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Supporting Information

Fenton-mediated thermocatalytic conversion of CO_2 to acetic acid by industrial waste-derived magnetite nanoparticles

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1 Experimental

Materials

IOD was purchased from TATA Steel Ltd., and all other chemicals were used as received without any further purification, such as 30% w/v H_2O_2 (CDH), Na_2S (Loba Chemie), CO_2 Gas (99.9998 %), Sodium Hydroxide (Thermo Fisher), Silicon Oil (ASES Chemicals), Imidazole (LOBA Chemie), Sodium formate (TCI), D_2O (Sigma Aldrich), De-Ionized water was purchased from Vision and purged with nitrogen gas before all experiments.

Synthesis of Fe_3O_4-NP

Briefly, 10 g of IOD was added to 100 mL of 6M of HCl in a 250 mL RB flask. Then, the mixture was refluxed at ~100 °C for 6 h. Then, after getting the red-colored solution, the whole solution was diluted to 400 mL by adding DI water. After that, 10 mL of a saturated solution of Na_2S was added to the mixture dropwise with the help of a burette. Later, black-colored iron nanoparticles were precipitated out by neutralizing the whole solution using NaOH solutions. The black precipitates were filtered, washed 3-4 times with water and acetone, and dried at room temperature. After getting the obtained, the black-colored magnetic powder was obtained and named Fe_3O_4-NP and characterized via various spectroscopic methods.

Material Characterization and Analysis

Powder X-ray diffraction (PXRD) analysis was performed by using an X-ray diffractometer instrument (Panalytical X Pert Pro). An ESCA+ omicron nanotechnology Oxford instrument performed X-ray photoelectron spectra (XPS) of Fe_3O_4-NP. Images taken from a Nova Nano FE-SEM 450 (FEI) electron microscope were used to analyze the geometry and morphology Fe_3O_4-NP. The pH of the solutions was checked by a LABMAN-LMPH-10 pH meter. The ^{1}H, ^{13}C NMR spectra were recorded using a JEOL ECS-400 spectrometer (operating at 400 MHz. CO gas was detected on a CO detector purchased from Honewell International, Inc.

Reduction of CO_2 to C_2 Products

Initially, Fe_3O_4-NP was added to the autoclave stainless steel (SS) batch reactor, then a solution of 20 mL mixture of H_2O_2 and H_2O (0-30 % v/v) was added to the reactor. After that, the autoclave was sealed carefully, and CO_2 gas was pressurized, ensuring all vents/valves were tightly closed. Then, the setup was heated continuously in an oil bath at various times (1, 2.5, 5, 10, 15 h), temperature (room temperature (RT), 100, and 180°C) and pressure (5, 10, 15 bar) in the presence of mechanical stirring in search of optimized conditions. The reaction was quenched at the desired time and the reactor was cooled down at RT. The CO gas was identified by CO detector. The recyclability of Fe_3O_4-NP was checked by regenerating the catalyst from the reaction mixture by distillation followed by separation using magnet. After that the catalyst was washed with DI water and dried in oven at ~70°C for 4 h.

The mixtures of gaseous products (mainly unreacted CO_2 and CO) collected after the completion of the reaction were analyzed using GC equipped with a thermal conductivity detector (TCD) and Hayesep-Q packed column. The retention peak time of CO_2 was ~ 4.5-5 min, and for CO was ~29-30 min. The liquid products (alcohols and acid: EtOH and AcOH) were separated by forming respective organic acid salts in 1N NaOH (~pH 12). Then the alcohols were collected from the distilled-out samples in the form of liquid. Later, both were quantified by ^{1}H and ^{13}C NMR spectroscopy, where HCOONa and imidazole were employed as internal standards for quantifying organic acids and alcohols, respectively. The concentrations of internal standards, i.e., sodium formate and imidazole, were fixed at 46.47 mM and 100 mM, respectively. The concentration of organic aid and alcohols was calculated by evaluating the integrated area of respective peaks of AcOH and HCOONa and alcohols and imidazole in the presence of D_2O as a reference, as shown in **Table 1**. The quantification of product yield (from ^{1}H NMR), was calculated using **Equation 1**.

$$Product\ Yield = \frac{\text{Normalized area of analyte } \times \text{ Standard Concentration}}{\text{Normalized area of standard}} \qquad 1$$

