The influence of hydrophobic/hydrophilic balance of the mesoporous solid acid catalysts in the selective dehydration of fructose into HMF

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Table of contents Page

1. Experimental Procedure

1.1 General

^{1}H NMR spectra were recorded on commercial instruments (400 MHz). Chemical shifts were reported in ppm with the solvent resonance as the internal standard ($CDCl_3$: δ= 7.26 and D_2O: δ=4.70). ^{13}C NMR spectra were collected on commercial instruments (100.60 MHz) with complete proton decoupling. Reagents obtained from commercial sources were used without further purification. Thermal treatments were conducted from room temperature to 800 °C and 1000 °C in nitrogen flow using a STA 409 PC analyzer (Netzsch).

1.1.1 Home designed reactor

1.2 Chemicals

TEOS (tetraethoxysilane), MPTMS (3-mercaptopropyl trimethoxysilane), PTES (phenyltriethoxysilane) and triblock co-polymer P123 (Eo_{70} Po_{20} Eo_{70}) were obtained from Aldrich and used as received. Also, CSPTMS [2-(4-chlorosulfonylphenyl) ethyltrimethoxysilane] was obtained from Gelest.

1.3 Catalysts preparation

1.3.1 Preparation of MCM-PrSO3H (1a)[1]

A mixture of (3-mercaptopropyl)trimethoxysilane (MPTS, 1 equiv.), tetramethoxysilane (TMOS, 2.5 equiv.), was prepared (solution 1). Solution I was rapidly added to a pre-prapared solution containing cetyltrimethoxy ammonium bromide, (CTAB, 0.42 equiv.) as template or structure directing agent (SDA), NaOH (0.96 equiv.), double distilled water (272 equiv.), and absolute MeOH (66 equiv.). The resulting solution was stirred at room temperature for 12 h, followed by heating at 95 ºC for 36 h in an autoclave. The surfactant was then extracted by refluxing with a solution of HCl/MeOH/H_2O (1.5 wt% HCl/ 2.5 Wt. % H_2O/MeOH) using a soxhelet apparatus for 24 h. Extracted mercaptopropyl-ordered nanoporous silica was then oxidized to the corresponding sulfonic acid derivative by first wetting the solid briefly with 20 wt% HNO_3, followed by careful addition of concentrated (100%) HNO_3 and stirring for 24 h at room temperature. The solid materials were thoroughly washed with a large volume of double distilled water until the pH of the filtrates reach to neutral level. The catalyst **1a** was then dried overnight at 120 ºC. TGA analysis of catalyst **1a** shows a first weight loss due to desorption of water below 100 ºC. This is followed by a second weight loss started at 240 ºC, corresponding to the loss of the covalently bound organic group. The ion exchange capacities of the sulfonic acid functionalized MCM-41 (**1a**) was determined to be 1 mmol.g^{-1} by acid–base titration.

1.3.2 Preparation of MCM-Ph-PrSO3H (1b)

To a suspension of **1a** (3 g) in dry toluene $PhSi(OEt)_3$ (PTES, 4 mmol) was added. The resulting mixture was first stirred at room temperature for 1 h and then refluxed for further 24

h. The solid materials was filtered and successively washed with toluene, EtOH, and Et_2O and dried overnight at 120 °C to afford the corresponding **1b** catalyst. The ion exchange capacities of the sulfonic acid functionalized MCM-41-Ph-$PrSO_3H$ (**1b**) was determined to be 0.9 $mmolg^{-1}$ by acid–base titration.

1.3.3 Preparation of SBA-15-PrSH

The synthesis of SBA-15-PrSH has been achieved using known procedure described by Stucky and his co-workers.[2] This procedure involved a synthetic strategy based on co-condensation of tetraethoxysilane (TEOS) and 3-mercaptopropyltrimethoxysilane (MPTMS) in the presence of Pluronic P123 as structure directing agent. In a typical preparation procedure, 4.0 g of Pluronic P123 (Aldrich, average Mw =5800) was dissolved in 125 g of 1.9 M HCl solution with stirring at room temperature. The solution was heated to 40 °C before adding 6.83g TEOS. After 3 h pre-hydrolysis of TEOS, 1.6 g thiol precursor MPTMS was added. The resultant solution was stirred for 20 h at 40 °C, after which the mixture was aged at 100 °C for 24 h under static conditions. The solid was recovered by filtration and air dried at room temperature overnight. The template was removed from the as-synthesized material by washing with ethanol using a Soxhelet apparatus for 24 h.

1.3.4 Preparation of SBA-15-Ph-PrSH[3]

To a suspension of SBA-15-Pr-SH (3 g) in dry toluene $PhSi(OEt)_3$ (PTES, 4 mmol) was added. The resulting mixture was first stirred at room temperature for 1 h and then refluxed for further 24 h. The solid materials was filtered and successively washed with toluene, EtOH, and Et_2O and dried overnight at 120 °C to afford the corresponding SBA-15-Ph-PrSH.

1.3.5 Preparation of SBA-15-PrSO3H (2a)

Typically, 0.3 g of SBA-15-Pr-SH was suspended in 10 g of aqueous 30 wt% H_2O_2. This suspension was stirred at room temperature in an Ar atmosphere for 24 h. After the oxidation treatment, the resulting solution was filtered and washed separately with water and ethanol. Finally the wet material was suspended in 1M H_2SO_4 solution for 2 h and then was washed several times with deionized water and ethanol and dried at 60 °C under vacuum overnight to give the corresponding catalyst.

1.3.6 Preparation of SBA-15-Ph-$PrSO_3H$ (2b)

Conversion of thiol groups of catalyst to sulfonic acid moiety was accomplished by hydrogen peroxide. Typically, 0.3 g of solid hodrophobic material was suspended in 10 g of aqueous 30 wt% H_2O_2. This suspension was stirred at room temperature in an Ar atmosphere for 24 h. After the oxidation treatment, the resulting solution was filtered and washed separately with water and ethanol. Finally the wet material was suspended in 1M H_2SO_4 solution for 2 h and then was washed several times with water and ethanol and dried at 60 °C under vacuum overnight to give the corresponding catalyst.

1.3.7 Preparation of SBA-15-$C_2H_4PhSO_3H$ (3a)[4]

This material was synthesized as follows: 4 g of Pluronic 123 (Aldrich) were dissolved with stirring in 125 g of 1.9 M HCl at room temperature. The solution was heated to 40 °C before addition of 0.0369 mol TEOS (Aldrich). After 45 min TEOS prehydrolysis, 0.0041 mol 2-(4-chlorosulfonylphenyl)ethyltrimethoxysilane [CSPTMS (Gelest)] was added and the resulting mixture was stirred at 40 °C for 20 h and aged at 100 °C for an additional 24 h under static conditions. The solid product was recovered by filtration and air-dried at room temperature overnight. The template was removed from the as-synthesised material by washing with ethanol using a Soxhelet apparatus for 24 h.

