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Adsorption and room temperature degradation of *N*-nitrosodiphenylamine on zeolites

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N-Nitrosodiphenylamine (NDPA) is selected as a model compound to reveal the specific adsorption and catalytic function of zeolites in the removal of carcinogenic nitrosamines from the environment. The bulky NDPA molecule is indeed adsorbed in the zeolite KA having a small aperture, by insertion of the –N–N=O group into the channel and involving a specific interaction between the nitrosamine and the zeolite. Degradation of NDPA at room temperature on zeolite is reported for the first time, revealing the potential applicability of zeolites to eliminate nitrosamines under mild conditions. The acidity of zeolite is the key factor determining its ability to degrade NDPA and, among the zeolites evaluated, Hβ is the most effective catalyst with an activity much higher than that of other zeolites at ambient temperature.

1. Introduction

The fight against cancer is one of the challenges facing scientists in the realm of life science in the 21st century and in this context the removal of carcinogenic compounds from the environment is an important step. Among the extensive efforts to be undertaken, one of the new developing areas of study is the application of zeolites, because they have unique functions in selective adsorption and catalysis. Zeolites and molecule sieves are employed in slow release drugs,[1] enzyme mimetic drugs,[2] anti-tumor drugs, *etc.*.[3] A noteworthy example is the addition of zeolites to cigarettes to remove carcinogenic agents like nitrosamines because smoking is a global problem causing serious health hazards.[4–7]

Cigarette smoke consists of more than 4000 individual components and the various toxic compounds include nitrosamines, strong carcinogens inducing cancers or tumors even when present in trace amounts.[8,9] Zeolites can selectively adsorb nitrosamines, due to a particular attraction for the –N–N=O functional group in nitrosamines,[6,10] so the zeolite was wrapped in a cigarette filter and removed a significant amount of nitrosamines.[11,12] Recently, Xu *et al.* have increased the selective adsorption properties of zeolites by modification with copper oxide.[7] Although the mechanism of adsorption requires further investigation, they provide evidence that the –N–N=O functional group of the nitrosamines interacts strongly with the copper species, thereby increasing the selectivity compared with that of the unmodified zeolite. On the other hand, zeolite alone was used as an additive in cigarettes, attached to the tobacco fibers to eliminate carcinogenic compounds like nitrosamines and polycyclic aromatic hydrocarbons by zeolite catalysis, which is activated as the hot zone approaches.[5,12] Of the nitrosamines some 40–50% could be removed from the mainstream (inhaled by the smoker) and around 50–70% from the side-stream (the smoke formed in-between puffs).[4,12] Apart from trapping nitrosamines in the gaseous phase, zeolites have been reported to selectively adsorb volatile nitrosamines like *N*-nitrosodimethylamine (NDMA) and *N*-nitrosopyrrolidine (NPYR) in organic or aqueous solutions,[13] which allows to reduce the amount of these carcinogens in beer and remove a hidden potential problem with drinking.[14]

However, doubts still exist about the usefulness of zeolites in the anti-cancer battle in removing carcinogenic compounds like nitrosamines from the environment. Firstly, zeolite has proven to be efficient in laboratory studies in adsorbing volatile nitrosamines such as NDMA or NPYR, whose molecule diameters are close to the zeolite pore size. Nonetheless, in actual applications, for instance when the zeolite is to be used as a drug component in human stomachs or used to remove harmful substances in the vent pipe of a building, the adsorbent often meets with nitrosamines like tobacco-specific nitrosamines such as *N*′-nitrosonornicotine (NNN) whose bulk volume that exceeds the aperture of zeolite, can the microporous material still selectively adsorb them? We have suggested an "inserting model" of adsorption in previously publications,[6,7,13] but lack direct evidences to support this suggestion. Secondly, degradation of nitrosamines on zeolites usually needs high temperature, at least above 100 °C, which is much higher than the human body heat. Do zeolites have the potential ability to degrade carcinogenic compounds at ambient temperatures? These questions prompted us to study the adsorption and degradation of *N*-nitrosodiphenylamine (NDPA) on zeolites.

NDPA is a man-made chemical instead of a naturally occurring substance; based on investigations on laboratory animals, it is carcinogenic for rats, producing transitional-cell carcinomas of the urinary bladder in animals given high doses. Therefore the U.S. Environmental Protection Agency considers NDPA to be a possible cancer-causing substance in humans. With two rigid phenyls connected to the N–N=O functional group, the molecular size of NDPA is significantly larger than that of NDMA or NPYR. In order to check the possibility of the inserting adsorption model of zeolites, KA and NaA with pore sizes of 0.3 and 0.4 nm were chosen to be adsorbents. Since the phenyls in the NDPA molecule cannot be distorted or bent, they should not enter the channels of zeolites NaA and KA; that is to say, the NDPA molecule cannot adsorb into the channel of the zeolite until it inserts the N–N=O group in the pore mouth of the adsorbent. On the other hand, the bond energy between the two nitrogen atoms in the NDPA molecule is only 11 kcal mol^{-1}, smaller than that in NDMA (dimethylnitrosamine, 52 kcal mol^{-1}),[15] it should be the easiest nitrosamine to degrade on zeolites at ambient temperature.

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Consequently, NDPA was chosen as a probe molecule to investigate the adsorption and degradation mechanism of nitrosamines in zeolites. However, dichloromethane solvent has to be used because of the insolubility of NDPA in water, though potential new applications of zeolites generally would take place in aqueous solutions. Nonetheless, different solvents employed in fundamental research experiments does not hinder the applications of zeolites, because A-type zeolites possess the ability to adsorb nitrosamines in both aqueous and dichloromethane solutions.[13]

2. Experimental

2-1 Materials

Zeolite NaY with an Si/Al ratio of 2.86, NaZSM-5 (Si/Al = 12.5) and NaA, CaA as well as KA were commercially available powders.[6] Sample HZSM-5 was obtained by ion exchange from the parent zeolite NaZSM-5 while sample HY was derived from NH_4Y by calcination at 500 °C for 3 h. MnY, BaY and ZnY samples were obtained by ion exchanging the parent zeolite NaY with the relevant metal salt solution for 2 h, followed by washing, drying and calcination.[6] Hβ zeolite with an Si/Al ratio of 29 and a surface area of 607 $m^2\ g^{-1}$ was a gift from BASF. CAS-1 is a zeolite-like porous material with a pore size close to that of zeolite NaA.[16] HZSM-11 (Si/Al = 25) was synthesized in the laboratory.[17] For comparison a sample of γ-Al_2O_3 with a surface area of 122 $m^2\ g^{-1}$ was employed. NDPA, synthesized through the reaction of $NaNO_2$ and diphenylamine (DPA) in acid solution,[18] forms light yellow needle crystals with a melting point of 67 °C and soluble in methylene chloride. All reagents used were AR grade.

