Effect of non-thermal plasma in the activation and regeneration of 13X zeolite for enhanced VOC elimination by cycled storage and discharge process

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1.1 Experimental set-up

The gas supply system consisted of two separate gas lines, each controlled by a mass flow controller (MFC, El-flow®, Bronkhorst) to produce the feed gas of toluene diluted in dry air. The temperature and humidity of the feed gas was monitored using a humidity measuring instrument (Testo 645). The pressure drop in the packed DBD reactor and in the bypass was monitored using a pressure indicator (DPI 705, Druck) and was kept constant using a pressure reducer (Swagelok).

The packed bed DBD reactor consisted of a quartz glass tube with a stainless-steel rod (diameter 0.4 cm) placed coaxially inside the tube, acting as high voltage electrode. The inner diameter, outer diameter and wall thickness of the quartz glass tube were 1.6 cm, 2.2 cm and 0.3 cm, respectively. The discharge length was maintained at 9 cm by using a stainless-steel mesh around the quartz tube which acted as grounded electrode. The discharge gap was filled with 2 g of MS-13X (Alfa Aesar), which is cylindrical in shape (length = 2.5 mm and diameter = 1.5 mm), and 25 g of round borosilicate glass beads (Sigma-Aldrich) of 3 mm diameter on both sides of the MS-13X pellets, as shown in Figure S2. An AC power supply with an operating frequency of 50 kHz, which was connected to the inner electrode, powered the packed DBD reactor. The calculation of the discharge power $P_{discharge}$ (W) is explained in detail elsewhere [9,25] and was determined using the following formula:

$$P_{discharge} = f \int_0^t V(t) I(t) dt \qquad 1$$

where $V(t)$ and $I(t)$ are the instantaneous voltage and current waveforms and f is the frequency of the discharge.

The flue gas composition during different stages of the experiment was investigated in-line with an FTIR spectrometer (Bruker, Tensor 27). The Tensor 27 FTIR was equipped with a DTGS (deuterated triglycine sulfate) detector and a gas cell with a 20 cm optical path length fitted with ZnSe windows. After reaching steady state conditions, FTIR spectra averaged over 20 samples were obtained with a resolution of 4 cm^{-1} and an aperture of 6 mm. OPUS (Bruker) software was used to collect and analyse the obtained FTIR spectra. The concentrations of toluene CO and CO_2 were obtained after FTIR calibration using standard gas mixtures. On the other hand, other by-products such as NO, NO_2 and N_2O were quantified using a more advanced FTIR spectrometer (Bruker, Matrix-MG2). The Matrix-MG2

FTIR was equipped with an IRcube module fitted with an MCT (mercury-cadmium-tellurium) detector and a gas cell with a path length of 5 m. The optical compartment of the IRcube was sealed against the gas cell using ZnSe windows. The gas cell was heated up to 191˚C and the inlet gas tube up to 50˚C to avoid gas condensation. FTIR spectra averaged over 50 samples were obtained with a resolution of 1 cm^{-1}. The peak positions used for the identification of the by-products and the wavenumber range used for the integration of the area under the peak for both qualitative and quantitative comparison are given in Table S1.

1.2 Cycled storage and discharge process

The total amount of toluene adsorbed on MS-13X (mol/g) was quantified from the toluene breakthrough curves using the following equation:

$$[Toluene]_{adsorbed} = \int_0^{t_1} \frac{(C_0 - C) \times f_1 \times dt_1}{24.4 \times m} \times 10^{-6} \quad (2)$$

where C_0 is the initial toluene concentration (ppm), C is the concentration of toluene in the outlet of the NTP reactor (ppm), f_1 is the dry air flow rate during adsorption (L/min), t_1 is the adsorption time (mins), and m is the mass of the MS-13X pellets packed in the DBD reactor (g).

The amount of toluene desorbed by flushing dry air (reversibly adsorbed toluene) and by switching on the NTP (unconverted toluene) (mol/g) was calculated using the following equation:

$$[Toluene]_{desorbed} = \int_0^{t_2} \frac{C_{Toluene} \times f_2 \times dt_2}{24.4 \times m} \times 10^{-6} \quad (3)$$

where $C_{Toluene}$ is the concentration of desorbed toluene by flushing dry air or by switching on the discharge (ppm), f_2 is the dry air flow rate used during flushing or NTP exposure (L/min), and t_2 is the flushing time or the NTP exposure time (mins).

The amount of toluene irreversibly adsorbed after flushing by dry air was calculated by $[Toluene]_{irreverble} = [Toluene]_{adsorbed} - [Toluene]_{desorbed\ by\ air}$. The amount of toluene converted by NTP exposure was calculated by $[Toluene]_{converted} = [Toluene]_{irreversible} - [Toluene]_{desorbed\ by\ NTP}$.

