Electronic Supplementary Material (ESI) for ChemComm. This journal is © The Royal Society of Chemistry 2020

## **Supplementary Information**

# CH₄ conversion over Ni/HZSM-5 catalyst in the absence of oxygen: decomposition or dehydroaromatization?

Yuebing Xu<sup>+</sup>, Mengyao Chen<sup>+</sup>, Bing Liu, Feng Jiang, Xiaohao Liu<sup>\*</sup>

School of Chemical and Material Engineering, Jiangnan University, 214122 Wuxi, China

\* Corresponding author: E-mail address: *liuxh@jiangnan.edu.cn*.

† These authors contributed equally to this work.

#### 1. Experimental details

#### 1.1 Catalyst preparation

Ni/HZSM-5 catalysts are prepared by ion-exchange method (IE) and incipient wetness impregnation (IWI) method and labeled as Ni/HZSM-5-IE and Ni/HZSM-5-IWI, respectively. The Ni-exchanged catalyst was obtained by adding a certain amount of HZSM-5 (Si/AI = 12.5) into a 2 mol/L Ni(NO<sub>3</sub>)<sub>2</sub> aqueous solution and continuously stirring at 90 °C K for 10 h, followed by filtration under vacuum and repeated washing with deionized water. Differently, Ni-impregnated catalysts were obtained by adding a certain amount of the same HZSM-5 into a Ni(NO<sub>3</sub>)<sub>2</sub> aqueous solution with a pre-calculated Ni concentration and volume according to the normal Ni content (2 wt% and 4 wt%) in catalyst and saturated water adsorption capacity of zeolite. All samples were dried at 110 °C K for 10 h and further calcinated at 550 °C for 5 h. Prior to activity test, the obtained powder was pressed and crushed into particles with a size range of 250-425 μm. The real Ni content in all catalysts was analyzed by ICP-AES.

#### 1.2 Catalyst characterization

X-ray diffraction (XRD) of sample was performed on a Bruker-AXS D2 Phaser Desktop X-ray diffractometer using a Cu K $\alpha$  radiation ( $\lambda$  = 0.15406 nm) at 40 kV and 40 mA under a scanning rate of 0.02 °/sec. FT-IR spectra of fresh catalyst samples were recorded on a Nicolet 6700 FT-IR spectrometer from Thermo Fisher Scientific Corporation. Raman spectra of spent samples were obtained over a confocal Raman system (Renishaw inVia Raman microscope) using a 785 nm excitation.

Thermo Scientific K-Alpha+ XPS system was used to analyze the surface of Ni species on HZSM-5 zeolite with an exciting source of Al-K $\alpha$  (1486.6 eV) at 12 kV and 6.0 mA in the CAE analyzer mode. Wide scan spectra were measured at 100 eV with a step of 1 eV under vacuum in the spectrometer chamber which is better than 10-7 mbar, while the narrow scan spectra was measured at 30 eV with a step of 0.1 eV for 5 times. Binding or kinetic energy data were referenced to the aliphatic C 1s peak at 284.8 eV.

SEM observations of spent catalyst samples were conducted over a SEM Hitachi S4800 at an accelerating voltage of 2 kV at room temperature. HAADF-STEM (high-angle annular dark field scanning transmission electron microscope) observation of fresh samples was conducted on a FEI-Tecnai G2 microscope. Before the measurement, the sample was dispersed ultrasonically in ethanol

and then deposited onto a TEM copper grid. SEM observation of spent catalyst samples was conducted over a SEM Hitachi S4800 at an accelerating voltage of 2 kV at room temperature.

