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REVIEW

Cleaning carcinogenic nitrosamines with zeolites

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Abstract *N*-nitrosamines are characterized with an *N*-nitroso group N–NO. *N*-nitrosamines are strong carcinogens or potent carcinogens. Nitrosamines occur widely in the environment, e.g., as tobacco smoke that causes cancers of lungs, larynx, oral cavity and pharynx, pancreas, kidney and bladder. It is difficult to capture selectively *N*-nitrosamines in the environment. Therefore, zeolite, which is a molecular sieve, may help to sequester *N*-nitrosamines. Zeolites are a class of aluminosilicates, characterized by ordered microporous structures with acidic–basic sites on the surface and energetic field inside the pores. They have been widely applied in industry as adsorbents and catalysts because of their unique shape selectivity. Here, we review the latest research on adsorption and catalytic degradation of *N*-nitrosamines by zeolite materials. The efficiency of zeolite is increased using metal oxides. Removal of *N*-nitrosamines in smoke is discussed.

Keywords Zeolite · *N*-nitrosamines (nitrosamines) · Selective adsorption · Cigarette smoke · Environmental protection · Tobacco-specific *N*-nitrosamines · Catalytic degradation · Health care

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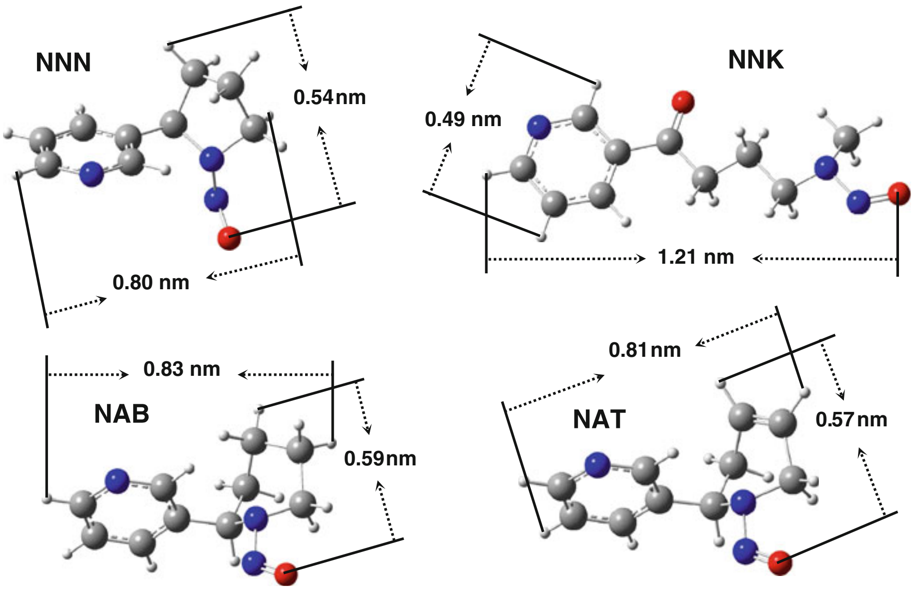
Introduction

Nitrosamines are probably the most widespread or potential carcinogens, they proverbially exist in workplace, processed meats, cigarette smoke and beer (Izquierdo-Pulido et al. 1996; Levallois et al. 2000; Hiramoto et al. 2001; Altkofer et al. 2005), and they are the chemical compounds characterized with *N*-nitroso group (N–NO). These compounds can be divided into three types: volatile nitrosamines (VNA), nonvolatile nitrosamines and tobacco-specific nitrosamines (TSNA) that are found only in tobacco products. Many nitrosamines, even in trace amounts, can induce tumors in a variety of organs, including liver, lung, kidney, bladder, pancreas, esophagus and tongue depending on the species (Lijinsky 1999). Apart from the health hazard caused by salted fish and preserved food, chemical exposure such as tobacco smoke and diet contributed to more than 65 % of human cancers (Doll and Peto 1981a). In particular, tobacco smoking was associated with about one-third of U.S. cancer deaths (Doll and Peto 1981b), or of all cancers of males in the world (Parkin et al. 1994). Cigarette smoke is a complex mixture of over 5,200 identified chemicals (Hoffmann et al. 1997; Branton et al. 2009), of which at least 150 are known to have specific toxicological properties (Meier and Siegmann 1999). Among these toxicants, tobacco-specific *N*-nitrosamines are well known to be the strong carcinogens (Fig. 1), including *N*′-nitrosonornicotine (NNN), 4-(methylnitrosamino)-1-(3-pyridyl)-1-butanone (NNK), *N*′-nitrosoanatabine (NAT) and *N*′-nitrosoanabasine (NAB) (Lee et al. 1996; Baker 1999; Hecht 1999; Koide et al. 1999).

Volatile nitrosamines also exist in the vapor or semivolatile phase of mainstream smoke inhaled by smokers (Meier and Siegmann 1999; Baker 1999; Zhuang et al. 2006). Most of volatile nitrosamines such as *N*-nitrosodimethylamine

Fig. 1 The molecular structure of four tobacco-specific *N*-nitrosamines (Lin et al. 2013b)



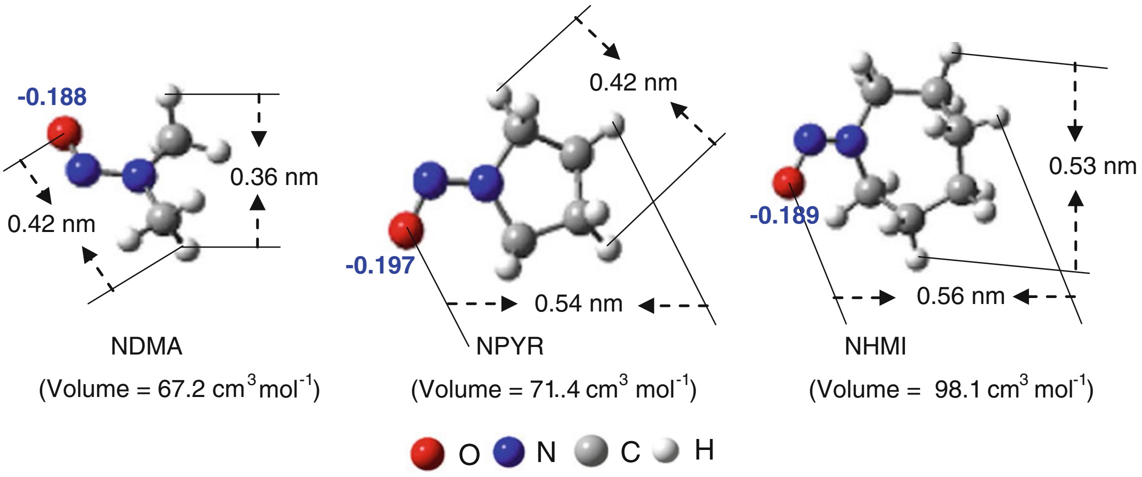


Fig. 2 Theoretically optimized geometry of volatile nitrosamines (the values of molecular weight and density are shown in *bracket*, and the *blue* data indicate the charge of atom) (Zhou et al. 2007). (Color figure online)

(NDMA) and *N*-nitrosopyrrolidine (NPYR) are also carcinogenic (Fig. 2), and they constitute a serious health risk for either smoker or the people around (Xu et al. 2003a; Sharp et al. 2005). Therefore, it is crucial to develop new functional materials and technologies to control the nitrosamine pollutants in environment, reducing the nitrosamine content of cigarette smoke and removing nitrosamines in food (Meier and Siegmann 1999; Ahn et al. 2003; Jo et al. 2003), and thus, the specific functional materials with selectivity are urgently required.

