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- 2 Lina Liu^{a,b}, Qiang Wang^{a,b}, Jianwei Song^a, Shakeel Ahmad^c, Xiaoyi Yang^{a,b}, Yifei Sun^{b,c,*}
- ^a School of Energy and Power Engineering, Beihang University, Beijing 100191, China
- 4 ^b Energy and Environment International Centre, Beihang University, Beijing, 100191, China
- ^c Beijing Key Laboratory of Bio-inspired Energy Materials and Devices, School of Space and
- 6 Environment, Beihang University, Beijing 100191, China
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^{*} Corresponding author Tel/ Fax: +86-10-82338120 E-mail address: <u>sunif@buaa.edu.cn</u> (Yifei Sun)

8 Abstract

9 The combination of non-thermal plasma (NTP) and transition metal catalysts is an alternative method for reducing tar derived from biomass gasification, converting it 10 11 to a mix of mainly H_2 and CO (syngas). In this study, Ni- and Fe-based steam reforming catalysts supported on CaO, SiO₂, γ-Al₂O₃ and ZSM-5 were combined with 12 a coaxial dielectric barrier discharge (DBD) plasma reactor for converting toluene, 13 14 selected as a simple tar model compound. The catalysts supported by ZSM-5 showed 15 the best potential in increasing toluene conversion, promoting the formation of syngas, 16 reducing the production of undesirable liquid by-products (such as benzene and 17 ethylbenzene) and corroborating the resistance to catalyst deactivation caused by 18 sintering and carbon deposition. Toluene cracking has been investigated in a 19 plasma-alone (PA), a post-plasma catalysis (PPC) and an in-plasma catalysis (IPC) 20 system. The IPC system exhibited the highest toluene conversion efficiency and 21 selectivity of syngas formation, compared with PA and PPC system. A maximum toluene conversion of 86.5% was achieved in the IPC system over Ni/ZSM-5, 22 23 together with a maximum gas selectivity (63.3% for H₂, 18.2% for CO, and 4.6% for 24 CH_4), and a minimum selectivity of undesirable liquid by-products (2.5% for benzene 25 and 0.66% for ethylbenzene and a low carbon selectivity of 6.7%). In addition, the 26 reaction mechanism was significantly different in the IPC system from that in the PA 27 and PPC system, since the catalyst in the IPC system might influence the discharge 28 properties and influence the reaction between excited and short lifetime reactive plasma species (OH, O, N_2^* ...) and toluene and its intermediates. Finally, a 29 30 mechanism of toluene cracking has been proposed, after analysis of gas and liquid 31 products and characterization of the fresh and used catalysts.

Keywords: biomass tar; toluene; catalytic steam reforming; Ni/Fe-based catalysts;
 syngas; DBD plasma-catalysis system

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35 **1. Introduction**

Syngas (a mixture of H₂ and CO) production by biomass gasification is 36 considered as an attractive and alternative treatment, meeting the increasing energy 37 demand and relieving the crisis of fossil energy.¹⁻³ Syngas can be used as the raw 38 39 materials for the synthesis of methanol, dimethylether (DME), ethanol and Fischer-Tropsch fuels.⁴ However, the formation of tar during gasification is one of the 40 major challenges that limit the commercial application of gasification techniques.⁵ Tar 41 42 is a complex and hazardous mixture of condensable hydrocarbons, including single-ring to five-ring aromatic compounds along with other oxygenates and 43 polycyclic aromatic hydrocarbons (PAHs).^{6,7} The formation of tar leads to the 44 decrease of the gasification efficiency due to the loss of chemical energy of tar.⁸ 45 Besides, the condensation of tar at low temperature leads to the clogging of pipe-lines 46 47 and contamination of process equipment such as gasifier, engine and turbine, and the deactivation of catalysts.^{9,10} As a consequence, more maintenance cost is needed for 48 the stable operation of gasification process.¹¹ Therefore, the efficient removal of tar is 49 essential for gaining clean biogas and increasing the process efficiency during 50 biomass gasification.¹² 51

Extensive studies have been reported for the elimination and reforming of tar, 52 and various strategies including mechanical separation,¹³ thermal cracking¹⁴ and 53 catalytic reforming^{15,16} have been proposed. Tar cracking and simultaneous reforming 54 to H₂, CO and CH₄ is more desirable than mechanical separation by filtration and 55 water or oil scrubbing, which lead to the secondary pollution and the chemical energy 56 loss of tar.^{3,6} However, both thermal cracking and catalytic reforming have been 57 restricted due to their shortcomings. Thermal cracking is generally conducted as high 58 59 temperature (>800 °C), leading to considerable energy consumption. Catalytic reforming is easily declining and even terminated because of the rapid deactivation of 60 catalysts by sintering, poisoning and carbon deposition.¹⁷ Therefore, non-thermal 61 62 plasma (NTP) shows significant potential in converting complex tar to energy gas, 63 due to its relative low energy consumption, high removal efficiency and universality

for various hydrocarbons.¹⁸ In recent years, NTP has been widely applied in the 64 removal of hydrocarbons such as volatile organic compounds (VOCs)^{19,20} and 65 biomass tar.^{11,21} However, NTP alone produced a great amount of undesirable 66 by-products, and showed less selectivity towards syngas than the catalytic steam 67 reforming.^{22,23} Therefore, coupling a NTP with heterogeneous catalysts seems a more 68 promising alternative, since NTP and catalysts may generate a synergistic effect, 69 enhancing tar conversion and syngas selectivity, inhibiting the formation of 70 undesirable by-products, and reducing energy consumption.^{24,25} Dielectric barrier 71 discharge (DBD) plasma is a potential option since it is easily integrated with 72 catalysts due to less carbon deposition.²⁶ 73

Various catalysts have been used for steam reforming of tar, including transition 74 metal catalysts (Ni-, Fe-, Co-based catalysts...), natural minerals (olivine, dolomite 75 ilmenite...), noble metal catalysts (Rh, Ru, Pd, Pt...) and char.²⁷⁻³⁰ Among these, 76 transition metal catalysts show high performance and low cost for biomass tar 77 reforming.³¹ The selection of support materials is an important issue since the catalyst 78 deactivation caused by sintering of the support surface is a great challenge for 79 catalytic steam reforming of tar. The most commonly used supports for steam 80 reforming of tar are alumina and its modifications.²⁴ Also CaO and MgO are 81 considered as active supports for tar reforming, as main components of dolomite.³² 82 Furthermore, zeolites, such as ZSM-5, SBA-15..., have been used for reforming 83 hydrocarbons because of their high surface area, thermal stability, and high affinity as 84 adsorbent for O-containing compounds.^{33,34} Although different support materials have 85 been applied for catalytic steam reforming of tar, few studies systematically 86 87 investigated the effect of supporting material on tar reforming, and the synergy of 88 plasma and catalyst is still unclear.