1.3.8 Preparation of SBA-15-Ph-$C_2H_4PhSO_3H$ (3b)

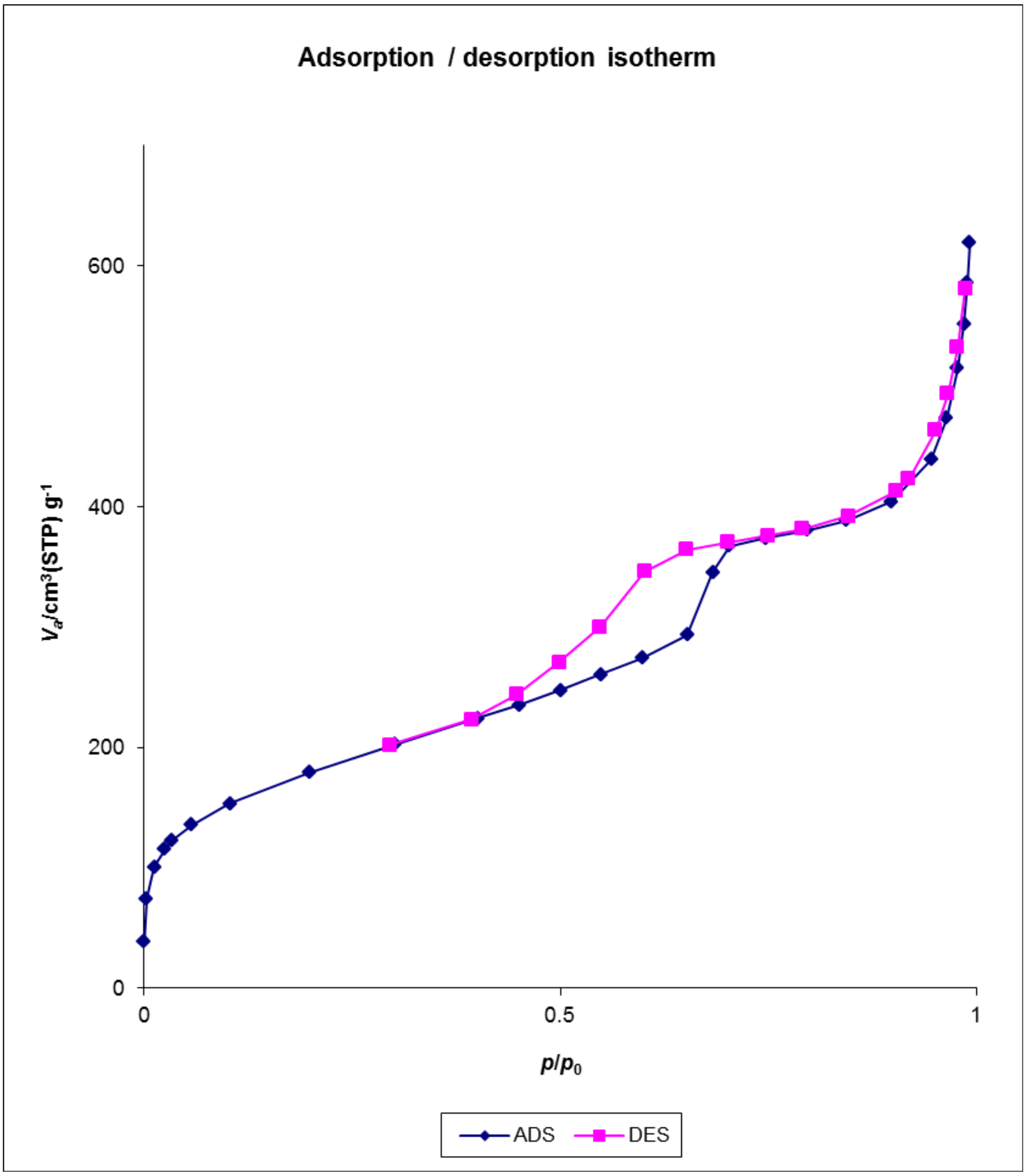
This material was synthesized as follows: 4 g of Pluronic 123 (Aldrich) were dissolved with stirring in 125 g of 1.9 M HCl at room temperature. The solution was heated to 40 °C before addition of 0.0369 mol TEOS (Aldrich). After 45 min TEOS pre-hydrolysis, 0.0041 mol 2-(4-chlorosulfonylphenyl)ethyltrimethoxysilane [CSPTMS (Gelest)] was added and the resulting mixture was stirred at 40 °C for 20 h and aged at 100 °C for an additional 24 h under static conditions. The solid product was recovered by filtration and air-dried at room temperature overnight. The template was removed from the as-synthesized material by washing with ethanol using a Soxhelet apparatus for 24 h. To a suspension of SBA-15-$C_2H_4PhSO_3H$ (1 g) in 25 ml dry toluene, $PhSi(OEt)_3$ (PTES, 2 mmol) was added. The resulting mixture was first stirred at room temperature for 1 h and then refluxed for further 24 h. The solid materials was filtered and successively washed with toluene, dichloromethane and dried overnight at 80 °C to afford the corresponding SBA-15-Ph-$C_2H_4PhSO_3H$.

