

Supplementary Information

Sulfonic acid functionalized dendrimer-grafted cellulose as solid acid catalyst for high-yield and green production of 5-hydroxymethylfurfural

Mahsa Niakan,^a Majid Masteri-Farahani,^{*a} Sabah Karimi^b and Hemayat Shekaari^b

^a Faculty of Chemistry, Kharazmi University, Tehran, Iran

^b Department of Physical Chemistry, Faculty of Chemistry, University of Tabriz, Tabriz, Iran

Email: mfarahani@khu.ac.ir

1. Chemicals and instrumentation

All reagents and solvents were obtained from Sigma-Aldrich and Merck companies and used without further purification.

Elemental analyses were performed by using a 2400 CHNS Series Perkin Elmer analyzer. Fourier transformed infrared (FTIR) spectroscopy data were recorded at room temperature using a Shimadzu FT-IR-8300 spectrophotometer. Scanning electron microscopy (SEM) images were performed using a TESCAN microscope (Model: MIRA3) equipped with energy-dispersive X-ray (EDX) spectroscopy. X-ray photoelectron spectroscopy (XPS) data was obtained using an ESCALAB 250 XI model X-ray photoelectron spectrometer (Thermo Scientific), with Mg X-ray source. X-ray diffraction (XRD) patterns of the samples were measured with a Philips TW-1730 equipped with a Cu-K α source. Transmission electron microscopic (TEM) images of the samples were taken by using a Zeiss-FM10C electron microscope operating at 200 kV. The experimental process was monitored by thin layer chromatography (TLC) on silica gel polygrams SIL G/UV 254 plates. High-performance liquid chromatography (HPLC) analysis of 5-HMF was recorded on a HPLC instrument (Agilent Technology Model: 1260 equipped with a UV-vis detector connected to eclipse XDB-C18), in which the mobile phase was a methanol:water (2:8) mixture with a flow rate of 1 mL min⁻¹ and the column and UV-vis detector temperatures were maintained at 30 °C and 35 °C, respectively. ¹H and ¹³C NMR spectra were recorded by using a Bruker Avance 400 MHz spectrometer (¹H using tetramethylsilane (TMS) as an internal reference and CDCl₃ as deuterated solvent).

2. Synthesis of Cell-G1.5

A mixture of Cell-G1 (1 g), 1,3,5-triacryloylhexahydro-1,3,5-triazine (10 mmol, 2.5 g), and AIBN (10 mmol, 1.64 g) in DMF (30 mL) was stirred at 100 °C for 24 h under N₂ atmosphere. The obtained product (Cell-G1.5) was isolated by filtration, washed repeatedly through soxhlet extraction with methanol, and dried under vacuum.

3. Synthesis of Cell-G2

1,2-ethanedithiol (20 mmol, 1.68 mL) and AIBN (20 mmol, 3.28 g) were added to a suspension of Cell-G1.5 (1 g) in 30 mL of DMF and the mixture was stirred at 100 °C for 24 h under N₂ atmosphere. The solid was separated by filtration and washed with hot ethanol. Cell-G2 was finally obtained by vacuum drying.

4. Synthesis of Cell-G2.5

Cell-G2 (1 g) was added into a mixture containing dimethylformamide (DMF, 30 mL), 1,3,5-triacryloylhexahydro-1,3,5-triazine (20 mmol, 5 g), and azobisisobutyronitrile (AIBN) as initiator (20 mmol, 3.28 g). The obtained mixture was stirred at 100 °C for 24 h under N₂ atmosphere. The end-product (Cell-G2.5) was separated by filtration, washed with hot methanol in a continuous extraction apparatus (Soxhlet), and dried under vacuum.

5. Synthesis of Cell-G3

To a suspension of Cell-G2.5 (1 g) in DMF (30 mL), 1,2-ethanedithiol (40 mmol, 3.36 mL) followed by AIBN (40 mmol, 6.56 g) was added and stirred at 100 °C for 24 h under N₂ atmosphere. The solid material (Cell-G3) was isolated by filtration, washed with ethanol, and dried under vacuum.