Based on the analysis above, it is essential to investigate the effect of different support materials on thermal stability, resistance to carbon deposition and catalytic activity of catalysts for steam reforming of tar. Additionally, few studies reported tar cracking and oriented reforming to syngas in the plasma-catalysis system, and the synergistic mechanism of plasma and catalysts is still unclear. Therefore, DBD plasma

was coupled with catalysts in order to promote the oriented conversion of tar to 94 95 syngas and reduce the formation of undesirable liquid by-products. Ni- and Fe-based 96 catalysts with different support materials, such as CaO, SiO₂, γ -Al₂O₃ and ZSM-5, were employed to investigate their performance on steam reforming of toluene as a 97 representative tar surrogate. The fresh and used catalysts were characterized by BET, 98 XRD, SEM, TG-DSC and XPS to study the influence of supports to catalytic 99 performances. In addition, the performance of toluene reforming in different types of 100 reactors (plasma-alone (PA), post-plasma catalysis (PPC), and in-plasma catalysis 101 (IPC) systems) was also investigated, along with the synergy of plasma and catalysts. 102 103 Finally, a reaction mechanism of toluene cracking was proposed by the analysis of liquid and gas products in the hybrid plasma-catalysis system. 104

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106 **2. Materials and Methods**

107 2.1 Preparation of catalysts

108 Different Ni- and Fe-based catalysts were prepared by wet impregnation:

- 1.58 g of Ni (NO₃)₂·6H₂O and 2.43g of Fe(NO₃)₂·9H₂O was dissolved in ~50 mL of deionized water. The aqueous solution was mixed with 9.7 g of CaO, SiO₂, γ-Al₂O₃ and ZSM-5 used as different supporting materials.
- The suspension was stirred under ambient condition for 12 hours, and
 subsequently at 333 K for 24 hours.
- Then the samples were dried at 378 K overnight and calcined in the atmosphere of air at 823 K for 6 hours in a tubular furnace (OTF-1200X, Hefei Kejing Material Technology Co. Ltd. China).
 - Therefore, the theoretical Ni and Fe loading of all catalysts was 3 wt.%. The Ni- and Fe-based catalysts prepared were defined as Ni/CaO, Ni/SiO₂,
- 119 Ni/ γ -Al₂O₃, Ni/ZSM-5, Fe/CaO, Fe/SiO₂, Fe/ γ -Al₂O₃ and Fe/ZSM-5. The catalysts 120 were sieved to 40-60 mesh and then reduced in 5 wt.% of H₂ diluted with N₂ (100 121 mL/min) at 650 °C for 6 h before use.

122 2.2 Selection of tar model compounds

Due to the complexity of tar, tar model compounds are generally selected for the 123 tar decomposition study.¹⁷ The most common model compounds are recognized as 124 benzene, toluene, phenol, naphthalene, etc.³⁵ In this study, we selected toluene as the 125 representative tar surrogate based on three reasons: (1) toluene is the dominant 126 component of biomass tar; (2) toluene shows a simple structure and high thermal 127 stability is well known; (3) toluene is less harmful and its high-temperature 128 129 characteristics are well known. Therefore, the utilization of toluene can help get realistic information of tar reforming over different catalysts.^{11,36} 130

131 2.3 Experimental setup and procedure

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The schematic diagram for biomass tar reforming is displayed in **Figure 1**. A 60 132 133 mm-long stainless steel wire surrounding a quartz tube (Length: 600 mm, I.D.: 44 mm, thickness: 3.0 mm) was used as grounded eletrode, and a stainless steel rod (length 60 134 mm and outer diameter 42 mm) was the high-voltage electrode of the DBD plasma 135 reactor. The discharge gap was 1 mm. The reactor was vertically installed in a shaft 136 137 tubular furnace (customized, Jinhua Hengfeng Electrical Instrument Co. Ltd., China). 138 The experiments were conducted in Mode A and Mode B. For Mode A, the catalyst 139 was held by silica wool at 50 mm downstream of the discharge area of a post-plasma 140 catalysis (PPC) system. For Mode B, the catalyst was placed in the discharge area of 141 an in-plasma catalysis (IPC) system. In addition, toluene cracking was also conducted 142 as a blank test in a plasma-alone (PA) system without catalyst. For each test 1.0 g of 143 new catalyst was used. Toluene was selected as surrogate of biomass gasification tar. 144 Toluene and water was injected into the DBD reactor by two syringe pumps (TJ-3A, 145 Baoding Longer Pump Co. Ltd., China) at a flow rate of 30 μ L/min for toluene and 35.5 μ L/min for water, respectively. The molar steam to carbon (S/C) ratio was 1.0. 146 Nitrogen (99.999 vol.%, Beijing Haipu Gas Co. Ltd, China) was used as carrier gas at 147 a constant flowrate of 100 mL/min. Toluene and water were evaporated in the upper 148 part of the reactor, kept at 473 K by a heating strip and then entered into the 149 discharging area of DBD plasma by the carrier gas. The discharge time and 150

temperature were 30 min and 573 K, respectively. The condensable products were 151 152 absorbed in ~200 mL of methanol using two impingers cooled in ice-water bath. 153 Finally, non-condensable gas products were collected in a sampling gas bag (10 L, 154 Dalian Delin Gas Packaging Co. Ltd., China) and their total volume was recorded by a wet gas flowmeter (LMF-2, Changchun Auto Filter Co., Ltd., China). The DBD 155 plasma reacter was connected to an AC high-voltage power supply with a maximum 156 peak to peak voltage of 30 kV and a frequency of 10 kHz. The discharge signals were 157 monitored by a digital oscilloscope (Rigol DS2102A). The average discharge power 158 159 and frequency were 60 W and 14.79 kHz, respectively.