2 Characterization

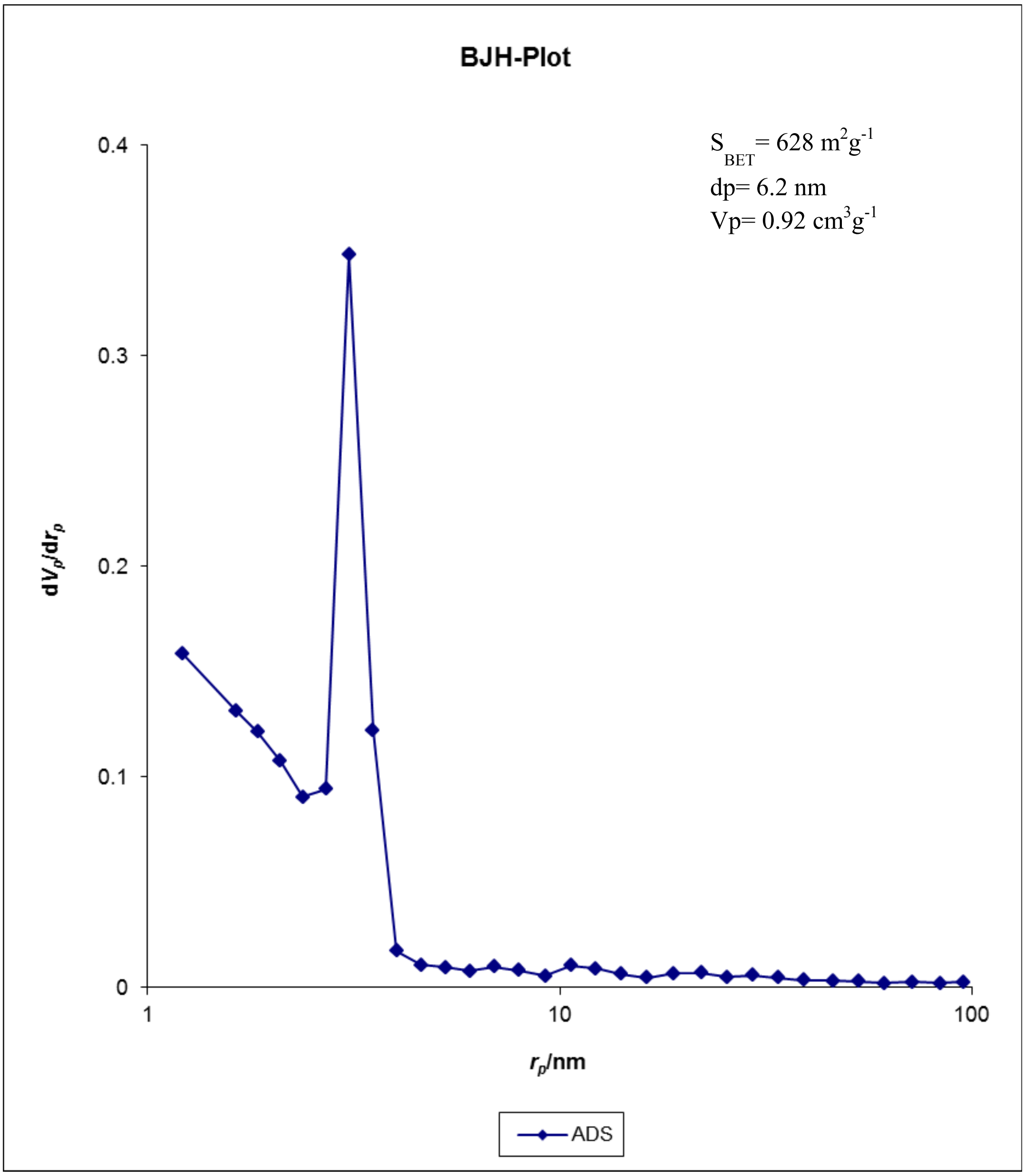
The textural properties of the functionalized mesoporous silicas were measured from nitrogen adsorption-desorption isotherms at 77 k with a BELSORB max system. The surface area and pore size distribution were calculated with the BET and BJH methods, respectively. Also, the surface hydophilicity was measured by water adsorption-desorption at 298 K with BELSORB max. Organic material present in the solids was determined by elemental analysis and the organic composition of the modified mesoporous materials was determined by thermogravimetric analysis (TGA) and differential thermoanalysis (DTA), with heating from room temperature to 800 °C and 1000 °C under Nitrogen flow. The ion exchange capacities of the sulfonic acid functionalized mesoporous catalysts were determined by acid-base titration.