6. XPS analysis

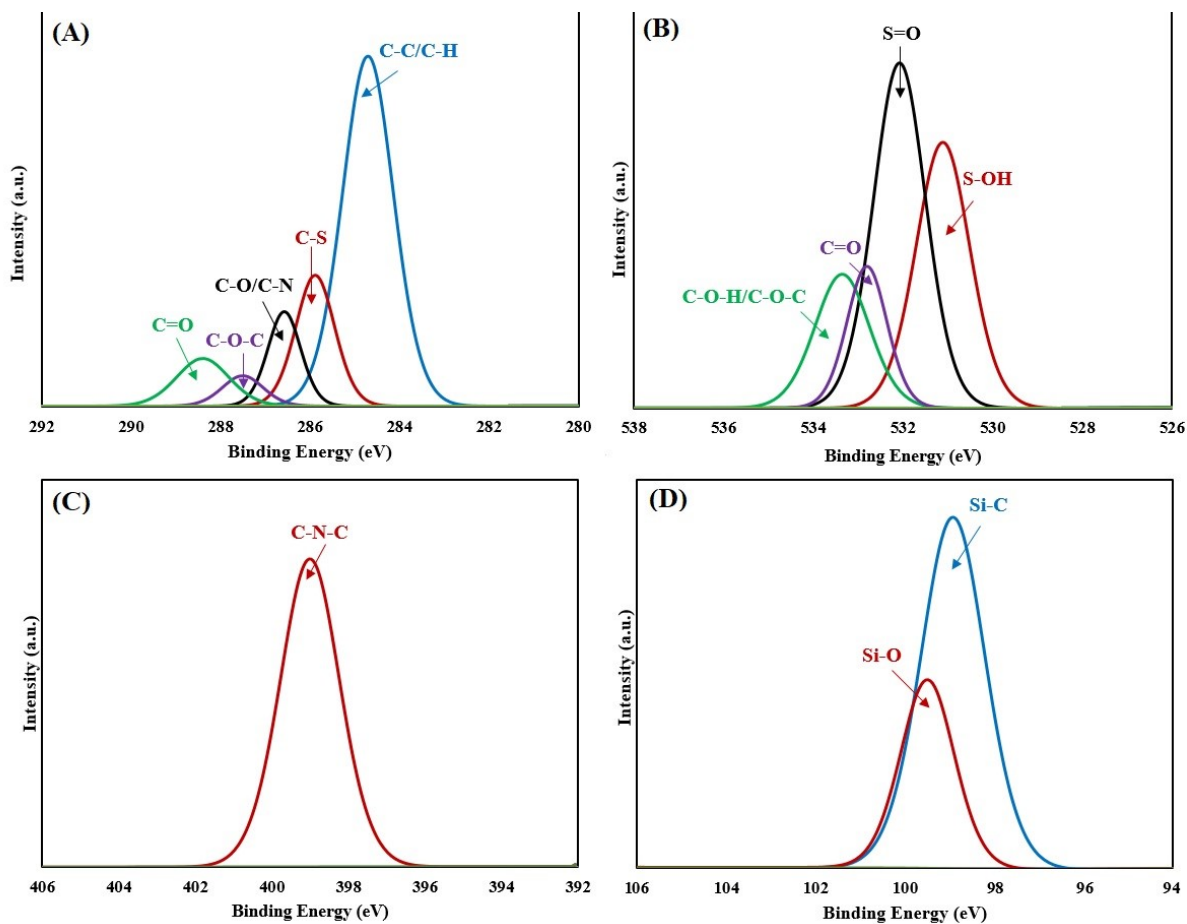


Fig. S1. High resolution XPS spectra of (A) C 1s, (B) O 1s, (C) N 1s, and (D) Si 2p of Cell-G3-SO₃H.

Table S1. Atomic percentage of various elements from XPS for Cell-G3-SO₃H.

Sample	C (%)	O (%)	N (%)	S (%)	Si (%)
Cell-G3-SO ₃ H	53.42	27.16	10.16	7.65	1.61

7. Calculation of the green chemistry metrics for the fructose dehydration to 5-HMF over Cell-G3-SO₃H in acetone:water (v:v=2:1)

Table S2. Calculation of the green chemistry metrics.