2-2 Measurements

Adsorption experiments of NDPA in solution were performed at 4 °C. All samples were activated by first heating at 500 °C for 2 h and then cooling down to 150 °C before being placed in desiccators. A 50 mg powder sample of zeolite was added into the tube containing 1 ml methylene chloride solution with 0.74 mg NDPA. After allowing 24 h for adsorption, the residual concentration of NDPA in solution was determined by an improved spectrophotometric method.[6] At the same time, the diffuse reflectance (DR) spectrum of the used zeolite adsorbent was determined after careful evaporation of the solvent. DR UV-VIS spectra were recorded on a UV-2401 (Shimadzu) spectrophotometer adapted with a praying mantis accessory, using $BaSO_4$ as standard.

Temperature programmed surface reaction (TPSR) of zeolite-adsorbed NDPA was carried out in a flow reactor.[19] A 40 mg zeolite sample, in 20–40 meshes, was activated at 500 °C in N_2 for 2 h, then cooled to 90 °C prior to pulse injection of the NDPA solution in a ratio of 235 μmol g^{-1}. After the sample was purged with N_2 for 0.5 h, the temperature was ramped to 500 °C at a rate of 10 °C min^{-1}. The NO liberated in the TPSR process was converted to NO_2 by passing through a CrO_3 tube[6] and then absorbed in a solution of sulfanilamide and *N*-1-naphthylethylene diamine di-HCl. The amount of NO_2 detected by a colorimetric method represents the amount of decomposed NDPA.[20]

In the degradation experiment on zeolite at room temperature, 9.42×10^{-7} mol NDPA dissolved in 10 ml dichloromethane were put into a test tube with an arm by which the carrier gas could pass through the bottom of the test tube (Scheme 1) and then 50 mg samples of H-type zeolites without activation or 50 mg γ-Al_2O_3 (activated at 500 °C for 4 h) was added to catalyze the degradation of the nitrosamines at ambient temperature.[6] The zeolite with sodium ion or the MnY, BaY, ZnY and CaA samples were activated at 500 °C for 2 h.

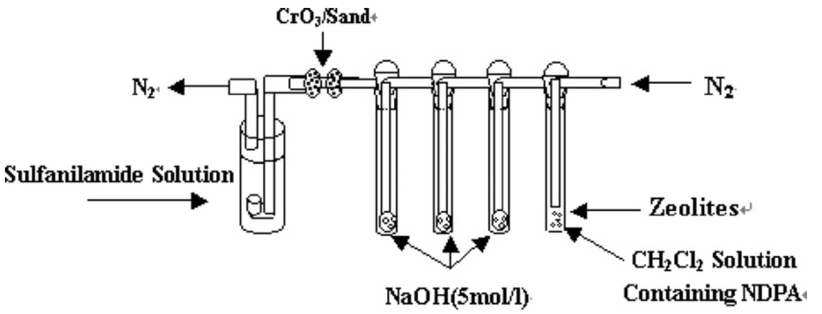
In the NH_3-TPD experiments all samples were activated at 600 °C for 2 h prior to adsorption of ammonia at 110 °C. After the physisorbed ammonia was purged by carrier gas, the sample was heated to 600 °C at a rate of 8 °C min^{-1} while the ammonia was detected using an *in situ* Varian 3380 gas chromatograph.[6] To study the role played by the degree of acidity of the zeolite in the degradation of nitrosamines, ammonia, acting as a poison, has been applied to an Hβ sample (50 mg Hβ activated at 600 °C for 2 h in a flux of N_2, then cooled to 400 °C). NH_3 (20 ml) was placed in contact with the sample for 10 min at 400 °C to poison the strong acid sites. Finally, the poisoned Hβ sample was purged by a flow of N_2 for 0.5 h to remove the physisorbed ammonia and cooled to room temperature.

FTIR tests were performed on a Bruker 22 FTIR spectrometer. Typically the spectrometer operated at 4 cm^{-1} resolution, collecting 40 scans in single-beam mode. Background spectra were collected on clean adsorbate-free samples to eliminate the overlap of IR adsorption features that originate from the zeolite structural vibrations and the adsorbed surface species. For IR measurements of the adsorbed species, the zeolite was pressed into plates with a density of 15 mg cm^{-2}. The resulting plate was slowly heated up to 500 °C and activated for 2 h in a flow of N_2. One microliter of a CH_2Cl_2 solution containing 1 mg NDPA was then introduced into the sample at 70 °C. After purging for 10 min with nitrogen flow, the IR spectrum was collected at the given temperature.

An optimized calculation of the NDPA molecular geometry in a solution of CH_2Cl_2 was made using Gaussian 98 W for UNIX, Rev. A9.[21b] The input files were compiled and the output files viewed in Gauss View 2.1. Gaussian 98 W for UNIX was run on a high performance ShuGuang3000 computer at the Chemistry Department of Nanjing University. Theory method/basis group was HF/STO-3G and the PCM solvation model was applied in the optimization process.[21a]

2-3 Precautions

Since nitrosamines are carcinogenic compounds, all experiments were carried out in an aerator and the operator should



Scheme 1 Experimental setup for the measurement of NDPA degradation at room temperature.

wear gloves. Waste solutions and residues were placed in an airtight container filled with dense lye, which efficiently destroys the nitrosamines, and was then sent to the appropriate waste disposal center.