2.1 SBA-15-PrSO$_3$H (2a)

2.1.1 Porosimetry data

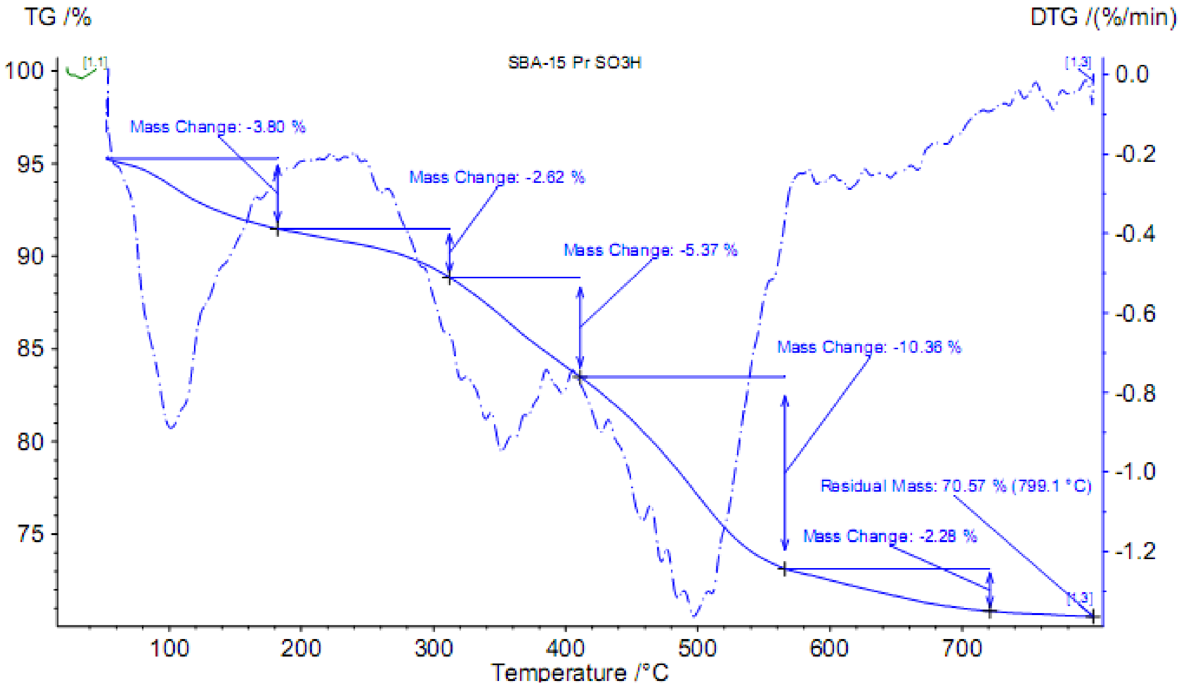


N$_2$ adsorption-desorption of SBA-15-PrSO$_3$H (2a) catalyst

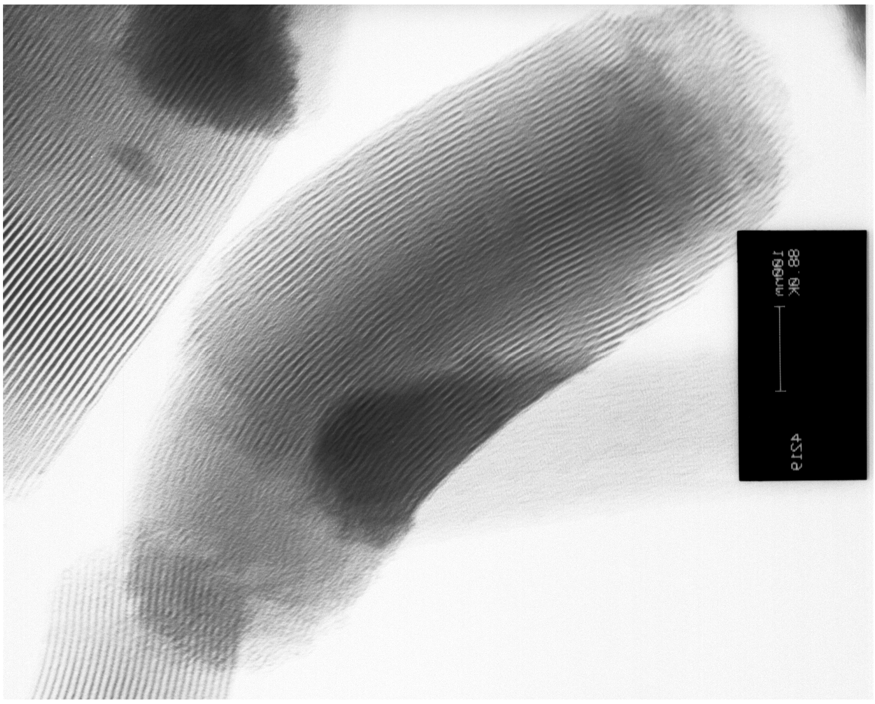


BJH analysis of SBA-15-$PrSO_3H$ (2a) catalyst