1	Atom economy	
	Atom Economy = (Exact molecular mass of 5-HMF / Exact Molecular mass of fructose) × 100%	= 126.11/180.16 × 100% AE = 70%
2	Reaction mass efficiency	
	Reaction Mass Efficiency = (Mass of 5-HMF / Mass of fructose) × 100	= (60/90) × 100 RME = 66.67%
3	E-factor	
	E-Factor = Amount of waste/ Amount of product	Total amount of reactant = 90 mg Amount of final product = 60 mg Amount of waste = (Total amount of reactant – amount of final product) = (90-60) mg = 30 mg E-factor = (30 /60) = 0.5
4	Eco-scale	
	Eco-scale = (100 – Sum of individual penalties)	Eco-scale = 100–15 = 85

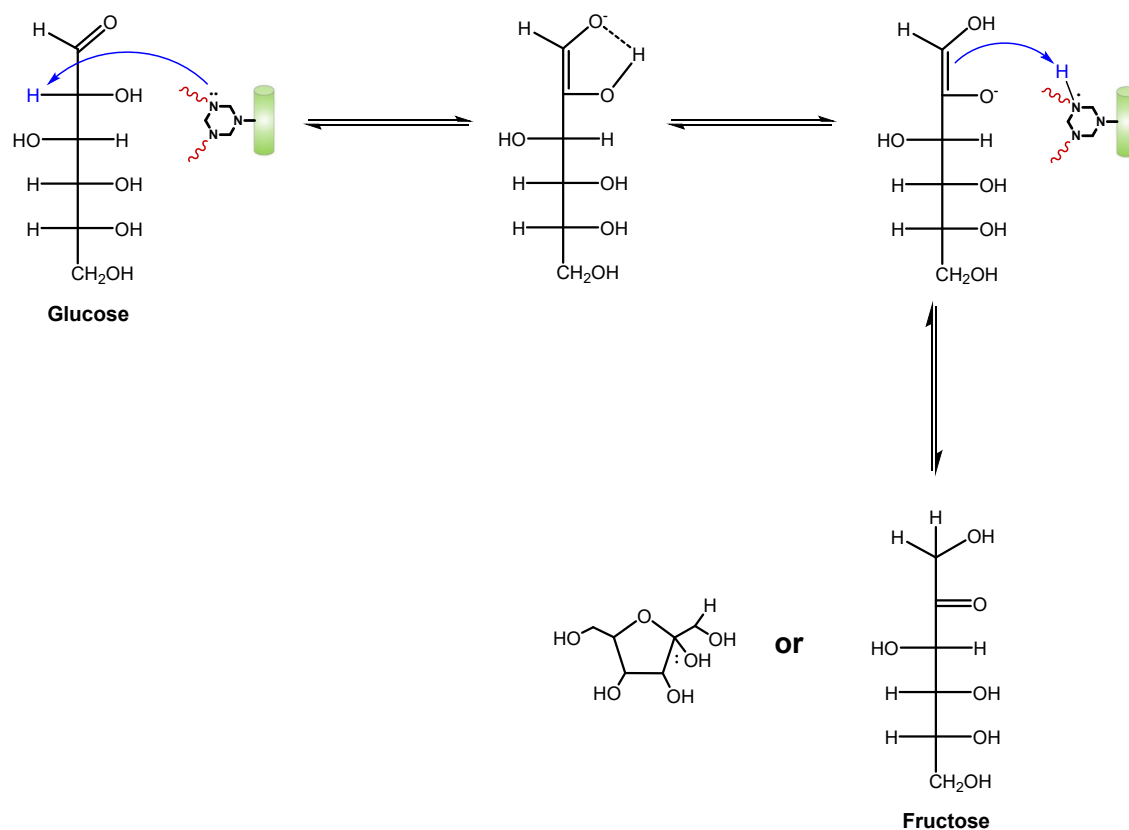
Table S3. Calculation of the penalty points for the Eco-scale calculation.

Calculation of penalty points		
	Parameters	Penalty points
1	Reaction Yield	
	Yield = 96%	2
2	Price of reaction components (to obtain 0.4 mmol of final product)	
	Catalyst components	3

3	Safety	
	Ethyl acetate, Catalyst components (Toxic)	5
4	Technical setup	
	Common setup	0
5	Temperature/Time	
	Heating, < 1 h	2
6	Work and Purification	
	Liquid-liquid extraction	3
	Total penalty points	15

