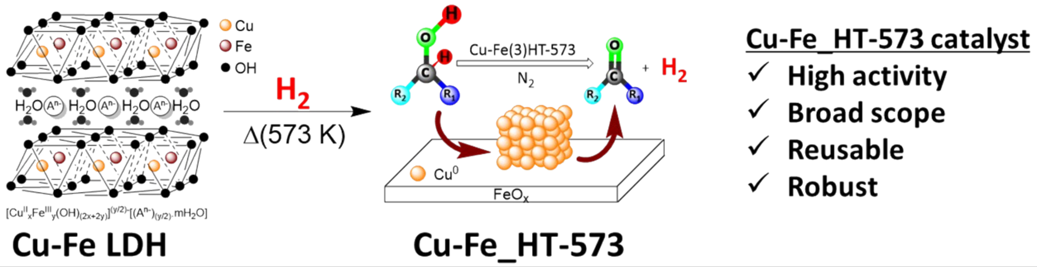
Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Acceptorless Dehydrogenation of Alcohols using Cu-Fe Catalysts Prepared from Cu-Fe Layered Double Hydroxides as a Precursor



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Experimental of Cu-Fe based catalysts synthesis method

Materials

Copper (II) nitrate trihydrate (WAKO), Iron (III) nitrate nonahydrate (WAKO), NaOH (WAKO), p-xylene (WAKO), and trans-decahydronaphthalene (WAKO) were purchased and used as received. Organic chemical compounds, such as 1-phenylethanol (WAKO) and DMSO (TCl, >98%) were purified using procedures recorded at Purification of Laboratory Chemicals.

Synthesis of Cu-Fe(3)LDH

The Cu-Fe(3)LDH sample was typically prepared in the following procedure: at room temperature, $Cu(NO_3)_2{\cdot}3H_2O$ (4 mmol) and $Fe(NO_3)_3{\cdot}9H_2O$ (2 mmol) was dissolved in 85 mL deionized water. The mixture solution was stirred 30 minutes at room temperature. About 15 M NaOH 2.0 M was dropwisely added to mixture solution. The solution was refluxed at 333 K for 24 h under air atmosphere.

Synthesis of Cu-Fe catalysts

Cu-Fe catalysts were produced by reduction process of the LDHs precursors. The reduction process followed three pathways to obtain Cu-Fe catalysts using various reductants, i.e. molecular H_2 or ethylene glycol. At the first pathway, the Cu-Fe LDHs were calcined at 923 K for 5 h under an air atmosphere (Cu-Fe_C-973), prior to the reduction process using 30 mL ethylene glycol in an autoclave reactor at 423 K for 24 h to give reduced-calcined Cu-Fe catalysts (denoted as R_Cu-Fe_C). At the second procedure, the reduction of calcined Cu-Fe catalysts with molecular H_2 at 573 for 1 h produced Cu-Fe catalysts, denoted as Cu-Fe_C_HT. Another process is the reduction of Cu-Fe LDHs (without calcination treatment) with molecular H_2 at 573 K for 1 h to give Cu-Fe_HT-573 catalysts.