The amount of CO_2 and CO (mol/g) formed during NTP exposure were calculated using the following equations:

$$[CO_2]_{produced\ or\ desorbed} = \int_0^{t_2} \frac{C_{CO_2} \times f_2 \times dt_2}{24.4 \times m} \times 10^{-6} \quad (4)$$

$$[CO]_{produced} = \int_0^{t_2} \frac{C_{CO} \times f_2 \times dt_2}{24.4 \times m} \times 10^{-6} \quad (5)$$

where C_{CO_2} and C_{CO} are the concentrations of CO_2 and CO produced during NTP exposure (ppm), respectively, f_2 is the dry air flow rate during NTP exposure (L/min), and t_2 is the NTP exposure time (mins).

The CO_x selectivity, S_{CO_x} (%) and CO_x yield, Y_{CO_x} (%) were defined as follows:

$$S_{CO_x} = \frac{C_{CO_x}}{7[C_{Toluene}]_{conv}} \times 100 \quad (6)$$

$$Y_{CO_x} = \frac{C_{CO_x}}{7[C_{Toluene}]_{ads}} \times 100 \quad (7)$$

where $C_{CO_x} = C_{CO_2} + C_{CO}$ and C_{CO_2} and C_{CO} are the concentrations of CO_2 and CO produced during NTP exposure. Finally, in this study, the energy cost E_c (kWh/m^3), which is the energy required to remedy 1 m^3 of air using the sequential process and the energy yield E_y (g/kWh), which measures the energy efficiency of the cycled storage and discharge process were calculated using the following equations:

$$E_c = \frac{P_{discharge}}{f_1} \times \frac{t_2}{t_1} \quad (8)$$

$$E_y = \frac{[Toluene]_{total\ adsorbed} \times 92.14 \times 60}{P_{discharge} \times t_2} \quad (9)$$

where f_1 is the dry air flow rate (m^3/h) during adsorption, and t_1 and t_2 are the adsorption and NTP exposure periods (mins), respectively.

1.3 Catalyst characterization

First of all, powder X-ray diffraction (PXRD) patterns of MS-13X were collected using a Thermo Scientific ARL X'Tra diffractometer, operating at 40 kV, 30 mA using Cu-Kα radiation (λ = 1.5406 Å). The PXRD patterns were recorded over the range 3˚ < 2θ < 55˚ using a step size of 0.02˚ and a scan rate of 0.5˚/min.

X-ray photoelectron spectroscopy (XPS) survey spectra and high resolution C1s, O1s, Al2p, Si2p and Na1s XPS spectra of different MS-13X samples were obtained using a PHI Versaprobe II XPS

spectrometer equipped with a monochromatic Al K_α X-ray source (hν = 1486.6 eV) operating with a beam size of 200 µm and a power of 50 W. The XPS measurements were conducted at a pressure of at least 10^{-6} Pa and the photoelectrons were detected by a hemispherical analyser positioned at an angle of 45° with respect to the normal of the sample surface. Moreover, X-ray induced secondary electron images (SXIs) of the sample were obtained by scanning a finely focused X-ray beam characterized by a sub-10 µm size across the surface. Such images are used to navigate the features of interest on the sample and precisely select the spot locations for analysis. The pass energies used for acquiring the survey and individual high resolution XPS spectra were 187.85 eV and 23.5 eV, respectively. The surface atomic elemental composition of the samples was calculated from XPS survey spectra using Multipak software. For this purpose, the adventitious carbon at 285 eV was used as internal standard and an iterated Shirley background was applied to determine the elemental composition. In addition, the deconvolution of the high resolution XPS spectra was also carried out in this study. To do so, Gaussian-Lorentzian peak shapes (80–100% Gaussian) were employed and a full width at half maximum (FWHM) set between 1.4 eV and 1.6 eV was adopted for each line shape dye.

Nitrogen adsorption-desorption measurements at the temperature of liquid nitrogen (-196˚C) were performed to analyse the specific surface area, pore volume and pore size distribution of the zeolites using a Micromeritics Tristar II 3020 device. Prior to the measurements, the MS-13X samples were degassed at 120°C overnight. The specific surface area and pore volume were determined using the Brunauer-Emmett-Teller (BET) method. In addition, argon sorption measurements were also recorded at -186°C to study, in particular, the distribution of the micropores using a Quantachrome Autosorb-1-MP automated gas sorption system. Prior to the measurements, the samples were degassed for 24 h under high vacuum at a temperature of 150°C.

Finally, the acidic properties of the MS-13X samples were determined by means of FTIR spectroscopy of chemisorbed pyridine (py-FTIR) using a Thermo Nicolet 460 Protegé spectrometer equipped with an MCT detector. Prior to FTIR analysis, the MS-13X samples were pressed to form self-supporting discs (6-8 mg/cm^2) and activated at 400°C overnight under high vacuum (< 10^{-7} mbar). Afterwards, the activated samples were saturated with pyridine vapour at 1.2 mbar for 30 minutes at 100˚C. In a next step, the desorption of pyridine under high vacuum was performed at different

temperatures (150˚C, 250˚C, 350˚C and 450˚C) and FTIR spectra averaged over 256 scans were recorded simultaneously with a resolution of 2 cm^{-1}. The surface concentration of the Brønsted and Lewis acid sites was calculated using the following formula:

$$n = \frac{A \times s}{\varepsilon \times m} \qquad 10$$

where n is the surface acidic site concentration (μmol/g), A is the integrated area under the absorbance band corresponding to pyridine adsorption (cm^{-1}) on Brønsted acid sites (1545 cm^{-1}) or Lewis acid sites (1445 cm^{-1}), s is the area of the pressed sample (cm^2), ε is the pyridine molar extinction coefficient (1.67 cm/μmol for Brønsted acid sites and 2.22 cm/μmol for Lewis acid sites) and m is the mass of the pressed sample (g).