3. Results and discussion

3-1 Inserting adsorption model

Fig. 1 illustrates the optimized geometry of the NDPA molecule in dichloromethane solution, in which the distance from the 1st to the 7th atom is 0.67 nm while that from the 6th to the 10th atom is 0.95 nm, so it possesses a transect size of 0.61 nm. The dimension of the phenyl group moiety in the NDPA molecule is about 0.5 nm. Considering the aperture size of KA (0.3 nm) or NaA (0.4 nm) zeolites, one might believe that NDPA cannot be adsorbed in these two zeolites, especially on KA. However, Fig. 2 demonstrates surprising results for NDPA adsorption on zeolites A at 4 °C. KA indeed adsorbs the bulky nitrosamine at a level of 17 mg g^{-1}. Although this value is relatively low if compared with that of NaA (27 mg g^{-1}) or CaA (49 mg g^{-1}), it is clearly not zero and directly confirms the occurrence of adsorption on this zeolite.

One could discredit this interpretation if some NDPA molecules are absorbed on crystal defects, cracks and crevices of the zeolite particles, or if they adsorb just on the external surface of the zeolite, but this suspicion can be excluded by consideration of the experimental facts. Firstly, KA has a similar particle size (3–4 μm) and surface area (740 m^2 g^{-1}) as that of NaA,[6] so the external surface is similar and the corresponding amount of NDPA adsorbed on the external surface should be similar under the same experimental conditions. Nonetheless, this is not the case. Since the KA sample was obtained from ion exchange of NaA zeolite, one may insist that ion exchanging may decrease the number of crystal defects, cracks and crevices of zeolite particles so that the amount of NDPA adsorbed on KA is lowered. However, sample CaA, also derived from NaA through ion exchange, shows that more NDPA is absorbed than on NaA, which means that the impact of crystal defects and cracks as well as crevices in the zeolite particles on the adsorption of NDPA, if any, is not a predominant factor. Secondly, several CaA samples were activated in different ways prior to adsorption of NDPA, in order to examine the influence of the pre-treatment on adsorption. One sample was heated at 500 °C in nitrogen for 2 h and another one was dried at 110 °C for 12 h, while a third sample was treated with microwave irradiation (800 W) in air for 3 min. These CaA samples showed different adsorption amounts: for the irradiated sample it was 9.7 mg g^{-1}, a fifth of that on the activated sample (49 mg g^{-1}), while on the dried sample no adsorption was observed. If NDPA only adsorbed on the external surface or crystal defects and crevices of the zeolite particles instead of in the channels, there should not be such obvious differences, because the water molecules located on the external surface and/or the crystal defects and crevices of zeolite particles could be removed by either microwave radiation or drying, while only the removal of those occupying the adsorption sites inside the channels would require activation at 500 °C. It is the residual water molecules that hinder adsorption of NDPA in the CaA sample, resulting in the different adsorption capacities.

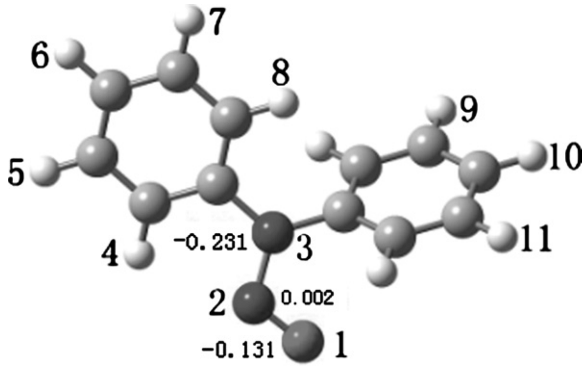


Fig. 1 The optimized geometry of NDPA in CH_2Cl_2 solution.

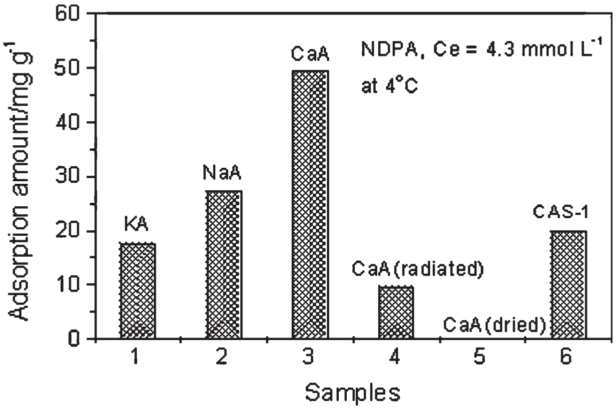


Fig. 2 Adsorption of NDPA on zeolites A in dichloromethane solution at 4 °C.

In order to prove the adsorption of bulky NDPA in microporous materials with small pore sizes, another calcosilicate zeolite-like material, CAS with small pore size (0.3 nm) but different ions (Na^+),[6,16] was selected because of its one-dimensional small pore channel system. A CAS-1 sample could also adsorb the bulky NDPA molecule and its adsorption capacity (19 mg g^{-1}) is close to that of KA zeolite (17 mg g^{-1}), as seen in Fig. 2.

NDPA is a fragile compound so one may ask if it is catalytically degraded instead of adsorbed at the pore mouths of the solid samples. FTIR tests were performed to check this possibility and Fig. 3 shows the results. Four small but identifiable IR bands emerged around 1591, 1494, 1445 and 1315 cm^{-1} in the spectrum of NDPA adsorbed on KA, assigned to the characteristic bands of phenyl (1590 cm^{-1}), N=O (1490–1440 cm^{-1}) and C–N (1310–1250 cm^{-1}) vibrations.[22] The CAS-1 adsorbed NDPA exhibited a similar IR spectrum with slightly stronger intensity, consistent with the adsorption results in which CAS-1 adsorbs more NDPA than KA zeolite. In the spectrum of NaA-adsorbed NDPA, the intensity of these bands was significantly increased and accompanied by a faint

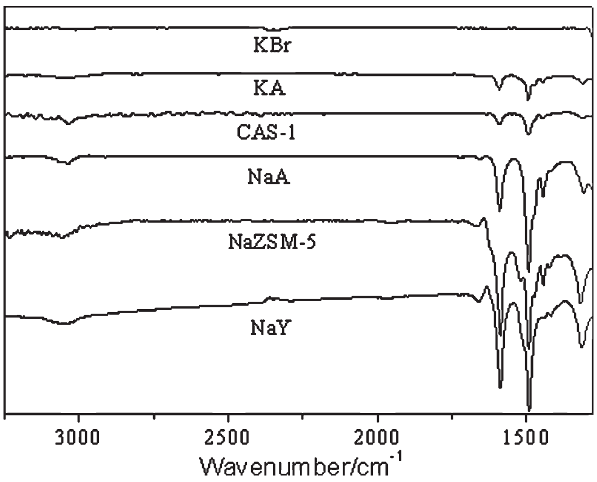


Fig. 3 FTIR spectra of NDPA adsorbed on different zeolites.