Zeolite is a crystalline aluminosilicate with a three-dimensional framework structure that forms uniformly sized pores of molecular dimensions (Maesen 2007), and its special structure is characterized by ordered microporous structures with acidic–basic sites on the surface and energetic field inside the pores (Fig. 3). With the unique shape selectivity, zeolites have been extensively utilized in petrochemical and chemical industry as adsorbents, catalysts and catalyst supports (Weitkamp and Hunger 2007; van Bekkum and Kouwenhoven 2007). Recently, the application of zeolites has been extended to life science and environment protection (Weiner 1997; Colella 2007). Actually, zeolites generally infiltrate our daily life, from purification of indoor air, water softening and decontamination to controllable releases of drugs, and capture of nitrosamines in complex system will be a new potential application of zeolites.

This short review will cover the issues and developments on the removal of nitrosamines in environment, especially in tobacco products by zeolites. Our group has

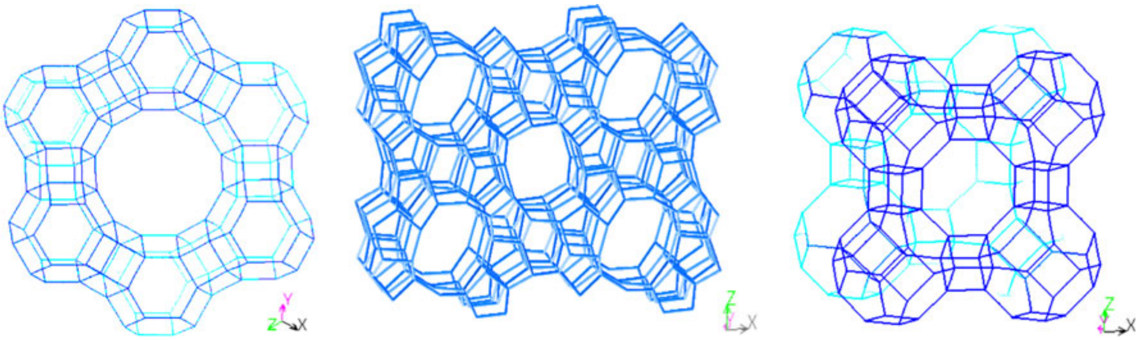


Fig. 3 The pore structure of zeolite Y with large micropore (*left*), ZSM-5 zeolite with middle micropore (*middle*) and the zeolite A with small micropore structure (*right*). (Yang et al. 2007)

carefully studied the adsorption and catalytic degradation of nitrosamines on zeolites in gas and liquid phases, exploring new methods to improve the catalytic activity of zeolite materials along with the new technique of microwave irradiation (Xu et al. 2008; Gao et al. 2009a, b). We also try to apply these results into practice, assessing the actual function of zeolite in tobacco smoke (Gao et al. 2008, Lin et al. 2013a, b; Wang et al. 2012). This review also summarizes our progresses on the liquid adsorption of nitrosamines by zeolite-based materials (Zhou and Zhu 2005; Yang et al. 2009; Wei et al. 2010, 2011), in order to offer new candidates for health care (This article is an abridged version of the chapter by Li et al. (2014); Chapter 9 Carcinogenic Nitrosamines: Remediation by Zeolites, published in the book series Environmental Chemistry for a Sustainable World) (http://www.springer.com/series/11480).

Adsorption of nitrosamines on zeolites

Gaseous adsorption of volatile nitrosamines

It is necessary to develop a reliable method for quickly assessing the efficiency of zeolites in adsorption of volatile nitrosamines in environment, and thus, a new test method, similar to concentration pulse chromatography (Harlick and Tezel 2000), is established for the instantaneous adsorption of volatile nitrosamines (Zhou et al. 2007). This instrument can be hermetically operated, suitable for the test of adsorbates with toxicity, mutagenic and carcinogenic properties. Practically, the instantaneous adsorption of volatile nitrosamines was performed in a stainless steel microreactor whose one end was inserted into the injector port of gas chromatograph (GC), while another end was connected with the separation column in the GC (Fig. 4). Adsorbents were filled up in the reactor where the temperature could be accurately controlled. The nitrosamine solution was pulse injected, passed through the adsorbent and then to the packed column and finally detected with thermal conductivity detector at the column outlet. And the decrement in the ratio of solute to solvent represents the amount of nitrosamines adsorbed by zeolite (Zhou et al. 2007).

N-nitrosopyrrolidine (NPYR) was chosen as the adsorbate because it is a typical volatile nitrosamine in food and tobacco smoke (Baker 1999; Ahn et al. 2002; Byun et al. 2004). *N*-nitrosopyrrolidine has a structure of five-membered ring with a molecular diameter of 0.42×0.54 nm^2, for which common zeolites show different adsorption characteristics: NaY, which is the crystal aluminosilicate possessing the channels with a largest pore size (0.74 nm) and the pore volume (0.31 cm^3 g^{-1}) among the zeolites used (Xu et al. 2003a), exhibited the highest adsorption capacity, and the weakly adsorbed moisture did not hinder the adsorption. Zeolite NaA that is an ordered porous material has a larger pore volume (0.28 cm^3 g^{-1}) and surface area ($\sim$800 m^2 g^{-1}), but a smaller pore diameter (0.4 nm) than NaZSM-5, the typical zeolite with middle pore size structure (0.11, 354 m^2 g^{-1} and 0.5 nm, respectively), and its adsorption ability was restricted by the narrow pore size (Fig. 5, Zhu et al. 2001; Yun et al. 2004). As the accumulated amount of *N*-nitrosopyrrolidine that passed through the zeolite rose to 2.5 mmol g^{-1}, 78.3 % was adsorbed by NaY, NaZSM-5 could trap 25.6 %, but the small microporous zeolite NaA only adsorbed 8.3 %. Since the molecular size of *N*-nitrosopyrrolidine is close to the pore diameter of middle microporous zeolite NaZSM-5, this zeolite exhibits some unusual properties in the adsorption. As the adsorption temperature was raised from 338 to 453 K, the proportion of *N*-nitrosopyrrolidine trapped by large microporous zeolite NaY and the small microporous zeolite NaA was lowered, but the zeolite NaZSM-5 with a middle pore size adsorbed 8.5 % more *N*-nitrosopyrrolidine. When the flow rate of the carrier gas was doubled from 15 to 30 mL min^{-1}, NaZSM-5 zeolite

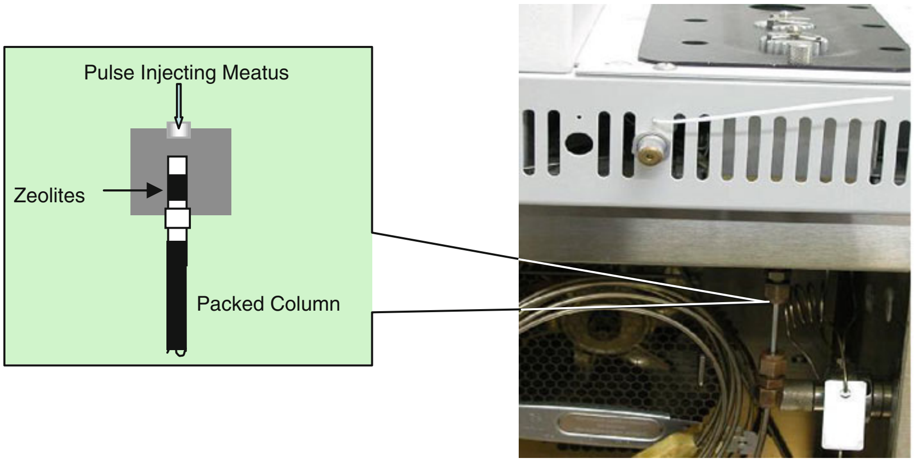


Fig. 4 Schematic representation of adsorption in gas chromatography (*left*) and diagram of experimental setup (*right*) (Zhou et al. 2007)