NH<sub>3</sub>-TPD, H<sub>2</sub>-TPR and CO-TPR profiles of fresh samples and O<sub>2</sub>-TPO profiles of spent catalysts were collected on a chemisorption instrument (BELCAT II, Japan) with a mass detector (BELMASS, Japan). For NH<sub>3</sub>-TPD measurement, 50 mg of a sample was charged into a reactor and heated in a He stream to 500 °C and kept there for 1 h, cooled down to 100 °C and then exposed to a 10%NH<sub>3</sub>/He stream for 30 min. After that, the NH<sub>3</sub> adsorbed sample was treated in a He stream at the same temperature for 1 h to remove physical adsorbed NH<sub>3</sub> and obtain a stable base line, and finally heated to 750 °C at a heating rate of 10 °C/min to obtain the NH<sub>3</sub>-TPD profile. For H<sub>2</sub>-TPR and CO-TPR measurement, after the same treatment at 500 °C for 1 h in a He stream to 800 °C to obtain the H<sub>2</sub>-TPR and CO-TPR profiles. For O<sub>2</sub>-TPO measurement, after kept at 313 K for 60 min in a He stream, 30 mg of a spent sample was heated in a 10%O<sub>2</sub>/He stream to 830 °C at a rate of 10 °C/min to obtain the TPO pattern. The signals of m/e = 18, 28, 32 and 44 were monitored in the measurement for detecting H<sub>2</sub>O, CO, O<sub>2</sub> and CO<sub>2</sub>, respectively.

The coke amount in spent catalyst sample was determined by TG measurement on a thermogravimetric analyzer (Mettler-Toledo TGA-1100SF), and the weight loss between 660 K and 873 K was used to estimate the amount.

#### 1.3 Catalytic test



**Scheme. S1**. Schematic diagram of reactor setup. ① Mass flow controllers; ② transparent gold furnace; ③ U-shaped reactor; ④ 10-way valve with two loops in a heating box; ⑤ gas chromatography with a TCD and an FID.

Catalytic performance of Ni/HZSM-5 catalyst for CH<sub>4</sub> conversion was evaluated in a U-shaped fixed-bed reactor (i.d. 8 mm). Scheme. S1 shows the schematic diagram of the reaction setup. In each

test, 300 mg of a catalyst was charged into the reactor. The catalyst was firstly heated in a N<sub>2</sub> stream of 25 mL/min to required temperature with a heating rate of 10 °C/min and maintained there for 15 min. After that, the 5%Ar/95%CH<sub>4</sub> stream was switched to replace the N<sub>2</sub> stream to flow the catalyst bed for starting of the reaction. The effluent from the reactor was sampled into two loops attached to a 10-way valve in a heating box and analyzed on-line by one gas chromatography (GC-14B) equipped with both TCD and FID. For avoiding the condensation of products, the pipe from reactor to GC and the heating box are kept at 200 °C. The separation of Ar, H<sub>2</sub>, CO and unreacted CH<sub>4</sub> was completed by a TDX-01 packed column at 40 °C, and that of hydrocarbons was done with a Chemipack PH packed column at 160 °C. Ar in feed is served as an internal standard for determination of flow rate and CH<sub>4</sub> conversion according to the equations (1) and (2), respectively. The formation rates of aromatics as well as their selectivities were obtained by external calibration technique and calculated by equations (3) and (4), respectively. The carbon balance is greater than 97%. After reaction, catalyst bed was cautiously cooled in an argon stream to room temperature and the spent catalyst was collected for characterizations.

$$F^{out} = \frac{F^{in} \times x_{Ar}^{in}}{x_{Ar}^{out}}$$
(1)

$$Conv = \frac{F^{in} \times x_{CH_4}^{in} - F^{out} \times x_{CH_4}^{out}}{F^{in} \times x_{CH_4}^{in}} \times 100\% = \left(1 - \frac{x_{CH_4}^{out} x_{Ar}^{in}}{x_{CH_4}^{in} x_{Ar}^{out}}\right) \times 100\%$$
(2)

$$R_i = A_i \times f_i \times n_i \times \frac{F^{out}}{V_{loop}} \times \frac{T_{loop}}{T_0} \times \frac{1}{m_{cat}}$$
(3)

$$S_i = \frac{0.0224 \times R_i \times m_{cat}}{F^{in} \times x_{CH_4}^{in} \times Conv} \times 100\%$$
(4)

where  $F^{in}$  and  $F^{out}$  are the flow rates of feed and effluent, respectively;  $f_i$  (µmol/area) is a calibration factor of aromatic compound *i* and is obtained by external calibration technique;  $A_i$  is an area of a peak in GC spectrum;  $n_i$  is a carbon number in product *i* (6 for C<sub>6</sub>H<sub>6</sub> and 10 for C<sub>10</sub>H<sub>8</sub>);  $V_{loop}$  (mL) is a volume of sampling loop;  $T_{loop}$  (°C) and  $T_0$  (°C) are the loop temperature and room temperature, respectively; and  $m_{cat}$  (g) is the weight of a catalyst sample.

