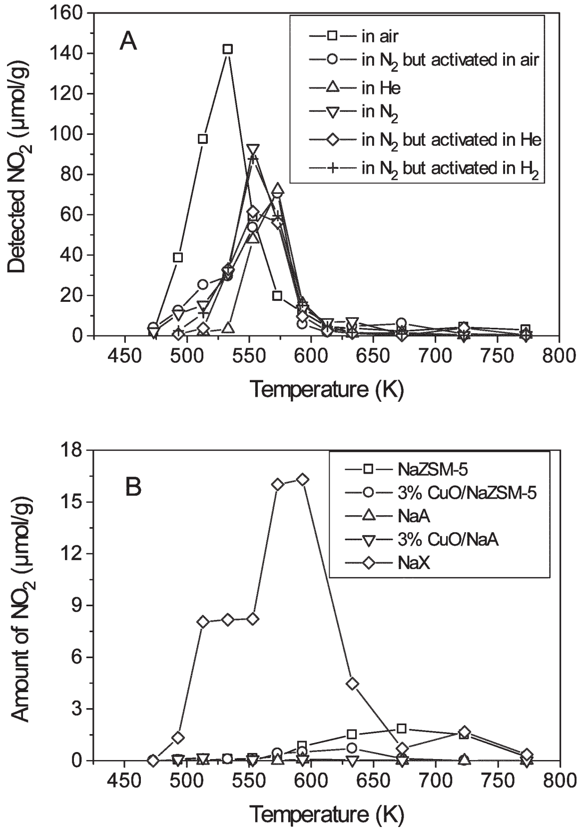

Fig. 6 Profile of NO_2 desorbed from (upper) 3%CuO/NaY in different carrier gases or (lower) from different zeolites in TPSR of NPYR in nitrogen.

undoubtedly lowered, so that only a little NO_2 formed on NaA zeolite.

To pursue the research on NO_2 formation further, the 3%CuO/NaY sample was activated in a different atmosphere from that used for the TPSR of NPYR in a different carrier gas and Fig. 6A shows the results. It is clear that the existence of air accelerated the formation of NO_2 in the degradation of nitrosamines, because NO was easily oxidized therefore the T_{max} shifted to lower temperature. However, if the sample was activated in air but the reaction performed in nitrogen, about half this amount of NO_2 formed. Existence of residual air adsorbed in the zeolite did not promote the production of NO_2. Activation or reaction in helium made the amount of NO_2 decrease further, leading to a variation of product distribution in nitrosamine degradation. Analysis of GC-MS revealed the formation of nitrogen: a strong MS signal of N_2 ($m/z = 28$ and $m/z = 14$) was observed.[13] It should not be unusual because of the function of copper dispersed on zeolite to decompose NO.[6,16] Activation in H_2 had a similar impact to that activated in air, however, some other nitrogen oxides were detected near 393 K, indicating the excellent catalytic activity of the sample in degrading nitrosamines at low temperature. According to the report of Sachtler and his co-workers,[37] this feature was related to the facile oxidization of Cu^0 active species in the zeolite by the reactant. From these results it is very likely that most of the NO_2 may be produced by disproportionation of NO fragments that occurs in the cavities of the zeolite but the valence of copper has a minor, if any, impact on the reaction. Of course NO_2 can result from the oxidation of NO fragments with oxygen in the gaseous phase, but it is not the main path when the reaction is performed in nitrogen. NO_2 can also be formed in the decomposition of NO, however, this seems not to be the main route because of two reasons. The first is that NO_2 formation is suppressed on CuO/NaZSM-5 whereas copper modified ZSM-5 zeolite represents the most promising catalyst for NO decomposition.[16] That means that the formation of NO_2 in the degradation of nitrosamines needs a larger space than the usual NO decomposition, probably due to the existence of adsorbed nitrosamines and other fragments in the channels. The second reason is that Cu^+ and Cu^{2+} ions in zeolites act as adsorption and/or reaction sites for the decomposition of NO[16] but activation of CuO/NaY in a different atmosphere to change the valence of copper did not significantly affect the formation of NO_2.