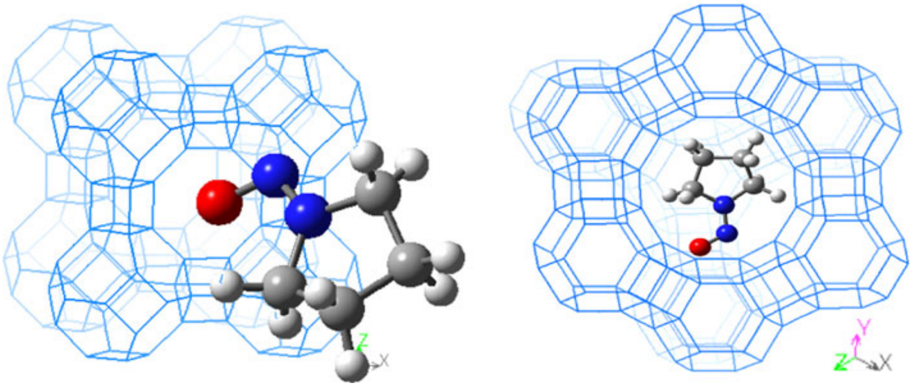


Fig. 5 The adsorption manner of *N*-nitrosopyrrolidine in (*left*) zeolite A with small micropore and (*right*) the Y zeolite with large micropore (Zhou et al. 2007)

with the middle pore size (0.5 nm) also trapped more *N*-nitrosopyrrolidine (Zhou et al. 2007). Freundlich equation can sensitively depict the difference in the adsorption of volatile nitrosamines in zeolites, but most of the isotherms deviate from Dubinin–Radushkevich or Langmuir equations (Zhou et al. 2007; Zhu et al. 2001).

Another two volatile nitrosamines were used to depict how the structure of adsorbate affected the adsorption of zeolite. One is *N*-nitrosodimethylamine (NDMA), a strong carcinogen with a molecular size of 0.42 × 0.36 nm^2, and another is *N*-nitrosohexamethyleneimine (NHMI), the strong carcinogen with a seven-membered ring and size of 0.56 × 0.54 nm^2 (Yun et al. 2004). The adsorption would be dramatically declined once the molecular size of nitrosamine exceeded the pore of zeolite, while the bulky nitrosamines might be chemisorbed on the external surface of zeolite with the nitroso functional penetrating into the pore mouth (Yun et al. 2004; Zhou et al. 2004). For the mixture of *N*-nitrosodimethylamine and *N*-nitrosopyrrolidine on different zeolites, the zeolite NaY with large micropore size (0.7 nm) preferentially adsorbed more negatively charged molecule *N*-nitrosopyrrolidine instead of the smaller one *N*-nitrosodimethylamine, while the middle microporous zeolite NaZSM-5 and the small microporous zeolite NaA willingly captured *N*-nitrosodimethylamine because of its smallness. Two major factors govern the adsorption, the geometric matching content and the electrostatic interaction between the adsorbate and the adsorbent; the former determines whether the molecule can be adsorbed by the zeolite or not, while the latter spurs and accelerates the adsorption (Zhou et al. 2007). For the given nitrosamine, the zeolite with a pore size slightly larger than its molecular diameter exhibits the highest adsorption capability (Zhu et al. 2001), since the effective attracting range of the cation in zeolite to pull the nitrosamine molecule is limited within about 0.05 nm (Yang et al. 2007). For a given zeolite, however, its aluminum content actually restricts its adsorption, because the cation concentration of zeolite relates to the aluminum content, and these cations form the electrostatic field to pull the *N*-nitroso functional group of nitrosamines toward the channels (Xu et al. 2003b; Zhou et al. 2004). Selective recognition of nitrosamine by the zeolite ZSM-5 possessing middle micropore structure with a pore size of 0.5 nm was confirmed through computational method (Pinisakul et al. 2008), in which the adsorption configurations of nitrosamines like *N*-nitrosodimethylamine were studied.

Impact of cation in zeolite on the gaseous adsorption of volatile nitrosamines

Cation of zeolite provides an essential electrostatic affinity on the *N*-nitroso group of nitrosamine, but occupies the space within the narrow channel of zeolite to hinder the entering and diffusion of adsorbate more or less; hence, it is necessary to understand the factual impact of the cation on the adsorption of nitrosamines by zeolite. For this purpose, four samples of zeolite A with different cations, CsA, KA, NaA and CaA, that have cesium, sodium, potassium or calcium ion in its frameworks in which pore size is varied by the introduction of the cation are chosen (Yang et al. 2008). These samples have similar particle diameter and structure, and the only difference is the alkali metal ion so that their pore size varies from 0.2 nm (CsA zeolite), 0.3 nm (KA zeolite), 0.4 nm (NaA zeolite) to 0.5 nm (CaA zeolite). In the adsorption of *N*-nitrosopyrrolidine at 338 K, NaA zeolite with a pore size of 0.4 nm showed the highest adsorption capacity, and the adsorption difference between zeolite NaA and others would be enlarged when the adsorption temperature rose to 453 K (Yang et al. 2008). Zeolite NaA has the channel structure with a pore size of 0.4 nm that matches with the smaller molecular diameter of *N*-nitrosopyrrolidine, which is advantageous for the adsorption. Although CaA zeolite that possesses the divalent calcium ion in framework has the larger pore size (0.5 nm), it fails to selectively adsorb *N*-nitrosopyrrolidine because of the competition for dichloromethane solvent (Cao et al. 2007a). Distribution of Ca^{2+} cation in the zeolite CaA badly affects the adsorption. There is no Ca^{2+} cation located in the window of eight-membered ring in the zeolite so that the electrostatic force of CaA microporous material is weak; hence, it cannot capture nitrosamine efficiently in gas stream. On the other hand, zeolite CsA containing cesium ion has a density larger than the zeolite NaA having sodium ion about 74.5 % in the dehydrated form, and its number of crystal cells is about 58 % of that of NaA zeolite in one gram hydrated sample (Yang et al. 2008), so that its number of pore opening per gram of sample is about 40 % less than that of NaA zeolite. Likewise, 1 g sample of KA zeolite possessing potassium ion has the number of pores about 10 % less than that of NaA zeolite, because of the heavier density of potassium ion than that of sodium ion. These differences in the pore number of per-gram sample among the small microporous zeolites CsA, NaA, KA and CaA inevitably affect their adsorption performance.

N′-nitrosonornicotine (NNN) is one of the tobacco-specific *N*-nitrosamines (TSNA), with 0.80 nm of length and 0.54 nm of width. However, it could be adsorbed by the small microporous zeolites CsA, KA and NaA that contain different alkali metal ion. In principle, *N*′-nitrosonornicotine may be adsorbed in zeolite by different ways depending on the pore diameter of the adsorbent. For the zeolite such as NaY, NaZSM-5 and CaA that have the wide channels with relative large pore size, *N*′-nitrosonornicotine can insert the five-membered ring into the channel, which requires the aperture of zeolite to be 0.541 nm at least. The small microporous zeolites NaA and KA only have a narrow channel; thereby, the most possible adsorptive manner of *N*′-nitrosonornicotine is to penetrate its *N*-nitroso group in the incommodious channel of zeolite, while the rest of the molecule retains on the external surface, which only needs a diameter of 0.123 nm. Compared with other zeolites such as NaZSM-5 and NaY, the small microporous zeolite-like NaA has the smallest pore size and the largest density of cation to provide the geometric confinement and the strong interaction to volatile nitrosamines, which strictly avoids desorption of the carcinogen (Yang et al. 2008).

