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## Supplementary Information

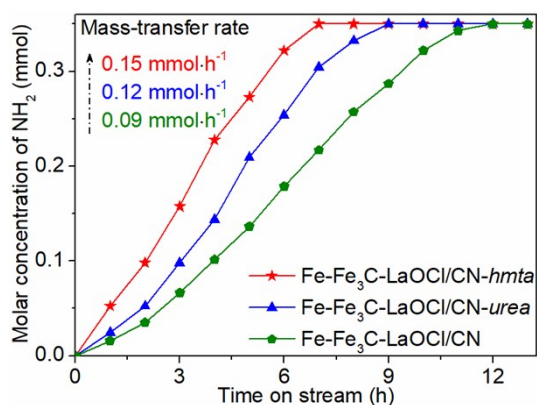
### **High efficiency LaOCl supported Fe-Fe<sub>3</sub>C-based catalyst for hydrogenation of nitroarenes fabricated by coordination-assisted- pyrolysis**

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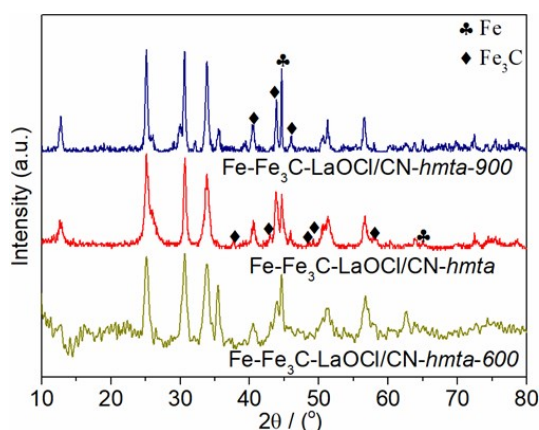
**Fig. S1** Mass-transfer tests of Fe-Fe<sub>3</sub>C-LaOCl/CN-*hmta*, Fe-Fe<sub>3</sub>C-LaOCl/CN-*urea* and Fe-Fe<sub>3</sub>C-LaOCl/CN catalysts.

As shown in Table S1, from the catalytic results, the LaOCl-800 and LaOCl/CN-*hmta*-800 showed very little catalytic activity. The Fe-Fe<sub>3</sub>C/CN-*hmta*-800 catalyst without introduction of LaOCl exhibited considerable catalytic activity, suggesting that the LaOCl support played very little effect on its performance. Therefore, for Fe-Fe<sub>3</sub>C-LaOCl/CN-*hmta* catalyst, the Fe-Fe<sub>3</sub>C is the determined active sites for the hydrogenation of nitrobenzene to aniline. In order to reveal the effect of the Fe and/or Fe<sub>3</sub>C content containing in Fe-Fe<sub>3</sub>C-LaOCl/CN-*hmta* catalyst on the hydrogenation performance, the catalytic activity of Fe-Fe<sub>3</sub>C-LaOCl/CN-*hmta* catalyst pyrolyzed at 600 °C (denoted as Fe-Fe<sub>3</sub>C-LaOCl/CN-*hmta*-600) and 900 °C (Fe-Fe<sub>3</sub>C-LaOCl/CN-*hmta*-900) for hydrogenation of nitrobenzene to aniline was tested. As shown in Table S1, the as-prepared Fe-Fe<sub>3</sub>C-LaOCl/CN-*hmta*-600 and Fe-Fe<sub>3</sub>C-LaOCl/CN-*hmta*-900 catalysts showed lower catalytic activity (21.8% and 24.7%, respectively) than that of developed Fe-Fe<sub>3</sub>C-LaOCl/CN-*hmta* (48.8%, pyrolyzed at 800 °C), suggesting that the different pyrolyzed temperatures have significant effect on the catalytic active sites (Fe-Fe<sub>3</sub>C) of prepared catalysts. Furthermore, crystalline structures of Fe-Fe<sub>3</sub>C species contained in Fe<sub>3</sub>C-LaOCl/CN-*hmta*-600 and Fe-Fe<sub>3</sub>C-LaOCl/CN-*hmta*-900 catalysts were analyzed by the XRD analysis (Fig. S2).

**Table S1** Comparison of the catalytic performance of different catalysts for the hydrogenation of nitrobenzene

Entry	catalyst	$T$ (°C)	(Eq.)/(P/bar)	$t$ (h)	Yield (%)
1	LaOCl-800	85	4.0	3.0	0.91
2	LaOCl/CN- <i>hmta</i> -800	85	4.0	3.0	5.8
3	Fe-Fe <sub>3</sub> C/CN- <i>hmta</i> -800	85	4.0	3.0	28.9
4	Fe-Fe <sub>3</sub> C-LaOCl/CN- <i>hmta</i> -600	85	4.0	3.0	21.8
5	Fe-Fe <sub>3</sub> C-LaOCl/CN- <i>hmta</i>	85	4.0	3.0	48.8
6	Fe-Fe <sub>3</sub> C-LaOCl/CN- <i>hmta</i> -900	85	4.0	3.0	24.7

Reaction condition:  $n_{\text{nitrobenzene}} = 0.81$  mmol,  $n_{\text{hydrazine hydrate}} = 3.2$  mmol,  $m_{\text{catalyst}} = 20$  mg,  $V_{\text{ethanol}} = 10$  mL.