2.1.2 TGA-DTG analysis for SBA-15-PrSO$_3$H (2a) catalyst



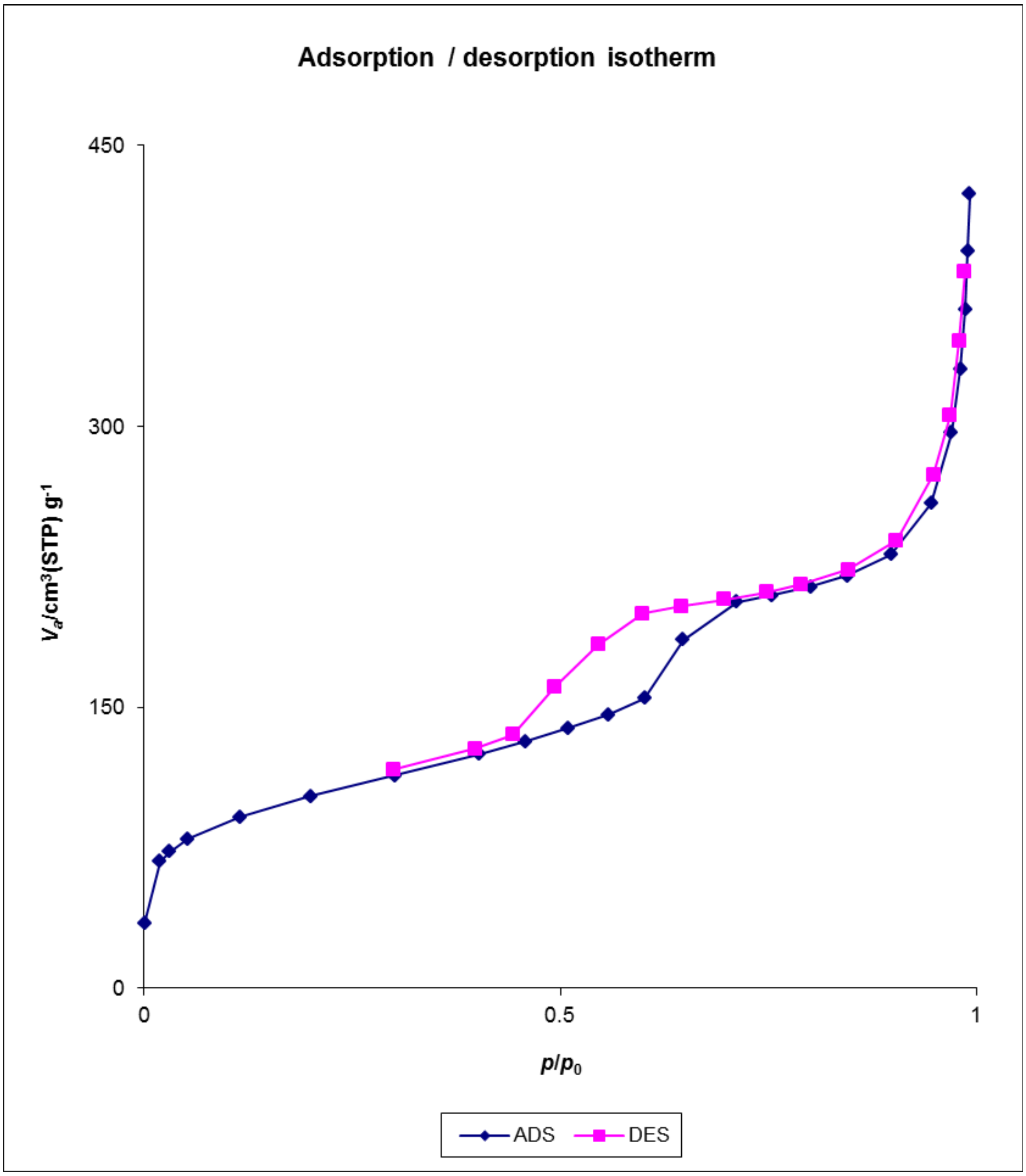
2.1.3 SBA-15-PrSO$_3$H (2a) catalyst TEM image



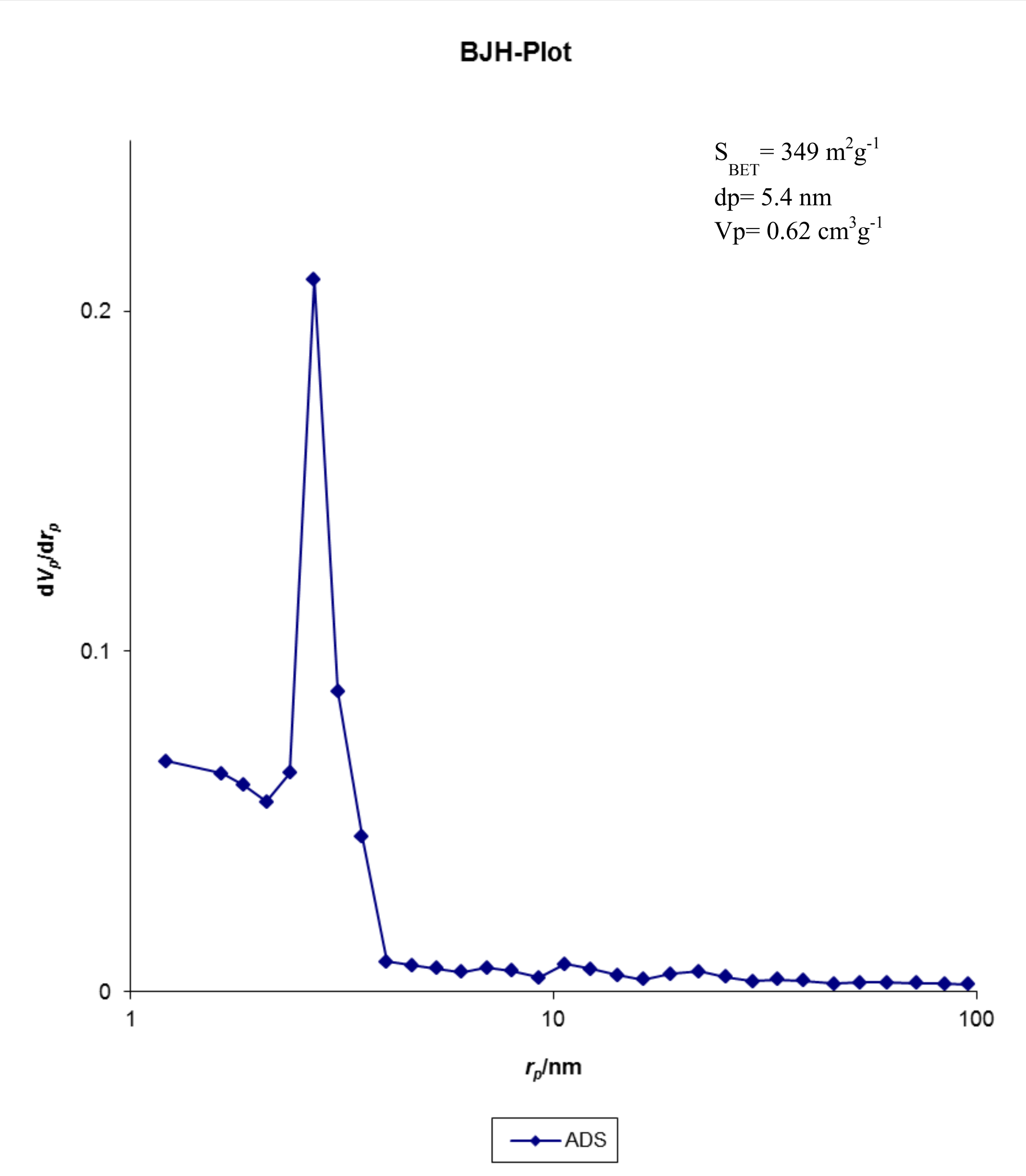
TEM image of SBA-15-PrSO$_3$H (2a) catalyst (bar=100 nm)