A subtle selectivity is found on two small microporous zeolites KA and CsA whose pore sizes are smaller than 0.4 nm due to the existence of potassium or cesium ion in the framework of zeolite. They can accurately identify *N*-nitrosodiphenylamine (NDPA), the bulky nitrosamine with two phenyl groups and nitrobenzene (Yang et al. 2009) no matter in dichloromethane or benzene solution, selectively adsorbing the larger molecule *N*-nitrosodiphenylamine, similar to the "molecular trapdoor" mechanism (Shang et al. 2012). Clearly, the pore structure of small microporous zeolites CsA and KA can identify two kinds of functional groups in molecules, *N*-nitroso and nitro (Yang et al. 2009), since the distance between two oxygen atoms in the nitro functional group is 0.36 nm, which exceeds the pore size of the small microporous zeolites KA and CsA. Instead, the *N*-nitroso group of *N*-nitrosodiphenylamine molecule has a diameter of only 0.2 nm so it can be inserted into the narrow pore mouth of the zeolite. If *N*-nitrosodiphenylamine and nitrobenzene were adsorbed into zeolite channels through "plug-in mode" (Yun et al. 2004; Zhou et al. 2004), similar to the "close fit" mechanism (de Ridder et al. 2012), it would be difficult for nitrobenzene to insert into the narrow channels with the fine size of <0.3 nm, but *N*-nitrosodiphenylamine could be adsorbed through embedding its *N*-nitroso functional group.

Enhancing the performance of zeolite in adsorption of nitrosamines with metal oxide modifiers

Introducing metal compounds is an effective way to improve the performance of zeolites in the adsorption of volatile nitrosamines (Cao et al. 2007b; Xu et al. 2003b).

Copper oxide is utilized to modify zeolite through impregnation (Xu et al. 2004), and the copper oxide nanoparticles in zeolite will attract the *N*-nitroso groups of nitrosamine and thus promote the adsorption (Xu et al. 2003b). Loading 3 % (weight percent) of copper oxide can increase the ratio of *N*-nitrosopyrrolidine adsorbed on the large microporous zeolite NaY from 57 to 75 % at 453 K. For the zeolite NaZSM-5 with the middle pore size of 0.5 nm, loading 3 % of copper oxide enables it to adsorb the same amount of *N*-nitrosodimethylamine as that by the NaY zeolite possessing the wide channel with the size of 0.7 nm. Impregnation of zeolite with zirconia or cobalt oxide also has a similar positive effect in nitrosamines adsorption (Zhuang et al. 2006; Cao et al. 2007b). For the large microporous zeolite NaY exchanged with copper cation (Gu et al. 2008), the total number of cation in the zeolite is reduced because one copper ion exchanges two sodium ions, and sodium ion has a radius (0.099 nm) larger than that of Cu^{2+} (0.073 nm); hence, the zeolite has a slightly larger pore size in comparison with the parent zeolite NaY. In succeeding adsorption, there is no promoted adsorption ability on the copper exchanged zeolites. In contrast, impregnation method not only remains most of the Na^+ ions in the large microporous zeolite NaY but also introduces additional copper species in the resulting composite (Xu et al. 2003b, 2004). As a result, the resulting modified zeolite CuO/NaY is superior to the primary zeolite NaY for trapping volatile nitrosamines at 453 K because the copper modifier interacts stronger with nitrosamines to suppress desorption of *N*-nitrosopyrrolidine (Xu et al. 2003b, 2004; Gu et al. 2008). Similar positive effect is also observed in the small microporous NaA zeolite. For the given porous support, the optimal amount of modifier is determined by the host structure; it should offer the strong electrostatic interaction to promote the adsorption of nitrosamines while kept the zeolite channel unblocked; 3 wt% is below the monolayer dispersion threshold of copper oxide in the large microporous zeolite NaY with a pore size of 0.7 nm (Xu et al. 2004); therefore, the modifier is well dispersed and accessible for nitrosamine adsorbate.

Ferric oxide can be loaded on the large microporous zeolite NaY through microwave irradiation; the resulting composite 3 %Fe_2O_3/NaY exhibits a higher adsorption capacity than NaY; it traps 86 % of *N*-nitrosopyrrolidine when the accumulated amount of *N*-nitrosopyrrolidine achieves 1.82 mmol g^{-1}, but the primary zeolite NaY adsorbs about 77 % (Cao et al. 2008). Similarly, cobalt-modified NaY zeolite can trap more volatile nitrosamines (Cao et al. 2007b). The parent large microporous zeolite NaY adsorbs about two-thirds of the *N*-nitrosopyrrolidine in gaseous phase at 338 K when the amount of *N*-nitrosopyrrolidine passed through the adsorbent accumulates to 2.66 mmol g^{-1}, while loading 1 wt% of cobalt oxide on the zeolite NaY enhances this proportion to 74 %. The sample modified with cobalt oxide of 3 wt% shows the highest adsorptive capability (92 %), but loading more cobalt oxide on the large microporous zeolite NaY cannot elevate the adsorptive capability further.

The influence of zeolite morphology on the gaseous adsorption of nitrosamines

The middle microporous zeolite MCM-22 is chosen for its specific roselike morphology (Yang et al. 2010, Wu et al. 2009). It has two independent pore systems: One involves two-dimensional, sinusoidal channels (0.4×0.5 nm^2) with the circular ten-membered rings such as ZSM-5 (Ravishankar et al. 1995), and another consists of 12-membered large cylindrical supercages ($0.7 \times 0.7 \times 1.8$ nm^3) similar to that of NaY (Daems et al. 2005). Surface morphology of zeolite assuredly affects its performance in the adsorption of nitrosamines. The zeolite MCM-22 with roselike morphology traps all *N*-nitrosopyrrolidine in gas stream at 338 K until the accumulated amount of *N*-nitrosopyrrolidine reaches 1.5 mmol g^{-1}, but the common middle microporous zeolite NaZSM-5 losses its ability at the amount of 0.58 mmol g^{-1}. When the flow rate of carrier gas increases from 10 to 30 mL min^{-1}, zeolite MCM-22 samples trap more *N*-nitrosopyrrolidine, similar to that observed in the middle microporous zeolite NaZSM-5 (Zhou et al. 2007). Rough surfaces of zeolite can provide more conducive sites for adsorption and collision of adsorbate (Reitmeier et al. 2008; Zhou et al. 2012). As the adsorption temperature rises to 453 K and the amount of *N*-nitrosopyrrolidine accumulates to 1.0 mmol g^{-1}, the zeolite MCM-22 with roselike morphology captures 0.92 mmol g^{-1}, and common zeolites NaY and NaZSM-5 adsorb 0.86 and 0.52 mmol g^{-1}, respectively. The MCM-22 zeolite with roselike morphology exhibits a high ability in the instantaneous adsorption of volatile nitrosamines at 453 K due to its inherent optimized aluminum content and the specific porous structure containing bell-mouthed pore mouth connected with the slightly narrow channel that are beneficial to intercept nitrosamines in air flow (Yang et al. 2010).

Liquid adsorption of nitrosamines by zeolites

Zeolites can capture nitrosamines in organic or aqueous solutions. NaY exhibits the largest adsorption capacity of nitrosamines among commercial zeolites in dichloromethane solution, and the amount of adsorption (Qe) increases as the residual concentration (Ce) is raised (Zhu et al. 2001). In the case that the residual concentration of *N*-nitrosodimethylamine is around 2,000 mg L^{-1}, the adsorbed amount value on NaY zeolite (175 mg g^{-1}) is higher than that on SiO_2 (25 mg g^{-1}) or Al_2O_3 (10 mg g^{-1}). Nitrosamines have a weak basicity (Ma et al. 2000); therefore, acid zeolite HZSM-5 adsorbs more nitrosamines than NaZSM-5 though their surface area and pore size are almost same. On the other hand, competition for solvent weakens the adsorption of nitrosamines. NaY can adsorb 59 mg g^{-1} of *N*-nitrosodimethylamine at the residual concentration of 320 mg L^{-1} in organic solution, but only 1.05 mg g^{-1} at the residual concentration of 478 mg L^{-1} in aqueous solution owing to the competitive adsorption of water (Zhu et al. 2001). In the liquid adsorption of *N*-nitrosopyrrolidine at 277 K, MCM-22 zeolite adsorbed two times more than NaY and NaZSM-5 (Yang et al. 2010). In addition to the special channels and proper hydrophilic/hydrophobic nature of MCM-22, its essential grain shape owns compact chip morphology and rich surface curvature to increase the collision probability between the nitrosamine and active sites, significantly improving the adsorption.