band appearing near 3036 cm^{-1}, which is another vibration of phenyl (3030 cm^{-1}) as seen in the standard spectrum of NDPA.[22] The apertures of ZSM-5 and Y zeolites allow NDPA to enter the channels, providing a prerequisite and necessary condition for adsorption. Once these samples are pre-treated with suitable procedures (dehydration, heating, *etc.*), adsorption of NDPA can occur. As seen in Fig. 3, the bands became stronger in the spectra of NDPA adsorbed on NaZSM-5 and NaY zeolites, mirroring their stronger adsorption capability, but the positions are the bands were still close to those in the standard spectrum of NDPA, indicating that the entire molecule is present. However, no NDPA bands were observed on KBr under the same conditions, which excludes the possibility of physisorption of NDPA on the solid samples. Otherwise, such adsorption should be observed on other solids like potassium bromide. From these results it is safe to conclude that the NDPA molecule is adsorbed instead of being catalytically degraded in the pore mouth of microporous materials at the temperature adopted in the experiments.

The TPSR results shown in Fig. 4 further confirm the adsorption of NDPA on KA zeolite. Since the N–NO bond is the weakest one in nitrosamines, degradation of the carcinogen should begin by the rupture of this bond to release NO.[23] Desorption of NO was observed from all NaA, CA and KA zeolites, showing a maximum concentration at around 200 °C. Due to the complexity of product formation in the degradation of nitrosamines,[6,23] the NO detected in TPSR could not be simply used to judge the actual amount of NDPA adsorbed. However, this experiment provides the proof for adsorption of NDPA on KA, because the nitrosamines need to be adsorbed on the zeolite prior to decomposition at elevated temperatures.[24] Otherwise, they would be removed by the purging carrier gas flow.

Judged from the results discussed above, it is without a doubt that NDPA indeed adsorbs in CAS-1, KA and NaA samples though its molecular diameter is assuredly larger than the aperture of the adsorbents. It is impossible for the whole NDPA molecule (0.61 nm) or its phenyl group (0.5 nm) to enter into the channels of these samples. Only the hypothesis of the inserting adsorption model can explain the two inconsistent results: NDPA adsorbs in KA zeolites by inserting its functional –N–N=O group into the channels, which is possible since the dimension of the –N–N=O group is only 0.22 nm, smaller than the aperture of KA zeolites. Of course, it is also possible that bulky NDPA is chemisorbed on the external surface with the nitroso functional group penetrating into the pore mouth. Additionally, the result of the optimized calculation shows that the charge on the –N–N=O group is strongly negative (0.36; see Fig. 1). Considering the fact that there are numerous cations in the channel of zeolites A, the electrostatic force fields generated inside the zeolite channels will aide in the adsorption of NDPA by insertion of –N–N=O into the channels. The smaller the radius of the cation located in the zeolite, the stronger the electrostatic field in the channels of the zeolite. Since the Na^+ radius (0.099 nm) is smaller than that of K^+ (0.133 nm), the intensity of the electrostatic field in NaA zeolites is stronger than that in KA zeolites, which may be a reason why more NDPA is adsorbed on NaA (27 mg g^{-1}) than on KA (17 mg g^{-1}).

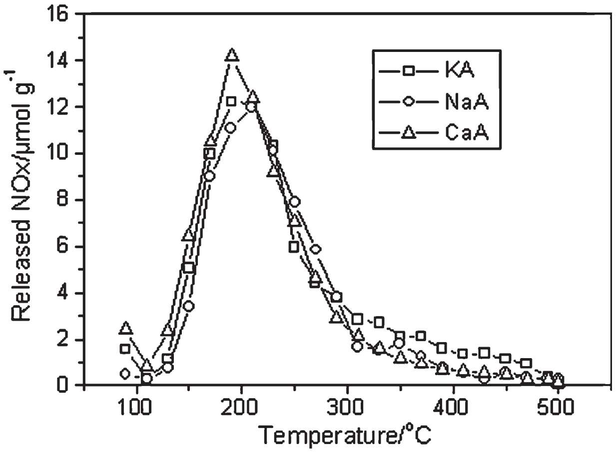


Fig. 4 Profile of NOx liberated from NDPA on zeolites A during the TPSR process.

The zeolite particles are indeed not perfect crystals and there must be some defects, cracks and crevices in the samples. However, considering the fact that both KA and CAS-1 samples cannot adsorb N_2,[16] the average size of the defects, cracks and crevices in zeolites should be smaller than the kinetic diameter of N_2 and further smaller than the size of NDPA; it is thus very difficult, if impossible, to believe that these defects and crevices play an important role in the adsorption of NDPA.

Validation of the inserting model adsorption on zeolites KA and NaA reveals a new mode of adsorption by zeolites through which even an adsorbent with a small aperture can still adsorb bulky nitrosamines. This is expected to expand the applications of zeolites to selectively remove carcinogens.

3-2 Degradation of NDPA at room temperature by zeolites

Selective removal of nitrosamines from the environment is a new application of zeolites, but the mechanism needs to be explored. Compared with the study on adsorption for which an inserting model of bulky nitrosamines is assumed and incorporation of copper in zeolites is suggested,[7] little is known about the elimination of the carcinogen on zeolites. Although nitrosamines can be denitrosated by HBr in acetic acid at room temperature,[25] on zeolites most nitrosamines decompose only at high temperature to form various products; the occurrence of pyrolysis side-reactions interfere with the analysis to deduce the reaction mechanism.