Synthesis of supported Cu/Fe_3O_4 catalysts

The supported Cu/Fe_3O_4 catalysts were synthesized by various methods, such as impregnation ($Cu/Fe_3O_4^{imp}$), co-precipitation ($Cu/Fe_3O_4^{co\text{-}p}$), and physical mixture ($Cu/Fe_3O_4^{pm}$) methods. The $Cu(20\%)/Fe_3O_4^{imp}$ catalysts were prepared by the following procedure: at room temperature, $Cu(NO_3)_2{\cdot}3H_2O$ (0.7609 g) was diluted to the 100 mL of deionized water. The Fe_3O_4 (0.8 g) was added to the Cu solution. The mixture was then stirred at 373 K to vaporized the water. The black powder was dried under vacuum condition overnight at room temperature. The dried powder was reduced with an H_2 treatment at 573 K prior to the catalytic test. The $Cu/Fe_3O_4(3)^{imp}$ catalysts were prepared with the same procedure with $Cu(20\%)/Fe_3O_4^{imp}$, but using $Cu(NO_3)_2{\cdot}3H_2O$ (3.624 g) and Fe_3O_4 (0.3859 g) as the starting materials. $Cu(20\%)/Fe_3O_4^{co\text{-}p}$ catalysts were prepared by the following pathway: $Cu(NO_3)_2{\cdot}3H_2O$ (0.7609 g) was diluted to the 85 mL of deionized water before the addition of Fe_3O_4 (0.8 g). The mixture was stirred and mixed with NaOH 2M 15 mL as a precipitator at room temperature. The suspension was subsequently placed in a sealed Teflon lined autoclave for the hydrothermal process at 423 K for 24 h. The black fluffy solid was filtered, washed using deionized water and acetone several times, and dried under vacuum overnight. The black powder was treated with H_2 at 573 K prior to the catalytic reaction. The $Cu/Fe_3O_4(3)^{co\text{-}p}$ catalysts were prepared with the identical procedure with $Cu(20\%)/Fe_3O_4^{co\text{-}p}$, but using $Cu(NO_3)_2{\cdot}3H_2O$ (3.624 g) and Fe_3O_4 (0.3859 g) as the starting materials. Finally, the $Cu(20\%)/Fe_3O_4^{pm}$ catalysts were prepared by following pathway: Cu metal (0.2 g) was simply added Fe_3O_4 (0.8 g) and ground into the mortar before taking H_2 treatment for activation. The $Cu/Fe_3O_4(3)^{pm}$ catalysts were prepared with the similar manner to $Cu(20\%)/Fe_3O_4^{pm}$, but using 0.66 g of Cu metal and Fe_3O_4 (0.8 g) as the starting materials.

Catalytic test

The mixture of catalyst (100 mg), 1-phenylethanol (1 mmol), *trans*-decahydronaphthalene (0.08 g), and solvent (p-xylene, 3 mL), was poured into the Schlenk tube, followed by filling with N_2. Then, the resulting mixture was stirred under reflux, and the reaction temperature was varied in the range of 100-130 ˚C. Conversion and yields of products were determined by GC using *trans*-decahydronaphthalene as an internal standard. The other unknown products were identified by GC-MS.

Analytical technique

Gas Chromatography (GC)

Substrate conversion was determined by GC (Shimadzu GC-14B) equipped with a flame ionization detector, and RT-βDexSm (30 m, DF=1.4 μm, 0.25 mm) for monitoring the dehydrogenation of 1-phenylethanol with *trans*-decahydronaphthalene as an internal standard. The GC was operated under the conditions as follow: injection temperature (230 ˚C), detection temperature (230 ˚C), initial temperature (120 °C), initial time (1 min) progress rate (10 ˚C/min), final temperature (180 ˚C), and final time (1 min). The other substrates of secondary alcohols are detected by using Rtx-BAC PLUS 1 or InertCap 624 column, depending on the peak separation. The sample was introduced into the column *via* split mode (1/50) and the system used nitrogen gas as a carrier gas with the rate of 50 kPa at carrier P1 and 100 kPa at carrier P2.

X-Ray Diffraction

XRD measurements were recorded on a D8 ADVANCE, Bruker using monochromatic Cu Kα radiation (λ = 0.15418 nm). The XRD was operated at 40 kV and 40 mA with divergence and scattering slit 1^{o}, a step width of 0.02^{o} and scan speed of 2^{o} min^{-1}.