Many carcinogenic agents such as nitrosamines or their precursors enter human stomach through diet and drinking, so it is necessary to trap the nitrosamines in gastric juice. Consequently, liquid adsorption experiments of nitrosamines are performed in hydrochloric acidic solution at pH 1, and *N*-nitrosopyrrolidine is selected as the adsorbate (Zhou and Zhu 2005). NaY and NaA zeolites are dissolved in the solution within 30 min, while NaZSM-5, ZSM-11 and Hβ are stable. And *N*-nitrosopyrrolidine is found to be also stable in the acidic solution for 3 h. The *N*-nitrosopyrrolidine uptake process on NaZSM-5 zeolite obeys the first-rate Lagergren equation, and the adsorption curve of ZSM-5 can be fitted with Langmuir formula. Zeolites are superior to amorphous silica and mesoporous silica SBA-15 for the adsorption of nitrosamines in acidic solution, and among them, the acidic zeolite Hβ has the largest adsorption capacity (Zhou and Zhu 2005).

Liquid adsorption of nitrosamines is also studied in fasting artificial gastric juice to examine the impact of additives such as NaCl and glycine on the adsorption of zeolite (Dong et al. 2007), and the acidic middle microporous zeolite HZSM-5 is treated with alkali corrosion to create mesoporosity (Van Der Voort et al. 2002). Creation of mesopores in the microporous zeolite ZSM-5 is beneficial for mass transport inside the channel to promote the adsorption of nitrosamines in artificial gastric juice, but zeolite surfaces become more uneven. The sample with a Si/Al ratio of 38 has the highest adsorption capacity, on which the cations provide enough electrostatic induction to pull *N*-nitrosopyrrolidine, but the competitive adsorption of water is not too serious (Dong et al. 2007). Since the hydrated radii of the cation bigger than 0.3 nm in the channels of zeolite will hinder the transport of adsorbate to decrease the adsorption capability (Rabo et al. 1966), acidic HZSM-5 zeolite with proton rather than other metal cation is more favorable for adsorption of *N*-nitrosopyrrolidine in artificial gastric juice. The adsorption of zeolite in artificial gastric juice is in accord with Freundlich equation instead of Langmuir equation (Dong et al. 2007). In the case that both *N*-nitrosopyrrolidine and lead ions exist in artificial gastric juice (Tao et al. 2010), the middle microporous zeolite NaZSM-5 ($Si/Al = 26$) captures more nitrosamines (4.36 mg g^{-1}) than lead ion (0.42 mg g^{-1}), while natural Na-clinoptilolite shows a selectivity toward lead ion in the solution, trapping more lead ions (6.88 mg g^{-1}) than nitrosamine (1.04 mg g^{-1}). Based on these results, a versatile zeolite functional material is developed to release NO at first and then captures the nitrosamines in mimic gastric juice (Wei et al. 2010).

Zeolite is able to selectively adsorb tobacco-specific *N*-nitrosamines (TSNA) in the extractable liquid of cut tobacco (Wei et al. 2009a). The bulky tobacco-specific *N*-nitrosamines molecules only insert their *N*-nitroso groups into the narrow channels of small microporous zeolite NaA due to the fine pore size of the zeolite (Zhu et al. 2003; Yun et al. 2004; Zhou et al. 2004), so that the zeolite NaA only adsorbed 0.58 μmol g^{-} of tobacco-specific *N*-nitrosamines, which is much lower than that of large microporous zeolite NaY with the pore size of 0.7 nm (1.37 μmol g^{-}). The adsorption capacity of middle microporous zeolite NaZSM-5 is about 1.11 μmol g^{-1}, same as that of the MCM-22 zeolite with roselike morphology whose pore opening is similar to ZSM-5 but pore structure different. These results indicate the crucial role played by the pore size of zeolite in the liquid adsorption, since the limitation of narrow channel on the mass transfer of adsorbate is unavoidable. Acidic zeolite such as HZSM-5 and Hβ exerts a higher capability than their basic analogues NaZSM-5 and Naβ for the liquid adsorption, because the proton in acidic zeolite can promote the adsorption of nitrosamines through forming hydrogen bond with the N atom in the nitroso group of nitrosamines (Meier and Siegmann 1999; Xu et al. 2003a; Wu et al. 2008). Calcium ion has a usual promotion on this liquid adsorption. Actually, the zeolite CaZSM-5 with calcium ion shows the enhanced adsorption capability of 1.41 μmol g^{-1} nitrosamines to exceed either NaZSM-5 or HZSM-5 zeolite, and higher adsorption ability is observed on CaA zeolite that also contains calcium ions in framework, because it can trap 1.68 μmol g^{-1} of nitrosamines in the solution, even exceeded activated carbon (Wei et al. 2009a). This may result from the specific high cation concentration of zeolite NaA or CaA that provides a powerful electrostatic interaction toward nitrosamines (Gao et al. 2008; Yang et al. 2008). On the basis of these studies, new efficient materials are developed to remove 70 % of tobacco-specific *N*-nitrosamines in the extractable liquid of cut tobacco (Wei et al. 2009b).

Capture of *N*′-nitrosonornicotine in aqueous solution by the acid-immerged zeolite is investigated. Zeolites NaY with large micropore, and ZSM-5 and MCM-22 with middle micropores are employed to study their structure variation after the acid leaching (Hou et al. 2013) and assessed to adsorb the *N*′-nitrosonornicotine in aqueous solution. The zeolites with Si/Al ratio of about 13 can keep their adsorption performance after acid treatment; rather, those with the Si/Al ratio of around 10 show the enhanced adsorption capability in deed. Further, the large microporous zeolite NaY and its dealuminated analogue NTY are proven to be safe for the human 293-T cells, and the dealuminated zeolite NaY can trap the *N*′-nitrosonornicotine in the aqueous solution to reduce toxicity so that it is a valuable candidate to trap nitrosamines in stomach juice (Hou et al. 2013).

Reducing nitrosamine level of smoke by zeolites

Zeolites had the ability to adsorb volatile nitrosamines in mainstream smoke of cigarettes (Xu et al. 2003a), and their adsorption capacity depends on the pore structure and surface acidity since protons form hydrogen bonds with the N atoms of nitroso groups in nitrosamine. Large microporous zeolite NaY and the acidic middle microporous zeolite HZSM-5 are the best adsorbents, while the NaZSM-5 with pore size of 0.5 nm is better than NaA zeolite whose pore size is 0.4 nm, and the residual nitrosamines in the smoke of cigarettes after adsorption on zeolite is very low (Xu et al. 2003a). Acidic zeolite HZSM-5 not only adsorbs more nitrosamines than its basic analogue NaZSM-5 but also keeps a high activity for the degradation of nitrosamines without interference of competitive adsorption of other components in smoke. To prevent desorption of nitrosamines from zeolite at high temperatures, copper oxide is used as the modifier for the zeolite containing sodium ion such as NaY, NaZSM-5 and NaA to strengthen their ability to adsorb volatile nitrosamines (Xu et al. 2003b, 2004). Due to the special interaction from the copper species in channel, nitrosamines are easily trapped by the modified zeolite so that about 70 % of the nitrosamines in smoke are eliminated.