Fig. 5 demonstrates an unusual experimental result: NDPA in dichloromethane solution can be degraded at room temperature on acidic zeolites without activation. When these non-activated samples were put into an NDPA solution, the samples changed color from white to blue; meanwhile NO was released from the reaction system. Zeolite Hβ was the most efficient catalyst, completely degrading NDPA (18.04 μmol per gram catalyst) within 2.5 h whereas about 84% of the nitrosamines was degraded on HY zeolite under the same conditions. HZSM-5 and HZSM-11 have different channel systems (the former has both straight and "z" type channels and the latter has only the straight ones) but a similar pore size; however, only 15% of the NDPA was degraded on either of

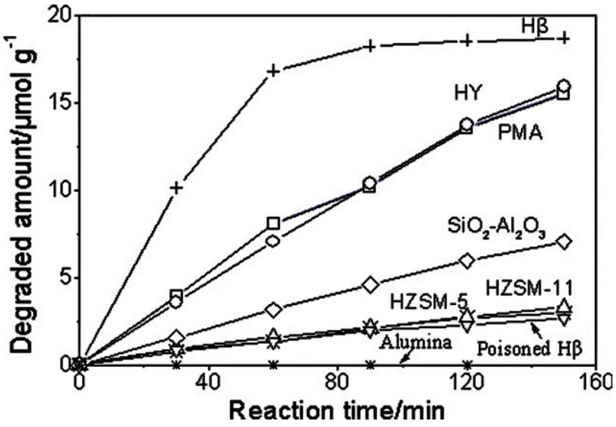


Fig. 5 Degradation of NDPA on zeolites at room temperature.

these zeolites. Phosphate molybdic acid (PMA) has the highest acidity among all the evaluated samples, even stronger than H_2SO_4 and HNO_3,[26] but its degradation ability is comparable to that of zeolite HY and obviously lower than that of Hβ (Fig. 5). The absence of a pore structure in PMA should be taken into account to explain this difference, since the surface area of PMA is only a few $m^2\ g^{-1}$ while that of zeolites exceeds $350\ m^2\ g^{-1}$.[6] To assess the influence of an ordered pore structure on the decomposition of nitrosamines, the amorphous SiO_2–Al_2O_3 was tested; its degradation ability is higher than that of HZSM-5 but lower than that of HY and Hβ. The kind of metal ion in the zeolite seems to be a critical factor for the degradation of NDPA at room temperature, because NO was not detected and no color changes were observed on zeolites NaA, NaZSM-5 and NaY, whether they were activated or not. As stated previously, the FTIR results in Fig. 3 also confirm that NDPA does not decompose on the zeolites with sodium ion. Nevertheless, CaA, BaY, MnY and ZnY can catalyze NDPA degradation at ambient temperature as will be discussed below.

Fig. 6 shows the NH_3-TPD spectra of acidic zeolites. All samples had two ammonia desorption bands, a strong one centered near 200 °C representing the weak acid sites and a weak one appearing above 450 °C characterizing the strong acidic sites. To determine which one plays the determinant role in the degradation of NDPA, one Hβ sample was poisoned by NH_3 at 400 °C, then used in the reaction at ambient temperature. As seen in Fig. 5, poisoning deactivated the Hβ sample so that its residual activity was close to that of HZSM-5 and HZSM-11. This is to say that the strong acid sites holding NH_3 at 400 °C are the main active centers for the degradation of NDPA at room temperature, even though they are few in number, while the weak acid sites desorbing NH_3 below 400 °C probably make only a minor contribution. To distinguish the contribution of Lewis acid sites in the degradation of NDPA, a sample of dehydrated γ-Al_2O_3 was employed, which has only Lewis acid sites and no Brønsted acid sites.[27] This γ-Al_2O_3 sample could not catalyze the degradation of NDPA at room temperature. Based on this result, the Brønsted acid sites in zeolites and other porous solid acid samples seem to be one of the main active centers for the degradation of NDPA. The possibility that Lewis acids of the same or lower strength than that of alumina catalyze NDPA degradation can be ruled out, but this possibility cannot be excluded for Lewis acids with a stronger acidity than alumina or those in zeolites poisoned by ammonia.

Among the acidic zeolites used here, HY possesses a larger surface area and a lower Si/Al ratio than Hβ and HZSM-5, hence HY zeolite should have the largest number of acid sites. In addition, HY can adsorb more volatile nitrosamines in CH_2Cl_2 solution.[13] However, the catalytic activity of HY zeolite in the degradation of NDPA at room temperature is obviously lower than that of Hβ zeolite. The activity of HZSM-5 zeolite is also lower than that of Hβ zeolite. The total acidity of HZSM-5 ($0.48\ mmol\ g^{-1}$) or HY ($0.62\ mmol\ g^{-1}$) is larger than in Hβ ($0.36\ mmol\ g^{-1}$), according to the NH_3-TPD results, and their strong acid sites seem to be more so than those of Hβ (Fig. 6). Although it is difficult to compare the catalytic activities of zeolites with differences arising from the pore structure, particle size, surface area, Si/Al ratio, Brønsted/Lewis acid site population and other relevant parameters, the excellent catalytic performance of Hβ still implies the impact of other factors, probably the geometric effect between the reactant and the catalyst, which is not simply the fit between NDPA and the zeolite but may involve an optimal location/assembly of active sites that needs further investigation.

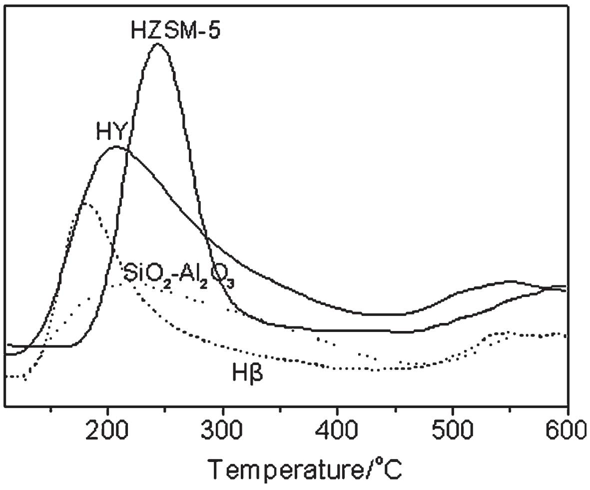


Fig. 6 NH_3-TPD spectra of acid zeolites.

