

# Electronic Supplementary Information

## Simultaneous catalytic reduction of *p*-nitrophenol and hydrogen production on MIL-101(Fe)-based composites

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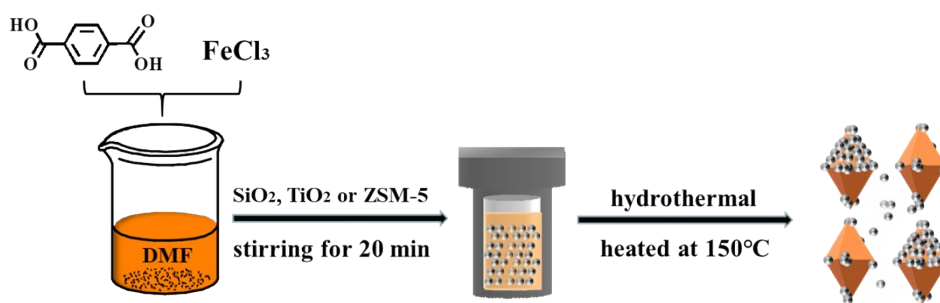
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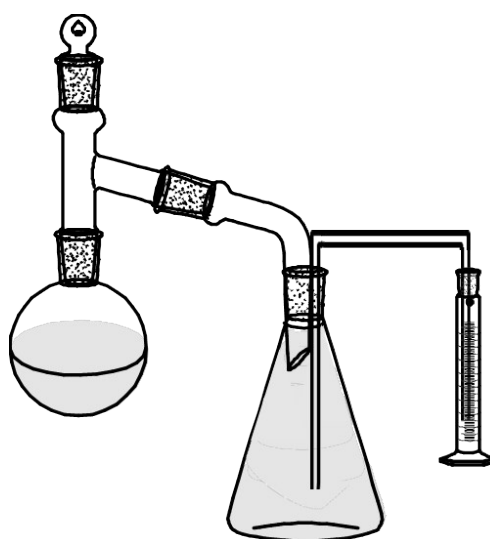
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### Preparation MIL-101(Fe)-base composites

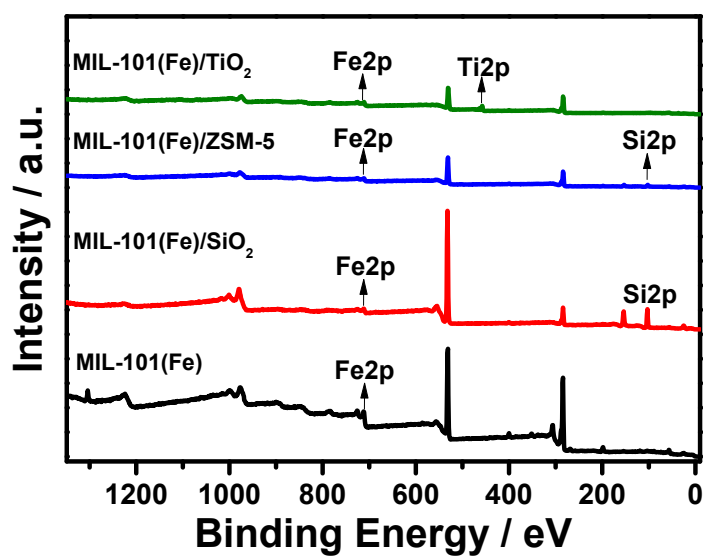
Fabrication of MIL-101(Fe)-base compositions catalyst was typically performed as follows, as outlined in Scheme 1. 0.01 mol  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and 0.01 mol PTA were added to a certain volume of DMF solution, and disperse in ultrasonic for 20 min. Next, the solution was stirred with a magnetic stirrer for 1 h. Then, 1.67g  $\text{SiO}_2$ ,  $\text{TiO}_2$  or ZSM-5 were added into the above solution. After stirring for 20 min, it was poured into a hydrothermal reactor, placed in an electric thermostatic drying oven, and heated at 150°C for 10 h. When the reaction vessel was cooled to room temperature illustrated that the reduction was completed. The precipitate was centrifuged washed with deionized water and ethanol. Last, drying the precipitate in an air atmosphere at 65 °C will obtain MIL-101(Fe)/ $\text{SiO}_2$ , of which the silica accounts for 50%.