Trapping tobacco-specific nitrosamines (TSNA) in smoke is a hard task for zeolite, because most tobacco-specific *N*-nitrosamines exist in the particles in tobacco smoke (Baker 1999) and the sizes of these particles exceed the micropores of zeolites. However, zeolite-like calcosilicate CAS-1 can effectively intercept the particles and thus reduces 30–60 % of the tobacco-specific *N*-nitrosamines in mainstream smoke (Gao et al. 2009b). The reduction can achieve about 30 % once 10 mg zeolite-like calcosilicate CAS-1 is added into the filter of cigarette, superior to the function of 30 mg zeolite NaA (11 %). As the amount increases to 20 and 30 mg per cigarette, the decrease in tobacco-specific *N*-nitrosamines achieves 55 and 58 %, respectively. Zeolite-like calcosilicate CAS-1 is not the simply physical filter, since the Ca^{2+} in framework provides a strong affinity to attract the *N*-nitroso group of nitrosamines. The fiberlike morphology of zeolite-like calcosilicate CAS-1 realizes the effective interception of particles in smoke, better than common zeolite, while plenty of cations plus zeolite-like microporous structure in zeolite-like calcosilicate CAS-1 enables the tobacco-specific *N*-nitrosamines adhered on particles to be captured.

Researches of nitrosamine degradation on zeolite

Catalytic decomposition of nitrosamines on zeolite

Zeolite has been tried as the cigarette additive to destroy the harmful components in smoke including tobacco-specific **N**-nitrosamines and volatile nitrosamines such as *N*-nitrosodimethylamine (Meier and Siegmann 1999). In fundamental research, the catalytic degradation of *N*-nitrosopyrrolidine is chosen as the model reaction, large microporous zeolites HY and NaY along with the middle microporous zeolite NaZSM-5 and HZSM-5 as the catalysts, and the temperature-programmed surface reaction (TPSR) is employed to examine the variation of degradation products of nitrosamines in these zeolites via different temperatures (Fig. 6, Wu et al. 2008). *N*-nitrosopyrrolidine can be decomposed to form NO, methylamine, dimethylamine and *N*-methyl-1-butanamine in the acidic large microporous zeolite HY at 773 K, but produces more complex products such as pentanedinitrile, 1-methyl-1-H-pyrrole, toluene, 1H-pyrrole and 1-H-2-methyl-pyrrole in the basic zeolite NaY at 773 K. Nitrogen, CO, water and propylene are the main species formed on basic zeolite NaY, while the portion of NO, N_2O and CO_2 in the products is small. Contrarily, majority of the products on the acidic large microporous zeolite HY are nitrogen-containing species and CO_2 or CO; only few hydrocarbons are detected due to the coking on acidic zeolite (Fig. 7). Decomposition of *N*-nitrosopyrrolidine on the acidic middle microporous zeolite HZSM-5 forms more products than that on zeolite HY, including toluene and 2-butanamine. On the basic middle microporous zeolite NaZSM-5, the nitrosamine is degraded to N_2O, 1-H-1-methyl-pyrrole and 1-H-pyrrole (Wu et al. 2008). The large microporous zeolite NaY with a pore size of 0.7 nm can adsorb and degrade more *N*-nitrosopyrrolidine than the middle microporous zeolite NaZSM-5 with pore size of 0.5 nm, and in general, the acidic zeolite shows a higher activity

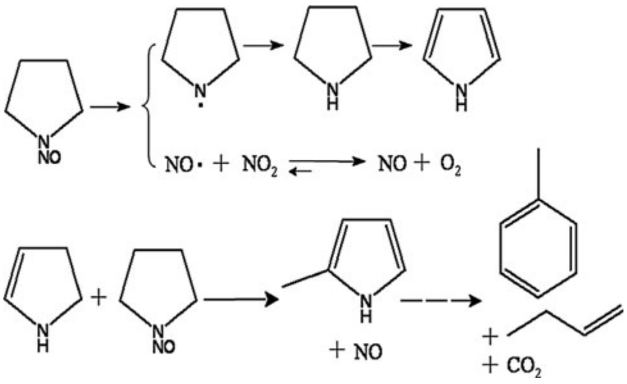


Fig. 6 The possible degradation of *N*-nitrosopyrrolidine on basic zeolite (Wu et al. 2008)

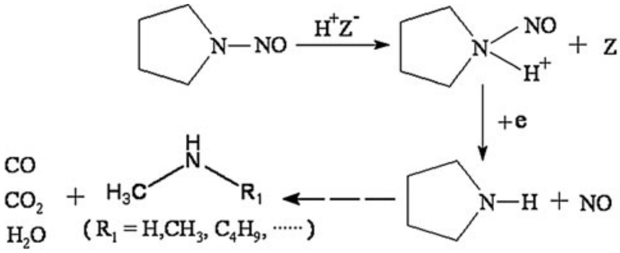


Fig. 7 The possible degradation of *N*-nitrosopyrrolidine on acidic zeolite (Wu et al. 2008)

than its basic analogue to decompose nitrosamines. Moreover, all of the adsorbed *N*-nitrosopyrrolidine could be degraded in the temperature-programmed surface reaction tests of *N*-nitrosopyrrolidine on the basic zeolite NaZSM-5 or NaY in nitrogen, in which NO and N_2O as well as pyrrolidine fragments appear in the range of 450–650 K, 2-methyl-1H-pyrrole and toluene emerge at 591 and 667 K, respectively, but their amounts are very small. Desorption of NO emerges on NaZSM-5 zeolite around 587 and 734 K, accompanied by propylene and 1H-pyrrole (Wu et al. 2008).

Different carrier gasses used in temperature-programmed surface reaction experiment affect the products distribution of nitrosamine degradation. In oxygen atmosphere, most NO_2 is produced from the oxidation of NO gasses (Wu et al. 2008); nonetheless, it comes from disproportionation reactions of N–O group in nitrosamines in inert and reductive atmospheres. NO_2 gas can form varieties of adsorption species on zeolite; for instance, NOx starts to strip at about 673 K, and decomposition of Na^+–NOy^-, Al^{3+}–NOy^- nitrate and nitrite begins at above 793 K. The basic large microporous zeolite NaY does not need to be protonated before performing the catalysis, and it is still active to catalyze nitrosamine degradation even in inert atmosphere (Wu et al. 2008). *N*-nitrosopyrrolidine can be adsorbed by ZSM-5 or Y-type zeolites regardless of what cation they possess (Zhou et al. 2007). The N–N bond in the *N*-nitroso group is the weakest bond in the structure of nitrosamine; hereby, the degradation of *N*-nitrosopyrrolidine starts from the cleavage of *N*-nitroso bond to release NO or NO^+ (Cheng et al. 1998; Miura et al. 2000), and the NOx and other fragments formed in the pyrolysis procedure can further react with each other at high temperature like 773 K to give complex products through different reaction paths. Either reaction temperature or products distribution of *N*-nitrosopyrrolidine has been changed on zeolite (Zhu et al. 2001). NO emerges near 450 K on the basic large microporous zeolite NaY, much earlier than that in pyrolysis (593 K); meanwhile, several other nitrogen oxides are formed resulting from the further reaction of NO. Also, acidic zeolite HY is used to eliminate the nitrosamines in smoke (Meier and Siegmann 1999; Wu et al. 2008).

