Supporting Information

Experimental:

The temperature program surface reaction (TPSR) experiments were done as follows. 20 mg sample (20-40 meshes) was activated in N_2 flow at 773 K for 2 h and then cooled to 423 K followed by the injection of 100 μ L NNN solution (5mg mL⁻¹). After adsorption, the sample was purged on N_2 flow for 0.4 h, then heated to 773 K at a rate of 10 K min⁻¹ while the gaseous cracking products were detected every 20 K by the spectrometric method as described previous [Microporous Mesoporous Mater. 2003, 60, 125-138].

The purification process of extracted solution is performed as follows: The obtained extractive solution was further cleaned-up by using the GX-274 ASPEC autosolid-phase extraction machine equipped with PCX solid phase extraction column (Agela, 60 mg, 3 mL), which was pre-activated by 3 mL methanol and 3 mL water successively. 5 mL acidic extracted solution was added and allowed to pass through the column, and then leached by 3 mL methanol, finally eluted by NH₃-methanol solution (5: 95, v/v). After that, the eluted solution was further cleaned-up by using filter membrane (0.22 μ m). About 1 ml of liquid was transferred to an autosampler vial and analyzed by Agilent 6410 Triple Quad LC-MS/MS.

The experiment of LC-MS/MS is carried out as follows: An Agilent 1200 LC system was used for chromatographic separation. The system was fitted with a XDB-C18 column ($4.6 \times 50 \text{ mm i.d. } 1.8 \mu\text{m}$) at 50°C and equilibrated with 72% solvent A (water) and 28% solvent B (methanol). 5 µl of sample or calibration standard was injected. An Applied Biosystems API 5000 mass spectrometer was used 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 350°C, curtain gas (N₂) at 9 psig, ion source gases at 35 psig, ion spray voltage at 5200 V, and collision gas pressure at 5 psig. Mass spectral data on precursor and product ions were collected in multiple reactions monitoring (MRM) mode.

Internal standard method by comparing the peak area of the target compounds to the one of their deuterated analogues was applied to quantify TSNA concentration in extracted solution. Then, each TSNA content in the cigarette was calibrated as follows: C*V/N, in which C, V and N are the concentration of each TSNA in the extracted solution, volume of the extracted solution and the number of smoked cigarettes in each channel of the Smoking Machine. Peak area determinations for all samples, blanks, standards were processed using the Analyst software version 1.2. Each ion of interest in the chromatogram was automatically selected and integrated. The peak integrations were manually inspected for errors and re-integrated if necessary.

Sample	Pressure drag	TPM	NNN	NNK	NAT	NAB	TSNA ^a (ng
	(Pa)	(mg cig ⁻¹)	(ng cig ⁻¹)	cig ⁻¹)			
AMM(1)	928	12.5	5.10	4.86	13.94	0.41	24.31
AMM(1)-P ^b	957	13.5	6.96	7.03	15.59	0.5	30.08
Al-MCM-41 ^c	1012	13.4	6.14	6.27	14.58	0.44	27.43
MCM-41 ^c	961	13.6	7.50	7.05	15.85	0.49	30.89
Blank	1054	13.5	8.10	7.74	17.33	0.46	33.63

Table S1. The TPM and TSNA content in the cigarette with different additives in the filter.

^a The content of TSNA are accumulation of NNN, NNK, NAT and NAB; b AMM(1)-P was prepared as follows: calcined AMM(1) sample was firstly ground to be powder, and then pressed in the pressure of 2 MPa, finally divided to be small pieces and sieved to be 20- 40 meshes; MCM-41 and Al-MCM-41 were synthesized in basic condition according to the reference [*J. Phys. Chem. C* 2010, **114**, 8431–8439], and the molar ratio of Si to Al for Al-MCM-41 was about 200, similar to AMM(1) sample.

Table S2. The ratio of TPM and TSNA eliminated by different additives in the filter.

Sample	TPM (%)	NNN (%)	NNK (%)	NAT (%)	NAB (%)	TSNA(%)
AMM(1)	7.41	37.04	36.69	19.79	10.87	27.71
AMM(1)-P	0.00	14.07	9.17	10.04	-8.70	10.56
Al-MCM-41	0.74	24.20	18.99	15.87	4.35	18.44
MCM-41	-0.74	7.41	8.91	8.54	-6.52	8.15

Table S3. The synthetic condition and the textural properties of rockery-like MCM-41 monolith.

Samuela	$(m^2 a^{-1})^a$	Released NO _x in TPSR			
Sample	$S_{BET}(m g)$	$(\mu mol g^{-1})^{b}$	(µmol m ⁻²) ^c		
MCM-41	1133	11	0.010		
MM	1302	15	0.011		
MM(1)	1367	14	0.010		
MM(2)	1514	18	0.012		

 a S_{BET}, BET surface area; b the accumulated NO_x detected per gram sample; c the accumulated NO_x detected per square meter.



Figure S1. SEM images of MCM-41 synthesized in basic condition.



Figure S2. The variation of TPM in the mainstream smoke gas with different additives in the filter.



Figure S3. Elimination ratio of different TSNA from the mainstream smoke gas.



Figure S4 The profile of NO_x released in the TPSR process of NNN, in which the NNN/dichloromethane solution was firstly vaporized, rapidly passed through and adsorbed by the sample in a gas flow, and then NNN was degraded at elevated temperature to release NOx that presents the degraded adsorbate. TPSR process can efficiently present the adsorptive and catalytic properties of the active sites in molecular sieves. All the MCM-41 type materials with different morphologies can gaseous adsorb and degrade NNN; however, the morphology had rarely influence on the TPSR process for these materials due to the same active site of them. The detected NOx on MP, MM, MM(1) and MM(2) were similar to each other, especially the ratio of NOx to surface area (Table S3), further validating the same adsorptive site to TSNA. This result clearly indicated there was no significant of the adsorptive sites to TSNA on MCM-41 materials with different morphology.