**Scheme 1.** Illustration for fabrication of MIL-101(Fe)-base compositions by a simple hydrothermal method.



**Fig. S1** Instrumentation diagram of H<sub>2</sub> production.



**Fig. S2** Elemental analysis of MIL-101(Fe) and MIL-101(Fe) composites by XPS.

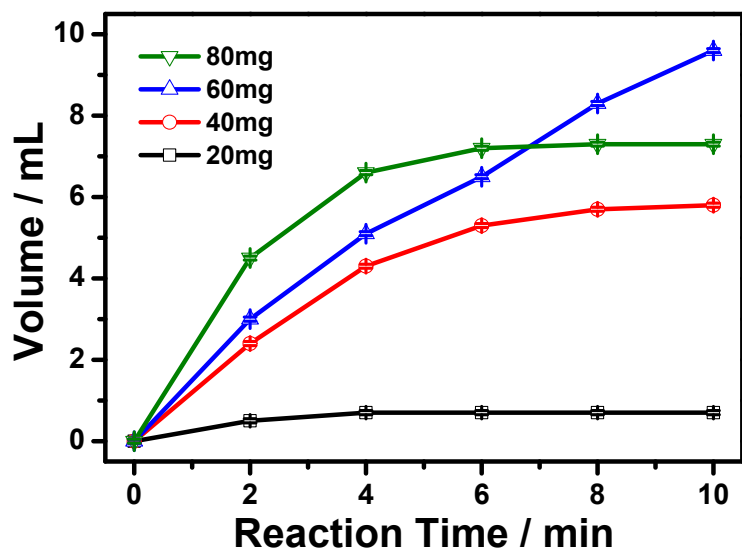


Fig. S3 Plot of the volume versus time for H<sub>2</sub> production with different amount of NaBH<sub>4</sub>.