As the bulky tobacco-specific *N*-nitrosamines with similar molecular size exceeded the pore mouth of zeolite (Cao et al. 2007a), *N*′-nitrosonornicotine is degraded on NaY zeolite at 423 K, causing new IR bands such as bridged nitrates at 1,590 cm^{-1} and giving the band of isolated nitrosonium ion or nitrite of *N*′-nitrosonornicotine (2,243 cm^{-1}) at 473 K. The bands of $-CH_2$, C–H and *N*′-nitrosonornicotine itself fade at 523 K because of both degradation of *N*′-nitrosonornicotine and desorption of the products. Degradation of *N*′-nitrosonornicotine occurs in the acidic middle microporous zeolite HZSM-5 at 423 K due to the promotion of protons in zeolite, and the degrading manner of *N*′-nitrosonornicotine adsorbed in zeolite depends on the pore structure of the adsorbent. Neither pyridine ($m/e = 79$) nor *N*-nitrosopyrrolidine ($m/e = 100$) is detected during the thermogravimetric–mass spectrometric test process of the *N*′-nitrosonornicotine adsorbed in zeolite NaY, and they are absent in that of copper-modified NaY, HY, NaZSM-5 and HZSM-5 zeolites. Also, a lot of fragments of *N*′-nitrosonornicotine deposit in zeolite, forming the coke of 0.4 and 1.2 % on the acidic zeolites HZSM-5 and HY, respectively. On the basic small microporous zeolite NaA, the fragments of *N*-nitrosopyrrolidine and pyridine as well as pyrrolidine appear. In principle, degradation of *N*′-nitrosonornicotine in zeolite sensitively depends on the pore diameter of catalyst. If the pore size of zeolite is smaller than 0.4 nm, *N*′-nitrosonornicotine inserts its *N*-nitroso group inside the narrow channel, while for the zeolite with a pore diameter equal to or larger than 0.5 nm, *N*′-nitrosonornicotine molecule enters in the channel, whole or partially. In both cases, the adsorbed *N*′-nitrosonornicotine molecule will be degraded from the rupture of N–N bond in *N*-nitroso group, forming nitrogen oxides and the residual carbon-containing parts. If the pore size of zeolite is between 0.32 nm and 0.54 nm, *N*′-nitrosonornicotine will be clipped in the pore mouth, decomposing through the rupture of the C–C bond linking five-membered ring and pyridine ring to form pyridine fragments (Cao et al. 2007a).

Nitrosamines can be decomposed in zeolite with the assistance of microwave irradiation (Xu et al. 2008). *N*-nitrosodiphenylamine (NDPA) has two rigid phenyls connected to the *N*-nitroso functional group; the large molecular size makes it usually adsorb on zeolite through the way of inserting its *N*-nitroso group into zeolite channel (Zhou et al. 2004). Without addition of zeolite, no *N*-nitrosodiphenylamine is degraded in dichloromethane solution under irradiation for 45 s no matter how the power of microwave changed from 0.1 kW to 1 kW. Under the condition of irradiating for 45 s with the power of 1 kW, the percentage of *N*-nitrosodiphenylamine adsorbed and decomposed in the basic zeolite with sodium ion such as NaA, NaZSM-5 and NaY reaches 4.1, 16.6 and 22.3 %, respectively (Xu et al. 2008). Ion exchange of zeolite NaA with Ca^{2+} can increase the conversion of *N*-nitrosodiphenylamine from 4.1 to 15.4 %, and the moisture in zeolite will promote degradation of *N*-nitrosodiphenylamine under the microwave irradiation. The volatility of *N*-nitrosopyrrolidine suppressed its microwave-induced degradation in NaY zeolite, but the narrow channel and plenty of cation of the basic zeolite tightly anchor the nitrosamine molecules. As a result, zeolite NaA also adsorbs all nitrosamines in solution, but no desorption of *N*-nitrosopyrrolidine occurs while 11.2 % is degraded under microwave irradiation.

There are two reasons to explain the promotion of microwave on the *N*-nitrosodiphenylamine degradation in zeolites. The first is heating effect, since zeolite cations can transfer heat energy to the adsorbed nitrosamines to degrade them. The second is the limited-domain effect, because nitrosamines are constrained in the channels after being adsorbed, while microwave irradiation makes the surrounding water molecules moving with a high speed to bump the carcinogen, promoting the degradation of nitrosamines. Based on the results of fundamental study, microwave degradation of nitrosamines is developed to be a new technology for reducing the harm compounds in tobacco smoke (Gao et al. 2009b). The finished cigarettes are directly irradiated with microwave in the optimized conditions, and the N–N bond of nitrosamines in tobacco fibers is fractured. After irradiation for 90 s with the microwave of 1 kW, 25–30 % of nitrosamines in tobacco and 50–60 % in mainstream smoke of the cigarette are reduced. Moreover, less mutagenic activity and higher CHO cell livability are found for the irradiated cigarette according to the results of in vitro tests, mirroring the declined biological toxicity of smoke (Gao et al. 2008, 2009a, b).

Researches of metal oxide-modified zeolite catalysts applied to the removal of nitrosamines

Zeolites can be modified with CuO nanoparticles (Xu et al. 2003b, 2004), and these copper oxide particles strengthen the attraction toward *N*-nitroso group of nitrosamines, elevating its catalytic degradation in temperature-programmed surface reaction test. The total amount of NOx product formed in temperature-programmed surface reaction experiment reflects the number of active centers in zeolite, while the T_{max}, a temperature at which the maximum concentration of NOx appears, indicates the activity of the active centers (Shen et al. 2000). The basic large microporous zeolite NaY can degrade 0.31 mmol g^{-1} of *N*-nitrosopyrrolidine with a T_{max} around 573 K. Introducing CuO of 1 wt% on the basic zeolite enhances the catalytic activity about 8 %, while loading 3 wt% makes the activity further increased about 12 %. In the latter case, the T_{max} is lowered from 573 K to 553 K, implying that more *N*-nitrosopyrrolidine is decomposed at relatively lower temperature. Rather, 5 %CuO/NaY microporous composite exhibits the best performance since it degrades the *N*-nitrosopyrrolidine 33 % more than the primary zeolite NaY. Further, loading more copper does not create a higher activity on zeolite (Xu et al. 2004). Loading CuO on either the basic middle microporous zeolite NaZSM-5 or the small microporous zeolite NaA also dramatically enhances their catalytic activity.

Introducing ferric modifier also elevates the activity of NaY zeolite in nitrosamine decomposition. Modification of NaY zeolite with ferric oxide of 1 % (w/w) increases the nitrogen oxides products desorbed in temperature-programmed surface reaction test from 0.308 to 0.474 mmol g^{-1} (Cao et al. 2008). Ferric modification has complex effect on the basic zeolite NaZSM-5. N_2O and 1H-pyrrole are detected at lower temperature on the composite of 3 %Fe_2O_3/NaZSM-5 than the primary zeolite NaZSM-5 zeolite, but the formation of 2-methyl-1-H-pyrrole and propionitrile is suppressed.

In the temperature-programmed surface reaction experiment on the cobalt-modified zeolite NaY above 500 K, *N*-nitrosopyrrolidine is first divided into a nitric oxide radical and pyrrolidine radical, which will quickly change into NO and pyrrolidine (Cao et al. 2007b). Through the disproportionation of nitric species, NO is converted to N_2O and NO_2, while the Co^{2+} cations in zeolites catalyze the decomposition of NOx to form N_2. At the same time, dehydrogenation of pyrrolidine occurs to form 1H-pyrrole and 2-methyl-1H-pyrrole, involving breaking of the five rings of *N*-nitrosopyrrolidine. As the temperature raises over 600 K, new Mass spectrometric signals of aromatic cyclic compound such as aniline emerge.