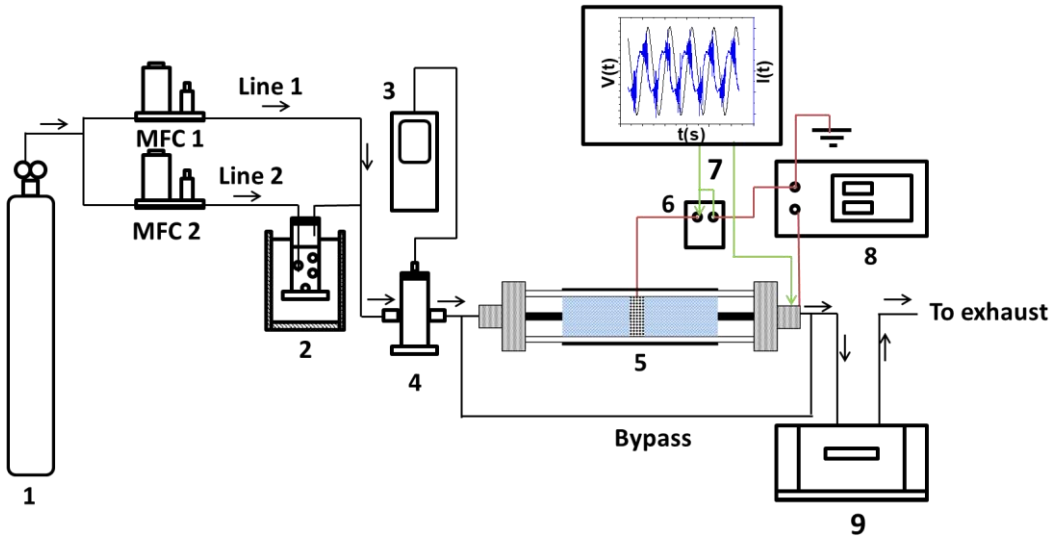
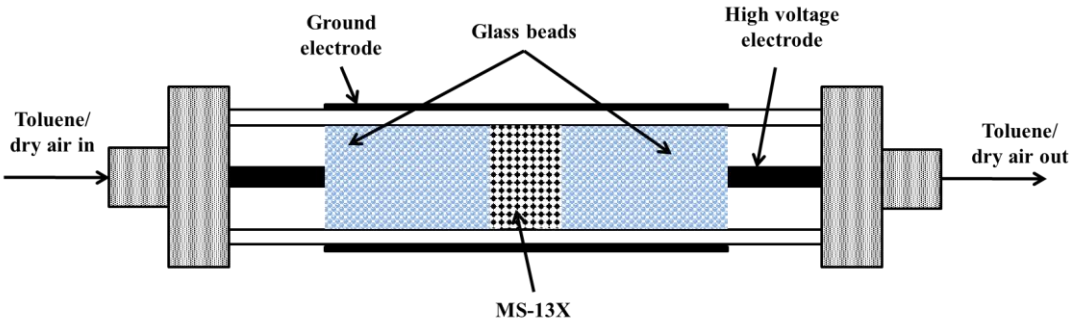


Figure S1 Schematic representation of the experimental set-up used for the cycled storage and discharge process of toluene removal: 1-dry air cylinder, 2-toluene bubbler, 3-humidity meter, 4-mixing chamber, 5-MS-13X/glass beads DBD reactor, 6-resistor (46.4 Ω), 7-high voltage and current probe, 8-AC power supply (50 kHz), 9-FTIR spectrometer



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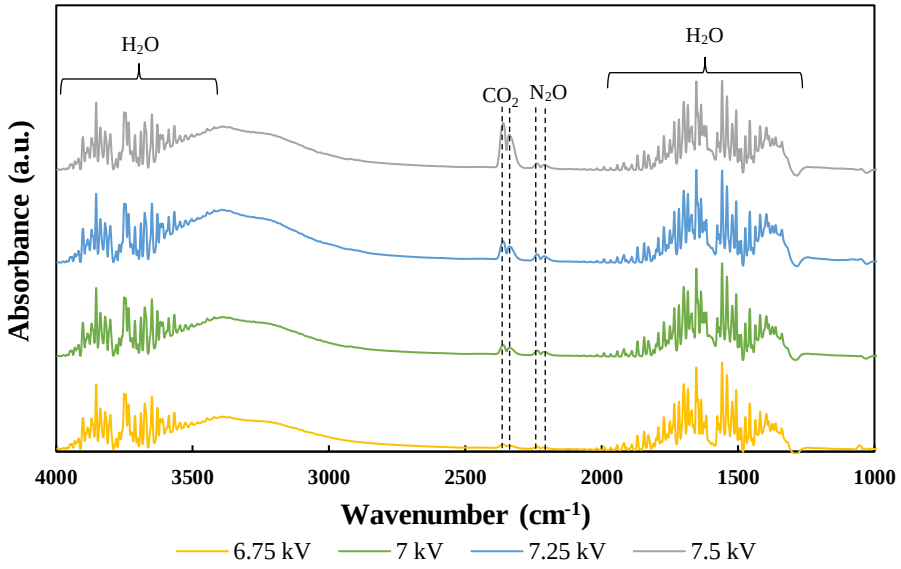
150 *Figure S2 Schematic representation of the MS-13X pellets & glass beads packed bed DBD reactor*