#### 2. Discussion

It can be seen from Fig. 3 in the main body that for the 4 wt% Ni/HZSM-5-IWI catalyst, different catalytic behaviors were observed at 700 °C and 750 °C: 1) the initial  $CH_4$  conversion at 10 min of TOS

(the first point) at 750 °C was obviously lower than that at 700 °C; 2) an increase but then a decrease in the  $CH_4$  conversion was especially observed at 750 °C.

In general, increasing reaction temperature could obviously increase the catalyst activity for an endothermic reaction thermodynamically and kinetically. Note that CH<sub>4</sub> conversion had reached about 45% at 10 min of TOS (the first point in Fig. 3(a)) at 700 °C and then decreased to only 3% at about 75 min of TOS. The rapid decrease during 0-75 min can be certainly ascribed to the complete decomposition of CH<sub>4</sub> into coke which continuously covered and deactivated the Ni active sites with time on stream. At the elevated temperature of 750 °C, the very initial CH<sub>4</sub> conversion should be greatly higher than 45% that was observed at 10 min and 700 °C, and at the same time the period for the rapid decrease in CH<sub>4</sub> conversion should be largely shortened to, for example, 0-10 min only. Therefore, the observed CH<sub>4</sub> conversion at the first point (10 min) must be much low because of a missed observation.

Regarding the increase but then decrease in the CH<sub>4</sub> conversion for the 4 wt% Ni/HZSM-5-IWI catalyst at 750 °C it can be understood as follows: as the CH<sub>4</sub> conversion decreased to a low level (about 5%), the remaining Ni species which were still active for activating CH<sub>4</sub> could favor the CNTs' formation by steadily decomposition of CH<sub>4</sub>, because a large amount of CNTs was observed in the spent 4 wt% Ni/HZSM-5-IWI catalyst (Fig. S4). Therefore, it is possible that due to the growth of the CNTs, some Ni species could have an opportunity to be exposed again for showing their activity by dis-agglomeration of the agglomerated nano-sized HZSM-5 crystals into smaller agglomerates. The improving effect of CNTs formation on catalyst activity and stability can be also found for Fe-modified Mo/HZSM-5 catalysts employed for CH<sub>4</sub> dehydroaromatization (MDA) in previous publications.<sup>1-4</sup> Especially, as the deactivated Mo/HZSM-5 catalyst without Fe addition was treated by ball-milling only for dis-agglomerating the zeolite agglomerates, the activity of the spent nanosized Mo/HZSM-5 catalyst for MDA could be obviously recovered in different degrees depending on the employed space velocity.<sup>5</sup> As a result, an increase in CH<sub>4</sub> conversion over the 4%Ni/HZSM-5-IWI catalyst could be expected during the period of 25-160 min (Fig. 3(b)). In fact, the similar increase could be also observed for the same catalyst at 700 °C from 100 min to the end of the reaction (Fig. 3(a)), and the similar CNTs formation was found on the spent sample (Fig. 4(a)). By comparison, the following decrease in CH<sub>4</sub> conversion is probably due to the termination of the formation of CNTs or/and deactivation of all Ni species by coke deposition.



Fig. S1. FT-IR spectra of parent HZSM-5 zeolite and fresh Ni/HZSM-5 catalysts.



Fig. S2. Ni 2p XPS spectra of fresh Ni/HZSM-5 catalysts.



**Fig. S3**. CH<sub>4</sub> conversion and the selectivity to total aromatics (benzene, toluene and naphthalene) as a function of time on stream over IE- and IWI-prepared Fe/ and Co/HZSM-5 catalysts reacted at 1023 K and 3000 mL/g/h. Co(NO<sub>3</sub>)<sub>2</sub> and FeSO<sub>4</sub> compounds were used as precursors for the preparation of Co/HZSM-5 and Fe/HZSM-5 catalysts, respectively.