The relatively low activity of HZSM-5 in the degradation of NDPA results from a geometric effect. The molecule dimension of NDPA is about 0.61 nm, larger than that of benzene due to the –N=O on the nitrogen atom connecting the two phenyls, whereas DPA possesses a similar molecular size to benzene. Adsorption of nitrosamines in zeolites is a determinant step in degradation,[24] but the intense electrostatic fields inside zeolites and the topological restrictions of the channels also affect it.[7] For instance, the close match between the pore size of ZSM-5 and the phenyl precludes any further reaction of the DPA radical.[28,29] In the same way, NDPA cannot enter into the channel of HZSM-5. Although NDPA may adsorb on the external surface of the zeolite or insert the –N–N=O group into the channel prior to degradation,[6,24] the corresponding conversion is relatively low because most of the channel is inaccessible to the reactant and successive adsorption cannot proceed until the degradation products desorb from the orifice. Hβ zeolite has a channel with a size ($0.66 \times 0.67\ nm^2$) that perfectly matches the NDPA molecule, which no doubt accelerates the adsorption and reaction of the guests because they can continuously adsorb and undergo degradation. In our experiments 1 g of Hβ zeolite could catalyze the degradation of 0.23 mmol of NDPA at room temperature; its efficiency is close to that of NaY for degrading NDMA ($0.26\ mmol\ g^{-1}$) at elevated temperature.[19] The reason why the HY zeolite with a larger pore size (0.74 nm) exhibits a relatively low activity in the degradation of NDPA is still unclear.

To check whether liquid acids and zeolites have the same function in the degradation of NDPA at ambient temperature, a series of experiments was designed. When NH_3-poisoned Hβ was used to degrade NDPA in solution at room temperature, only 13.2 nmol of the nitrosamines were degraded in 2.5 h while the color of the sample became light blue. In succession 50 mg fresh Hβ was put into the reaction system but it can only degrade 50 nmol NDPA within 0.5 h, one tenth of the amount usually degraded on Hβ, as seen in Fig. 5. Moreover, part of the newly added Hβ in the solution turned blue and the rest remained white. Finally 0.5 ml HBr–acetic acid was added into the system, which degraded 62.6 nmol NDPA; meanwhile the entire amount of Hβ came back to white. The NH_3 poison led to the lost of Hβ's strong acidity so it could not degrade NDPA as usual, but its adsorption capacity was unaffected so that NDPA was still adsorbed in the channels, though it could not be fully protonated and degraded. The added fresh Hβ could not recapture the adsorbed NDPA from the poisoned sample, so it only degraded the nitrosamines remaining in solution. In contrast, the added HBr and acetic acid molecules could enter the zeolite channels to degrade the adsorbed NDPA. In addition, the radicals on zeolite, which give a blue color, can obtain a proton from the acid solution to form DPA, so that the blue color of the zeolite disappears. Although acid solutions and acidic zeolite can degrade NDPA at room temperature, and in principle one should expect the behavior of liquid and solid acids to be the same, they play different roles in this reaction; the former is only a reactant but the latter is a catalyst. To support our statement, the degradation of NDPA in the presence of a catalytic amount of liquid acids was measured at room temperature. Benzyl acid was inactive while a given amount of hydrochloride acid containing 1.18×10^{-6} mol of proton produced 1.08×10^{-6} mol of NO product, in good agreement (within experimental error) with the stoichiometric relation that each NO forms at the expense of one proton. On the other hand, the amount of strong acid sites of Hβ is about, if not less than, a quarter of the total amount of acid sites (0.36 mmol g^{-1}), consulting the NH_3-TPD spectrum in Fig. 6, but the roughly 0.09 mmol g^{-1} of acid sites makes 0.23 mmol of NO as mentioned above, which confirms the catalyst function of the zeolite acid sites in the degradation of NDPA.

3-3 Degradation products of NDPA formed in zeolites

Adsorption of NDPA in acidic zeolites activated at 500 °C for 2 h led to a color change of the sample from white to blue in dichloromethane solution at room temperature. Afterwards, the color of HY zeolites in solution became green with decay of the blue and the same phenomenon was also observed on Hβ zeolites. Upon exposure to air, the HY sample changed its color from green to dark yellow while Hβ changed to light yellow after washing and evaporation of the solvent. Nonetheless, the HZSM-5 sample kept its blue color for 2 weeks. Diffuse reflectance (DR) UV/VIS and *in-situ* FTIR techniques were utilized to analyze the degradation products of NDPA in zeolites; Fig. 7 shows the UV spectrum. A long-wavelength adsorption band assigned to the $\mathrm{DPA}^{+\bullet}$ radical cation, with $\lambda_{\max} = 690$ nm and a shoulder near 630 nm, and a short-wavelength band ($\lambda_{\max} = 420$ nm) of the $\mathrm{DPA}^{\bullet}$ radical were observed in the spectrum on HZSM-5.[29] The intensity and shape of these bands did not change much with increasing time as seen in Fig. 7 (curves a). The IR bands of NDPA on HZSM-5, shown in Fig. 8, have similar vibrational frequencies to those in the standard spectrum of DPA,[22] too, but no bands due to NO_x were detected. Relying on these results the degradation of NDPA on HZSM-5 zeolite can be supposed: NDPA molecule is degraded in the pore mouth of HZSM-5 due to the geometric limitation of the channels, and NO, the fragment indicating that the degradation of nitrosamines starts with the rupture of the N–NO bond, escapes from the reaction system owing to the weak interaction between NO and protons;[1] meanwhile, the other moiety is adsorbed into the channels of the zeolite.

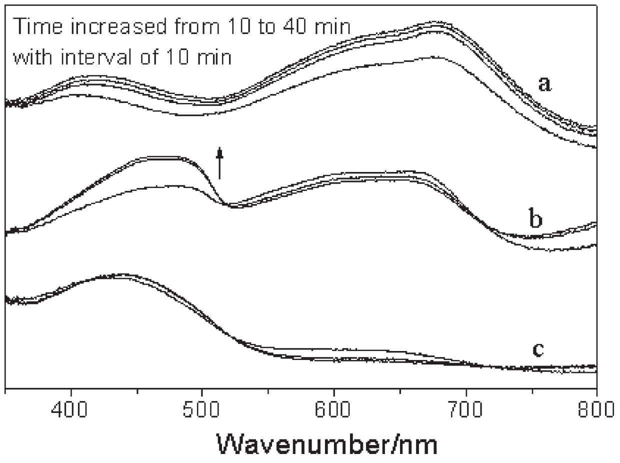


Fig. 7 DR spectra of the zeolites (a) HZSM-5, (b) Hβ and (c) HY used in the degradation of NDPA at ambient temperature for different times with an interval of 10 min.