2.2 SBA-15-Ph-PrSO$_3$H (2b)

2.2.1 Porosimetry data

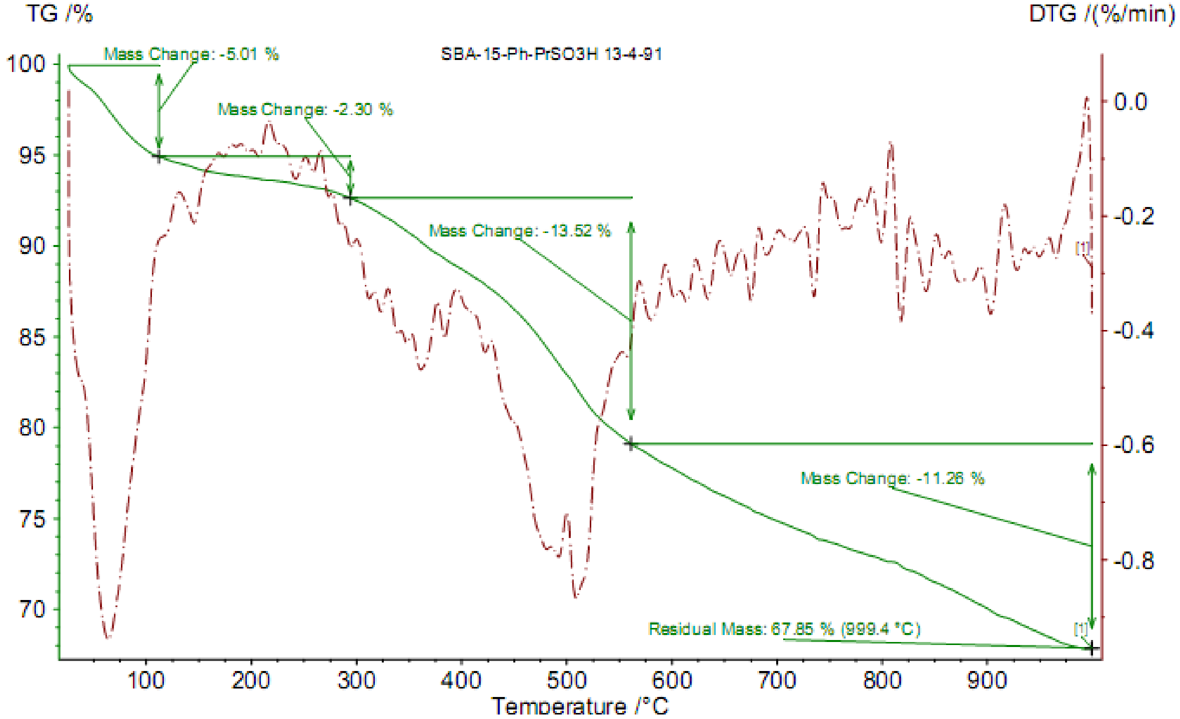


N$_2$ adsorption-desorption of SBA-15-Ph-PrSO$_3$H (2b) catalyst



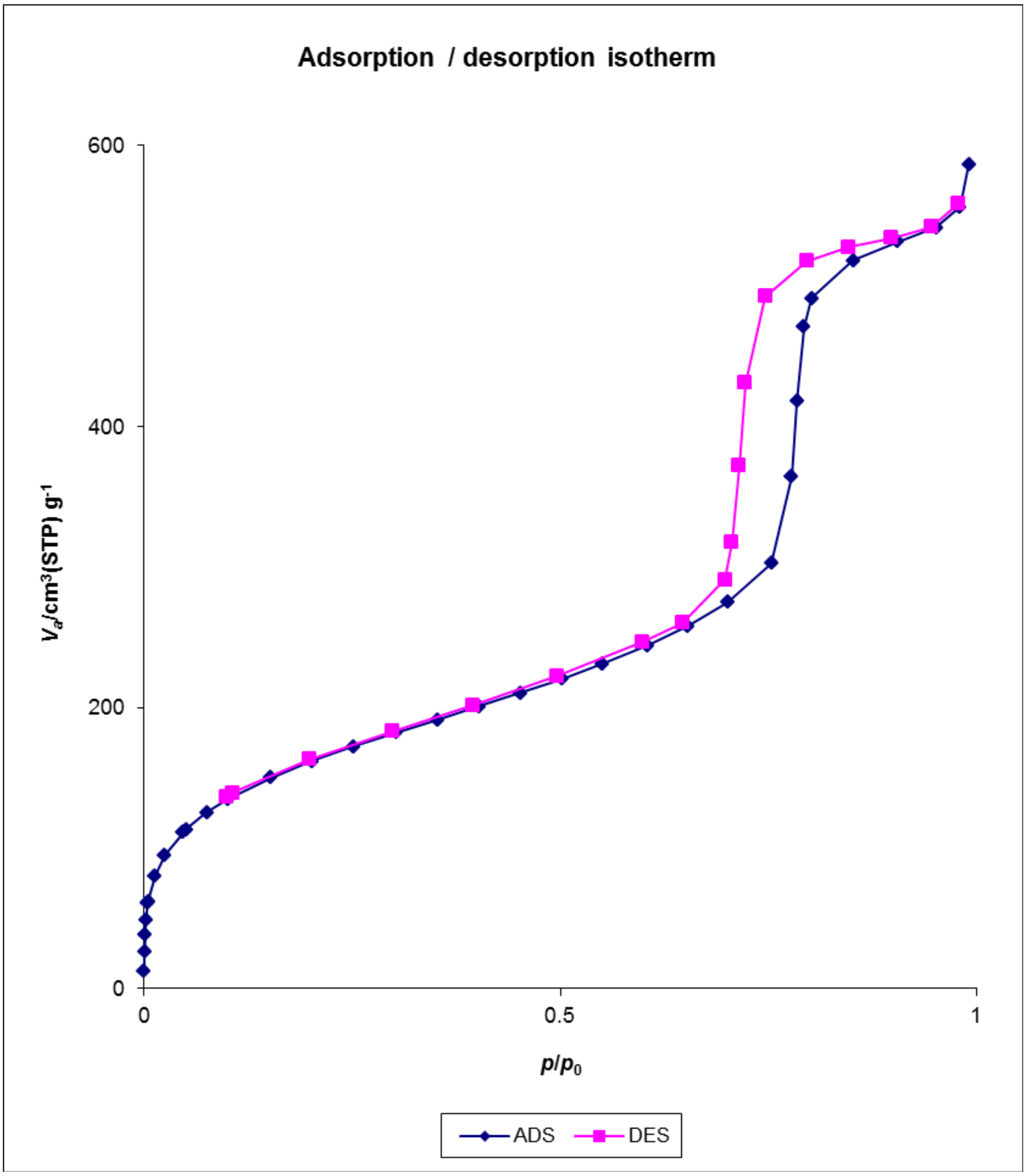
BJH analysis of SBA-15-Ph-$PrSO_3H$ (2b) catalyst