**Fig. S2** XRD patterns of Fe-Fe<sub>3</sub>C-LaOCl/CN-*hmta*- $T$  with different pyrolysis temperatures.

As shown in Fig. S2, it can be observed that the pyrolysis temperature has obvious effect on the phases and contents of Fe-Fe<sub>3</sub>C contained in the three catalysts. The metallic Fe is the dominant phase when pyrolysis temperature at 600 °C, whereas metallic Fe and Fe<sub>3</sub>C become the dominant phases when pyrolysis temperature at 800 °C (developed Fe-Fe<sub>3</sub>C-LaOCl/CN-*hmta* catalyst). When pyrolysis temperature increased to 900 °C, the metallic Fe became the dominant phase again contained in Fe-

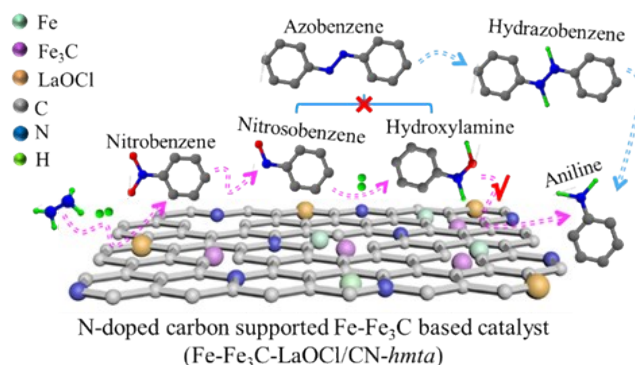
Fe<sub>3</sub>C-LaOCl/CN-*hmta*-900. Correlated with above catalytic results, the change towards the contents of Fe-Fe<sub>3</sub>C suggested the synergy effect of Fe-Fe<sub>3</sub>C could effectively promote the catalytic performance of developed Fe-Fe<sub>3</sub>C-LaOCl/CN-*hmta* (pyrolyzed at 800 °C) for hydrogenation of nitrobenzene to aniline.

**Table S2** Comparison of the catalytic performance of different catalysts for the hydrogenation of nitrobenzene

Entry	catalyst	Hydrogen source	<i>T</i> (°C)	(Eq.)/(P/bar)	<i>t</i> (h)	Yield (%)
1	Fe-Fe <sub>3</sub> C-LaOCl/CN- <i>hmta</i>	N <sub>2</sub> H <sub>4</sub> ·H <sub>2</sub> O	85	4.0	6.5	98.7
2	Fe <sub>2</sub> P@C <sup>S1</sup>	H <sub>2</sub>	120	50	12	>99.0
3	Fe-phenanthroline/C <sup>S2</sup>	N <sub>2</sub> H <sub>4</sub> ·H <sub>2</sub> O	100	4.0	10	99.0
4	FeO <sub>x</sub> @CN- <i>hpes</i> -400 <sup>S3</sup>	N <sub>2</sub> H <sub>4</sub> ·H <sub>2</sub> O	85	4.0	7.0	96.0
5	Co-Co <sub>3</sub> O <sub>4</sub> @carbon-700 <sup>S4</sup>	H <sub>2</sub>	110	40	15	99.0
6	Ni/C <sup>S5</sup>	H <sub>2</sub>	25	5.0	7.0	100
7	PdNPore-3 <sup>S6</sup>	H <sub>2</sub>	25	2.0	7.0	99.0

On the basis of previous works and above characterization results, the plausible catalytic reaction process over Fe-Fe<sub>3</sub>C-LaOCl/CN-*hmta* for the hydrogenation of nitrobenzene to aniline was proposed.<sup>S7</sup> As illustrated in Fig. S3, the LaOCl-CN-*hmta* support with abundant structural defects serves as stronger Lewis basic sites for absorbing nitrobenzene molecule in comparison with Fe-Fe<sub>3</sub>C-LaOCl/CN-*urea* and Fe-Fe<sub>3</sub>C-LaOCl/CN (identified by UV analysis). Meanwhile, the synergy effect of Fe-Fe<sub>3</sub>C species confined in large specific area of Fe-Fe<sub>3</sub>C-LaOCl/CN-*hmta* could facilitate the absorption/dissociation of N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O into the active H species. The enhanced ability of mass transfer facilitates the absorption of nitrobenzene reacting with the generated active H species to nitrosobenzene, with subsequent quickly the nitrosobenzene converted to intermediate hydroxylamine.

Finally, the hydroxylamine molecule is quickly hydrogenated to final product of aniline. Notably, the strong ability of dissociation  $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$  molecules could also suppress the condensation reaction between nitrosobenzene and hydroxylamine to azobenzene.



**Fig. S3** Plausible catalytic process over Fe-Fe<sub>3</sub>C-LaOCl/CN-hmta catalyst for hydrogenation of nitrobenzene to aniline.

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