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161

162	Figure 1. Schematic diagram of the experimental setup with (a) the post plasma-catalysis
163	system and (b) the plasma-catalysis system.

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165 *2.4 Analysis method of the products*

The non-condensable gas products were analyzed by a gas chromatograph (GC-17A, Shimadzu, Japan) equipped with a thermal conductivity detector (TCD) and a Carboxen-1010 PLOT capillary column (30 m \times 0.53 mm \times 30 µm, Supelco Corporation, USA). The liquid products absorbed in the methanol solution were analyzed by a high-resolution gas chromatograph-low resolution mass spectrometer (HRGC-LRMS, QP2020, Shimadzu) equipped with an HP-5MS capillary column (60 m \times 0.25 mm \times 0.25 µm; Agilent Technologies, USA). and carbon deposition were calculated as follows,

175
$$C_{T}(\%) = \frac{\text{moles of toluene input-moles of toluene output}}{\text{moles of toluene input}} \times 100\% \quad (1)$$

176
$$S_{H_2}(\%) = \frac{\text{moles of } H_2 \text{ output}}{4 \times \text{moles of toluene converted } + \text{ moles of } H_2 \text{ O input}} \times 100\% \quad (2)$$

177
$$S_{CO}(\%) = \frac{\text{moles of CO output}}{7 \times \text{moles of toluene converted}} \times 100\% \quad (3)$$

178
$$S_{C_mH_n}(\%) = \frac{m \times \text{moles of } C_mH_n \text{ output}}{7 \times \text{moles of toluene converted}} \times 100\%$$
(4)

179
$$S_{C}(\%) = \frac{\text{moles of carbon output}}{7 \times \text{moles of toluene converted}} \times 100\%$$
(5)

180 The yield of gas products such as H_2 , CO and CH_4 was calculated as Eq. (6).

181
$$Y(mol/mol) = \frac{moles of gas products output}{moles of toluene input}$$
 (6)

182 The energy efficiency is defined as the ratio of the mass of toluene converted per 183 hour to the discharge power as shown in Eq. (7).

184
$$\eta(g/kWh) = \frac{\text{mass of toluene converted }(g)}{P(W) \times 0.5/1000}$$
 (7)

185 *2.5 Characterization of catalysts*

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186 The fresh and used Ni- and Fe-based catalysts were characterized as follows.

Ni and Fe loading. About 0.1g of each catalyst was digested in a microwave system (Mars 6, CEM, USA) using 6 mL of 36% HCl and 2 mL of 65% HNO₃ and generating an aqueous solution of Ni or Fe. This solution was diluted and then analyzed using inductively coupled plasma- mass spectrometry (ICP-MS, XSERIES 2, Thermo Scientific, USA) to determine the actual Ni and Fe loadings on different supports.

The Brunauer-Emmett-Teller (BET) surface area, pore volume and average pore
diameter of the fresh catalysts were determined by the adsorption-desorption isotherm
using a Quantachrome NOVA 2200e analyzer (USA).

X-Ray Diffraction (XRD, D6000, Shimadzu, Japan) was used to examine the
crystal species of different catalysts before and after reforming. The scanning range
20 was 10-90° with a speed of 5°/min.

A scanning electron microscope (SEM, Quanta FEG 250, FEI, USA) allowed to
 analyze the morphology and particle size of different catalysts.

X-ray photoelectron spectra were recorded by an imaging X-ray photoelectron
 spectrometer (XPS, Axis Ultra, Kratos Analytical, UK) to characterize the catalyst
 surface.

The carbon content of fresh and used catalysts was characterized using thermogravimetry-differential scanning calorimetry (TG-DSC, STA449F3 Jupiter, Netzsch-Gerätebau GmbH, Germany). About 40 mg of catalysts were heated in air from room temperature to 800°C, at a heating rate of 10 °C/min.

208 3. Results and Discussion

209 *3.1 Catalyst characterization*

210 **Table 1** shows the Ni or Fe loading, specific surface area, pore volume, average 211 pore diameter and the crystallite size of different supports and catalysts. The Ni or Fe 212 loading was measured by ICP-MS as 1.91-2.54 wt.% for Ni-based catalysts and 1.95-2.84 wt.% for Fe-based catalysts, slightly lower than the 3 wt.% desired. 213 214 However, the Ni/Fe loading of almost all catalysts was about 2 wt%, indicating the 215 reliability of the preparation method of the catalysts. The specific surface area was 216 calculated by the BET method, and the pore diameter distribution was determined by 217 the adsorption-desorption isotherm of catalysts. The nitrogen adsorption-desorption 218 isotherms of different Ni- and Fe-based catalysts and the pore diameter distribution 219 are shown in Figure S1 and Figure S2. The results showed that the catalyst supports 220 (CaO, SiO₂, γ -Al₂O₃ and ZSM-5) influence the adsorption-desorption isotherm and 221 pore diameter distribution these more than the active metal (Ni and Fe). The catalysts 222 with different supports displayed absolutely different adsorption-desorption isotherms. 223 M/CaO and M/SiO₂ catalysts (M: Ni or Fe) exhibit the type III adsorption-desorption 224 isotherm of non-porous materials (Figure S1a and b). M/γ -Al₂O₃ show a type V 225 adsorption-desorption isotherm with H1 hysteresis loop, clearly related to a diameter in the mesopore range³⁷ (Figure S1c). M/ZSM-5 display a type I-like 226 227 adsorption-desorption isotherm characteristic of cellular materials (Figure S1d). The

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pore diameter distributions shown in Figure S2 confirmed the results. The pore 228 229 diameter of M/γ -Al₂O₃ ranges 5-15 nm, i.e. mesoporous. Most M/ZSM-5 catalyst pores are micropore in the range of 0-2 nm. However, M/ZSM-5 catalysts also 230 contain mesopores, leading to multilayer adsorption in a N_2 adsorption-desorption 231 isotherm. It is shown in **Table 1** that the addition of both Ni and Fe led to a decrease 232 in the BET surface area, pore volume and average pore diameter of supporting 233 materials. It might be caused by the coverage of Ni and Fe particles on the surface of 234 supporting materials and even the migration of the metals in pores of the supporting 235 materials, which leads to the contraction of pores.³⁸ Among all catalysts supported by 236 different materials, M/ZSM-5 exhibited the highest BET surface area of 340.1-359.6 237 m²/g, comparing with 145.2-156.6 m²/g for M/ γ -Al₂O₃, 5.9-7.5 m²/g for M/SiO₂ and 238 16.4-19.5 m²/g for M/CaO. However, the pore volume of M/ γ -Al₂O₃ was 0.46-0.49 239 cm³/g, much higher than the 0.07-0.13 cm³/g of M/ZSM-5. The difference might be 240 attributed to the abundant amounts of mesopores in M/y-Al₂O₃. 241

242

Table 1 Physicochemical properties and Ni/Fe loadings of the catalysts.

