Catalysis Today 212 (2013) 52–61

Contents lists available at SciVerse ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Applying heterogeneous catalysis to health care: *In situ* elimination of tobacco-specific nitrosamines (TSNAs) in smoke by molecular sieves

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ARTICLE INFO

Article history:
Received 11 January 2012
Received in revised form 13 July 2012
Accepted 22 July 2012
Available online 25 September 2012

Keywords:
Zeolite
Mesoporous silica
Tobacco-specific nitrosamines (TSNAs)
Catalysis
Pyrolysis
Smoke

ABSTRACT

To expand heterogeneous catalysis to health care and to control the carcinogens in environment, molecular sieves are put into the tobacco rod of cigarettes as the cigarette-catalyst (cig-cat) to *in situ* eliminate tobacco-specific nitrosamines (TSNAs) in mainstream smoke during the combustion of cigarette. Several zeolites and mesoporous silicas are utilized for comparison, in order to assess the impact of pore size, Al content, morphology as well as acid–base property of additives on the reduction of TSNA content in smoke. When these additives are activated as the hot zone in burning cigarette approaches, they will remove TSNAs once these carcinogens transfer or form in the smoke. Actually they can remove the TSNA up to 35% in the smoke of Burley type tobacco, and most of these additives can keep their structure after tobacco combustion. These latest results are beneficial for controlling the environment pollution caused by smoking.

1. Introduction

Smoking is the global problem of environment pollution. Among thousands of components in tobacco smoke, nitrosamines, especially the tobacco-specific nitrosamines (TSNAs) that present abundantly in the particulate phase of cigarette smoke, *N*′-nitrosonornicotine (NNN), 4-methylnitrosarnino-1-3-pyridyl-1-butanone (NNK), *N*′-nitrosoanatabine (NAT), and *N*′-nitrosoanabasine (NAB) are well known to be the strong carcinogens [1]. In general, about 40–46% of NNN and 26–37% of NNK in the mainstream smoke were transferred from tobacco [2,3], and the residual resulted from pyrosynthesis during combustion. They exist in not only the mainstream smoke (inhaled by smoker), but also the side stream smoke to make non-smokers suffer from the risk of various diseases. Therefore, eliminating these hazardous substances is an important task for environmental protection.

Recently removal of nitrosamines by porous material is thoroughly investigated in laboratorial scale. Among them zeolites can efficiently adsorb and catalytically degrade volatile nitrosamines [4–7], their special pore structure offers the geometric confinement toward the target [5], while the cations inside the channel attach the N—NO group of nitrosamines through electrostatic interaction, inducing the nitrosamine to be adsorbed in the way of inserting the N—NO into the channel [6]; likewise, the catalytic degradation of nitrosamines in zeolite starts from rupture of N—N bond [6]. Incorporation of metal oxide in zeolite is able to further improve the adsorption and catalytic degradation of nitrosamines [4]. Moreover, mesoporous silica such as MCM-41, SBA-15 and their modified analogs are also employed to trap the bulky nitrosamines such as TSNAs [4,7].

In the cigarette smoke, however, removal of nitrosamines is different and complex. Most TSNAs exist in the particulate matter whose size exceeds the pore diameter of zeolites [8,9], so that the selective reduction of TSNAs in smoke by the zeolite additive in filter seems intrinsically impossible. Thus, a new strategy is tried to add a candidate zeolite directly into the tobacco blend of cigarette. In this way, the zeolites will play the role of catalyst as they are activated when the hot zone in the burning cigarette approaches [10], degrading nitrosamines into the non-carcinogenic fragments [4,11] and sometimes suppressing the formation of TSNAs through eliminating their precursors [6]. However, it is unknown the actual function of mesoporous materials when they are added into the tobacco rod. Is the mesoporous silica superior to zeolite in trapping TSNAs due to its larger pore size? Can the mesoporous silica with the fiber-like morphology more efficiently intercept the particulate matter in smoke than zeolite crystalline? This spurs us to examine the practical performance of mesoporous silica. Also, suspicions still exist on the actual function of zeolite in reducing TSNAs content of smoke. Zeolite Y and A had been tried as the component of catalyst for cigarette [10,11], but their performances included

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http://dx.doi.org/10.1016/j.cattod.2012.07.045

the contribution of assistants such as binder. Tobacco smoke contains more than 5200 compounds [12], and the zeolite additive into tobacco rod will experience high temperature during the puffing of cigarette when the hot zone approaches, such a complex environment makes the catalytic abilities become dubious. How the pore structure and cation of zeolites affect their actual function? Can they keep their framework during tobacco combustion? Does the acidic zeolite exhibit a higher activity than basic analog? What is the degraded process and products of TSNA? To answer these questions is important not only for controlling the pollution induced by smoking, but also for understanding how the molecular sieves work in the extremely complex system with thousands of compounds.

Therefore, a series of experiment was carried out in present study to directly test the actual functions of mesoporous silica and zeolites on elimination of TSNAs in the mainstream smoke. MCM-41 and SBA-15 with similar mesostructure but different pore size were chosen for the representatives of mesoporous silica. Three common zeolites NaA, NaZSM-5 and NaY with different pore size and Si/Al ratio were employed while HZSM-5 was adopted to assess the influence of acid–base property. MCM-41 and SBA-15 with similar mesostructure but different pore size were chosen as the representative of mesoporous silica, along with their Al-containing analogs prepared in different ways. The investigations would examine the performance of molecular sieves in the *in situ* removal of carcinogens in tobacco smoke. For this aim the new analysis technique of TSNAs, Liquid Chromatography–Tandem Mass Spectrometry (LC–MS/MS) together with the internal-standard of deuterated TSNAs [13], were employed to accurately detect the TSNAs content in cigarette smoke. Moreover, GC–MS method was used to dissect the substances resulting from NNN pyrolysis, while the structure of additive after combustion in cigarette was carefully assessed by X-ray diffusion method.

