**In situ X-ray absorption spectroscopic studies of magnetic Fe@FexOy/Pd nanoparticle catalysts for hydrogenation reactions**

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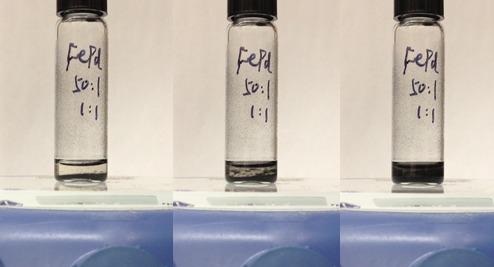
c *Canadian Light Source, University of Saskatchewan, Saskatoon, SK S7N 2V3, Canada*

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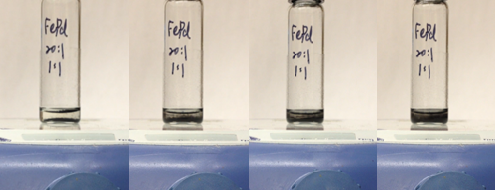
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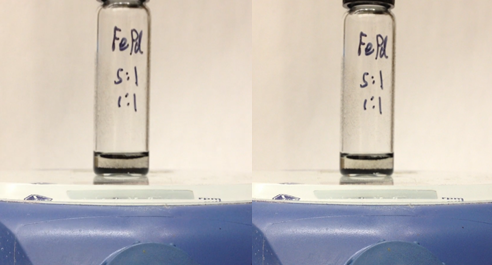
**Fig. S1.** Low-magnification TEM images of the 50:1 Fe@FexOy/Pd NPs.



0s 10s 20s

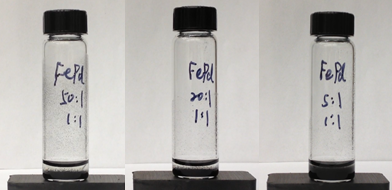


0s 20s 40s 60s



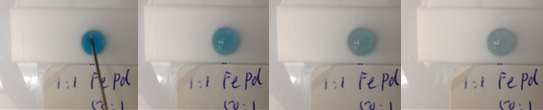
0s 60s

**Fig. S2.** The comparison of stirring ability of different molar ratios of Fe@FexOy/Pd NPs on a magnetic stirrer at a speed of 1600 rpm.



**Fig. S3.** The comparison of magnetic recycling ability of different molar ratios of Fe@FexOy/Pd NPs on a magnet after 9s.

**50:1 Fe@FexOy/Pd NPs**

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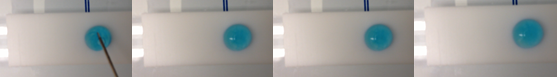
0s 10s 20s 25s

**20:1 Fe@FexOy/Pd NPs**



0s 10s 20s 25s

**Without Fe@FexOy/Pd NPs**

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0s 10s 20s 25s

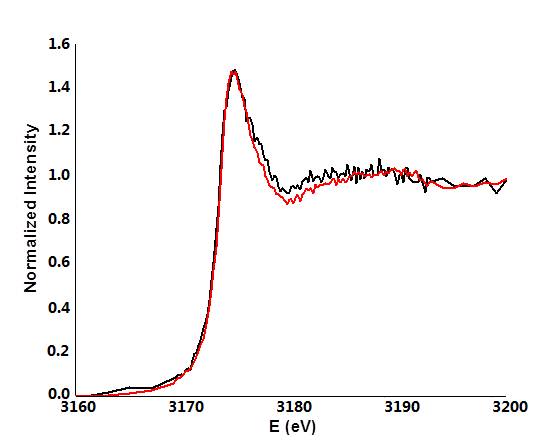
**Fig. S4.** The comparison of the hydrogenation of methylene blue by NaBH4 in smaller volume liquid droplet with and without the stirring of Fe@FexOy/Pd NPs.

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**Fig. S5.** Reaction rate versus temperature for 20:1 Fe@FexOy/Pd NPs (0.0050 mmol based on Pd content) to catalyze the hydrogenation of 2-methyl-3-buten-2-ol (1.9 mmol)in 5.0 mL waterwhile stirring with a stir-bar.

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**Fig. S6.** Reaction rate versus temperature for 5:1 Fe@FexOy/Pd NPs (0.0050 mmol based on Pd content) to catalyze the hydrogenation of 2-methyl-3-buten-2-ol (1.9 mmol)in 5.0 mL water, with no stir-bar.

** Fig. S7.** The Pd L-edge XANES spectra of the 20:1 Fe@FexOy/Pd NPs before (black) and after (red) a hydrogenation reaction using ethanol as a solvent.



**Fig. S8.** TEM images of the 20:1 Fe@FexOy/Pd NPs after 3 cycles of hydrogenation reactions in ethanol.

**Table S1.** XANES fitting results depicting the changes of Fe@FexOy NPs in the Fe@FexOy/Pd NPs during the hydrogenation reaction.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Sample** | **Reaction Time (min)** | **Fe (0)%** | **Fe(II)%** | **Fe(III)%** |
| Fe@FexOy/Pd NPs | 0 | 56(0) | 31(0) | 14(1) |
| 15 | 51(0) | 31(0) | 18(1) |
| 30 | 49(0) | 34(0) | 17(1) |

**Table S2.** XANES fitting results of the changes to Fe@FexOy NPs in the Fe@FexOy/Pd NPs before and after 6 cycles of hydrogenation reactions.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Sample** | **Cycle** | **Fe (0)%** | **Fe(II)%** | **Fe(III)%** |
| Fe@FexOy/Pd NPs | 0 | 56(0) | 31(0) | 14(1) |
| 6 | 0(0) | 60(0) | 40(0) |