**Fig. S4**. SEM observations of (a) fresh HZSM-5 zeolite and (b) spent 4 wt% Ni/HZSM-5-IWI sample reacted at 750 °C.

Catalyst	Preparation method <sup>a)</sup>	Active	Metal loading/wt%	Reaction condition			Catalytic performance b)			Net rate	
				Temp.	SV	CH <sub>4</sub> content	CH <sub>4</sub> conv.	Select. to total	Yield of total	$/\times 10^{-3}  \mathrm{s}^{-1}  \mathrm{c}$	Ref.
				/K	/mL/g/h	in feed /%	/%	aromatics /%	aromatics /%		
Ni/HZSM-5	IE	Ni	1.4	973	3000	95	3.6	61	3.1	4.6	This study
Ni/HZSM-5	IE	Ni	1.4	1023	3000	95	9.0	63	7.2	10.7	This study
Ni/HZSM-5	IWI	Ni	2.0	973	3000	95	2.5	0.0	0.0	0.0	This study
Ni/HZSM-5	IWI	Ni	4.4	973	3000	95	45	0.0	0.0	0.0	This study
V/HZSM-5	SOL	V	2.0	1023	800	90	0.6	35.4	0.2	0.01	6
V/HZSM-5	IM	V	2.0	1023	800	90	3.2	37.9	1.2	0.3	6
Mn/HZSM-5	IM	Mn	4.0	973	1600	100	2.1	91.5	1.9 <sup>d)</sup>	0.5	7
Mn/HZSM-5	IM	Mn	4.0	1023	1600	100	4.4	91.5	4.0 <sup>d</sup>	1.1	7
Mn/HZSM-5	IM	Mn	4.0	1073	1600	100	8.2	91.5	7.5 <sup>d</sup>	2.0	7
Mn/HZSM-5	IM	Mn	2.0	1073	1620	90	5.5	90.0	5.0	2.5	8
Co/HMCM-2	IM	Ca	2.7	072	1500	00.5		0.0	0.0		0
2		CO	5.7	975	1500	90.5	-	0.0	0.0	0.0	9
Cr/HZSM-5	SOL	Cr	2.0	1023	800	90	0.5	28.2	0.1	0.01	6
Cr/HZSM-5	IM	Cr	2.0	1023	800	90	1.1	75.7	0.8	0.2	6
V/HZSM-5	SOL	V	2.0	1023	800	90	0.6	35.4	0.2	0.01	6
V/HZSM-5	IM	V	2.0	1023	800	90	3.2	37.9	1.2	0.3	6
W/HZSM-5	IM	W	2.0	1023	800	90	2.4	50.8	1.2	1.0	6
W/HZSM-5	IM	W	2.0	1073	1500	100	5.7	100.0	5.7 <sup><i>d</i></sup>	9.7	10
Fe/HZSM-5	SOL	Fe	2.0	1023	800	90	3.9	45.5	1.8	0.4	6
Fe/HZSM-5	IM	Fe	2.0	1023	800	90	4.1	89.5	3.7	0.9	6
Fe/HZSM-5	IE	Fe	0.95	973	3750	50	1.5	30.0	0.5	0.6	11
H-(Fe)ZSM-5	IS	Fe	0.73	973	3750	50	0.56	45.0	0.3	0.4	11
Fe/HZSM-5	IM	Fe	5.0	1023	3000	90	4.1	50.1	2.1	0.8	12
Fe/HZSM-5	IM	Fe	2.0	1023	1500	90	11.0	57.8	6.4	3.0	13
Fe/HZSM-5	IM	Fe	4.0	1023	1500	90	13.2	53.8	7.1	1.7	13

**Table. S1.** Survey of net rates of aromatics formation in carbon basis (s<sup>-1</sup>) over various catalysts from references.