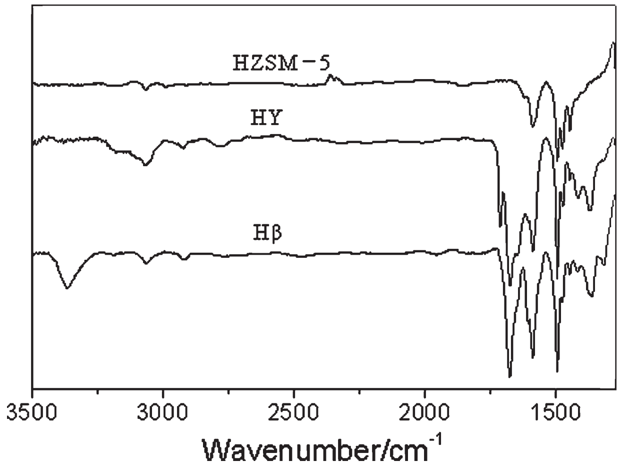
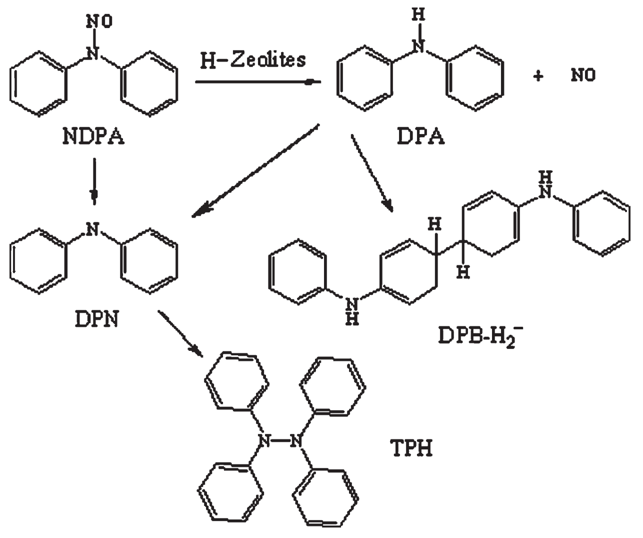


Fig. 8 FTIR spectra of NDPA adsorbed on acidic zeolites.

When Hβ was added into the NDPA solution, the zeolite turned blue, accompanied with the release of NO. After evaporating the solvent, the DR spectrum of the used zeolites showed two long-wavelength bands with $\lambda_{\max}$ of 465 and 670/610 nm (Fig. 7), which could be assigned to the diphenylbenzidine (DPB) radical cation (denoted as $\mathrm{DPB}^{\bullet+}$) and the DPA radical cation (denoted as $\mathrm{DPA}^{\bullet+}$), respectively.[29] Upon prolonged exposure to air, the color of the sample changed from blue to green and then to yellow, while in the meantime the absorption band at 465 nm in the DR spectrum increased at the expense of the 630 nm band, indicating the deprotonation of $\mathrm{DPA}^{\bullet+}$ to $\mathrm{DPB}^{\bullet+}$.[29] Degradation of NDPA could occur on Hβ even at 4 °C but 24 h were needed for the color of the zeolite to change to blue, while $\mathrm{DPA}^{\bullet+}$ and $\mathrm{DPB}^{\bullet+}$ products appeared in the DR spectrum of the sample. The IR spectrum of NDPA adsorbed on Hβ (Fig. 8) not only includes the bands of DPB similar to those in the standard spectrum[22] but also contains some new bands. The ones at 1311 and 1676 cm^{-1} can be assigned to the adsorbed NOx[30] and the band at 1363 cm^{-1} originates from the symmetric stretch of the aromatic $-NO_2$ group, which implies the nitrification of DPB in the channels of Hβ. Thus, NDPA can be adsorbed in the Hβ zeolite and degraded to $\mathrm{DPA}^{+\bullet}$ radical cation and NO. For unknown reasons NO forms NOx in zeolite, as reflected in the IR spectrum (Fig. 8). Since no pyrolysis side-reactions can occur in this low temperature, the NOx and DPA product species mean that degradation of nitrosamines like NDPA on zeolite begins assuredly from rupture of the N–NO bond. The presence of protons is helpful for the degradation of nitrosamines, protonating the adsorbed NDPA molecule and accelerating the N–N bond breaking in the electrostatic field provided by the channels of the acid zeolite, forming $\mathrm{DPA}^{\bullet+}$ as the primary product. The enthalpy of the N–N bond in NDPA is 46 kJ mol^{-1}, much smaller than that of acyclic nitrosamines (217–225 kJ mol^{-1}).[31] This bond can also be broken on acid zeolite as in pyrogenation, $Ph_2NNO \rightarrow Ph_2N^{\bullet} + NO$, since a variety of organic radical cations can be generated spontaneously by inclusion of their precursors into zeolite,[32] stabilized by the rigid microporous solid.[33] Moreover, two $\mathrm{DPA}^{+\bullet}$ radical cations could polymerize to $\mathrm{DPB}^{+\bullet}$ such that the 670/610 nm bands of $\mathrm{DPA}^{+\bullet}$ decay while the 465 nm of $\mathrm{DPB}^{+\bullet}$ increases, as the DR spectra demonstrated.

The products of NDPA degradation in HY zeolite differ from those in HZSM-5 and Hβ. Only one band appeared in the DR spectra of HY with a $\lambda_{\max}$ of 445 nm (Fig. 7), due to the $\mathrm{DPN}^{\bullet}$ radical resulting from tetraphenylhydrazine (TPH) illuminated by UV light;[34] the intensity and shape of this band did not change with the time of exposure to air.



Scheme 2 The possible degradation pathways of NDPA in acidic zeolites.

DPN• radical in zeolite Y is very reactive so it is easy for two DPN• radicals to react with each other, forming TPH in the super-cage of HY zeolites. IR tests confirm that TPH is the final product of NDPA degraded in HY zeolite, since the recorded bands coincide with those in the standard spectrum of TPH.[22] At the same time, the IR bands of NO_2 (1311 and 1676 cm^{-1}) and N_2O_4 (1713 cm^{-1}) appeared,[30] accompanied by the band at 1363 cm^{-1} assigned to the $–NO_2$ functional group as seen in Fig. 8. TPH in HY may also be nitrified like DPB in Hβ.