2. Experiment

2.1. Materials preparation

Zeolite NaA, NaZSM-5 and NaY are commercially available powder samples provided by the Catalyst Plant of Nankai University (China). HZSM-5 sample was obtained from NaZSM-5 (Si/Al = 12.5) by ordinary ion exchange [5]. Mesoporous silica MCM-41 and SBA-15 were synthesized in normal basic and acid condition, respectively [14,15]. Table 1 lists the relevant parameters of these samples. SBA-15 with the particle instead of fiber morphology was prepared according to literature [16] at 313 K without stirring, denoted as SBA-15(p). Al-MCM-41 and Al-SBA-15 were synthesized by one-pot method and solvent-free approach [17,18], respectively; and the final aluminum contents were both adjusted to 1%.

The commercial Burley type fine cut tobacco with 13 mg tar and 1.2 mg nicotine per cigarette was used in the experiment. To prepare the sample cigarette, 0.75 g tobacco and 30 mg powder additives were placed together into an agate mortar, and then kneaded manually until they were homogeneously mixed without residual powder remaining in the mortar. The treated tobacco was backfilled one by one into a commercial cigarette pipe with filter tip. Through the same procedure, control cigarette without additive was made. Each set of the hand-made cigarettes was carefully selected to ensure their error of weight and pressure drop were below ±2% and ±5%, respectively.

Table 1
Relevant parameters of the zeolites and mesoporous silica samples.

Sample	Si/Al	Pore size (nm)	Surface area ($m^2\ g^{-1}$)	Pore volume ($cm^3\ g^{-1}$)
NaA	1	0.4	800	0.28
NaZSM-5	12.5	0.54 × 0.56	354	0.11
HZSM-5	12.5	0.54 × 0.56	346	0.11
NaY	2.86	0.74	766	0.31
MCM-41	–	2.8	1342	1.01
SBA-15	–	8.5	918	1.18

2.2. Measurement

The XRD patterns of samples were recorded on an ARL XTRA diffractometer with Cu K_α radiation in the 2θ range of 0.5–6.0°. The morphology of these materials on tobacco leaf was determined by scanning electron microscopy (SEM) using a Hitachi S4800 FE-SEM system with 10 kV accelerating voltage and 0.005 mA of beam current for imaging. A little piece of tobacco leaf after treatment was cut out and adhered on conducting resin. The sample disks were prepared by sputtering a thin layer of gold onto their outer surface. EDX analysis of sample was performed on this instrument with an acceleration voltage of 20 kV.

The pyrolysis of NNN on molecular sieves was performed as follows: about 5 mg of sample was pre-activated at 773 K in helium flow for 3 min in a pyrolyzer. After the sample was cooled to 313 K, 10 μL of NNN solution (5 mg NNN: 3 mL CH_3OH) was injected into the sample followed by the purge of 10 min in helium flow. And then the sample was heated from 313 K to 773 K with a rate of 50 K min^{-1} meanwhile the resulting products were collected in a cold trap of 213 K. Later, the collected compound were injected into GC and detected by MS. Peak assignments in the GC–MS chromatograms were made using an on-line library, the Wiley Registry of Mass Spectral Data, 6th edition, by F.W. McLafferty.

2.3. Sample collection and extraction

These hand-made cigarettes, with or without porous additives, were conditioned for at least 48 h at 295 K and 60% R.H. before smoking test. Ten cigarettes were smoked by using SM450 smoking machine (Borgwaldt) under ISO standard conditions (35 cm^3 puff, 2 s duration every 60 s). The particulate phase of the smoke was separated from the gas phase by passing smoke through a standard Cambridge filter pad [13]. After the last replicate was smoked, the intact Cambridge pad filter was transferred from the pad holder to a 100 mL erlenmeyer flask followed by adding 100 μL internal-standard (50 ng for each deuterated TSNA) and 20 mL ammonium acetate solution, then the erlenmeyer flask was shaken for 1 h at the rate of 140 rpm. The obtained extractive solution was further cleaned-up by using the Agela PCX extraction column and finally cleaned-up with filter membrane (0.22 μm). About 1 mL of liquid was transferred to an auto-sampling vial and analyzed by Agilent 6410 Triple Quad LC–MS/MS. In order to investigate whether zeolite and mesoporous silica can keep their structure in tobacco combustion, the ash of sample cigarettes was collected and denoted as "B-*x*%" where *x* means amount of additive. For comparison, the ash of control cigarette was mixed with a given amount of additives to form M-*x*% sample, and they were detected by X-ray diffusion.

2.4. Liquid Chromatography–Tandem Mass Spectrometry (LC–MS/MS) analysis

An Agilent 1200 LC system was used for chromatographic separation. The system was fitted with a XDB-C18 column (4.6 mm × 50 mm i.d. 1.8 μm) at 313 K and equilibrated with 72% solvent A (water) and 28% solvent B (methanol). Five microliter of sample was injected each time.

An Applied Biosystems API 5000 mass spectrometer was utilized for the MS/MS analysis. The instrument was operated in positive ESI mode. The Turbospray settings were as follows: the source temperature (TEM) was set to 623 K, curtain gas (N_2) at 9 psig, ion source gases at 35 psig, ion spray voltage at 5200 V, and collision