Ordered Mesoporous Materials. Novel Catalyst for Degradation of *N*′-Nitrosonornicotine

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Temperature-programmed surface reaction (TPSR) of *N*′-nitrosonornicotine (NNN) was firstly reported on zeolite and ordered mesoporous materials. Among the catalysts SBA-15 and MCM-48 exhibited an activity much higher than zeolite NaY. They could also adsorb nitrosamines without interference of organic solvent, which will be helpful for environmental protection.

Existence of carcinogenic agents like nitrosamines in the smoke of cigarettes is one important reason why smoking caused health hazard. Among these nitrosamines the tobacco specific nitrosamines (TSNA) receive much attention because their strong carcinogenesis no matter they are transferred from tobacco or pyrosynthesized during combustion.[1] While filtration with cellulose acetate has proven very effective for the volatile nitrosamines, such is not the case for the TSNA. Therefore new material is sought to eliminate the TSNA. Recently zeolites were directly added in cigarette therefore a significant amount of carcinogenic compound was removed from smoke,[2] including 40-50% of TSNA from the mainstream and around 50-70% from side-stream. Unfortunately, suspicions still remain since there is no direct experimental evidences on the degradation of TSNA over zeolite. TSNA is well-known to have a big molecular volume so it may be difficult to be adsorbed in the channel of zeolite like Y and ZSM-5. Ordered mesoporous materials like SBA-15 can provide the ordered pore with the size of approximately 10 nm, so they are expected to be superior to zeolite in the case of bulky reagents exceeding the size of the zeolite pores.[3] However, there is no open literature on the reaction of TSNA over mesoporous materials up to date; Moreover, MCM-41 was found not to possess the selectivity in adsorption of *N*-nitrosodimethylamine (NDMA) or *N*-nitrosopyrrolidine (NPYR),[4] which hinders its application in removal of nitrosamines from environment. Can SBA-15 have the feature of selectively adsorbing nitrosamines in solution? Does the ordered mesoporous material exhibit an excellent catalytic activity in the degradation of TSNA in comparison with zeolites? These questions prompt us to study the TPSR of NNN, the representative of TSNA, on zeolite and ordered mesoporous materials.

NDMA, NPYR, and *N*-nitrosohexamethyleneimine (NHMI) was purchased from Sigma.[4] NNN, provided by Yunnan Tobacco Institute, can also be purchased from Sigma and was dissolved in methylene chloride at the ratio of 7:5 mg/mL. Zeolite NaY (Si/Al = 2.86) and NaZSM-5 (Si/Al = 23) were commercially available powder, and HZSM-5 obtained by an ion exchange method.[4] Silicic hexagonal mesoporous material SBA-15 and cubic MCM-48 were synthesized according to literatures.[5,6] Their surface area was 918 m^2/g and 983 m^2/g and the pore size was 8.0 nm and 2.8 nm respectively. The purity of carrier gases N_2 and H_2 were 99.99%, and all agents used were of AR grade.

Adsorption of nitrosamines was performed in micro-reactor filled with 5 mg of sample and the decrement in the ratio of solute to solvent was utilized to calculate the amount of adsorbed nitrosamines.[4] In the process of TPSR,[4] the NNN solution of 0.1 mL was injected after the sample was activated at 773 K. The amount of NO_x liberated during TPSR process was determined by spectrophotometric method and represented the decomposed nitrosamines.[7]

The structure of NNN looks like that an H atom in the five-membered ring of NPYR is replaced by a pyridine, so its molecular size can reach 0.75 × 0.80 nm which is slightly larger than the pore size of zeolite NaY (0.74 nm). Unlike NDMA and NPYR that had been decomposed more than 70 μmol/g owing to relative small volume,[4] NNN seemed quite difficult to be adsorbed and decomposed on NaY so the concentration of NOx formed was always below 1 μmol/g as seen in Figure 1. A weaker catalytic activity was observed on NaZSM-5 zeolite because of its smaller pore size (0.56 × 0.54 nm). The NNN molecule may be adsorbed in the channel of ZSM-5 by inserting with the characteristic group of –N-N=O as that assumed in the adsorption of NPYR on zeolite NaA,[7] and thus the N-N bond can be broken at elevated temperature since it is the weakest bond in the structure of nitrosamines, therefore the decomposition of nitrosamines and elimination of the carcinogenic compound is realized. Otherwise the special restriction will inhibit the adsorption. Similar profile of NOx desorption was also found on HZSM-5 zeolite in the TPSR process, but the maximum value exceeded 1 μmol/g. Such different catalytic behavior between HZSM-5 and NaZSM-5 had been reported in TPSR of NDMA and NPYR and attributed to the strong acidity of zeolite HZSM-5, since proton could accelerate degradation of nitrosamines.[8] In contrary, SBA-15 was much more active for degradation of NNN than these common zeolites under the same condition. The NNN began to decompose on SBA-15 at 473 K, and a maximum concentration appeared near 593 K exceeding 3 μmol/g, twice as high than that on HZSM-5. Since HZSM-5 is an acidic zeolite but the acidity of silicic SBA-15 does not exceed that of amorphous

