



Liquid adsorption and catalytic degradation of 4-methylnitrosamino-1-3-pyridyl-1-butanone (NNK) by zeolite



Xiao Dan Sun^{a, b}, Shuo Hao Li^{a, b}, Xin Yu Ming Dong^a, Lei-jun Wang^b, Wen-bo Gu^b, Wei-miao Wang^b, Zheng-yu Yang^{b, **}, Ying Wang^{a, c, ***}, Jian Hua Zhu^{a, *}

^a Key Laboratory of Mesoscopic Chemistry of MOE, College of Chemistry and Chemical Engineering, Nanjing University, Nanjing, 210023, China

^b Technology Center of Shanghai Tobacco (Group) Company, Shanghai, 200082, China

^c Ecomaterials and Renewable Energy Research Center, Nanjing University, Nanjing, 210093, China

ARTICLE INFO

Article history:

Received 29 November 2016

Received in revised form

17 January 2017

Accepted 29 January 2017

Available online 2 February 2017

Keywords:

Zeolite

Liquid adsorption

4-Methylnitrosamino-1-3-pyridyl-1-

butanone (NNK)

Catalytic degradation

Environment protection

ABSTRACT

Adsorption of 4-methylnitrosamino-1-3-pyridyl-1-butanone (NNK) along with *N*-nitrosanornicotine (NNN) in water is studied for the first time with the monitoring of LC-MS/MS. In the mixed aqueous solution of NNK and NNN, NaZSM-5 zeolite uniquely captured NNK but refused NNN. And the influence of initial concentration, adsorption time and type of sorbents were systemically investigated. Degradation of NNK adsorbed on zeolite is studied with TG/MS and FTIR methods for the first time. It was degraded to NO, pyridine, amine and propanal at around 600 K, avoiding formation of volatile nitrosamines and secondary pollution.

© 2017 Elsevier Inc. All rights reserved.

1. Introduction

Tobacco specific *N*-nitrosamines (TSNA) are the derivatives of nicotine characterized with *N*-nitroso group (N-NO) and they can induced oral, lung, pancreatic and esophageal cancers in laboratory animals [1]. Apart from smoking and esophageal pollution, TSNA in water is becoming an unexplored environmental health risk [2]. Thus, control of TSNA pollution is important for public health. Among four components of TSNA, 4-methylnitrosamino-1-3-pyridyl-1-butanone (NNK) and *N*'-nitrosanornicotine (NNN) have been evaluated as the carcinogens to humans (Group 1) [3], and NNK owns a higher carcinogenicity. The other two are *N*'-nitrosoanatabine (NAT) and *N*'-nitrosoanabasine (NAB) [4]. NAT is a weak carcinogen though it is the most component in TSNA while

NAB apparently lacks activity [5,6]. Hence seeking efficient and low-cost sorbent that can recognize and selectively capture NNK in water is the real challenge for accurate removal of environmental carcinogen to protect human health. Zeolites are deemed to be promising candidate and tried to trap nitrosamine in solution because of their shape selectivity in adsorption [7,8]. KA and CsA zeolites even distinguished the functional group of *N*-nitrosodiphenylamine (NDPA) and nitrobenzene, and captured the bulky former rather than the smaller latter [7]. Recently, zeolites were tried to adsorb TSNA in tobacco extract solution [4,6], in which NaZSM-5 zeolite displayed a kind of selectivity forwards NNK but the reason remains unknown [6]. In fact, little research reports adsorption and/or catalytic removal of NNK though NNK is the most toxic member of TSNA and listed as one of the 7 representative hazardous chemicals in mainstream smoke by Chinese tobacco industry [9].

Safety disposal of the trapped TSNA is another unexplored environmental health risk. Pyrolysis of TSNA can disrupt whole compound but has two drawbacks. One is the high temperature, and another is formation of new nitrosamines [10]. Actually, it is only required to eliminate the carcinogenicity of TSNA [11]. *N*-Nitroso group of nitrosamine is a leading cause of cancer [12], and

* Corresponding author.

** Corresponding author.

*** Corresponding author. Key Laboratory of Mesoscopic Chemistry of MOE, College of Chemistry and Chemical Engineering, Nanjing University, Nanjing, 210023, China.