Result

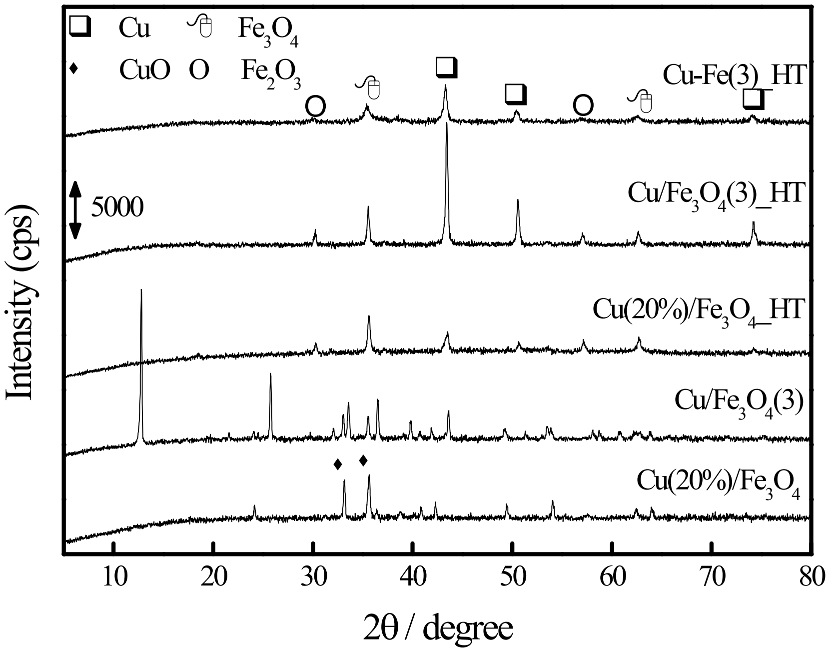


Fig. S1 XRD patterns of Cu-Fe(3)_HT-573 and various treatments of Cu/Fe_3O_4 catalysts prepared by co-precipitation method.

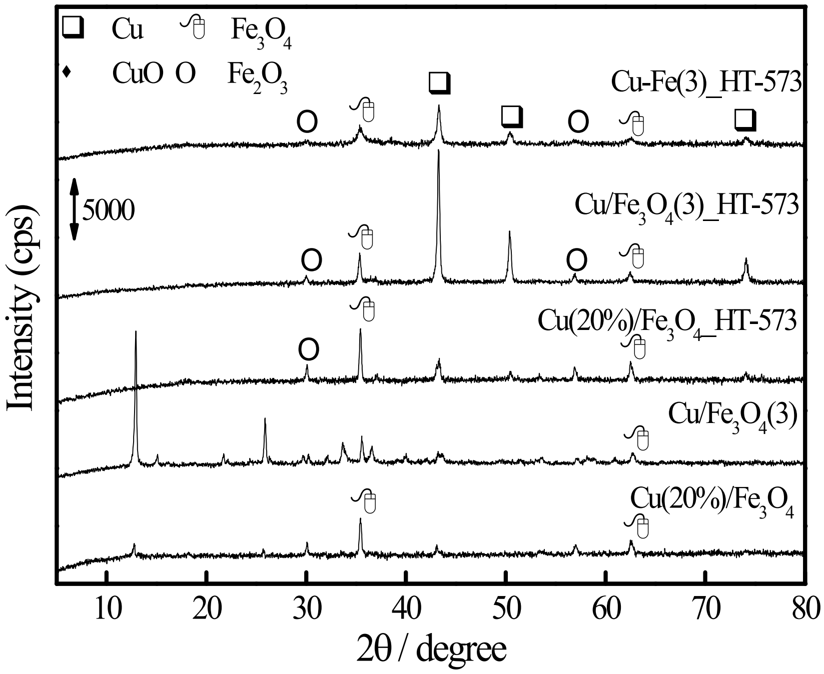


Fig. S2 XRD patterns of Cu-Fe(3)_HT-573 and various treatments of Cu/Fe_3O_4 catalysts prepared by impregnation method.

