Supplementary information

Tailoring MIL-100(Fe)-derived Catalyst for Controlled Carbon Dioxide Conversion and Product Selectivity

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1. Supplementary figures

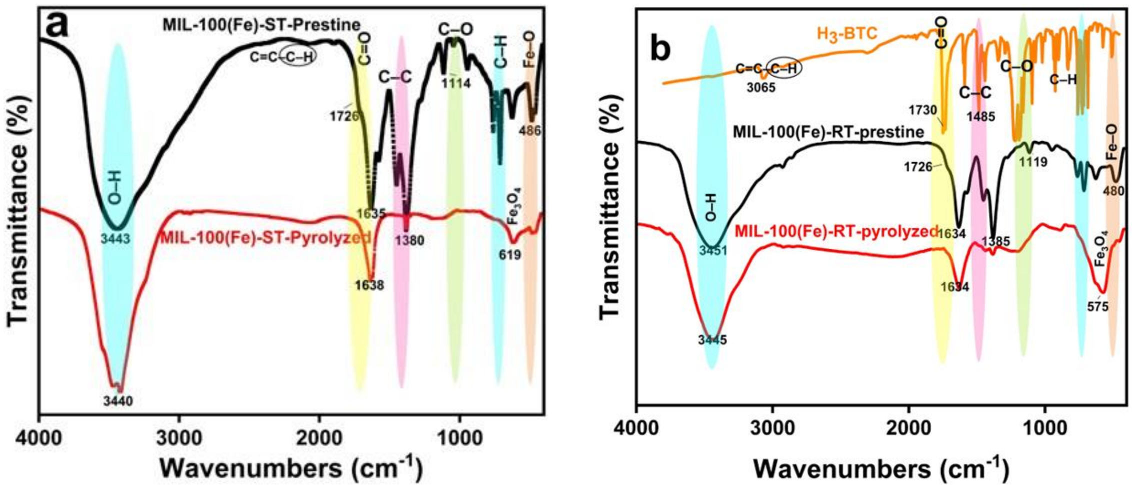

Fig. S1. FTIR spectra of a) pristine and pyrolyzed ST-based-MIL-100(Fe), and b) trimesic acid, pristine, and pyrolyzed RT-based-MIL-100(Fe).

The coordination between iron ions (Fe^{+3}) and the H_3BTC linker is characterized by a robust affinity, leading to a discernible reduction in the intensity of the characteristic bands attributed to H_3BTC [1]. The benzene ring demonstrates vibrational modes of in-plane and out-of-plane bending and stretching, with respective frequencies of 1453, 1119, and 770 cm^{-1}. Also, the vibrations of the carbonyl group of trimesic acid at 1730 cm^{-1} have weekend strongly due to the coordination effect and a new peak appeared in the range from 1300 to 1700 cm^{-1} related to the carboxylate group symmetrical and asymmetrical vibrations changes [1]. Furthermore, there are discernible Fe-O bands that can be detected at frequencies of 631 and 475 cm^{-1} [2]. After pyrolysis, the carboxylate vibrations in the range from 1300 to 1700 cm^{-1} disappeared and the remaining vibrations at 1638 and 1634 cm-1 in case of ST- and RT-based catalysts, respectively, are attributed to the C=C vibrations in the carbon framework.