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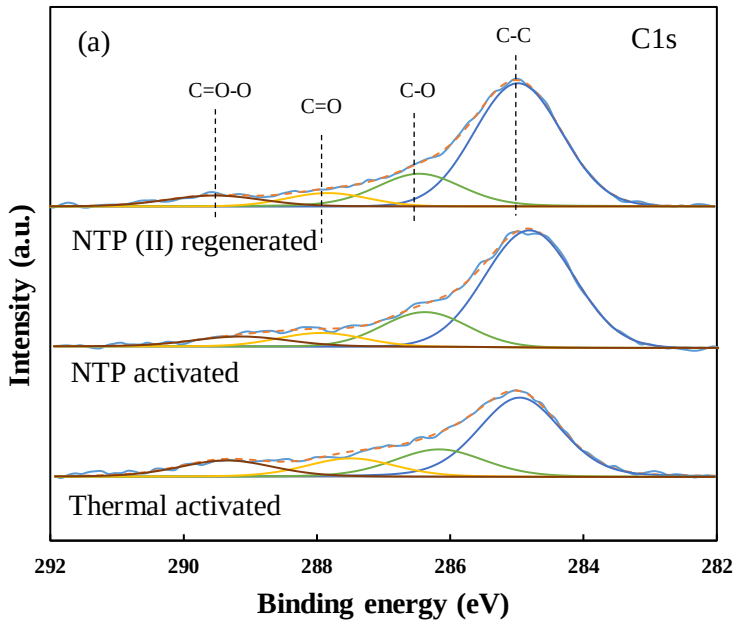
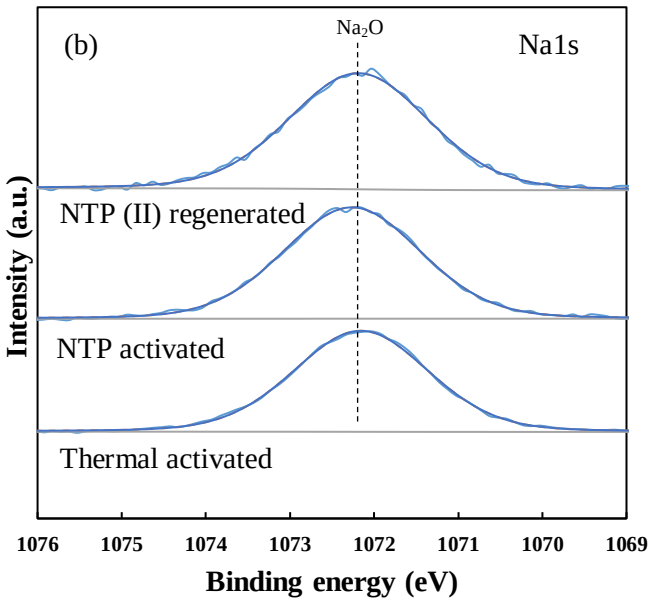
152 *Figure S3 FTIR spectra of the outlet gas after 10 minutes of NTP activation using different applied*

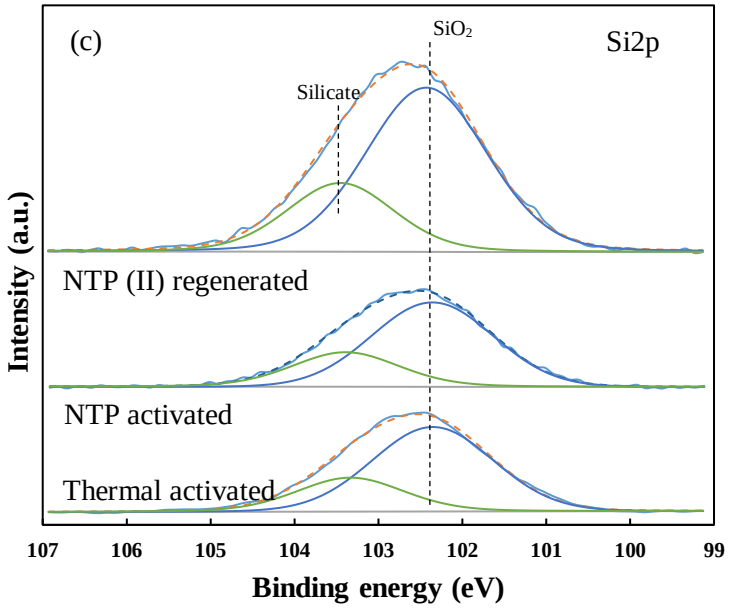
153 *voltages (dry air flow rate=0.5 L/min)*