											Continued
Re/HZSM-5	IWI	Re	5.0	1023	1440	90	9.3	52.0	4.8	3.0	14, 15
Re/HZSM-5	IWI	Re	5.0	973	1440	90	7.0	59.0	4.1	2.4	14, 15
Zn/HZSM-5	IM	Zn	2.0	973	1440	100	3.0	100.0	3.0 <sup><i>d</i></sup>	1.8	16
Zn/HZSM-5	IM	Zn	2.0	973	1440	100	3.0	100.0	3.0 <sup><i>d</i></sup>	1.8	16
Zn/HZSM-5	IM	Zn	2.0	973	1680	100	6.2	5.1	0.3	0.2	17
ZnO/HZSM-5	IM	Zn	6.4	973	3750	50	1.1	59.1	0.7	0.2	18
Zn/HZSM-5	IE	Zn	0.75	973	3750	50	1.2	71.0	0.9	1.7	18
Cu/HZSM-5	IE	Cu	0.75	1023	1440	100	2.2	70	1.5	1.6	19

a) Preparation methods including ion-exchanged (IE), impregnation (IM), isomorphous substitution (IS), solid ion-exchange (SOL), physical mixing (PM) and incipient-wetness impregnation (IWI).

<sup>b)</sup> The CH<sub>4</sub> conversion and selectivity to total aromatics are taken from references for maximizing the yield of aromatics

<sup>c)</sup> The net rates of aromatics formation in carbon basis is defined to mol of CH<sub>4</sub> converted to aromatics per mol of metal atom per second (s<sup>-1</sup>), and calculated by the following equation:

$$(s^{-1}) = \frac{space \ velocity}{3600 \times 22400} \times CH_4 \ content \ in \ feed \times the \ maximum \ yield \ of \ aromatics \div \ metal \ loading \ in \ catalyst \times \ atomic \ weight$$

*d)* Without considering the selectivity to coke formation.

### References

- 1. Y. Xu, Y. Song, Y. Suzuki and Z.-G. Zhang, Catal. Sci. Technol., 2014, 4, 3644-3656.
- 2. Y. Xu, J. Wang, Y. Suzuki and Z.-G. Zhang, CAtal. Today, 2012, 185, 41-46.
- 3. Y. Xu, J. Wang, Y. Suzuki and Z.-G. Zhang, Appl. Catal., A, 2011, 409-410, 181-193.
- 4. Y. Xu, Y. Suzuki and Z.-G. Zhang, Appl. Catal., A, 2013, 452, 105-116.
- 5. Y. Xu, Y. Song, Y. Suzuki and Z.-G. Zhang, Catal. Sci. Technol., 2013, 3, 2769.
- 6. B. M. Weckhuysen, D. Wang, M. P. Rosynek and J. H. Lunsford, J. Catal., 1998, 175, 338-346.
- 7. P. L. Tan, C. T. Au and S. Y. Lai, Catal. Lett., 2006, 112, 239-245.
- 8. T. E. Tshabalala, N. J. Coville and M. S. Scurrell, Catal. Commun., 2016, 78, 37-43.
- 9. D. Ma, Y. Shu, M. Cheng, Y. Xu and X. Bao, J. Catal., 2000, 194, 105-114.
- 10. J. L. Zeng, Z. T. Xiong, H. B. Zhang, G. D. Lin and K. R. Tsai, Catal. Lett., 1998, 53, 119-124.
- 11. Y. Lai and G. Veser, Catal. Sci. Technol., 2016, 6, 5440-5452.
- 12. F. Denardin and O. W. Perez-Lopez, Fuel, 2019, 236, 1293-1300.
- 13. P. Tan, J. Catal., 2016, 338, 21-29.
- 14. L. S. Wang, R. Ohnishi and M. Ichikawa, Catal. Lett., 1999, 62, 29-33.
- 15. L. Wang, R. Ohnishi and M. Ichikawa, J. Catal., 2000, 190, 276-283.
- L. S. Wang, L. X. Tao, M. S. Xie, G. F. Xu, J. S. Huang and Y. D. Xu, *Catal. Lett.*, 1993, 21, 35-41.
- 17. B. S. Liu, Y. Zhang, J. F. Liu, M. Tian, F. M. Zhang, C. T. Au and A. S. C. Cheung, *J. Phys. Chem.*, *C*, 2011, **115**, 16954-16962.
- 18. Y. Lai and G. Veser, Environ. Prog. Sustain. Energy, 2016, 35, 334-344.
- 19. S. Li, C. Zhang, Q. Kan, D. Wang, T. Wu and L. Lin, Appl. Catal., A, 1999, 187, 199-206.