8. Proposed mechanism for the conversion of glucose to 5-HMF

Step 1: Isomerization of Glucose to Fructose



Step 2: Dehydration of Fructose to 5-HMF

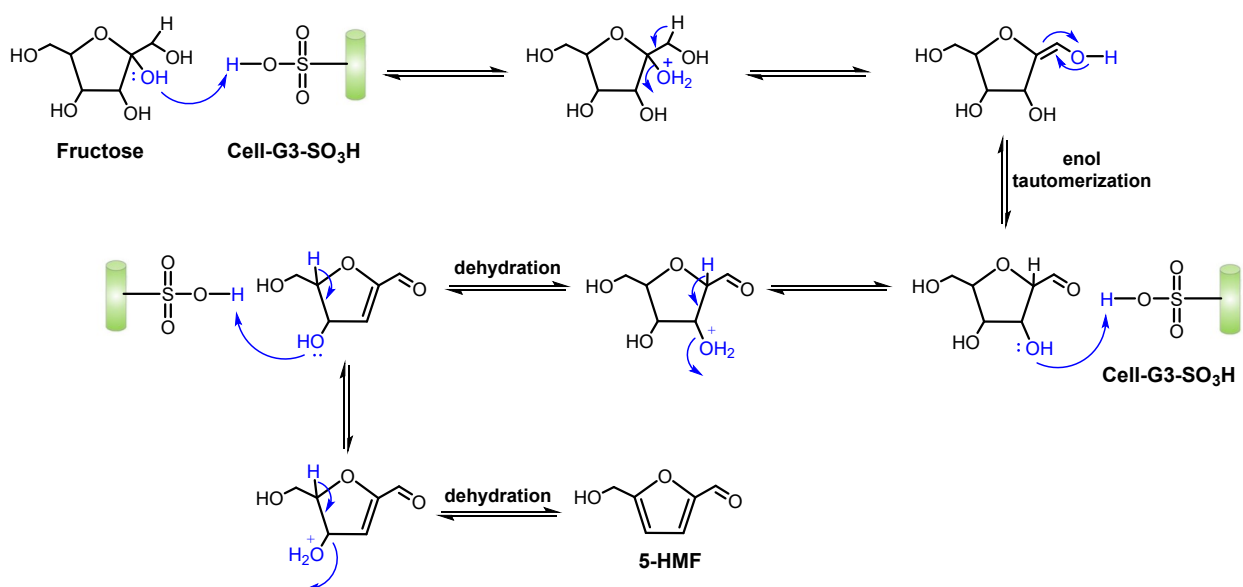


Fig. S2. Proposed mechanism for the conversion of glucose to 5-HMF catalyzed by Cell-G3-SO₃H.

9. Characterization of 5-HMF

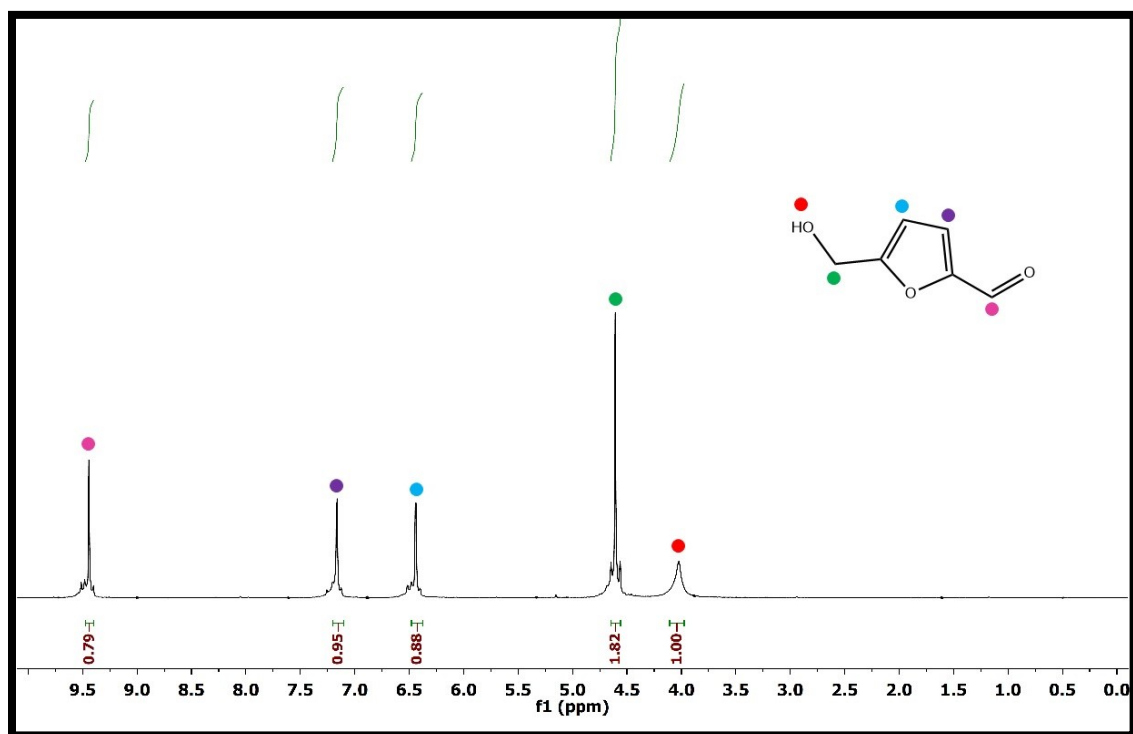


Fig. S3. ¹H NMR spectrum of the isolated 5-HMF in CDCl₃.