Ni-based Catalysts	Ni/HZSM-5	Ni/γ-Al ₂ O ₃	Ni/SiO ₂	Ni/CaO
BET Surface Area (m ² /g)	359.6	156.6	5.9	16.4
Average Pore Diameter (nm)	1.68	7.91	1.47	3.84
Pore Volume (cm^3/g)	0.13	0.49	0.01	0.04
Crystallite Size ^{<i>a</i>} (nm)	21.6	8.8	75.6	56.0
Ni loading (%)	1.91	2.54	1.93	2.10
Fe-based Catalysts	Fe/ZSM-5	Fe/y-Al ₂ O ₃	Fe/SiO ₂	Fe/CaO
BET Surface Area (m ² /g)	340.1	145.2	7.5	19.5
Pore Diameter (nm)	0.91	9.76	2.47	3.82
Pore Volume (cm^3/g)	0.07	0.46	0.02	0.05
Crystallite Size ^{<i>a</i>} (nm)	16.4	4.7	61.2	44.1
Fe loading (%)	1.95	2.84	1.95	2.47
Supports	ZSM-5	γ-Al ₂ O ₃	SiO ₂	CaO
BET Surface Area (m ² /g)	383.0	165.6	10.7	20.1
Pore Diameter (nm)	2.26	15.6	3.05	7.14
Pore Volume (cm^3/g)	0.22	0.55	0.02	0.05

²⁴³

^a Calculated by the Scherrer equation based on the XRD results.

Figure 2 presents the XRD patterns of freshly calcined and used Ni-based 244 245 catalysts. In addition, the supporting materials were also analyzed using XRD, as 246 shown in Figure S3. It is obvious that the presence of NiO particles showed little 247 effect on the diffraction patterns of supporting materials. Almost all catalysts show clear NiO diffraction peaks at $2\theta=37.8^{\circ}$, 43.7° and 62.7° , except for Ni/ γ -Al₂O₃. The 248 difference might be attributed to two reasons: (1) the diffusion peaks of NiO falling in 249 the broad diffusion peak range of Al₂O₃ at 42.5-49.6° and 58.9-70.7°, (2) a better 250 dispersity of NiO particles on Al₂O₃. In addition, similar results were observed for the 251 Fe-based catalysts, as presented in Figure S4. The XRD results of Fe/SiO₂, Fe/CaO 252 253 and Fe/ZSM-5 all showed the diffusion peaks at 2θ =33.2° and 35.7°, corresponding to 254 the characteristic peaks of Fe_2O_3 . However, they were not observed in Fe/Al_2O_3 .

255 The average crystallite size of different catalysts was determined by the Scherrer

equation, as shown in **Table 1**:

$$d=0.89\lambda/\beta cos\theta \tag{8}$$

where d represents the average size of the crystallite; λ represents the X-ray wavelength; β represents peak width at half height and θ is the Bragg angle, respectively.

The crystallite size of the Ni-based catalysts supported by different materials varied from 8.8 nm to 75.6 nm, generally higher than 4.7-61.2 nm for the Fe-based catalysts, which is in agreement with the N_2 adsorption-desorption experiment in this study (**Table 1**).





Figure 2. XRD analysis of the (a) Ni/SiO₂, (b) Ni/CaO, (c) Ni/γ-Al₂O₃ and (d) Ni/ZSM-5 before
and after toluene reforming.

The SEM pictures of the fresh and used Ni-based catalysts are shown in Figure 3. 271 272 Ni-based catalysts with different supports show absolutely different particle shape and 273 size. Ni/SiO₂ and Ni/γ-Al₂O₃ catalysts consist of sphere-like particles and Ni/ZSM-5 274 catalyst shows rod-shaped particles aggregated into clusters. The Ni/CaO catalyst is 275 composed of larger particles with irregular shapes. Among all catalysts, Ni/γ -Al₂O₃ 276 has a minimal size in nano-scale. During a comparison of fresh and used catalyst, 277 Ni/SiO₂, Ni/CaO and Ni/γ-Al₂O₃ all show obvious sintering, but Ni/ZSM-5 catalyst 278 presents no obvious changes before and after toluene reforming, indicating absence of 279 sintering.

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285 *3.2 Catalytic steam reforming of toluene*

Transition metals, such as Ni and Fe, are promising catalysts for cracking tar, due to their high efficiency, low cost, and easy regeneration.³⁹ Their support is an important influencing factor since metal catalysts are not actively supported by inert oxides.⁴⁰

The conversion efficiency of toluene and the selectivity of forming benzene and 290 ethylbenzene catalyzed by Ni-based catalysts in the post-plasma catalysis (PPC) 291 system are shown in Figure 4 (a). The combination of catalyst and DBD plasma 292 293 obviously enhanced toluene cracking than the DBD plasma without catalysts. The 294 conversion of toluene catalyzed by Ni-based catalysts with different supports varied 295 in a range of 67.0-79.5%, i.e. 1.05-1.24 times that with plasma alone. The catalytic activities of different Ni-based catalysts followed the order: Ni/ZSM-5 > Ni/ γ -Al₂O₃ > 296 $Ni/SiO_2 > Ni/CaO > Blank$, which was positively related to the BET surface area. 297 298 Catalyst with high surface area and pore volume has higher adsorption ability for 299 reactants and promoters such as H_2O and free radicals ($H_{\cdot}, OH_{\cdot}, O\cdots$). They provide 300 more active sites for toluene cracking. Benzene and ethylbenzene are the leading 301 liquid by-products of toluene cracking. Their selectivity was in the range of 4.2-8.5 % and 1.4-2.9 %, respectively. Contrary to toluene conversion, the selectivity of benzene 302 and ethylbenzene obtained their minimum when catalyzed by Ni/ZSM-5 and their 303 maximum with plasma alone (Figure 4a). The results showed that the addition of 304 Ni-based catalysts, especially Ni/ZSM-5, inhibited the conversion of toluene to liquid 305 306 by-products.