(a)
C1s
C-C
C=O-O
C=O
C-O
NTP (II) regenerated
NTP activated
Thermal activated
Intensity (a.u.)
292
290
288
286
284
282
Binding energy (eV)

154


(b)
Na1s
Na2O
NTP (II) regenerated
NTP activated
Thermal activated
Intensity (a.u.)
1076
1075
1074
1073
1072
1071
1070
1069
Binding energy (eV)

155

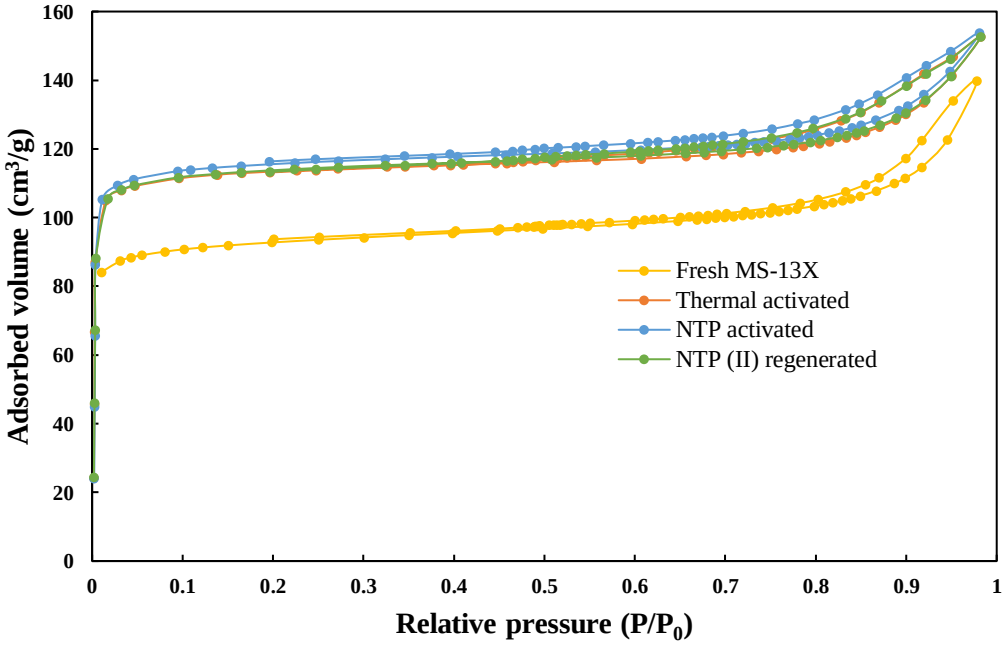


156

157 *Figure S4 XPS high-resolution spectra of (a) C1s, (b) Na1s and (c) Si2p for thermal activated, NTP*