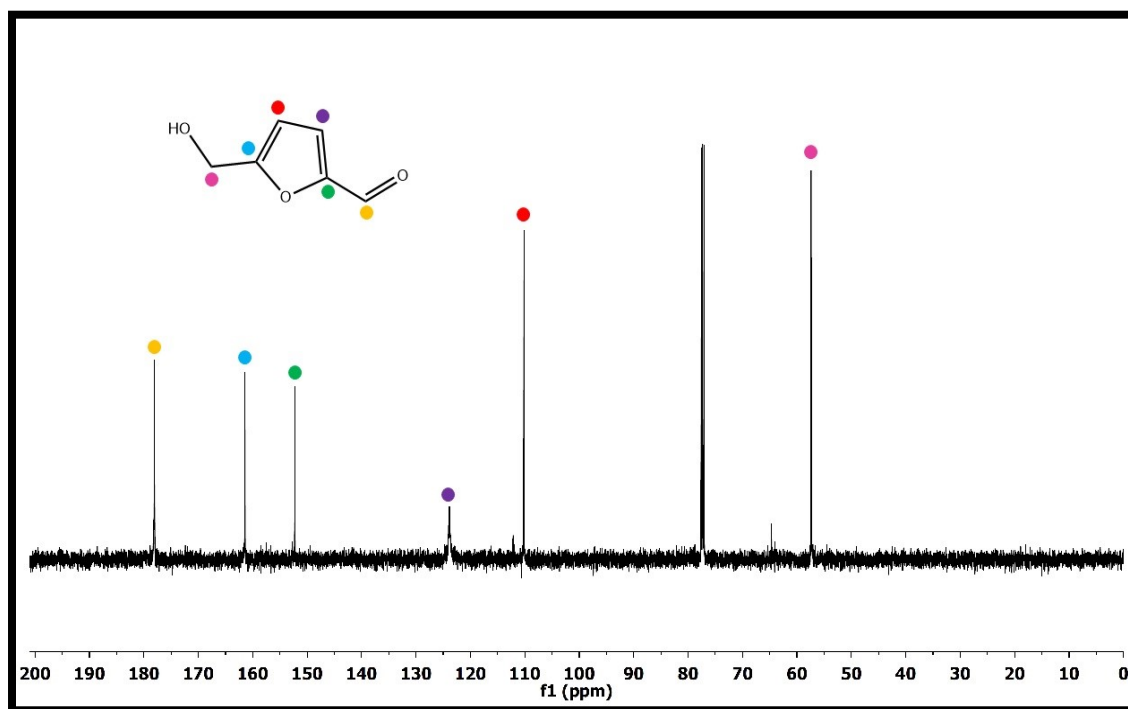


Fig. S4. ¹³C NMR spectrum of the isolated 5-HMF in CDCl₃.