307 Apart from the liquid by-products, H₂ and CO were the most important gas 308 products. The selectivity and yield of H_2 and CO is shown in Figure 4(b). Ni/ZSM-5 309 and Ni/ γ -Al₂O₃ present comparable catalytic activity on the formation of syngas, 310 higher than Ni/SiO₂ and Ni/CaO. Most Ni-based catalysts promote the formation of H₂ and CO, except Ni/CaO. Ni-based catalysts stimulate the conversion of toluene to 311 H_2 and CO, promoting steam reforming and the water-gas shift (WGS) reaction.⁴¹ 312 313 However, both the yield and selectivity of syngas decreased catalyzed by Ni/CaO compared with the DBD plasma system without catalysts. In previous studies, 314 14

315 MgO-CaO and dolomite were effective supports in the suppression of coke and their resistance to sulfur poisoning during biomass tar reforming.⁴¹ However, Ni/CaO 316 showed little catalytic activity in toluene cracking and syngas formation in this study, 317 which might be attributed to the consumption of H₂O by CaO. CaO could react with 318 319 H_2O to generate $Ca(OH)_2$ and thus the steam reforming reaction (9) and water-gas shift reaction (10) were weakened. This assumption was supported by the 320 XRD-results of Ni-based catalysts before and after reforming (Figure 2). The XRD 321 322 results of Ni/SiO₂, Ni/γ-Al₂O₃ and Ni/ZSM-5 did not show obvious difference before 323 and after reforming. However, the fresh Ni/CaO-catalyst contains crystals of NiO and CaO, and the characteristic diffraction peaks of Ca(OH)₂ at 2θ =29.0°, 34.4°, 47.5°, 324 51.0° and 54.6° were also observed in used catalysts, cf. Figure 2(b). 325

- 326 $C_7H_8 + 7H_2O \rightarrow 7CO + 11H_2$ (9)
- 327

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We also tested the catalytic activity of ZSM-5, SiO_2 , Al_2O_3 and CaO without NiO loading on toluene reforming in the PPC system. The results indicated that the supporting materials did not show obvious catalytic activity on toluene conversion and formation of H₂ and CO, as shown in **Figure S5**. It can be concluded that Ni was the main active component for toluene conversion and syngas production.

 $CO+H_2O\rightarrow CO_2+H_2$

(10)





Figure 4. Effect of Ni-based catalysts on the (a) conversion efficiency of toluene, selectivity of benzene and ethylbenzene, and (b) selectivity and yield of H₂ and CO.

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The catalytic activity of Fe-based catalysts was also evaluated with different supports (**Figure 5**). The results showed that the catalytic activity of Fe-based catalysts with different supports showed similar trend with Ni-based catalysts,⁴² following a sequence of Fe/ZSM-5 > Fe/ γ -Al₂O₃ > Fe/SiO₂ > Blank > Fe/CaO. Fe/ZSM-5 exhibited the highest catalytic activity with the highest toluene conversion efficiency of 74.6% and the lowest benzene and ethylbenzene selectivity of 4.1% and 1.6%, respectively (**Figure 5a**).

The selectivity for H_2 and CO, catalyzed by Fe/ZSM-5 and Fe/ γ -Al₂O₃, was comparable, yet much higher than for Fe/SiO₂ and Fe/CaO. Fe/CaO showed no catalytic effect on syngas formation and CO was not even detected during toluene cracking. The yield of H_2 and CO attained a maximum of 2.25 mol/mol-toluene for H_2 and 0.92 mol/mol-toluene for CO.

In addition, Ni-based catalysts exhibited relatively higher activity on the conversion of toluene than Fe-based catalysts, 67.0-79.5% for Ni-based catalysts and 63.8-74.6% for Fe-based catalysts. However, Fe-based catalysts were more potential on syngas formation. The results can be explained by the characteristics of Ni- and

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356 Fe-based catalysts. Ni-based catalysts exhibit higher catalytic activity than Fe-based catalysts for toluene conversion due to the higher reactivity of C-C and C-H bonds in 357 hydrocarbons on the surface of Ni particles.⁴³ However, syngas production is better 358 catalyzed by Fe-based than by Ni-based catalysts. Since Fe has higher oxygen affinity 359 than Ni,⁴⁴ Fe-based catalysts can increase the coverage of oxygen-contained 360 compounds (H₂O, O[,], OH^{,...}) on the catalyst surface during the steam reforming 361 362 reactions. Thus the formation of syngas is promoted by enhancing the steam 363 reforming reaction of toluene and the attack of free radicals to toluene. Therefore, adding Fe or other oxytropic materials (OMs) such as CeO₂⁴⁵ in Ni-based catalysts. 364 might improve the conversion of toluene and syngas production simultaneously. 365 366 Developing modified catalysts by adding different kinds of OMs and adjusting the OMs/Ni ratio should be an alternative choice to enhance the conversion of tar and the 367 368 formation of syngas.

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Figure 5. Effect of Fe-based catalysts on the (a) conversion efficiency of toluene, selectivity of benzene and ethylbenzene, and (b) selectivity and yield of H₂ and CO.