158 *activated and NTP (II) regenerated MS-13X*

159



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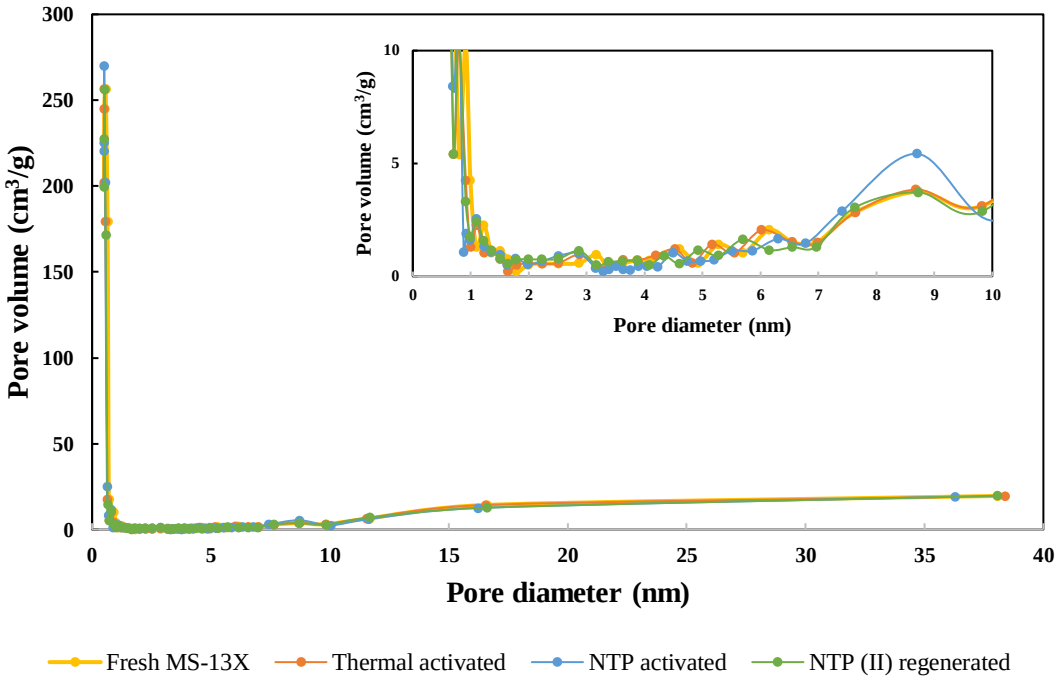
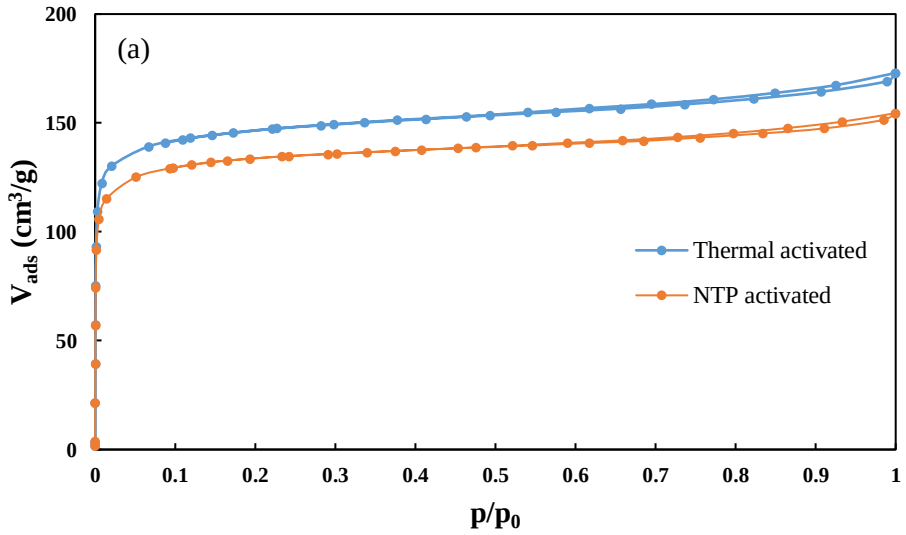


161

162 *Figure S5 (a) Nitrogen adsorption-desorption isotherms and (b) BJH pore size distribution for fresh,*

163 *thermal activated, NTP activated and NTP (II) regenerated MS-13X*



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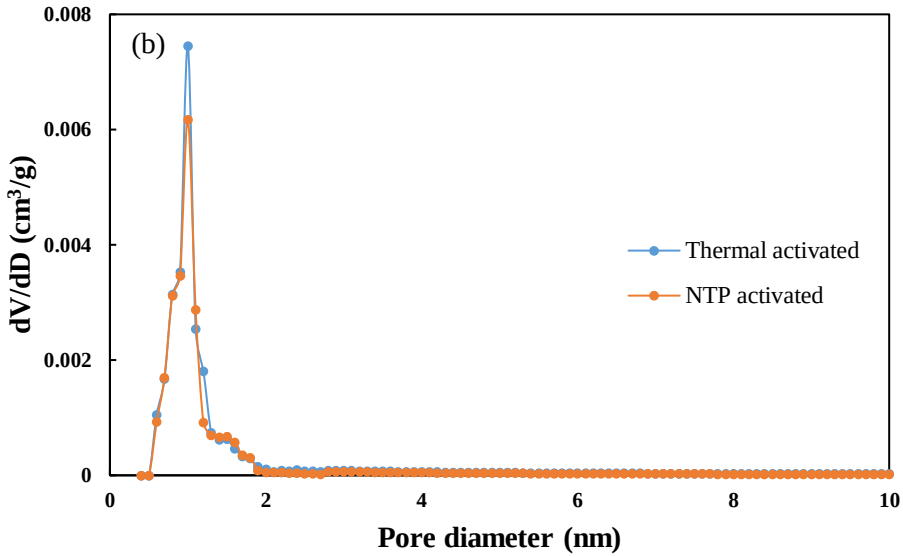
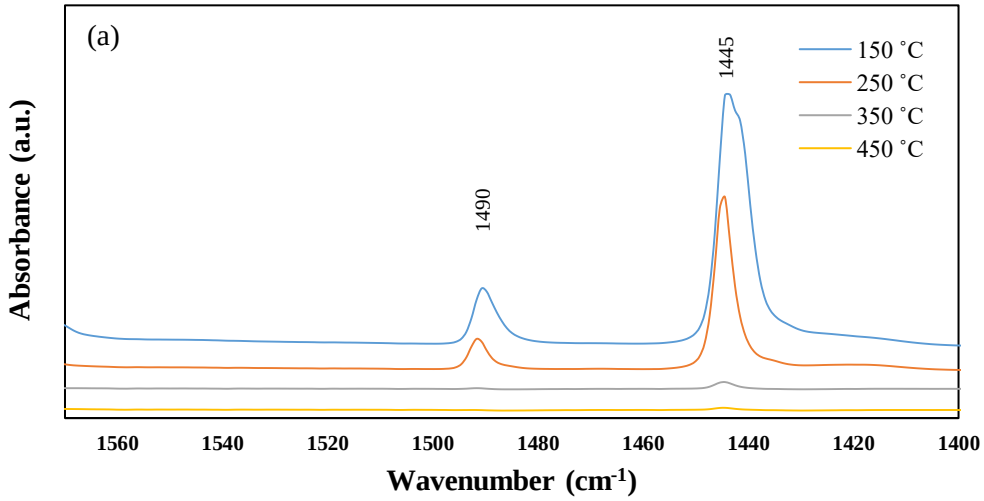


