**Supporting Information**

High catalytic performance of Fe-rich/Palygorskite supported Ni catalyst for steam reforming of toluene

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The toluene conversion, gas yields, gaseous product distributions and the molar ratios of H2/CO were calculated based on the equations (1-6).

where C and Cout T are the inlet and outlet concentration of toluene.

where Cout B is the concentration of benzene in the products.

where [Hin S] and [Hin T] are the concentration of H2 in the steam and toluene, [H2]out is the outlet concentration of H2.

The following equations (7-13) represented the possible reactions in the CSRT.

C7H8(g) + 7H2O(g) → 7CO(g)+11H2(g) (S/C = 1.0)

C7H8(g) + 14H2O(g) → 7CO2(g) + 18H2(g) (S/C = 2.0)

Hydrodealkylation reaction：

C7H8(g) + H2(g) → C6H6(g) + CH4(g)

Water gas shift reaction (WGSR):

CO(g) + H2O(g) ↔ CO2(g) + H2(g)

Boudouard reaction:

C(s) + CO2(g) → 2CO(g)

Water gas reaction (WGR):

C(s) + H2O(g) → CO(g) + H2(g)

C(s) + 2H2O(g) → CO2(g) + 2H2(g)

The kinetic model could be expressed with Eq. 14.

(14)

where rt is the consumption rate of toluene. Kapp is the apparent rate constant. Ct and CH are the inlet concentration of toluene and H2O, respectively.

Based on the previous literatures (Li et al., 2009; Tang et al., 2020), the consumption rate of toluene can be assumed as first-order reaction related to the toluene concentration, as shown in Eq. 15:

(15)

The apparent rate constant can be fitted to Eq. 16, and the apparent activation energy is calculated by Eq. 17.

(17)

where Xt, W and V are the toluene conversion, sample weight and volumetric flow rate, respectively.

The accumulation rate of coke deposition was calculated by Eq. 18.

where Vc, Mc and h are the accumulation rate of coke deposition, the amount of coke and reaction time, respectively.

The reaction conditions for the kinetic study were presented below.

A quartz tube with an inner diameter of 8 mm was used and the catalyst was crushed to 0.075 mm to avoid the back mixing, fluid channeling and the internal mass-transfer resistance. The experiment was carried out by varying the gas flow rate to investigate the effect of external mass transfer on the toluene conversion of Ni14/FePal, while the catalyst mass, reaction temperature, toluene concentration and S/C molar ratio were kept at 3 mg, 700 oC, 3000 ppm and 1.0, respectively.



**Fig. S1.** XRD patterns of Nix/FePal (a) and Ni14/FePal calcined in air at different temperatures (b).





**Fig. S2.** Gas distributions (a), H2/CO molar ratio (b) for steam reforming of toluene over Ni14/FPal at different reaction temperatures. Reaction conditions: calcination temperature=600 °C, reduction temperature=700 °C, sample weight=0.3 g, toluene concentration=3000 ppm, S/C=1, reaction time=120 min, GHSV=17052 h-1.





**Fig. S3.** Gas distributions (a), H2/CO molar ratio (b) for steam reforming of toluene over Ni14/FPal at different S/C ratio. Reaction conditions: calcination temperature=600 °C, reduction temperature=700 °C, reaction temperature=700 °C, sample weight=0.3 g, toluene concentration=3000 ppm, reaction time=120 min.



**Fig. S4.** Effect of total flow rate on catalytic activity of Ni14/FPal. Reaction conditions: sample weight =3 mg, flow rate=200 mL/min, GHSV=3.4×106 h-1, toluene concentration=3000 ppm, S/C=1, reaction time=30 min.

**Table S1.**

|  |  |  |  |
| --- | --- | --- | --- |
| Catalyst | Reactants | Conversion (%) | Reference |
| Ni14/FePal | Toluene, H2O | 98 | This work |
| Ni-Fe/α-Al2O3 | Toluene, H2O | 73.6 | (He et al., 2020) |
| Ni0.15Fe0.15@m-Char | Tar | 95.5 | (Lin et al., 2021) |
| NiFeCe-HTc/WC | Toluene, H2O | 98.5 | (Zhang. et al., 2022) |
| Fe3Ni8/De | Toluene, H2O | 98 | (Zhang et al., 2022) |
| Fe3Ni8/Palygorskite | Toluene, H2O | 97 | (Zou et al., 2018) |

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