2. Table S1: Detectable ^{1}H NMR peaks positions of internal standards and CO_2 reduced products.

Analytes	Detectable number of protons (splitting)	Peak position
Sodium formate (Internal standard for AcOH)	1 (s)	~8.38
AcOH	3 (s)	~1.85
Imidazole (Internal standard for EtOH and MeOH)	2 (s) 1 (s)	~7.10 ~7.74
EtOH	2 (q)	~3.63
MeOH	3 (s)	~3.32

3. FESEM analysis of Fe_3O_4-NP

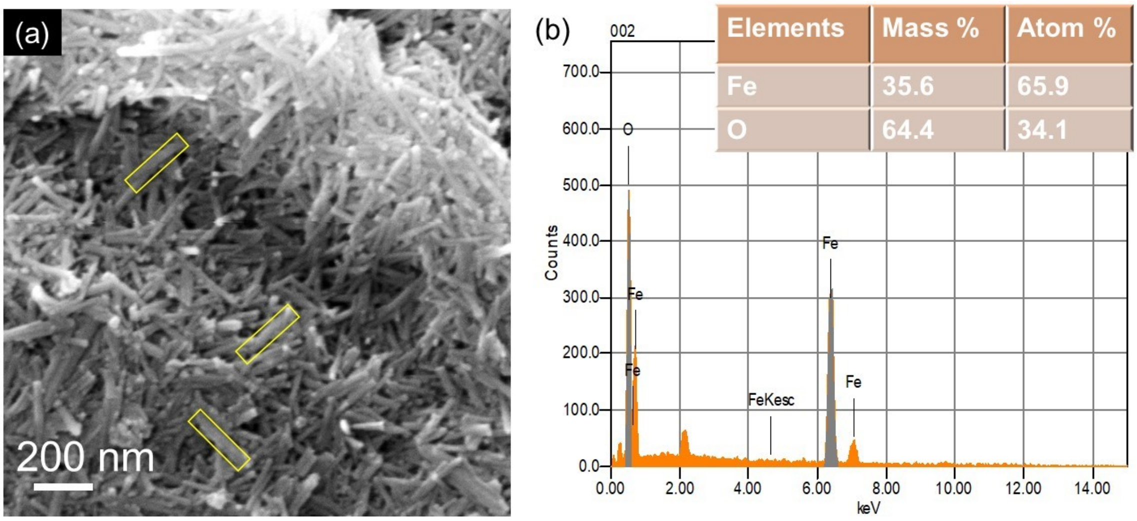

Fig. S1: (a) Low-resolution SEM image of Fe_3O_4-NP and (b) corresponding EDS analysis.

4. Recyclability of Fe_3O_4-NP

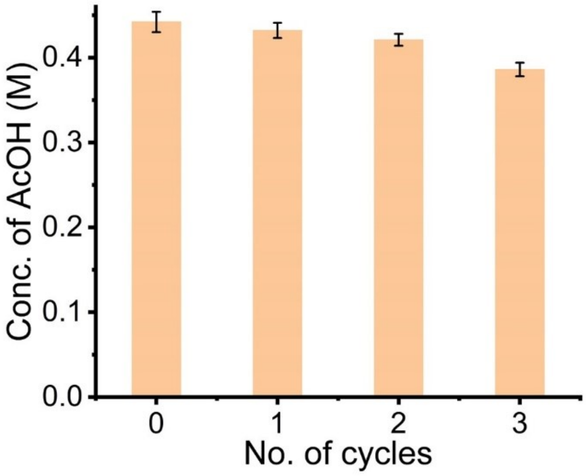

Fig. S2: Recyclability of Fe_3O_4-NP towards the conversion of CO_2 to acetic acid.

5. TEM analysis of spent-Fe_3O_4-NP and comparative pXRD analysis of Fe_3O_4-NP before and after the CO_2 reduction reaction