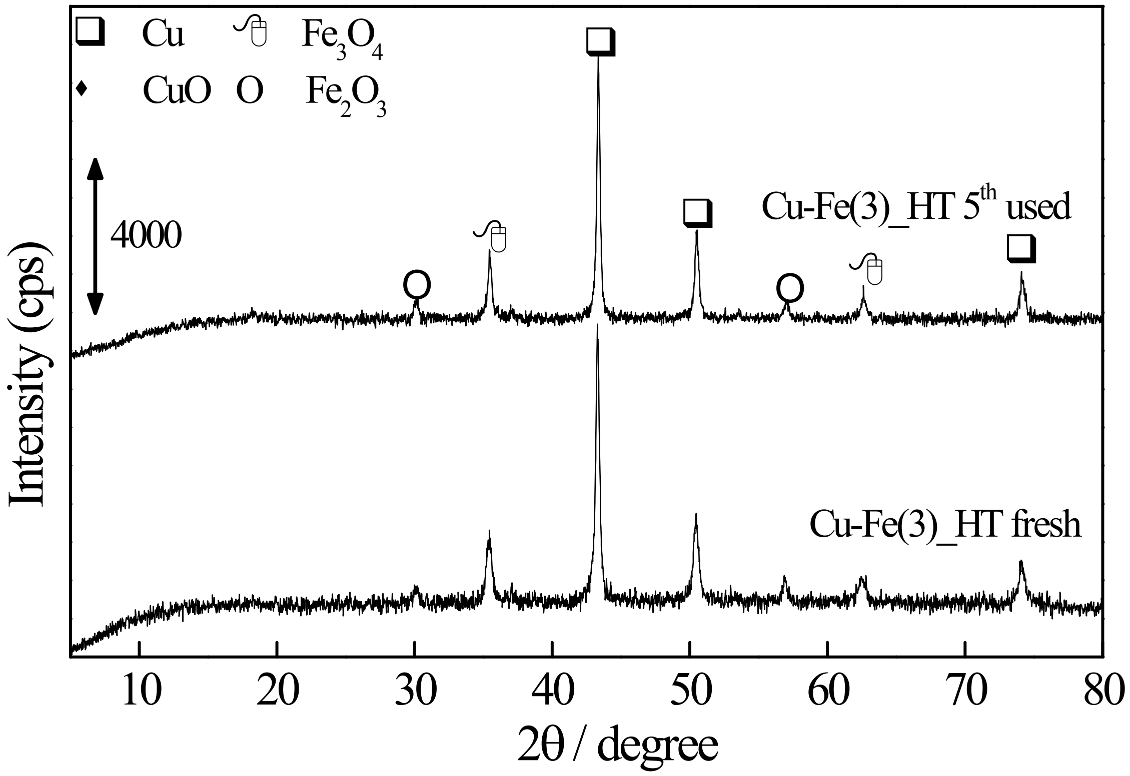
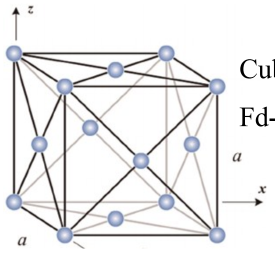


Fig. S3 XRD patterns of fresh and used Cu-Fe(3)_HT-573 catalysts

Table S1. The crystallite size of Cu metal on Cu-Fe catalysts after taking various treatments

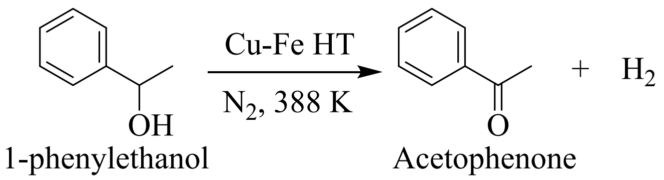
Entry	Catalyst	D(nm)	*a* (Å)
1	Cu-Fe(3)_HT-573	33.2	3.62
2	Cu-Fe(3)_C_HT-573	48.1	3.62
3	Cu-Fe(3)_C_R	56.3	3.62
4	Cu-Fe(3)_HT-573 (used)	32.1	3.62



Cubic (FCC)
Fd-3m

The crystallite size, D, was calculated using Debye-Scherrer equation from the XRD of Cu (111) peak at 2θ ~ 43°. The lattice constant, *a*, was calculated from the peak of Cu(111) based on the index of cubic (FCC) with a space group of Fd-3m.

Table S2. The quantification data of H_2 and acetophenone formation with time progress.



Time	Conv.	Product	Product	Product	H_2 production			H_2 sel.[c]
(h)	(%)	(%)	(mmol)	sel.[a] (%)	V1	V2	H_2[b]	(%)
0	0	0	0	—	50.8	0	0	—
1	37.3	37.3	0.41	100	42	8.8	0.39	95.1
2	50.3	50.3	0.56	100	39.3	11.5	0.51	91.1
4	69.5	69.1	0.77	99.4	34.6	16.2	0.72	93.5
8	90.1	89.3	0.99	99.1	30.4	20.4	0.91	91.9
12	93.5	92	1.02	98.4	29.5	21.3	0.95	93.1
16	97.1	95.5	1.06	98.4	29.3	21.5	0.96	90.6
20	100	97	1.08	97	29.1	21.7	0.97	89.8

[a]Selectivity of product (acetophenone). V1 = volume monitored in volumetric flask (mL). V2 = volume of H_2 gas formed (initial volume monitored – volume monitored at a certain time) (mL). [b]Mole of H_2 (mmol) is converted in turns of V_{STP} (22.4 L.mol^{-1}). [c]H_2 selectivity (H_2 Sel. = mole of H_2 / mole of product * 100%)