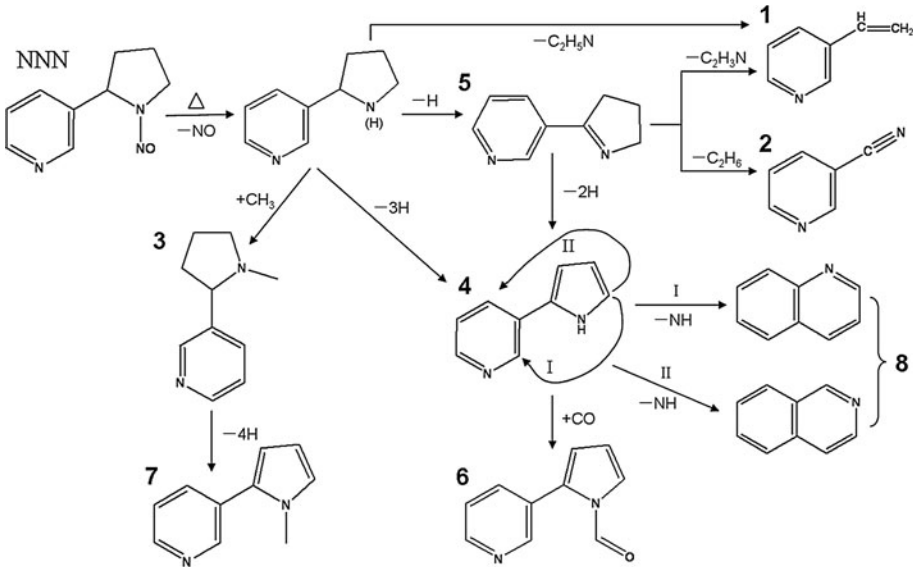


Fig. 8 The possible pyrolysis process of N'-nitrosonornicotine (Lin et al. 2013a). (*1*) 3-vinyl pyridine; (*2*) 3-cyano pyridine; (*3*) 3-(*N*-methylpyrrolidine-2-yl) pyridine; (*4*) 3-pyrrol-2-yl pyridine; (*5*) 3-(4,5-dihydro-3H-pyrrol-2-yl) pyridine; (*6*) 3-(*N*-carbonylpyrrol-2-yl) pyridine; (*7*) 3-(*N*-methylpyrrol-2-yl) pyridine; (*8*) quinoline and isoquinoline

Degradation of nitrosamines usually releases nitrogen oxides NOx due to the rupture of *N*-nitroso bond. Zirconia is thus chosen to replace copper oxide for zeolites to obviously reduce the release of NOx (Zhuang et al. 2006). Dispersing zirconia of 3 wt% on the basic large microporous zeolite NaY through microwave irradiation enhances the catalytic activity of the zeolite. When the carrier gas of temperature-programmed surface reaction is changed to air, however, the maximum concentration of NOx released from the sample of 10 %ZrO_2/NaY is abruptly decreased to below 10 μmol g^{-1}, and similar phenomenon is also observed on 5 %ZrO_2/NaY sample. In contrast, 54.5 μmol g^{-1} NOx desorbs from the primary zeolite NaY instead.

A strange degradation of *N*-nitrosodiphenylamine on zeolite at room temperature is reported for the first time (Zhou et al. 2004). The degradation manner of *N*-nitrosodiphenylamine on acidic zeolite is started from the cleavage of *N*-nitroso band without interference of side reactions such as pyrolysis. Among various zeolites evaluated, the acidic zeolite Hβ is the most effective catalyst. Bronsted acid sites are the main active centers while existence of metal ion such as Ca^{2+} or Ba^{2+} in zeolite is helpful to trap the NOx products and to prevent from secondary environment pollution.

Degradation of nitrosamines in tobacco smoke by zeolites

Zeolite was tried to be added into blended cigarette as catalyst to reduce carcinogenic compounds in smoke (Meier and Siegmann 1999). Basic zeolite NaY catalysts were activated when they were approached by the hot zone in the burning cigarette. Of the nitrosamines, some 40–50 % could be eliminated from the mainstream (inhaled by smokers), and around 50–70 % from the side stream (Meier and Siegmann 1999). In a pilot experiment performed lately, the additives consisting of zeolite NaA with a small pore size of 0.4 nm were added into alginate-based slurry and sprayed onto the tobacco before the Chinese Virginia cigarette manufacturing, in order to prepare the test sample cigarettes containing 3 % (w/w) of zeolite (Gao et al. 2008). The zeolite added into the tobacco rod is more effective in reducing the volatile nitrosamines than the tobacco-specific *N*-nitrosamines in the smoke of cigarette: The mean reduction of nitrosamines in smoke is around 61 % (Gao et al. 2008). Also, the total toxicity of smoke is evaluated in some in vitro and in vivo investigations. As proven in further experiments, zeolite additive does not form particles in the burned tobacco to escape into smoke. Either the tobacco-specific *N*-nitrosamines or the total nitrosamines level of the mainstream smoke is lowered, as proven by liquid chromatography–tandem mass spectrometry and photometric methods (Wang et al. 2012). For the reduction of tobacco-specific *N*-nitrosamines content in smoke (Lin et al. 2013a), basic zeolites NaA and NaZSM-5 and acidic zeolite HZSM-5 eliminate about 18–19 % of tobacco-specific *N*-nitrosamines, while the basic large microporous zeolite NaY removes 31 %. Pyrolysis of tobacco-specific *N*-nitrosamines such as N'-nitrosonornicotine starts from the dissociation of nitroso group and forms less or noncarcinogenic fragments (Fig. 8). Concerning the components of tobacco-specific *N*-nitrosamines in smoke, less N'-nitrosonornicotine (16 %) is removed than N'-nitrosoanatabine (23 %) by the basic small microporous zeolite NaA, while the reduction of four components of tobacco-specific *N*-nitrosamines is similar on the middle microporous zeolites

NaZSM-5 and HZSM-5. In contrary, more *N*′-nitrosonornicotine (35 %) than *N*′-nitrosoanatabine (28 %) in smoke is eliminated by the basic zeolite NaY with a pore size of 0.7 nm (Lin et al. 2013a).

Basic zeolites NaZSM-5 and NaY are modified by ferric species through aqueous ion-exchange and impregnation methods. Since the Fe cations in zeolite framework are more active than Fe_2O_3 nanoparticles in catalyzing the decomposition of nitrosamines, ion-exchanged ferric zeolite shows a higher catalytic activity than its impregnated analogue. Ferric Y zeolite can selectively reduce 26 % of tobacco-specific *N*-nitrosamines in mainstream smoke of burley-type tobacco (Lin et al. 2013b). On the reduction of four tobacco-specific *N*-nitrosamines components, no preference is observed on both the primary basic zeolite NaZSM-5 and NaY, but these ion-exchanged ferric zeolites have the orderliness of *N*′-nitrosonornicotine >4-(methylnitrosamino)-1-(3-pyridyl)-1-butanone > *N*′-nitrosoanatabine.

Conclusion

Adsorption and catalytic degradation of nitrosamines by zeolites are two efficient strategies for the removal of carcinogens in environment, which derives from the unique selectivity of zeolites. The electrostatic field inside channel and the pore size of zeolite are two determinative factors governing the selective adsorption of nitrosamines, the former drives the nitrosamine molecule inserting closely into zeolite channels, wholly or partly, while the latter provides the fine geometric constraints to imprison the carcinogen. Owing to these special factors, zeolite is able to not only selectively adsorb/catalyze the volatile nitrosamines whose molecular diameter is less than or equal to the pore mouth of zeolite, but also capture/degrade the bulky nitrosamines like tobacco-specific *N***-**nitrosamines whose cross section exceeds the channel size through special group-embedded mode. Besides, some zeolites can even distinguish the tiny differences between the functional groups of nitrosamines and nitrobenzene. Understanding of these new characteristics of zeolite will promote the design and development of new versatile materials, while introducing modifiers such as metal oxides can greatly improve the performance of zeolites, supplying many powerful candidates for the potential application of zeolite in environment protection and life science.

Researches of selective adsorbing and degrading nitrosamines also promote the development of new technology to deal with environmental pollutants. The fact that *N*-nitroso bond of nitrosamines is easily breakable once they are adsorbed in zeolite not only reveals the new strategy of degrading nitrosamines through microwave irradiation in limited domain, but also implies a new concept of eliminating environment pollution: It is possible to transform or exploit the environment pollutants by “lop off” their harmful groups. Through the strategy of transforming and utilizing the large numbers of pollutants, people can protect their ecological environment more effectively.

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