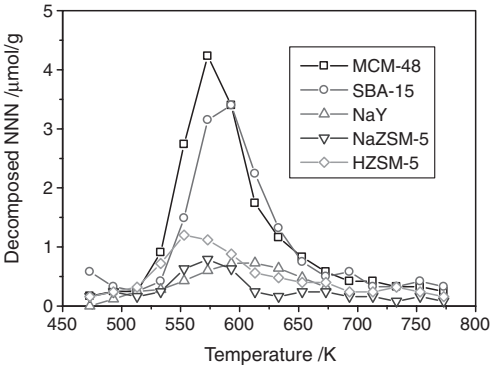

Figure 1. Profile of NOx liberated in the TPSR process of NNN.

aluminumsilicates,[3] it is clear that pore structure of catalyst has a stronger impact than the surface acidity on the degradation of NNN. MCM-48 showed a slightly higher activity in the TPSR of NNN with a maximum concentration of NOx exceeding 4 μmol/g though its pore size is smaller (Figure 1). The ordered mesoporous materials are the better catalysts for decomposition of bulky molecule like NNN than zeolites, since their pore size allows the whole pore system to be used while zeolitic pore is inaccessible.[9] Nitrosamines should be adsorbed on catalyst at first in the process of TPSR,[4] which is easy on SBA-15 or MCM-48 because of their enormous pore but it is hard on zeolite owing to the narrow channel. Consequently the more the product is degraded the more NOx is formed on SBA-15 and MCM-48. Although the pore dimensions, size and wall thickness of the two samples is quite different, the two mesoporous materials give identical activities originating from the existence of large pore. A further proof on this inference came from silica whose catalytic activity was also higher than zeolites in the degradation of NNN though its surface area (350 m^2/g) was smaller than that of NaY (766 m^2/g), which would be discussed in detail elsewhere.

Selective adsorption of nitrosamines is of great importance for the porous material to eliminate the carcinogenic compound in tobacco smoke. NDMA is a volatile nitrosamines with the smallest molecular size, so its solution is usually used to check if the sample possesses the ability of selectively adsorbing nitrosamines.[4,7] Unlike MCM-41 that did not have the function of selective adsorption,[4] SBA-15 could adsorb NDMA in methylene chloride solution at 453 K or 523 K as illustrated in Figure 2. Although only 39% of NDMA were separated from solution by use of SBA-15 at 453 K when the total amount reached 1.77 mmol/g, an indication was obtained that SBA-15 can adsorb nitrosamines without interference of organic solvent. Contrarily amorphous silica showed a much lower ability to selectively adsorb NDMA resulting from the absence of ordered pore structure. Increasing the adsorption temperature deceased the capacity of SBA-15 to adsorb NDMA, the adsorbed proportion was lowered to 24% at 523 K when the total amount reached

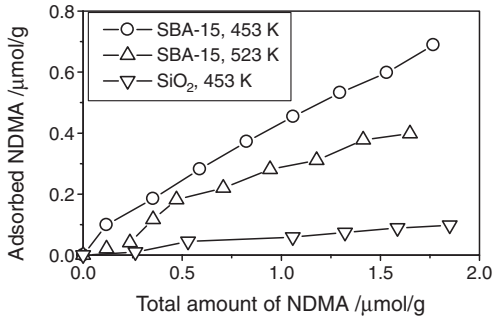

Figure 2. Adsorption of NDMA on SBA-15 and SiO_2.

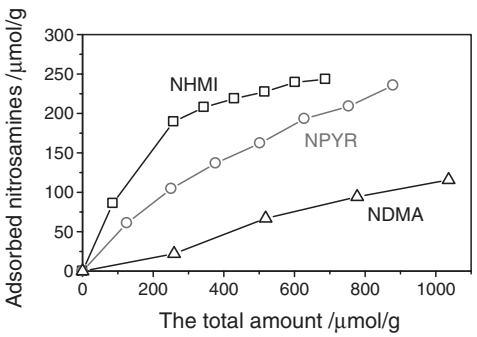

Figure 3. Adsorption of nitrosamines on MCM-48 at 453 K.

2.12 mmol/g, implying the ordered mesoporous material should be used as a catalyst instead of adsorbent to remove nitrosamines at high temperature.

Further investigation reveals the adsorbent-adsorbate effect in the adsorption of nitrosamines on ordered mesoporous material, similar to that found on zeolite.[7] As the molecular dimensions of adsorbate increased from 0.45 nm (NDMA) to 0.59 nm (NHMI), the amount of nitrosamines adsorbed on MCM-48 significantly increased as demonstrated in Figure 3. This indicates the potential application of ordered mesoporous material to adsorb those bulky pollutants from environment. Together with the high activity exhibited in catalytic degradation of bulky nitrosamines like TSNA, SBA-15 and MCM-48 will be the candidate for eliminating the smoking pollution in environmental protection.

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