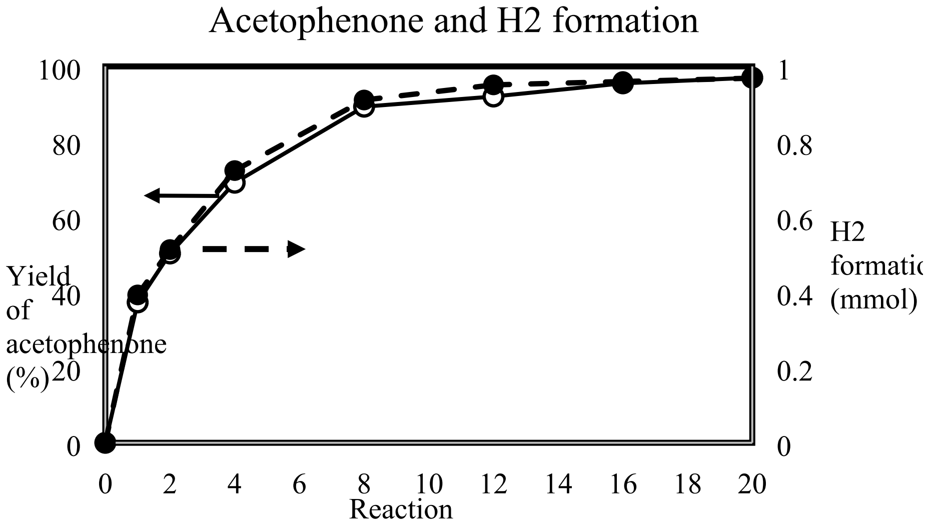


Fig. S4 The evolution of H_2 and acetophenone formation with the time progress.

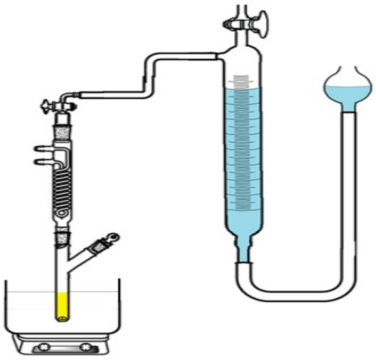
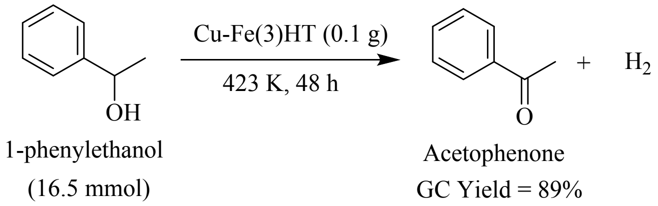
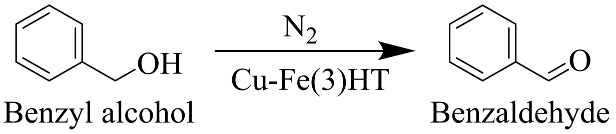


Fig. S5 Reaction setup for the measurement of evolved hydrogen gas.



Scheme. S1 The large-scale dehydrogenation of 1-phenylethanol (16.5 mmol).

Table S3. AD reaction of benzyl alcohol using Cu-Fe(3)HT with the various condition.



Entry	T(K)	Additive	Solvent	Conversion (%)	Yield (%)
1	388	—	p-xylene	34	31
2	398	—	p-xylene	63	38
3	408	—	p-xylene	81	46
4	388	La_2O_3	p-xylene	27	16
5	388	Y_2O_3	p-xylene	27	25
6	388	MgO	p-xylene	70	21
7	388	KOH	p-xylene	80	4
8	388	$KHCO_3$	p-xylene	46	10
9	388	t-BuOK	p-xylene	98	6
10	388	—	DMF	13	13
11	388	—	o-xylene	51	34
12	388	—	DMSO	15	15

Reaction conditions: $W_{CAT} = 100$ mg; $W_{ADD} = 25$ mg; $C°_{SUBS} = 0.37$ M; $V_{SOLV} = 3$ mL; t = 20 h; N_2 atmosphere.