2.2.2 TGA-DTG analysis for SBA-15-Ph-PrSO$_3$H (2b) catalyst

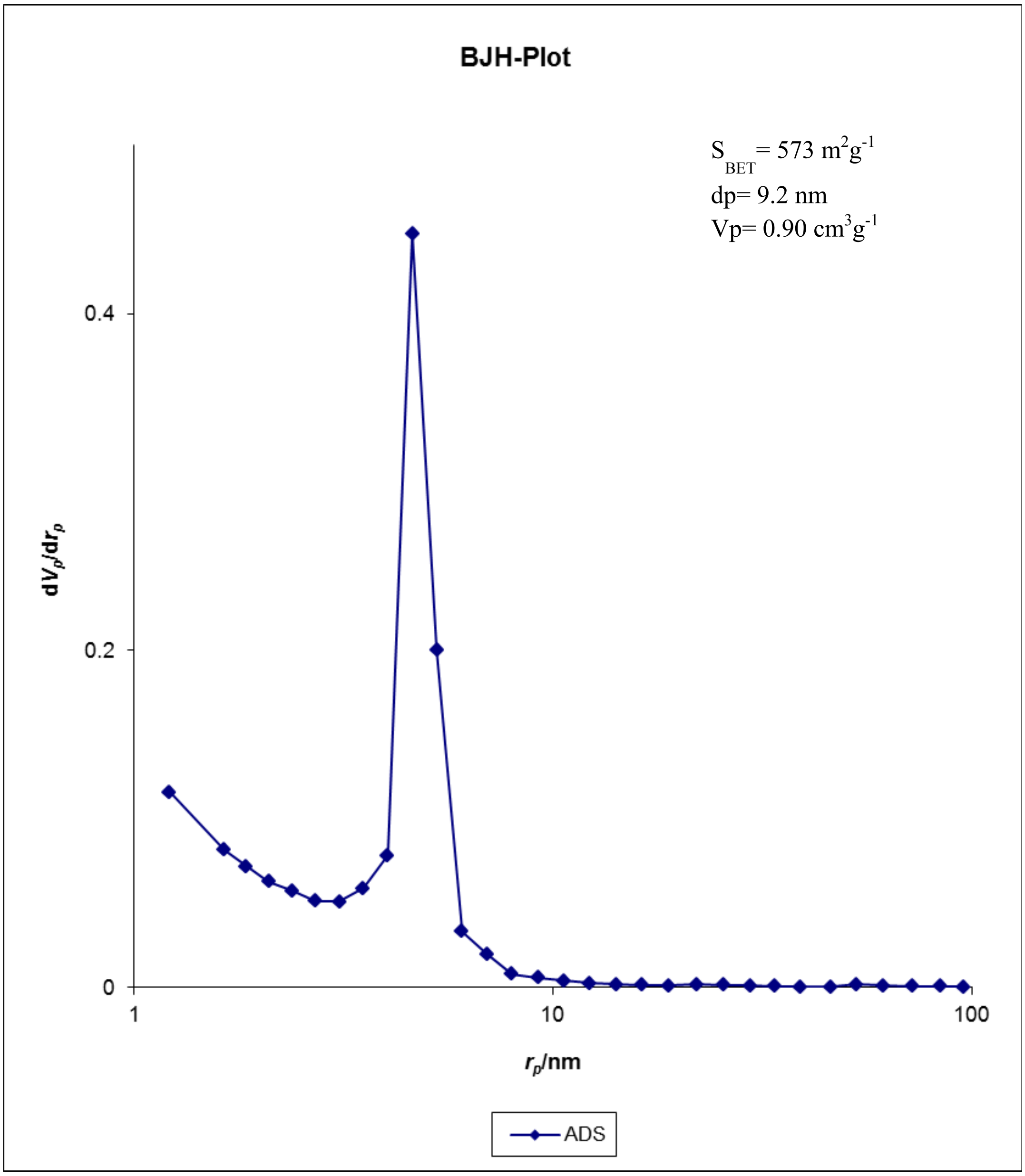


2.3 SBA-15-$C_2H_4PhSO_3H$ (3a)

2.3.1 Porosimetry data

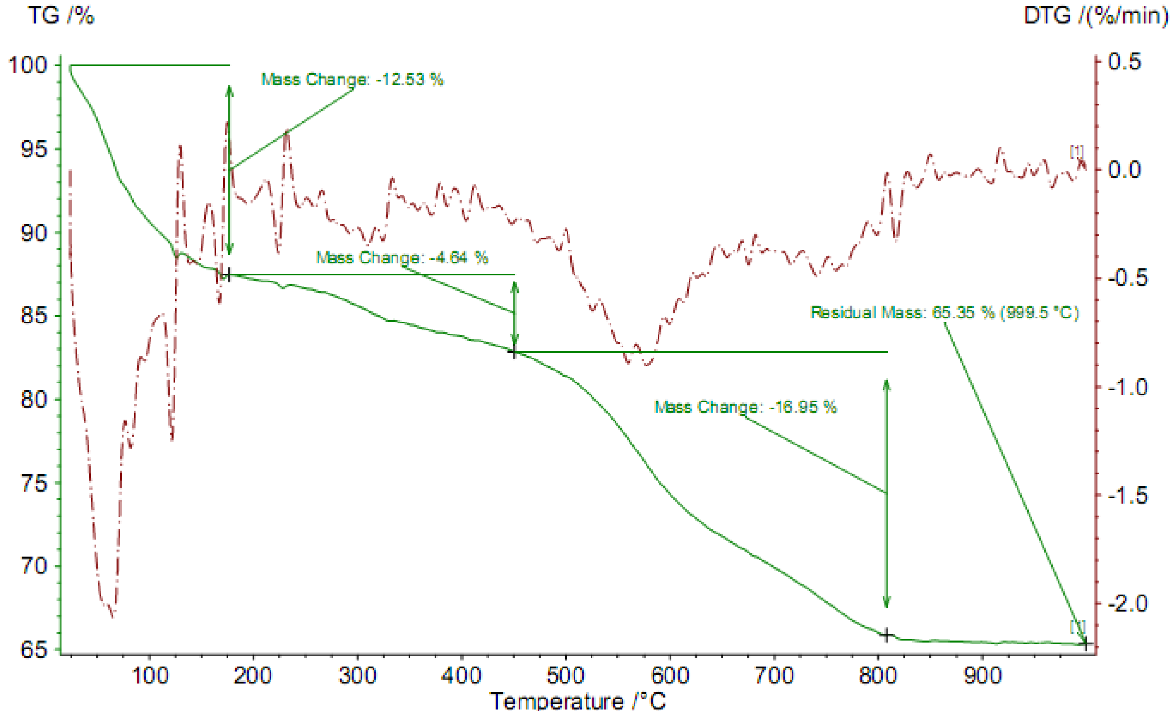


N_2 adsorption-desorption of SBA-15-$C_2H_4PhSO_3H$ (3a) catalyst

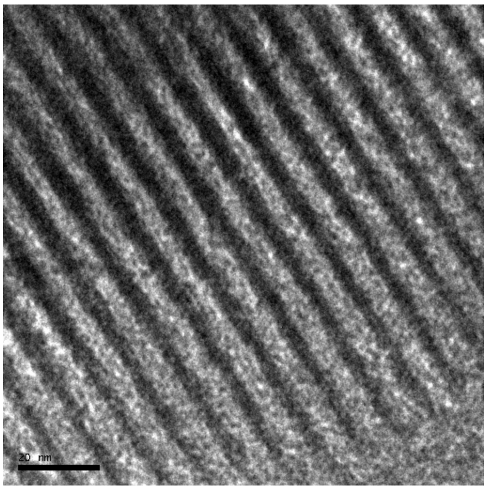


BJH analysis of SBA-15-$C_2H_4PhSO_3H$ (3a) catalyst

2.3.2 TGA-DTG analysis of SBA-15-$C_2H_4PhSO_3H$ (3a) catalyst

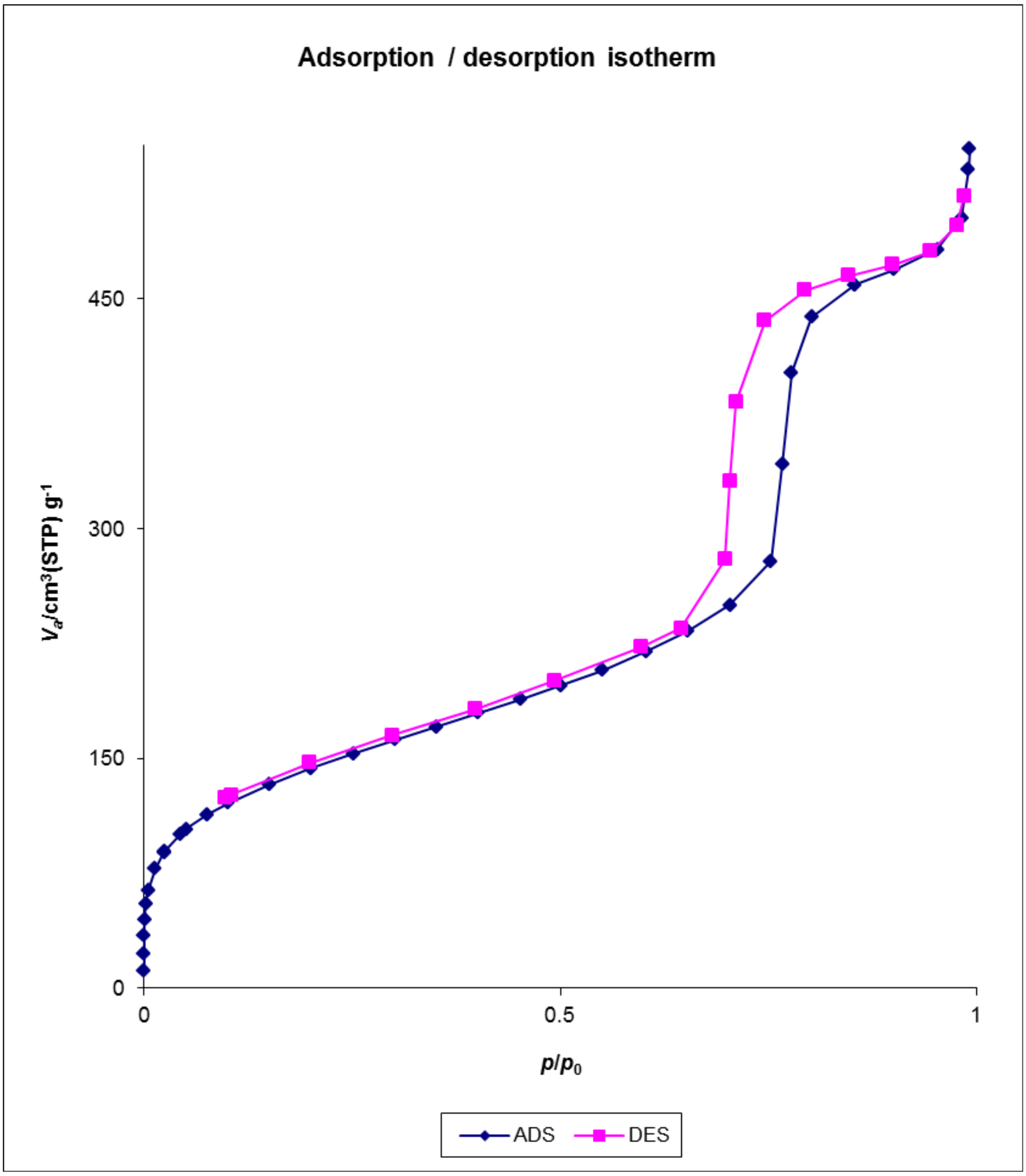