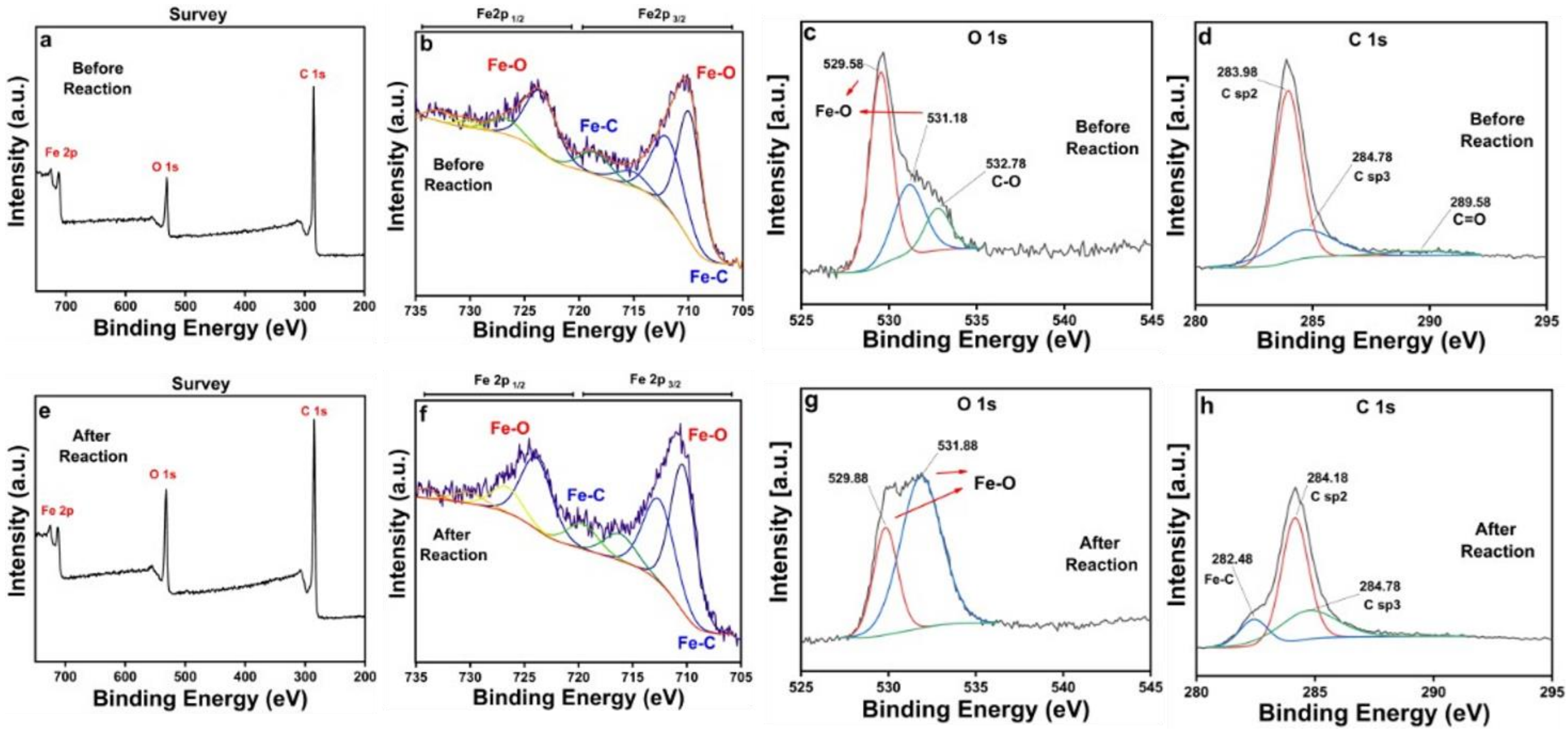

Fig. S2. XPS survey spectra before (a) and after (e) reaction, high-resolution Fe 2p spectra before (b) and after reaction(f), high-resolution O 1s spectrum before (c) and after reaction (g), and high-resolution C 1s spectrum before (d) and after reaction (h).

XPS analysis on the catalyst before (after treatment in CO: H_2 (2:1) gas mixture to prepare active phase (iron carbide and oxide)) and after the reaction was done. The survey spectrum before and after catalysis in **Fig. S2 (a and e)** illustrates that it comprises three elements: Fe, O, and C. The high resolution of Fe spectra **(Fig. S2 (b, f)** shows two peaks at 708 and 720 eV which are attributed to iron carbides [3]. The peaks seen at 712.6 and 710.6 eV correspond to Fe(III) and Fe(II) 2p3/2, respectively. The peaks at 726 and 724 eV are attributed to Fe(III) and Fe(II) 2p1/2, respectively [4]. The peak ratio of FeCx/FeOx dropped slightly following the reaction without reducing catalytic activity, as demonstrated by the stability test in **Fig. 4(c).** The high-resolution spectra of O 1s before the reaction show a 532.78 eV peak referred to C-O bond which remains from MOF structure after pyrolysis. This peak was removed after the reaction due to reduction by hydrogen and the feed gas. The peaks at 529 and 531 eV correspond to the Fe-O in magnetite. The high-resolution C 1s spectrum before the reaction also shows a peak at 289.5 eV, which indicates the presence of C=O remaining from the MOF structure [5]. The peak at 282.5 eV on the C 1s spectrum after the reaction is attributed to the Fe-C. The peaks at 284 and 284.8 eV match the Sp^2 and Sp^3 carbon, respectively.

2. Supplementary tables

Table S1. The crystal size of MIL-100(Fe) prepared at room temperature and solvothermal and pore properties of the derived catalysts.

Sample	Average crystal size of MIL-100(Fe) via TEM (nm)	Fe nanoparticles average size via TEM (nm)	$A_{s,BET}$[a] (m^2g^{-1})	V_{total}[b] (cm^3g^{-1})	D_{mean}[c] (nm)
RT-based catalyst	210	3	204	0.4	7.74
ST- based catalyst	249	10	54	0.2	15.3

[a] *specific BET surface area.* [b] *Total pore volume at* ($\frac{P}{P_0} = 0.999$). [c] *Mean pore diameter according to BJH method.*

Table S2. H_2 consumption for pyrolyzed catalyst by TPR, and H_2 and CO_2 chemisorption on reduced catalyst by TPD.

Sample	H_2 consumption (mmole g^{-1}) Pyrolyzed catalyst	H_2 Uptake (mmole g^{-1}) Reduced catalyst	CO_2 Uptake (mmole g^{-1}) Reduced catalyst	Normalized H_2-TPD peak area	Normalized CO_2-TPD peak area
RT-based catalyst	0.268	4.320	0.898	1	0.699
ST- based catalyst	0.184	3.625	1.285	0.839	1

3. Supplementary equations

$$CH_4\ Selectivity = \frac{CH_{4\,outlet}}{\sum C_nH_{m\,outlet}} \times 100\%$$

$$C_2{-}C_4\ Selectivity = \frac{\sum_2^4 C_nH_{m\,outlet}}{\sum_1^n C_nH_{m\,outlet}} \times 100\%$$

$$C_{5+}\ Selectivity = \frac{\sum_5^n C_nH_{m\,outlet}}{\sum_1^n C_nH_{m\,outlet}} \times 100\%$$

4. References

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