To survey the promotion of copper on the catalytic activity of zeolite for the degradation of volatile nitrosamines, decomposition of NPYR was carried out on the copper modified zeolite NaY at 423 K and Fig. 7 shows the results of the impulse reaction. Zeolite NaY exhibited a faint activity at the relatively low temperature and it became inactive at the 3rd and 4th injections. Modification with CuO dramatically increased the activity of the zeolite and a fifty times higher concentration of NOx was produced on the sample of 3%CuO/NaY at the 1st injection. However, its activity declined badly as the time of reaction was prolonged. Lowering the reaction temperature to 413 K suppressed NPYR decomposition on 3%CuO/NaY, but its activity was still superior to that of NaY itself. The true reason for the deactivation of zeolite in NPYR decomposition is not yet clear, probably resulting from the occupation of fragments like amines on the active sites to hinder the succeeding reaction. However, such deactivation does not cause serious influence on CatCig because CatCig is only used as a one-off. When the cigarette is lit, a burning zone is formed at the end of the tobacco rod. Tobacco is heated, causing moisture and volatile materials to distil out of it, and its components to thermally decompose (pyrolysis), both resulting in the generation of volatile gases and leaving a residual, carbonized char.[1] At this point the CatCig can be activated and begins to adsorb the nitrosamines and to catalyze them decompose before the carcinogenic compounds escape toward the gaseous phase. After the char reacts readily with oxygen in air, producing combustion gases to form smoke and leaving the inorganic content of the tobacco as ash,[1] the used CatCig finishes its work and is thus mixed in the ash. As far as a piece of tobacco concerned, the heating, pyrolysis and combustion of it is relatively fast, no matter whether in a puffing or natural smoldering process, since the whole cigarette can be smoked within 10 min under the standard ISO machine smoking regime.[24] So, the activation, adsorption and/or catalysis processes are performed on a particle of CatCig within a short time, hence there are no stability and regeneration demands for CatCig; on the contrary the cheap cost and high initial activity are indeed rather important.

Owing to the limitations of the spectrophotometric method, nitrogen oxides were detected while other products could not be determined in both TPSR and impulse reaction of NPYR. Therefore, TG-MS techniques were employed to monitor the products formed during TPSR experiments on the NaY zeolite before and after loading CuO. From the TG-MS results and relevant literature,[38,39] it is found that the products of NPYR degraded on NaY zeolite contain NO ($m/z = 30$), 1*H*-pyrrole ($m/z = 67, 68$) and 2*H*-pyrrole ($m/z = 68, 69$), 1-methyl-1*H*-pyrrole ($m/z = 79, 81$) *etc.* N_2O ($m/z = 44$) and pyrrole ($m/z = 42, 43, 70, 71$) were also observed among the products formed on 3%CuO/NaY sample. Besides, the desorbed NPYR ($m/z = 100$) in the TPSR process from 430 K to 580 K was 1.67% in comparison with those degraded to NO (Fig. 8). However, this proportion was significantly reduced to one third on the sample of 3%CuO/NaY. That is to say, copper modified zeolite indeed catalytically decomposes, instead of desorbing, nitrosamines at high temperatures, which is crucial in reducing environmental pollution. Another significant

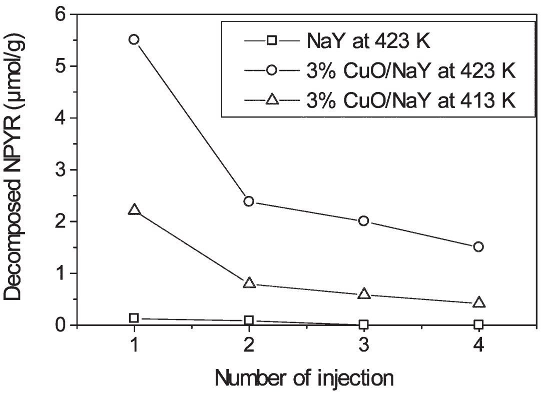

Fig. 7 Decomposition of NPYR on copper modified zeolite NaY.