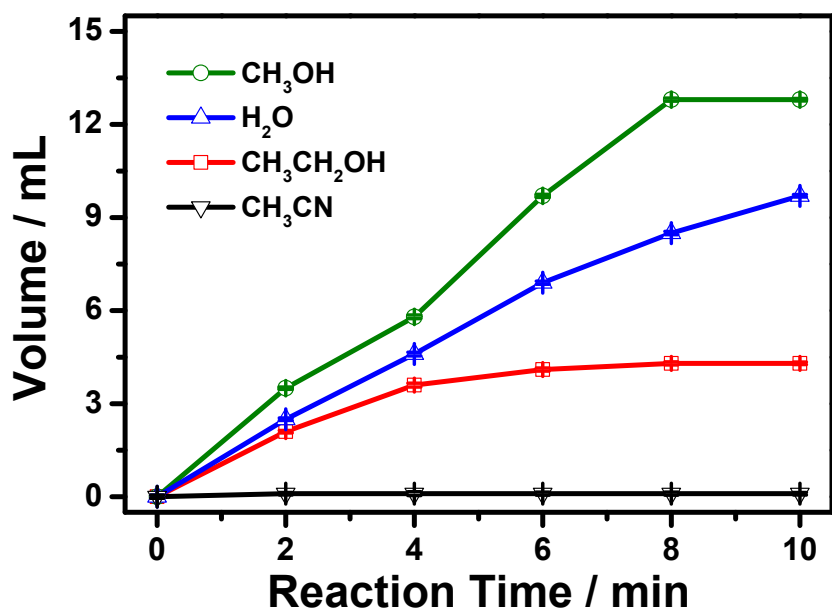
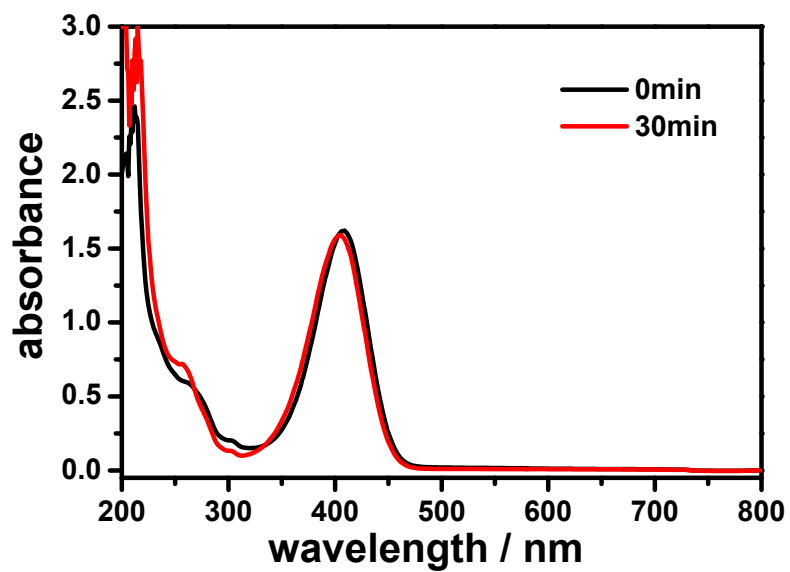
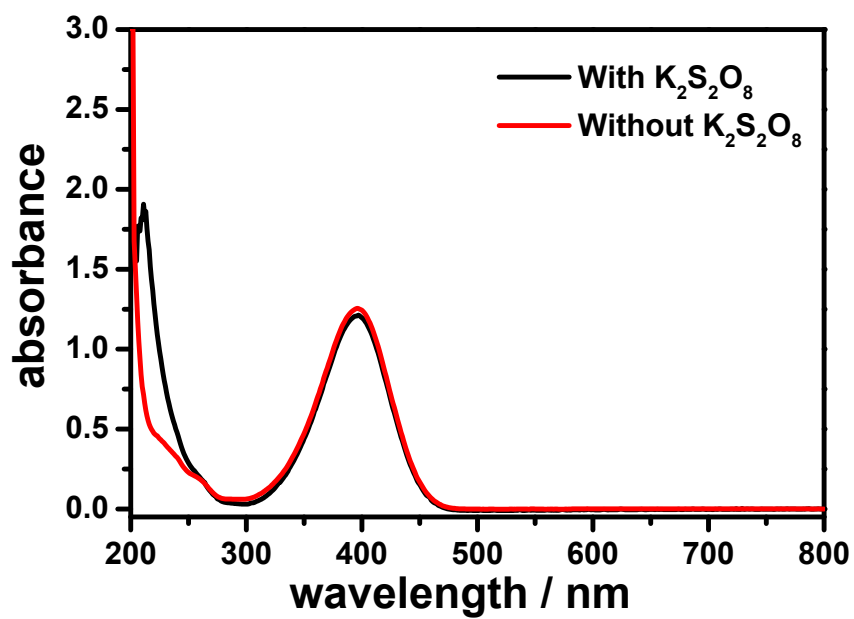


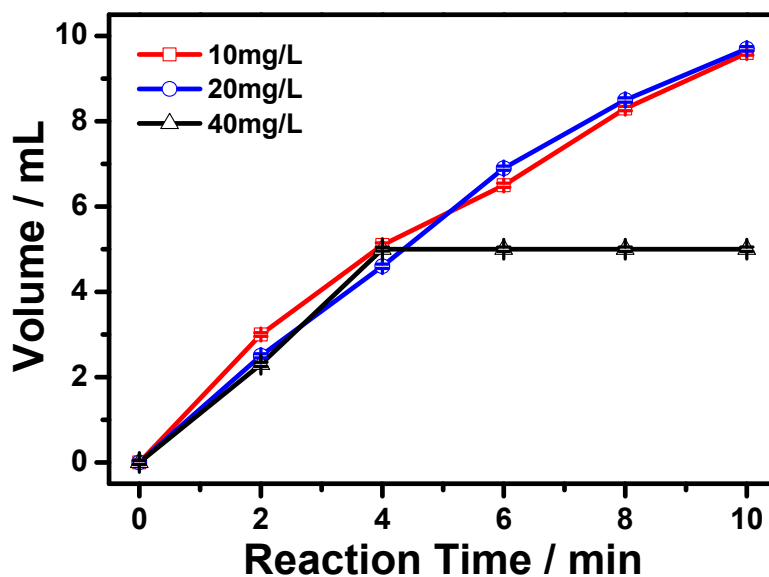
Fig. S4 Plot of the volume versus time for H<sub>2</sub> production in different solvents.