165

166 *Figure S6 (a) Ar adsorption isotherms and pore size distribution obtained from Ar sorption for thermal*

167 *and NTP activated MS-13X*



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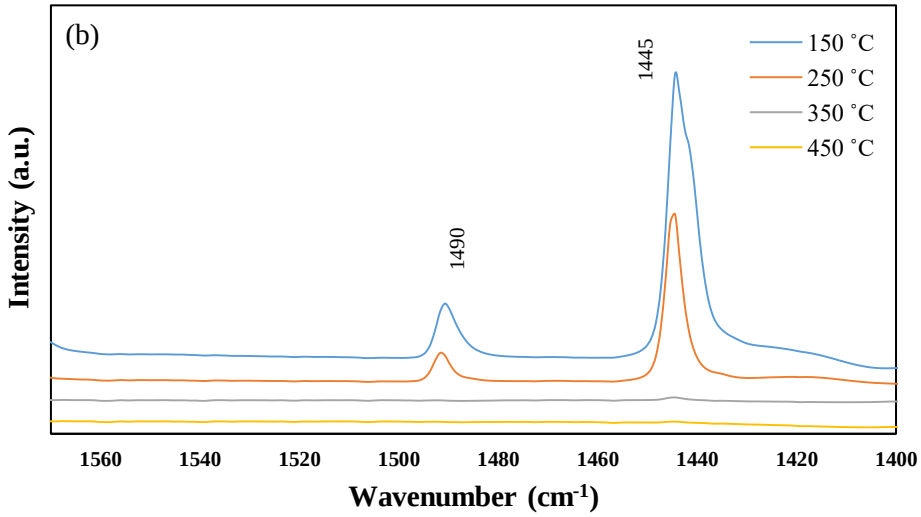

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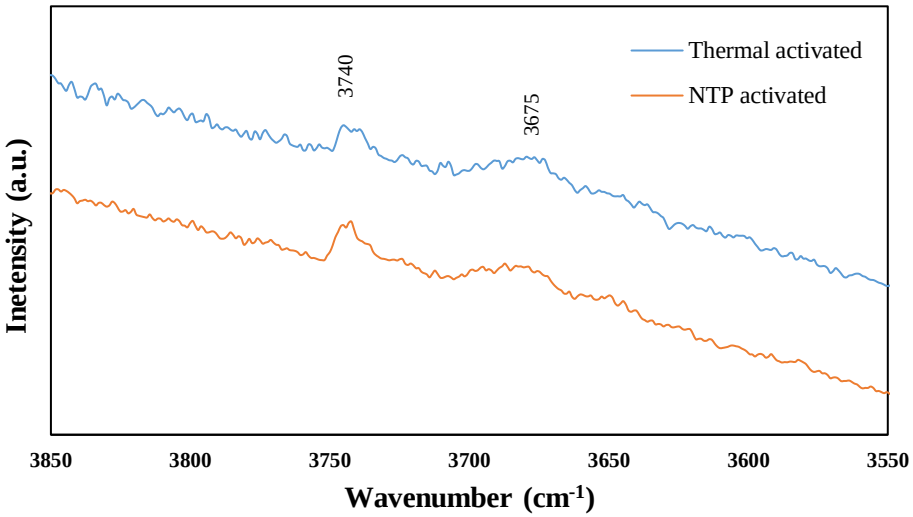
170 *Figure S7 Subtracted FTIR spectra in the region 1570 – 1400 cm^{-1} obtained after desorption of pyridine*

171 *at different temperatures for (a) thermal activated and (b) NTP activated MS-13X*



172

173 *Figure S8 Reprocessed FTIR spectra in the region 3850 - 3550 cm^{-1} obtained after desorption of pyridine*