The pore structure of zeolites affects the formation of the degradation product of NDPA. In HZSM-5 zeolite with a pore diameter smaller than the molecular size of NDPA, the nitrosamine is cleaved to $DPA^{+\bullet}$ radical cation and NO. In Hβ and HY zeolites with wider channels, the $DPA^{+\bullet}$ radical cations undergo several further reactions (Scheme 2) and form different products: DPB is produced in the channels of Hβ while TPH forms in the super-cage of HY zeolites. Although the intermediates and product selectivity of zeolites have long been well-known, the influence of the formation of different products on the degradation of NDPA at ambient temperature is not clear and further research is thus desirable.

When CaA zeolite, activated at 500 °C for 2 h, was used to catalyze the degradation of NDPA at room temperature, no NOx gaseous products were detected but the sample in dichloromethane solution became light blue. No sooner was the solvent evaporated that the color of the sample faded immediately and its DR spectra showed no bands in the range of 400–800 nm. The IR bands of the sample changed gradually with prolonged purge time (Fig. 9). The bands of the phenyl group at 1613 and 1464 cm^{-1}, along with the ones 2997 and 3060 cm^{-1} (not shown in Fig. 9), vanished,[22] whereas the bands at 1640, 1592 and 1492 cm^{-1} increased in intensity. Since the 1640 and 1592 cm^{-1} bands appear and increase isochronously, they are assigned to the same species, bidentate NO_3^-.[35] At the same time, the C–N band at 1276 cm^{-1} split into two new ones, emerging near 1315 (NO_2) and 1262 (N_2O) cm^{-1}.[22,30,36] When the IR measurements were finished, the color of the CaA plate that only adsorbed NDPA in the gaseous phase had also changed to light blue, indicating the presence of DPA radical cations. These phenomena reveal the considerable catalytic activity of the calcium ion in zeolite A, which may originate from the generation of protons through dissociation of water from $Ca(H_2O)_2^{2+}$ during the activation process,[37] and imply that NDPA is adsorbed in the pore mouth of CaA zeolites and degraded to form DPA radical cation and NO. However, NO is adsorbed in the channels of CaA and forms a series of reactive products, different from those on acidic zeolite from which NO desorbs.

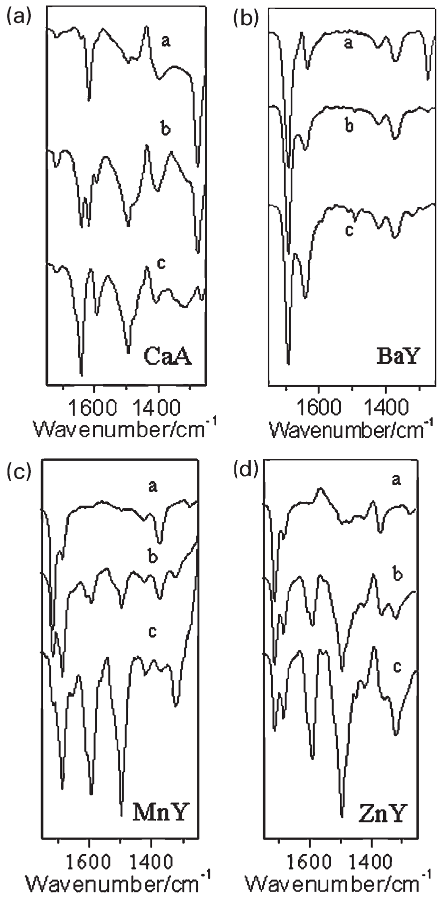


Fig. 9 FTIR spectra of NDPA adsorbed on (a) CaA, (b) BaY, (c) MnY and (d) ZnY zeolites after purging with a nitrogen flow for 11, 12 and 13 min or longer for traces a, b and c, respectively.

BaY, MnY and ZnY zeolites could also degrade NDPA in dichloromethane solution at room temperature, provided they were activated at 500 °C, but their catalytic activity was quite low, similar to that of CaA. The difference between them and HY is in the IR bands of the adsorbed NOx species. After BaY adsorbed NDPA the IR spectra exhibited some bands of TPH, but their intensity was very weak (Fig. 9). In contrast, the 1640 cm^{-1} band of bidentate NO_3^- became the strong one and its intensity increased as the time was increased,[35] overlapped the band of the phenyl group at 1587 cm^{-1}. At the same time, a very weak band of unidentate nitrate appeared at 1556 cm^{-1} with prolonged time, though the band of the $–NO_2$ functional group (1363 cm^{-1}) remained unchanged.[38,39] In the IR spectra of MnY and ZnY with adsorbed NDPA, bands of NO_2 (1676, 1311 cm^{-1}) and N_2O_4 (1713 cm^{-1}) were detected (Fig. 9).[30] From these phenomena, it is very likely that NOx and the fragments from degraded NDPA are trapped in MnY, ZnY and BaY zeolites instead of escaping into the atmosphere, which is beneficial for environmental protection and opens a new application of zeolites.

4. Conclusions

Some conclusions can be tentatively drawn from these results described above.

(1) Because of the interaction between the –N–N=O group and electrostatic fields in the channels of the zeolites, a zeolite with a small pore size can still selectively adsorb bulky nitrosamines like NDPA through a specific mode of inserting

adsorption, in which the adsorbate inserts its –N–N=O functional group into the channel. In this study, we have presented the first laboratory evidence directly supporting the inserting adsorption model on zeolite.

(2) Degradation of nitrosamines at room temperature by zeolites is observed for the first time and confirmed; the kinds of metal ions in the zeolite are proven to influence the catalytic activity of the samples. In addition, the degradation of nitrosamines on acidic zeolites is directly shown for the first time to be from cleavage of the N–NO band without interference from side-reactions like pyrolysis.

(3) The acidity of zeolite is an important factor affecting the degradation of NDPA at ambient temperature and Brønsted acid sites are the main active centers. The product selectivity of zeolite is observed in the degradation of nitrosamines. The presence of metal ions such as Ca^{2+} or Ba^{2+} in the zeolite is helpful to trap the NOx products and to prevent secondary environmental pollution.

Acknowledgements

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