**Fig. S5** UV-vis absorbance map during catalyzed reduction of *p*-NP using NaBH<sub>4</sub> in CH<sub>3</sub>CN.



**Fig. S6** UV-vis absorbance map for catalyzed reduction of *p*-NP with or without K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>.



**Fig. S7** Plot of the volume versus time for H<sub>2</sub> production in different concentrations of *p*-NP.

### Catalytic mechanism

The effects of NaBH<sub>4</sub>, SiO<sub>2</sub> and MIL-101(Fe)/SiO<sub>2</sub> catalysts on the spectral absorption peak of *p*-NP has been studied to explore the mechanism of the reaction. A characteristic absorption peak at 317 nm of *p*-NP is shown in in Fig. S9 (Supplementary Materials), When NaBH<sub>4</sub> is used, absorption peak shifted from 317 nm to 400 nm due to the hydroxyl group in *p*-NP is deprotonated and converted to *p*-NP anion under alkaline conditions. NaBH<sub>4</sub> is a strong reducing agent, however it cannot directly reduce *p*-NP ions. It's infeasible in kinetics owing to the strong mutual repulsion between *p*-NP anions and BH<sub>4</sub><sup>-</sup> and the difference of oxidation-reduction potential between ( $E_{\text{H}_3\text{BO}_3(\text{aq})/\text{BH}_4^-(\text{aq})} = -1.33\text{V}$  and  $E_{p\text{-NP}(\text{aq})/p\text{-AP}(\text{aq})} = 0.76\text{V}$ ). SiO<sub>2</sub> that as catalyst reduced *p*-nitrophenol are of no effect. There is unsaturated coordination Fe center in the MIL-101 (Fe), which will affect catalytic performance toward *p*-NP reduction. It is worth noting that Fe<sup>3+</sup> does not supply electrons, BH<sub>4</sub><sup>-</sup> easily releases electrons.

After the addition of MIL-101(Fe) catalyst, NaBH<sub>4</sub> will adsorb on the surface of the unsaturated metal coordination site, which will dissociate H-donating electrons. Then, with oxidation reaction occurring in NaBH<sub>4</sub> and MIL-101(Fe), electrons are transferred to the coordination Fe surface and reacts with the *p*-NP compound adsorbed on the surface of the catalyst. Finally, electron obtained by *p*-NP, reduced to *p*-aminophenol, thereby achieving the intended purpose, Accordingly, a probable catalytic reaction mechanism for selective reduction of *p*-NP to *p*-

aminophenol over MIL-101(Fe)/SiO<sub>2</sub> is proposed, as displayed Fig. S10.