377 3.3 Toluene cracking in the PPC and IPC reactor

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378 Although Ni- and Fe-based catalysts in the post-plasma catalysis (PPC) reactor 379 somewhat promoted the conversion of toluene and syngas formation than that in the plasma system without catalysts, the promoting effect was limited. Therefore, the 380 381 catalytic steam reforming of toluene in the in-plasma catalysis (IPC) reactor was studied. Considering the higher activity of Ni-based catalysts, they were selected for 382 the steam reforming of toluene in the IPC system. The comparative results of PPC and 383 384 IPC reactors are presented in Figure 6. It can be seen from Figure 6(a) that the catalytic activity of Ni-based catalysts exhibited similar trend in the IPC reactor with 385 386 that in the PPC reactor. However, the catalytic activity of Ni-based catalysts was obviously improved in the IPC reactor. The conversion efficiency of toluene and 387 388 energy efficiency showed higher values of 66.6-86.5% and 17.3-22.5 g/kWh in the IPC reactor, compared with 67.0-79.5% and 17.4-20.7 g/kWh in the PPC reactor. 389

The selectivity of benzene and ethylbenzene both decreased in the IPC reactor than the PPC reactor catalyzed by Ni/SiO₂, Ni/ γ -Al₂O₃ and Ni/ZSM-5, as shown in **Figure 6(b)**. The selectivity and yield of H₂, CO and CH₄ are displayed in **Figure**

6(c). The main gas products are H_2 and CO, and CH_4 is newly detected during toluene reforming in the IPC reactor compared with that in the PPC system. As the minor gas product, the selectivity of CH_4 was in the range of 3.2-4.6%, much lower than that of H_2 and CO. We can find from **Figure 6(c)** that the formation of H_2 , CO and CH_4 is greatly promoted in the IPC reactor. Ni/ZSM-5 is the most promising catalyst also in the IPC reactor, with the highest gas selectivity of 63.3% for H_2 , 18.2% for CO, and 4.6% for CH_4 .



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Figure 6. (a) Conversion of toluene and energy efficiency, (b) selectivity of benzene and ethylbenzene, (c) selectivity and yield of H₂, CO and CH₄ in the post-plasma and in-plasma system.

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In order to demonstrate the effect mechanism of catalyst on toluene reforming, 410 411 XPS technique was used to characterize the chemical changes on the surface of 412 Ni/ZSM-5 and Ni/SiO₂ catalysts before and after toluene reforming. Figure 7 shows the XPS spectra of Ni 2p. Ni/ZSM-5 and Ni/SiO₂ displayed similar Ni 2p spectra. 413 Both the Ni 2p3/2 spectra of the fresh Ni/ZSM-5 and Ni/SiO₂ catalysts showed two 414 main peaks, confirming the presence of Ni⁰ with a peak binding energy of ~852.9 eV, 415 and the presence of Ni²⁺ with a peak binding energy of ~856.4 eV, and its 416 corresponding shakeup resonance at ~861.8 eV.⁴⁶ The presence of satellite peaks 417 confirmed that partial nickel atoms were present in oxygen environment.⁴⁷ Therefore, 418 the main chemical states of Ni were zero-valent metallic nickel and NiO. Ni⁰ was 419 proved to be the dominant active component for toluene reforming,⁴¹ and the ratios of 420 Ni^0/Ni^0+Ni^{2+} were 30% for Ni/ZSM-5, higher than 27.9% for Ni/SiO₂, as presented in 421 **Table 2.** In addition, Ni/ZSM-5 contained a higher Ni ratio of 0.79 than 0.70 for 422 Ni/SiO₂. These phenomena both lead to a higher catalytic activity of Ni/ZSM-5 than 423

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Ni/SiO₂. Differently, the Ni 2p3/2 spectra exhibited only one main peak centered at
~855.5 eV, along with its shake-up peaks at ~861.3 eV for the used Ni/ZSM-5 and
Ni/SiO₂ catalysts. The results showed that the main Ni specie presented in the used
Ni/ZSM-5 and Ni/SiO₂ catalysts was NiO.

The O species is one the key factor influencing toluene cracking. Table 2 428 429 showed the element composition on the surface of the catalysts. It can be seen from **Table 2** that the amount of surface O species in Ni/ZSM-5 catalyst is higher than 430 Ni/SiO₂. This suggests the higher affinity of ZSM-5 towards O species than SiO₂. 431 432 This property is beneficial to promote the steam reforming reaction by reducing carbon depositions and enhancing WGS reaction during toluene steam reforming.⁴⁸ In 433 addition, the O 1s spectra of the fresh and used Ni/ZSM-5 and Ni/SiO₂ catalysts are 434 shown in Figure 8. Three components (O-I, O-II, O-III) are identified by 435 deconvoluting the main peak at ~533 eV. O-I component located at ~531.0 eV might 436 be °Cassigned to Ni-O bonds in NiO.49 The dominating O-II component at ~533.3 eV 437 was obviously related to O²⁻ species in the support SiO₂.⁵⁰ Both the O-I and O-II 438 439 components were defined as lattice oxygen (O_{lat}). The O-III component at ~534.0 eV 440 may be attributed to the Si-OH groups with O 1s at BE \sim 533.9 eV or adsorbed oxygen (O_{ads}).⁵⁰ It can be seen from Figure 8 and Table 2 that the adsorbed oxygen in the 441 fresh Ni/ZSM-5 decreased sharply after toluene reforming, and the ratio of 442 O_{ads}/O_{ads}+O_{lat} decreased from 24.2% to 8.23%. However, the lattice oxygen showed 443 no obvious change before and after toluene reforming. It can be concluded that the 444 445 adsorbed oxygen species is the dominant promoter for the steam reforming reaction compared with lattice oxygen. Moreover, the ratio of O_{ads} on the surface of Ni/SiO₂ 446 447 catalyst showed much less decrease than Ni/ZSM-5, which lead to a lower catalytic 448 activity of Ni/SiO₂ catalyst.



Table 2 Surface composition of elements presented in fresh and used Ni/ZSM-5 and Ni/SiO₂

Catalusta	Surface element composition (%)						
Catalysis	Ni	0	Si	Al	Ni ⁰ /Ni ⁰ +Ni ²⁺	Ni ²⁺ /Ni ⁰ +Ni ²⁺	$O_{ads} / O_{ads} + O_{lat}$
Fresh Ni/HZSM-5	0.79	62.2	27.6	0.19	30 (852.9eV)	70 (856.4 eV)	24.2 (533.8eV)
Used Ni/HZSM-5	0.44	53.1	23.4	0.19	0	100 (856.5 eV)	8.23 (534.0eV)
Fresh Ni/SiO ₂	0.70	57.4	21.8	0	27.9 (852.3eV)	72.1 (856.9 eV)	16.2 (533.1eV)
Used Ni/SiO ₂	0.40	49.5	29.8	0	0	100 (856.6 eV)	10.2 (533.0eV)





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459 Figure 8. Typical O 1s XPS spectra of fresh and used (a) Ni/ZSM-5 and (b) N