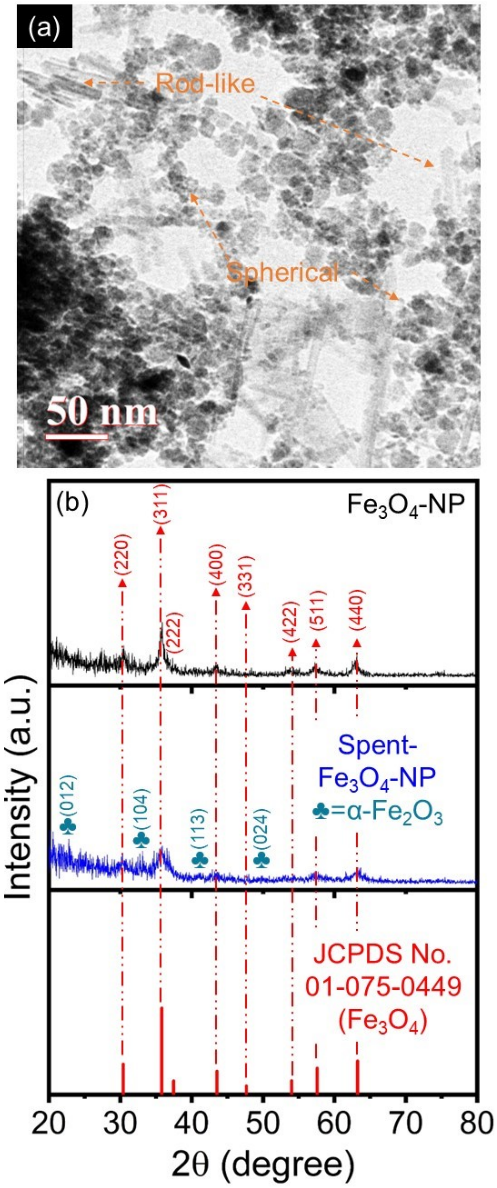

Fig. S3: (a) TEM analysis of spent-Fe_3O_4-NP catalyst after 3 cycles and (b) pXRD analysis of Fe_3O_4-NP before (black colour line) and after (blue colour line) the CO_2 reduction reaction along with the corresponding JCPDS data.

6. Table S2: Radical scavenging data showing yield of AcOH in presence of different scavengers.

Scavengers	Radical	Yield of AcOH (M)	% Reduction in Yield of AcOH
control	--	0.442	0
BZQ	$O_2^{\bullet -}$	0.137	69.00
t-BuOH	**$OH^{\bullet}$**	**0.008**	**98.19**

K_2S_2O8	electrons	0.037	91.63

7. Table S3: Comparison of various materials available in the literature with d-ZCu based on the thermal reduction of CO_2 to C_2 products in batch reactor.

S. No.	Catalyst Precursors	Catalyst	Product	Catalyst Loading	Isolated Yield	Temperature (°C)	CO_2:H_2 Pressure (Bar)	Time (h)	Technique	Remark	Ref.
1	$Fe(NO_3)_3.H_2O$, CBEA, $CrCl_3.H_2O$, H_2BDC, NaOH, DMF	MIL-88B	AcOH	400mg/ 40mL	0.59 M/g	150	35:35 (70)	21	Thermal	Hydrogen gas was used externally	[1]
2	C. aceticum, C. carboxydivoran, NH_4Cl, vitamins stock solution, HCl, NaOH	Zerovalent Iron	AcOH	25g/L	~0.03 M	121	1.5:0 (1.5)	0.33	Thermal Bioconversion	NH_4Cl and vitamin stock solutions were used	[2]
3	$In(NO_3)_3.4.5H_2O$, NH_3, H_2IrCl_6	Ir_1–In_2O_3	EtOH	20mg/3 mL	0.99 mmol $g^{-1}h^{-1}$	200	10:50 (60)	5	Thermal	Hydrogen gas was used externally	[3]
4	$Pd(acac)_2$, $Cu(acac)_2$, $FeCl_3.6H_2O$, Ascorbic acid, Oleylamine,TOP	Pd−Cu Nanoparticles	EtOH	5mg/5 mL	40 mmol $g^{-1}h^{-1}$	200	8:24 (30)	5	Thermal	Hydrogen gas was used externally	[4]
5	$[Ru(bpy)_2Cl_2]$, BPYDC, $CuNO_3.3H_2O$, phosphate buffer solution	Cu−Ru−MOF	EtOH	10mg/ N.A. mL	9.65 mmol $g^{-1}h^{-1}$	150	5:15 (20)	24	Photo-Thermal	450nm LED light, H_2 gas was used externally	[5]
6	TALH, Urea, $HAuCl_4$, NaOH, NH_3	Au/a-TiO_2	EtOH	100mg/ 5mL (0.3 mg Au)	0.63 M $g^{-1}h^{-1}$	200	15:45 (60)	10	Thermal	Reaction media DMF, H_2 gas was used externally	[6]
7	**Waste Industrial Iron Dust, HCl, NaOH**	**Fe_3O_4-NP**	**AcOH**	**100mg/ 20 mL**	**0.44 M**	**100**	**10:0 (10)**	**2.5**	**Thermal**	**H_2O_2 is used**	**This work**
					0.22 M	**25**	**10:0 (10)**				

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