174 *at 450 ˚C for (a) thermal activated and (b) NTP activated MS-13X*

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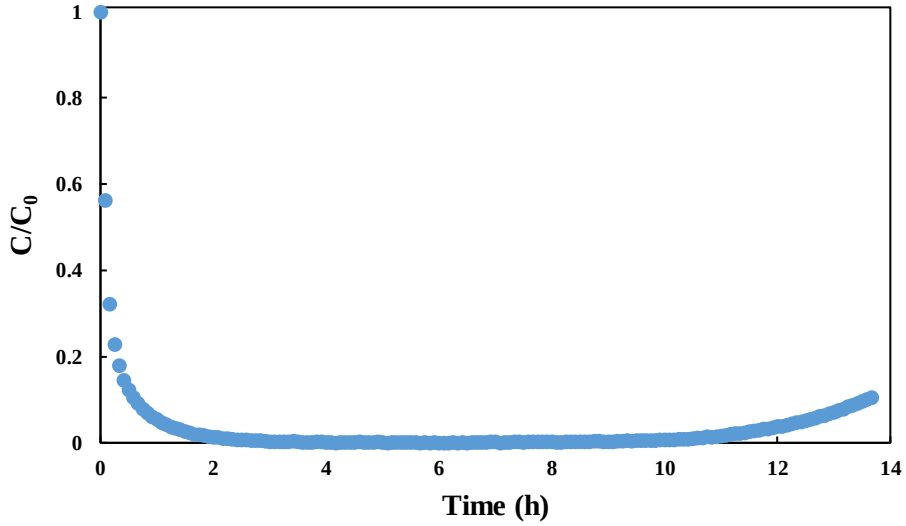

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177 *Figure S9 Breakthrough curve for the adsorption of toluene from dry air until the concentration in the*
178 *outlet reaches a critical concentration (10% of the initial concentration) on NTP activated MS-13X*
179 *pellets (flow rate=0.1 L/min; toluene initial concentration=1000 ppm)*

180

181 *Table S1 Parameters used for flue gas analysis using FTIR*

Compound	**Peak position (cm^{-1})**	**Wavenumber range (cm^{-1})**
Toluene	3074, 3038, 2938, 2882, 1610, 1500, 729, 694	3059-3010
CO	2175, 2120	2143-2030
CO_2	3729, 3703, 3627, 3599, 2360, 2341	2394-2283
H_2O	--	1881-1353
O_3	2108, 1055, 1032	1070-1044
N_2O	2236, 2211	2260-2223
NO	1903, 1845	1929-1883
NO_2	2918, 2894, 1628, 1601	1655-1574

182

Table S2 Experimental parameters used during the different steps of the cycled storage and discharge process for the abatement of toluene in dry air using a MS-13X pellets & glass beads packed DBD reactor

Plasma activation	
Gas source	Dry air
Flow rate	0.5 L/min
Applied voltage	7.25 kV
Discharge power	58 W
Treatment time	60 mins
Toluene adsorption	
Gas source	Dry air
Flow rate	0.1 L/min
Inlet toluene concentration	1000 ± 10 ppm
Toluene desorption by air	
Gas source	Dry air
Flow rate	0.5 L/min
Temperature	RT (=18 ˚C)
NTP exposure (for oxidation and regeneration)	
Gas source	Dry air
Flow rate	0.5 L/min
Applied voltage	7.5 kV
Discharge power	65 W
Treatment time	70 mins

190 *Table S3 Amount of toluene adsorbed and desorbed, CO_2, CO and CO_x formation during NTP*

191 *exposure for NTP activated and NTP(I) regenerated MS-13X*

	NTP activated	**NTP (I) regenerated**
	MS-13X	
Total adsorbed toluene (mmol/g)	2.45 ± 0.06	2.49 ± 0.03
Toluene desorbed by flushing dry air (reversibly adsorbed toluene) (mmol/g)	0.12	0.12
Irreversibly adsorbed toluene (mmol/g)	2.33 ± 0.05	2.37 ± 0.03
Toluene desorbed by NTP exposure (unconverted toluene) (mmol/g)	1.04	1.09
Converted toluene by NTP exposure (mmol/g)	1.29 ± 0.03	1.28 ± 0.01
CO_2 formation (mmol/g)	1.90	1.66
CO formation (mmol/g)	0.72	0.64
CO_x formation (mmol/g)	2.62	2.30

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Table S4 The total amount of toluene adsorbed on MS-13X pellets (until the critical concentration), the regeneration efficiency, and the CO_2 and CO_x selectivity during NTP exposure for different cycles of cycled storage and discharge process for the abatement of toluene

Cycle No.	Adsorbed toluene (mmol/g)	Regeneration efficiency (%)	CO_2 selectivity (%)	CO_x selectivity (%)
1	1.84 ± 0.01	NA	26.0 ± 0.1	35.9 ± 0.1
2	1.83 ± 0.01	99	25.8 ± 0.1	35.9 ± 0.1
3	1.79 ± 0.01	97	25.7 ± 0.1	35.8 ± 0.1
4	1.78 ± 0.01	97	26.0 ± 0.1	36.1 ± 0.1
5	1.84 ± 0.01	100	24.1 ± 0.0	33.5 ± 0.1
6	1.86 ± 0.01	101	25.5 ± 0.1	35.3 ± 0.1
7	1.89 ± 0.01	103	25.6 ± 0.1	34.1 ± 0.1
8	1.90 ± 0.01	103	23.9 ± 0.0	33.2 ± 0.1
9	1.79 ± 0.01	97	26.1 ± 0.1	36.3 ± 0.2
10	1.78 ± 0.01	97	27.2 ± 0.0	37.9 ± 0.1