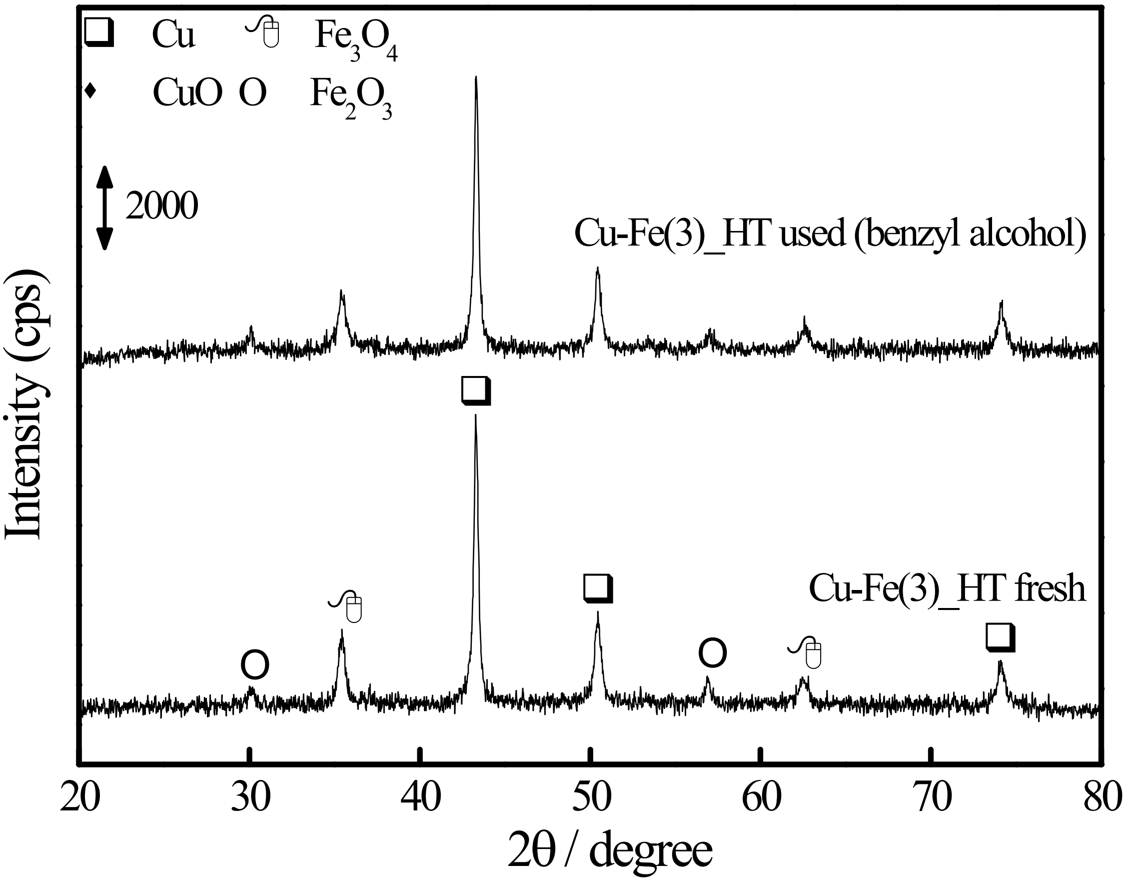
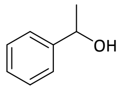
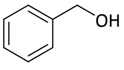
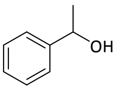
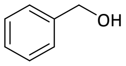


Fig. S6 XRD patterns of fresh Cu-Fe(3)_HT-573 catalyst and Cu-Fe(3)_HT-573 catalyst after used for dehydrogenation of benzyl alcohol.

Table S4. The effect of various substrate on the AD reaction using Cu-Fe(3)_HT catalysts

Entry	Substrate I	Substrate II	Conversion (%)	Yield (%)
1	 1-Phenylethanol	—	100	97
2	 Benzyl alcohol	—	32	32
3	 1-Phenylethanol	 Benzyl alcohol	Substrate I = 42 Substrate II = 26	Substrate I = 38 Substrate II = 22

Reaction conditions: W_{CAT} = 100 mg; $C°_{SUBS}$ = 0.37 M; $V_{P\text{-}XYLENE}$ = 3 mL; T = 388 K; under N_2 atmosphere.