E-mail addresses: zyyang@sh.tobacco.com.cn (Z.-y. Yang), wangy@nju.edu.cn (Y. Wang), jhzhu@nju.edu.cn (J.H. Zhu).

its fracture will remove the carcinogenicity of TSNA. It is possible to break the N-N bond of TSNA if the carcinogen is trapped by zeolite [10], but little is known whether the function of zeolite is altered by the interference of water. Also, the degradation of NNK has not been reported though its carcinogenicity was widely studied. Herein we utilize the mixed aqueous solution of NNN and NNK to examine the adsorption of zeolites by LC-MS/MS monitoring. Furthermore, the catalytic degradation of NNK adsorbed on zeolite is studied with *in-situ* FTIR and TG/MS technologies.

2. Experiments

Zeolites NaZSM-5, NaA and NaY were commercial available powders samples from the Catalyst Plant of Nankai University (China). CaA zeolite was provided by Shanghai Zeolite Molecule Sieve Co, LTD [4,6]. MCM-41 sample was synthesized according to literature [13]. NNN, NNK were bought from Toronto Research Chemical. All of reagents were of analytical grade and used as received without further purification.

X-ray diffraction (XRD) pattern of sample was recorded on an XRD-6000 diffractometer using Cu-K α radiation in the 2θ range of 10–80° for zeolites or 0.5–10° for MCM-41 when the voltage, current and scan rate are 40 V, 40 mA and 6° min⁻¹, respectively. The N₂ sorption isotherms at 77 K were measured using a Micromeritics ASAP 2020 volumetric adsorption analyzer, and about 100 mg of sample was evacuated at 573 K for 4 h in the degas port prior to test. The BET surface area was calculated using adsorption data in the relative pressure (P/P_0) range from 0.04 to 0.2, while the total pore volume was determined from the amount adsorbed at a relative pressure of about 0.99 and the pore size distribution curve was calculated from the analysis of the absorption branch of the isotherm using the Barrett Joyner Halenda (BJH) algorithm for MCM-41 or Density Functional Theory method for zeolites [6].

The initial concentrations (C_0) of mixed aqueous solution with equimolar amount of NNN and NNK were 8.98 and 9.94 $\mu\text{mol L}^{-1}$, respectively, and it was then diluted by denionized water to get the solution with reduced concentration 1/2 C_0 , 1/4 C_0 , 1/8 C_0 and 1/16 C_0 . Liquid adsorption of TSNA was performed as follows: a certain amount (usually 50 mg) of adsorbent without any pretreatment was added into 10 mL solution with the solid to liquid ratio of 5 ($S/L = 5$), and the mixture was in a thermostatic shaker at 303 K for a given time (usually 1 h) [4]. Finally, it was centrifuged at 4000 rpm for 20 min to separate the solid and liquid. In other tests, the sample was added into the solution for different time such as 5, 15, 30 or 45 min to explore the time required for adsorption equilibrium with the adsorption process same as above mentioned. In addition, single NNN or NNK aqueous solution was prepared and both kept the same concentration (C_0) as that of NNN or NNK in mixed solution, that is, C_{NNN} of 1850 ng mL^{-1} or C_{NNK} of 2070 ng mL^{-1} . Then, 50 mg adsorbent was put into the single solution to perform the adsorption as that in mixed solution in the same condition.

To explore the catalytic degradation of TSNA adsorbed by zeolite, diffuse reflectance FTIR test was performed on a Nicolet 5700 FT-IR spectrometer, in which background spectra were collected on the activated adsorbate-free NaZSM-5 zeolite to exclude the overlap of infrared adsorption features that originate from the zeolite structural vibrations and the adsorbed surface species. And the background spectrum was recorded as follows: the blank NaZSM-5 zeolite was purged with N₂ flow at 303 K for 0.2 h to remove the physically adsorbed impurities. Then, the sample was heated at the rate of 10 K min⁻¹ and the signal was recorded at given temperature (323 K, 423 K, 573 K and 723 K). After NaZSM-5 adsorbed NNK in aforementioned single NNK aqueous solution, the zeolite solid was obtained by centrifugation and dried overnight in an oven. Then, the zeolite powder adsorbed NNK was purged for