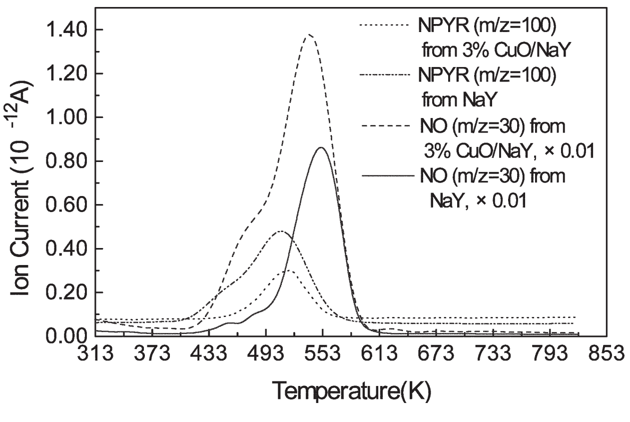

Fig. 8 TG-MS spectrum of NPYR and NO desorbed from zeolite NaY and 3%CuO/NaY sample that adsorbed NPYR and was heated in TPSR process.

difference between the two samples is the temperature at which the maximum concentration of product NO appeared. On the sample of 3%CuO/NaY it was near 540 K, but on zeolite NaY it emerged around 560 K. No doubt the activity of CuO modified zeolite is increased for catalytic degradation of nitrosamines, hence the carcinogen can be decomposed at lower temperature.

It should point out that the conditions for TPSR do not match those that are operative in the ultimate application of zeolites in cigarettes. The carrier gas is pure nitrogen in the TPSR test while the fresh tobacco smoke contains more than a thousand chemicals; the temperature of the zeolite rises at a constant rate in TPSR, while in smoking, the zeolite in the hot zone underwent heating, combustion and cooling within a minute. In TPSR the zeolite is in contact with pure nitrosamines but in the ultimate application zeolites are mixed with fine tobacco fibers. So, although TPSR tests can give much valuable information on the copper modified zeolite, actual application of the composites in cigarettes is necessary to assess their ultimate use. Fig. 9 shows the influence of loading CuO on the elimination of nitrosamines by zeolites in the smoldering smoke of cigarette. 36.2 nmole per cigarette of nitrosamines were determined in the smoke, less than the value reported by Meier and Siegamann in sidestream smoke,[3] because the Virginia type cigarettes used here contain fewer nitrosamines. Adding zeolite NaY could reduce 13.7% of nitrosamines in smoldering smoke, but it does not mean that the efficiency of zeolite is inferior to that in the mainstream. Although this removal proportion seems smaller than that of zeolite treatment downstream of the tobacco (47%), it is not the truth if the absolute removal of nitrosamines is calculated. In adsorption experiments the mainstream smoke of 16 cigarettes was treated by 0.5 g of zeolite and 17.9 nmole of nitrosamines reduced, so an efficiency of 35.8 nmol g^{-1} can thus be calculated. In the smoldering experiments, however, each cigarette contained 23 mg zeolite but 4.9 nmole of nitrosamines was eliminated, indicating a higher efficiency of 213 nmol g^{-1}. Incorporation of CuO in the zeolite appears to promote the removal of nitrosamines in smoldering smoke, since about quarter of the carcinogen can be reduced by the use of 1%CuO/NaY or 3%CuO/NaY additive (Fig. 9). The highest proportion was observed on the sample of 5%CuO/NaY where one-third of nitrosamines were eliminated, mirroring its best performance in the TPSR of NPYR as stated earlier. Zeolite NaA could eliminate a similar amount of nitrosamines to that removed by NaY in smoldering smoke, and its activity was doubled after modification with 3 wt% of CuO. The activity of 3%CuO/NaZSM-5 was lower (Fig. 9), but NaZSM-5 itself only removed 4% of nitrosamines under the same conditions, inferior to NaY or NaA. Two factors should be taken into account for this difference. One is the smaller surface area of NaZSM-5 (Table 1) and another is its higher Si/Al ratio relating to the concentration of metal ions in the zeolite. The concentration of sodium ions in the zeolite was of great significance with regard to the adsorption of NO_2,[15] since the metal ions could interact with NO_2 to produce primarily surface nitrites and nitrates.[32,40] To check which factor is predominant, a further experiment was performed on the ordered mesoporous material SBA-15 with a large surface area (Table 1). Only 1% of nitrosamines in smoldering smoke could be removed by the siliceous sample, which proves that it is the metal ions and not the surface area of molecular sieves that have the definitive influence on the removal of nitrosamines, otherwise more nitrosamines should be eliminated on SBA-15 with a much larger surface area than NaZSM-5. Incorporation of copper promoted the activity of SBA-15 and quarter of the nitrosamines was eliminated on 5%CuO/SBA-15. In contrast to the treatment downstream of tobacco by zeolites under mild conditions, elimination in smoldering smoke is usually carried out at higher temperatures. Even nitrosamines adsorbed on SBA-15 could desorb soon at high temperatures without catalytic degradation owing to the lack of active sites on the siliceous material. So, the mean concentration of nitrosamines in the smoldering smoke was slightly lowered. Loading CuO brought a significant catalytic activity to SBA-15, implying a new way to create efficient CatCig materials for removing the carcinogens.