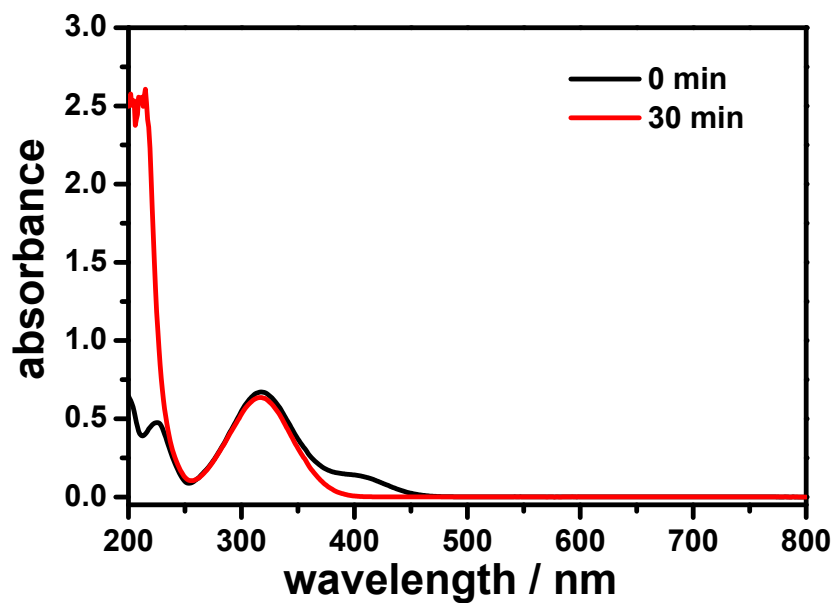


Fig. S8 UV-vis absorbance map for catalyzed reduction of *p*-NP without NaBH<sub>4</sub>.

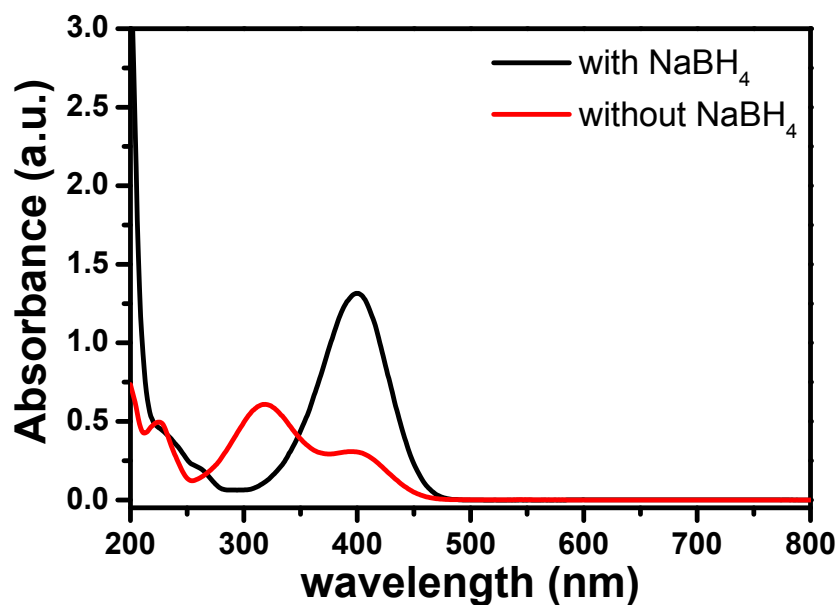
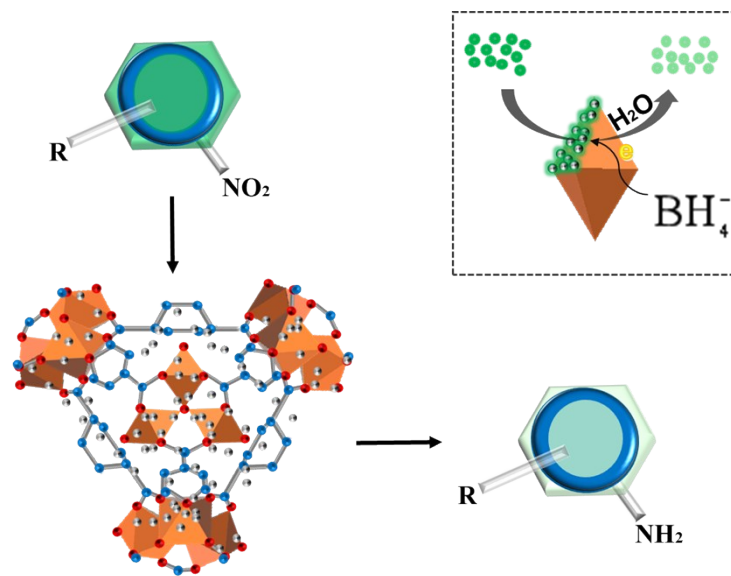


Fig. S9 UV-Vis spectra of *p*-NP before and after the addition of NaBH<sub>4</sub>.



**Fig. S10** Schematic illustration of the proposed mechanisms of the conversion of NP to AP by MIL-101(Fe)/SiO<sub>2</sub>.