461 *3.4 Characterization of carbon deposition*

Carbon deposition on metal catalysts is a troublesome issue limiting their 462 large-scale application. The nature and amount of carbon deposition on the catalyst 463 464 surface was determined by TG-DSC analysis of the used Ni-based and Fe-based catalysts. The used catalysts were heated up to 800°C and their TG-DSC curves are 465 466 shown in **Figure 9**. It can be seen that the catalysts supported by the same kind of materials showed similar TG-DSC curve. The TG-curves showed a one-stage weight 467 468 loss between 300-600°C except for CaO-supported catalysts. The total mass loss in 469 the temperature range of RT-800°C was 0.27-1.41% for SiO₂-supported catalysts, 470 5.49-8.95% for ZSM-5-supported catalysts, 9.22-10.3% for γ -Al₂O₃-supported 471 catalysts and 28.8-30.1% for CaO-supported catalysts. No obvious weight loss was 472 observed for SiO₂-supported catalysts. The DSC profile of catalysts supported by 473 γ -Al₂O₃ and ZSM-5 showed obvious exothermic peaks at around 400-500°C, corresponding to the oxidation of amorphous carbon.⁵¹ However, CaO-supported 474 475 catalysts exhibited a different TG-DSC profile. The TG curve of used CaO-supported catalysts presented two-stages of mass loss at 390-460°C and 560-740°C, respectively. 476 The mass loss in the first stage was due to Ca(OH)₂ dehydration at 370-465 °C, and 477

the second stage loss was caused by the calcination of $CaCO_3$ present in the catalysts.⁵² These mass losses were confirmed by the two endothermic peaks at around 440°C and 700°C in the DSC curve. In addition, the consumption amount of H₂O by reacting with CaO could be estimated by the TG results, approximately 14.2-16.2% of the overall feed of H₂O.

The yield and selectivity of carbon deposition on the used Ni- and Fe-based catalysts is shown in **Table 3**. It can be seen that the yield and selectivity of carbon deposition on Fe-based catalysts was generally higher than that for the Ni-based catalysts in the PPC system. In addition, the catalysts in the IPC system showed higher resistance to carbon deposition than in the PPC system, especially for Ni/ZSM-5. Ni/SiO₂ and Ni/ZSM-5 were the most potential in the resistance to carbon deposition, much better than the metal catalysts reported in previous studies. ^{51,53,54}

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 $(c)\gamma$ -Al₂O₃ and (d) ZSM-5.

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501		Table .	3 Selectivity	y of carbo	on deposition	n on the catal	ysts		
	PPC system						IPC system		
Catalust	PPC syst	em					IPC syste	em	
Catalyst	PPC syst	tem Ni/γ-Al ₂ O ₃	Ni/ZSM-5	Fe/SiO ₂	Fe/y-Al ₂ O ₃	Fe/ZSM-5	IPC system Ni/SiO ₂	em Ni/γ-Al ₂ O ₃	Ni/ZSM-5
Catalyst Yield (g/g-cat)	PPC syst Ni/SiO ₂ 0.003	nem Ni/γ-Al ₂ O ₃ 0.092	Ni/ZSM-5 0.066	Fe/SiO ₂ 0.014	Fe/γ-Al ₂ O ₃ 0.103	Fe/ZSM-5 0.089	IPC system Ni/SiO2 0.003	em Ni/γ-Al ₂ O ₃ 0.098	Ni/ZSM-5 0.055

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503 3.5 Mechanism of toluene reforming

The reaction mechanism of toluene cracking in DBD plasma-catalysis system is 504 complex, containing multiple electronic, ionic and free radical reactions.⁵⁵ The liquid 505 506 by-products were analyzed for a better understanding of the reaction pathway and mechanism of toluene cracking, as shown in Figure 10. It can be seen from Figure 10 507 (a) and (b) that the liquid by-products from toluene cracking in the plasma-alone (PA) 508 and the post-plasma catalysis (PPC) system contained almost the same components. 509 Benzene and ethylbenzene were identified as the dominant liquid by-products, 510 however, the selectivity of them was much less than that of H_2 and CO. Some other 511 hydrocarbons, such as o-xylene, styrene, cumene, n-propylbenzene, isobutylbenzene, 512 513 1, 2-diphenylethane and 2-methyl-3-phenylbutane, were also detected as the minor composition in the liquid by-products. The formation of N-containing benzonitrile 514 suggested that the N radicals also participate in the reaction. However, the amount of 515 benzonitrile was limited, which indicated that the cleavage of N_2 was difficult and 516 most N_2 was kept as a stable molecular state or nitrogen excited state (N_2^*) .³⁶ The 517 formation of oxygenates (dimethyl phthalate and diethyl phthalate) could be attribute 518 to the presence of H_2O , OH and O during toluene cracking. Besides, the chain 519 520 hydrocarbons, 1, 6-Heptadien-3-yne and 1, 6-heptadiyne, were also detected due to the cleavage of the benzene ring followed by the hydrogenation.²¹ The only difference 521 between the liquid by-products in the PA system and PPC system seems to be that the 522 peak area of liquid by-products in the PPC system was much less than that in the PA 523 system. This result indicated that the addition of catalysts in the downstream of the 524 discharge zone decreased the formation of liquid by-products, however, it had little 525

526 effect on the reaction mechanism of toluene cracking.

527 Figure 10 (c) presented the GC-MS spectrogram of liquid by-products in the IPC system with Ni/ZSM-5 catalyst. The formation of liquid by-products was undesirable, 528 which would lead to the secondary pollution and weaken the discharge.⁵⁶ It can be 529 530 seen that the amount of the liquid by-products in the IPC system decreased sharply and the composition was quite different from that in the PO and PPC systems. The 531 dominant liquid by-products were identified as benzene, ethylbenzene and 1, 532 2-diphenylethane, similar with that in the PO and PPC systems. However, other 533 hydrocarbon species, such as p-xylene, biphenyl, diphenylmethane, (E)-stilbene and 2, 534 535 3-diphenylbutane, were newly formed in the IPC system with Ni/ZSM-5. In addition, the species of oxygen-containing compounds in the IPC system (benzyl benzoate and 536 meso-hydrobenzoin) were also different, and their amounts were minor compared 537 with the PO and PPC systems. All the differences might be attributed to that the 538 539 catalysts in the IPC might influence the reaction mechanism of toluene cracking. In the IPC system, the oriented formation of H₂ and CO, through the reaction of the 540 active species (H₂O, OH \cdot , O \cdot , N₂^{*}...) with toluene and its cracked intermediates, was 541 542 enhanced in the effect of Ni-based catalysts in the IPC system. Although the same active free radicals might also be formed in the PO and PPC systems, the formation of 543 products was uncontrollable in PA system without catalysts.²³ For the PPC system, the 544 short lifetime reactive plasma species, such as OH_{\cdot} , O_{\cdot} and N_2^* , were not able to 545 reach the catalysts installed in the downstream of the plasma zone.²² Therefore, the 546 reaction mechanism in the PPC system was almost not changed compared with that in 547 the PA system. This result suggested that the IPC system with Ni/ZSM-5 was the most 548 549 potential in inhibiting the formation of undesirable liquid by-products and promoting 550 the formation of H_2 and CO.