0.2 h prior to recording the FTIR spectrum with the same procedure as that in background spectra. Finally, the background spectrum was deducted to obtain the spectrum of NNK in NaZSM-5. To explore the catalytic degradation of TSNA adsorbed by zeolite, the adsorbed sample was dried and transferred into the crucible of TG-MS instrument to run the experiment of Temperature Programmed Surface Reaction (TPSR). It was degassed at 303 K for 0.2 h at first and then the TGA was operated from 303 K to 1073 K at the rate of 10 K min⁻¹ in the flow of argon or air, meanwhile the released components were sent to the mass spectrometer for analysis [10,14]. The gas line between TG and MS was heated to 463 K to avoid cold points and thus condensation of some gaseous products.

The NNN and NNK contents of aqueous solution were determined by Applied Bio systems 4000 Q TRAP mass spectrum combined with an Agilent 1200 liquid chromatogram system equipped with a column of CAPCELL PAK C18 MG2 (4.6 mm \times 150 mm, 3 μm). At first, 1 mL internal standard solution was added into 2 mL aqueous solution, and then the mixture was diluted to 10 mL and passed through 0.2 μm filter membrane. The obtained clarified solution was measured on the LC-MS/MS system using an internal standard method. And the procedure and parameters used in the detection were same as that reported previously [4,6].

3. Results

3.1. The structural properties of sorbents

Three types of zeolites showed their typical crystal in the XRD pattern [6] (Fig. S1a), while mesoporous silica MCM-41 displayed three well-defined peaks (Fig. S1b), assigned to (100), (110) and (200) face for $p6mm$ symmetric respectively [6]. The texture properties of different sorbents were listed in Table S1. CaA zeolite had a smaller surface area (636 $\text{m}^2 \text{g}^{-1}$) than NaA did (800 $\text{m}^2 \text{g}^{-1}$) due to the larger volume of calcium ion, though they had the same pore structure and the Si/Al ratio. MCM-41 had the pore size of 2.8 nm and a larger surface area than that of these zeolites. The stability of NNN and NNK in aqueous solution was carefully examined by LC-MS/MS method, and there was no obvious change in concentration within experimental error ($\pm 4\%$) even if this solution was stirred for 24 h, implying that stirring did not make TSNA decomposed (Fig. 1a).

3.2. Adsorption of TSNA in aqueous solution

Various sorbents were employed to remove NNN and NNK in the mixed aqueous solution. The adsorption efficiency of NaZSM-5 zeolite reached 97.3% at 1 h for NNK but zero for NNN in the mixed solution (Table 1), which meant the selectivity of NaZSM-5 toward NNK in aqueous solution. According to the analysis of LC-MS/MS, 76% NNK was captured by NaZSM-5 zeolite in the first 5 min, almost all of NNK (95.7%) in solution were trapped at 30th min and this value remained for 24 h, but there was no NNN trapped throughout the adsorption, which demonstrated again the selectivity of NNK by NaZSM-5 zeolite (Fig. 1b). A difference observed in time of 5 min in reduction level between C_0 (76%) and other lower concentrations (>90%) reflects different diffusion of NNK that induces different adsorption equilibrium times. For instance, NaZSM-5 reached the adsorption equilibrium of NNK at 5 or 15 min when the initial concentration was diluted to 1/16 C_0 or 1/8 C_0 , respectively, and at 30 min as the initial concentration rose to 1/4 C_0 or above. On the other hand, no NNN was trapped by NaZSM-5 zeolite in the aqueous solution until the C_0 was decreased to one fourth (1/4 C_0) and the adsorptive time extended to 60 min, and the reduction of NNN was low (2%). In case that the concentration decreased to 1/8 C_0 , the value rose to 4.4%. NaZSM-5 started to trap NNN at

Download English Version:

<https://daneshyari.com/en/article/4758418>

Download Persian Version:

<https://daneshyari.com/article/4758418>

[Daneshyari.com](https://daneshyari.com)