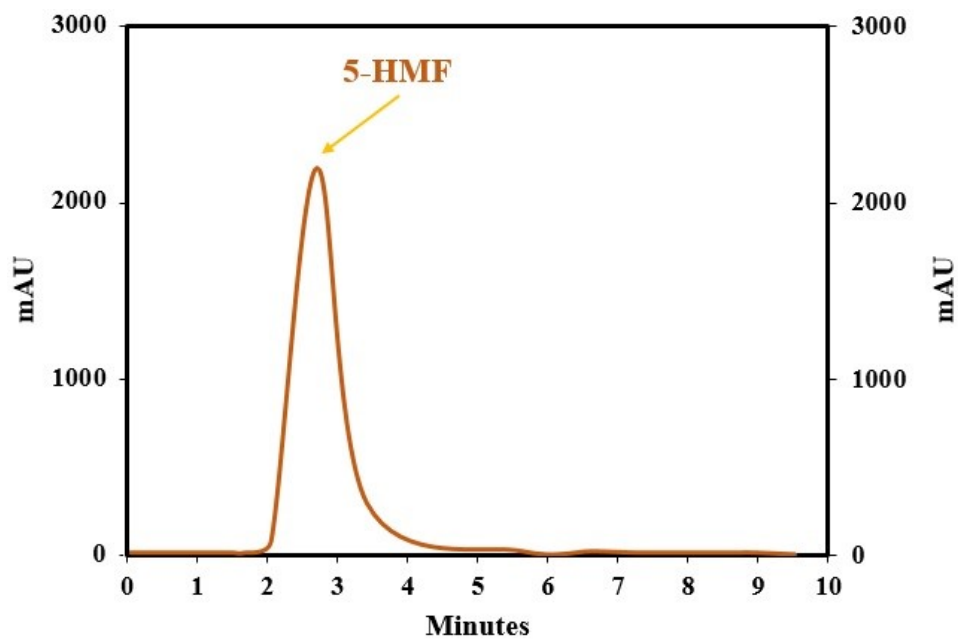


Fig. S5. HPLC analysis result of the isolated 5-HMF.

10. Characterization of the recovered catalyst

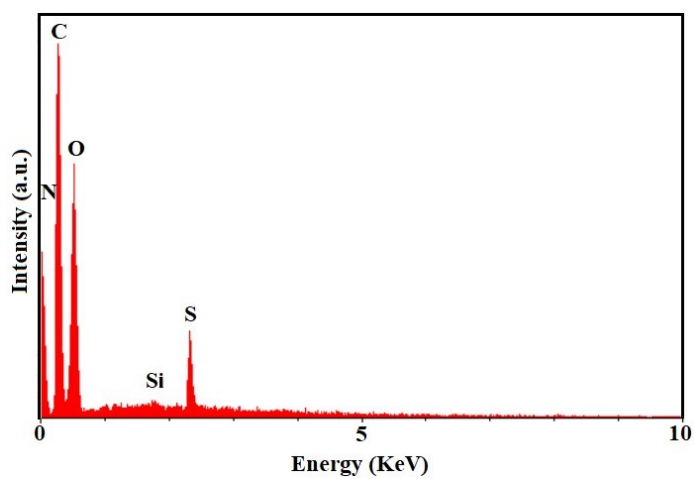


Fig S6. EDX spectrum of the reused catalyst after five runs.

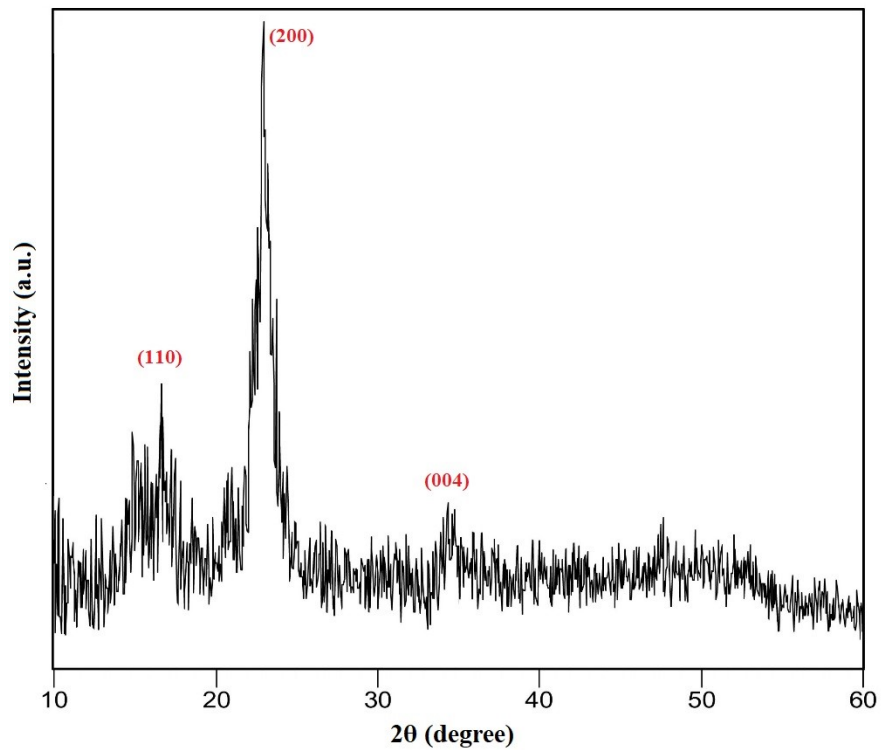


Fig. S7. XRD pattern of the reused catalyst after five runs.