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13. 1, 2-diphenylethane, 14. 2-methyl-3-phenylbutane, 15. diethyl phthalate, 16. p-xylene, 17. biphenyl,
18. benzyl benzoate, 19. phenol, 20. diphenylmethane, 21. meso-hydrobenzoin, 22. (E)-stilbene, 23. 2,
3-diphenylbutane)

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566 The possible reaction pathway of toluene in the IPC system with Ni/ZSM-5 was 567 shown in Figure 11. The major reactions of toluene reforming occurred in the plasma were activated by the high-energy electrons, free radicals (i.e., OH, O, N) and 568 excited species (i.e., N_2^*).⁵⁷ The toluene destruction mainly contained two processes: 569 direct destruction and secondary oxidation. The direct destruction of toluene 570 proceeded as route I-V and VII. Compared with the C-H bonds in the benzene ring 571 (4.3 eV), C-C bones between the benzene ring and methyl (4.4 eV), the C-C bones 572 (5.0-5.3 eV) and C=C bones (5.5 eV) in the benzene ring, the C-H bonds in the 573 methyl are easier (3.7 eV) to be cleavage.⁵⁸ Therefore, the H atoms in the methyl were 574 firstly removed to form benzyl ($C_6H_5CH_2$), benzylidene ($C_6H_5CH=$) and benzenyl 575 $(C_6H_5C\equiv)$. The benzyl combined with a methyl (CH_3) , phenyl (C_6H_5) and hydroxyl 576 (OH) to generate ethylbenzene, diphenylmethane and benzyl alcohol. The produced 577 578 benzyl alcohol and ethylbenzene would auto-combined to produce 579 meso-hydrobenzoin and 2, 3-diphenylbutane. Ethylbenzene could also react with a methyl or benzyl to form n-propylbenzene or 1, 2-diphenylethane. Although the 1, 580 581 2-diphenylethane could also be produced by the recombination of n-propylbenzene 582 and phenyl, n-propylbenzene and phenyl were more difficult to be obtained and their amounts were also limited compared with ethylbenzene and benzyl as shown in 583 Figure 10. Therefore, 1, 2-diphenylethane, as the one of dominant liquid by-products, 584 585 was tended to be produced by the combination of ethylbenzene and benzyl. Benzonitrile in the liquid products comes from the combination of benzenyl and N 586 free radical. The C-C bone between methyl and benzene ring was easy to be broken 587 by N_2^* and energetic electrons to produce benzyl. Benzyl radicals reacted with H-, 588 OH and benzyl, forming benzene, phenol and biphenyl. The H atom on the 589 590 para-position of methyl could also be activated and replaced by a methyl, generating 591 p-xylene. The secondary oxidation as shown in route VI and VIII might be explained as the oxidation of toluene in the presence of O· and OH·, and form benzyl benzoate 592 eventually.⁵⁷ The formation of CO could also be attributed to the oxidation of toluene 593 and its intermediates by O and OH.²¹ 594

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Figure 11. Reaction pathway of toluene reforming over Ni/ZSM-5 (in-plasma catalysis system).

599 4. Conclusion

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600 The oriented conversion of model tar compound toluene to H₂-rich syngas was 601 conducted in a hybrid DBD plasma-catalysis system. Ni- and Fe-based catalysts with different supports (CaO, SiO₂, γ-Al₂O₃ and ZSM-5) were characterized and their 602 catalytic activity was evaluated. The catalytic activity decreased in sequence of 603 604 $M/ZSM-5 > M/\gamma-Al_2O_3 > M/SiO_2 > M/CaO$ (M represents Ni or Fe), which was 605 positively related to the BET surface area. Catalysts supported by ZSM-5 showed the 606 most potential in converting toluene to syngas, inhibiting the formation of undesirable 607 liquid by-products and carbon deposition, and resistance of deactivation caused by 608 sintering and carbon deposition. M/CaO had little effect on toluene conversion, and 609 the formation of syngas was almost decreased in the presence of M/CaO. It was 610 attributed to that the support CaO reacted with H_2O , forming Ca(OH)₂, and thus the 611 steam reforming reaction and water-gas shift reaction were weakened. Ni-based 612 catalysts exhibited higher catalytic activity than Fe-based catalysts on toluene 613 cracking, due to the higher activity of C-C and C-H bonds in hydrocarbons on the 614 surface of Ni particles. However, the syngas production was higher catalyzed by 29

615 Fe-based catalysts than Ni-based catalysts, since Ni showed higher oxygen affinity 616 than Ni. The performance of toluene cracking in plasma-alone (PA) system, 617 post-plasma catalysis (PPC) system, and in-plasma catalysis (IPC) system was also compared. The toluene cracking in the IPC system exhibited higher conversion 618 619 efficiency of toluene, higher selectivity and yield of H₂, CO and CH₄, lower 620 production of unwanted liquid by-products. In addition, the mechanism of toluene cracking in IPC system was significantly different with that in the PA and PPC system. 621 622 It might be attributed to the short lifetime reactive plasma species (OH \cdot , O \cdot , N₂^{*}...) reacted with toluene and its intermediates on the surface of catalysts in the IPC system. 623 624 The possible mechanism and reaction pathway in the IPC system have been proposed and discussed in detail based on the analysis of the gas and liquid products and the 625 626 characterization of catalysts.

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Ni/ZSM-5 in the in-plasma catalysis system was potential in toluene conversion, syngas formation, and inhibiting undesirable by-product and coke formation.