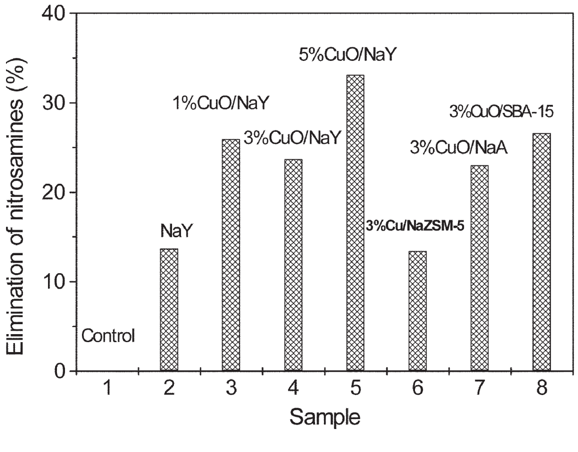

Fig. 9 Elimination of nitrosamines in the smolder smoke of cigarette by use of zeolite modified with CuO.

Selective removal of volatile nitrosamines in cigarette smoke is a problem. One may argue that choosing a suitable adsorbent with optimised pore structure would overcome this puzzle, but it has been proven to be very difficult, if not impossible. Neither zeolites nor the ordered mesoporous materials can give satisfactory performances. Based on the special "insertion adsorption" model of nitrosamines,[4,17] it seems practical to utilize the inducement effect to promote the selective adsorption and/or catalysis ability of zeolite. That means that some materials like copper located into zeolite will attract the –N–N=O functional group of nitrosamines so that the adsorption can thus be accelerated owing to the optimised adsorbate–adsorbent interaction. However, for practical reasons more investigations are desirable because only a limited number of experiments have been performed. Hand-rolled sample cigarettes are different from machine-made cigarettes in many features like ventilation and firmness, and natural smoldering differs also from smoking because of the different temperature profile along the length of the burning zone, which may have an impact on the reaction of nitrosamines. Besides, although tobacco leaves themselves contain plenty of metal ions,[41] the potential health effects of copper-modified zeolite addition need to be explored, and *in vitro* tests can be utilized for the complete toxicological assessment of cigarette smoke.

4. Conclusion

(1) Modification of zeolite and mesoporous siliceous molecular sieves with copper significantly promotes the selective adsorption and catalytic degradation of volatile nitrosamines, beneficial for the removal of nitrosamines in cigarette smoke.

(2) After running tests on various concentrations of CuO/NaY, the optimum composite was found to be a 3%CuO/NaY zeolite that could adsorb 75 per cent of *N*-nitropyrrolidine (NPYR), compared with just 56.8 per cent for the NaY zeolite alone. This increase in selectivity and efficiency is because the –N–N=O functional group of nitrosamines has a strong interaction with the copper in the zeolite.

(3) Pore structure affects the capacity of CuO modified molecular sieves to adsorb nitrosamines. Incorporation of copper helps adsorption of nitrosamines on SBA-15, but partially

blocks the channel of zeolite ZSM-5 and A and hinders the adsorption sometimes.

(4) Either in treatment downstream of tobacco or added into the tobacco, CuO modified molecular sieves can remove more nitrosamines in the mainstream or smoldering smoke of cigarettes than the materials themselves.

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