2.3.3 TEM image of SBA-15-$C_2H_4PhSO_3H$ (3a) catalyst

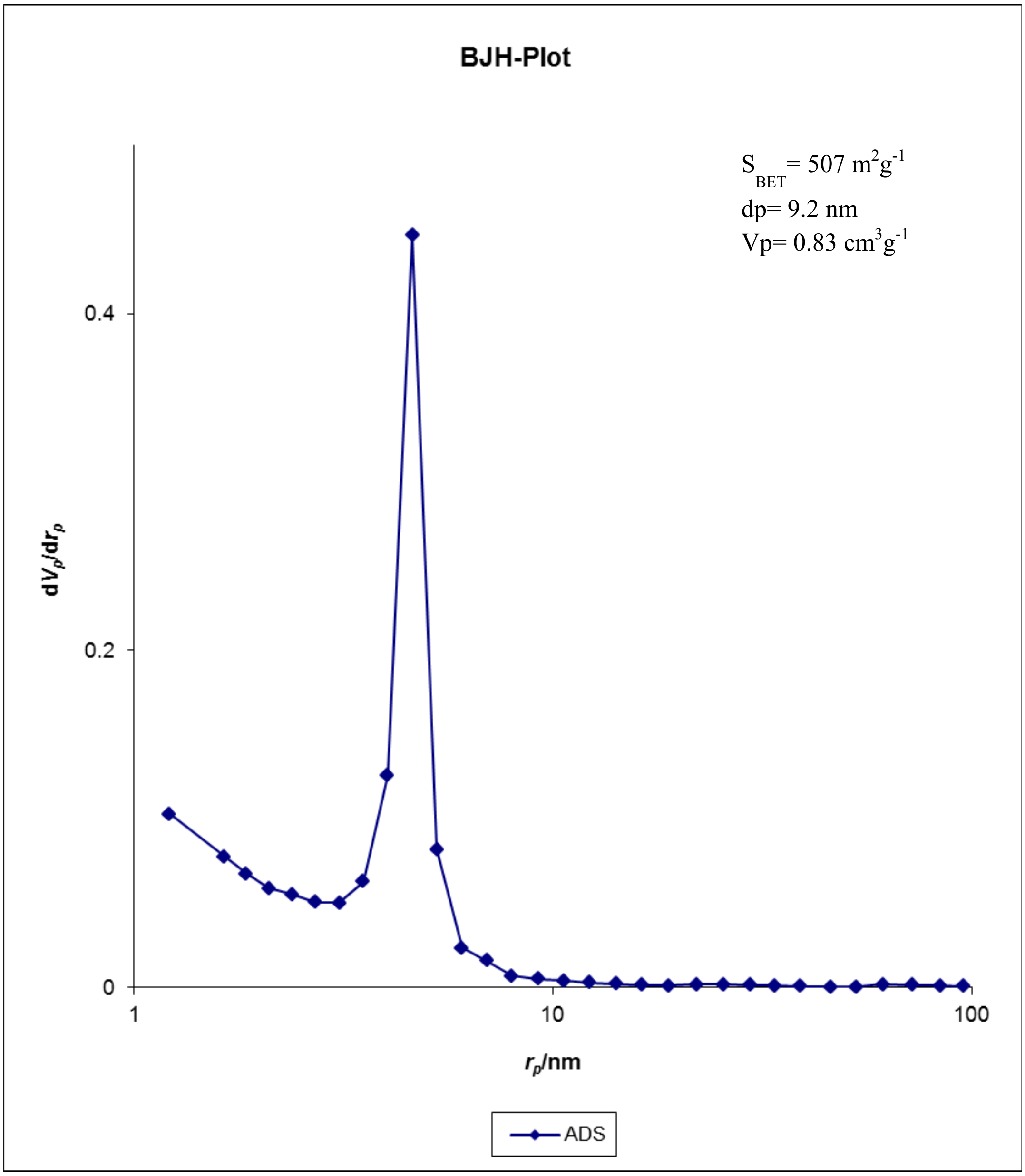


2.4 SBA-15-Ph-$C_2H_4PhSO_3H$ (3b)

2.4.1 Porosimetry data

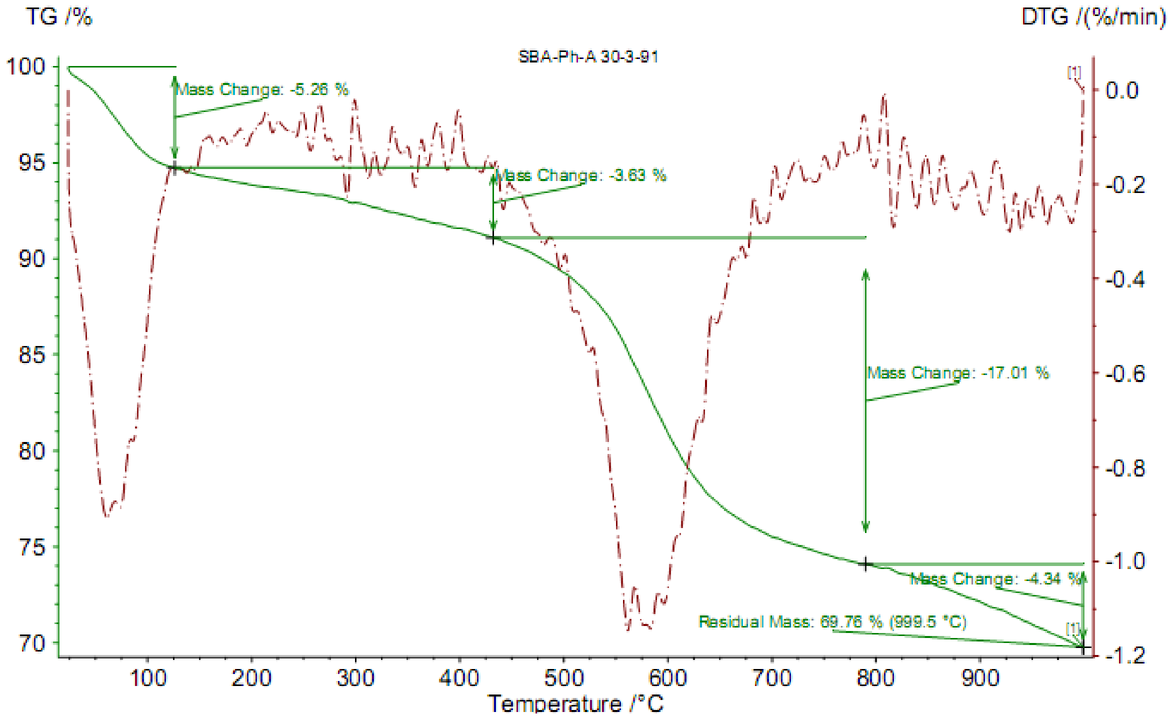


N_2 adsorption-desorption of SBA-15-Ph-$C_2H_4PhSO_3H$ (3b) catalyst

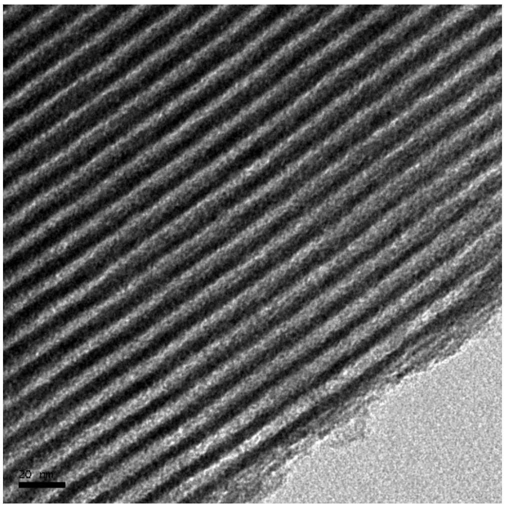


BJH analysis of SBA-15-Ph-$C_2H_4PhSO_3H$ (3b) catalyst

2.4.2 TGA-DTG analysis of SBA-15-Ph-$C_2H_4PhSO_3H$ (3b) catalyst

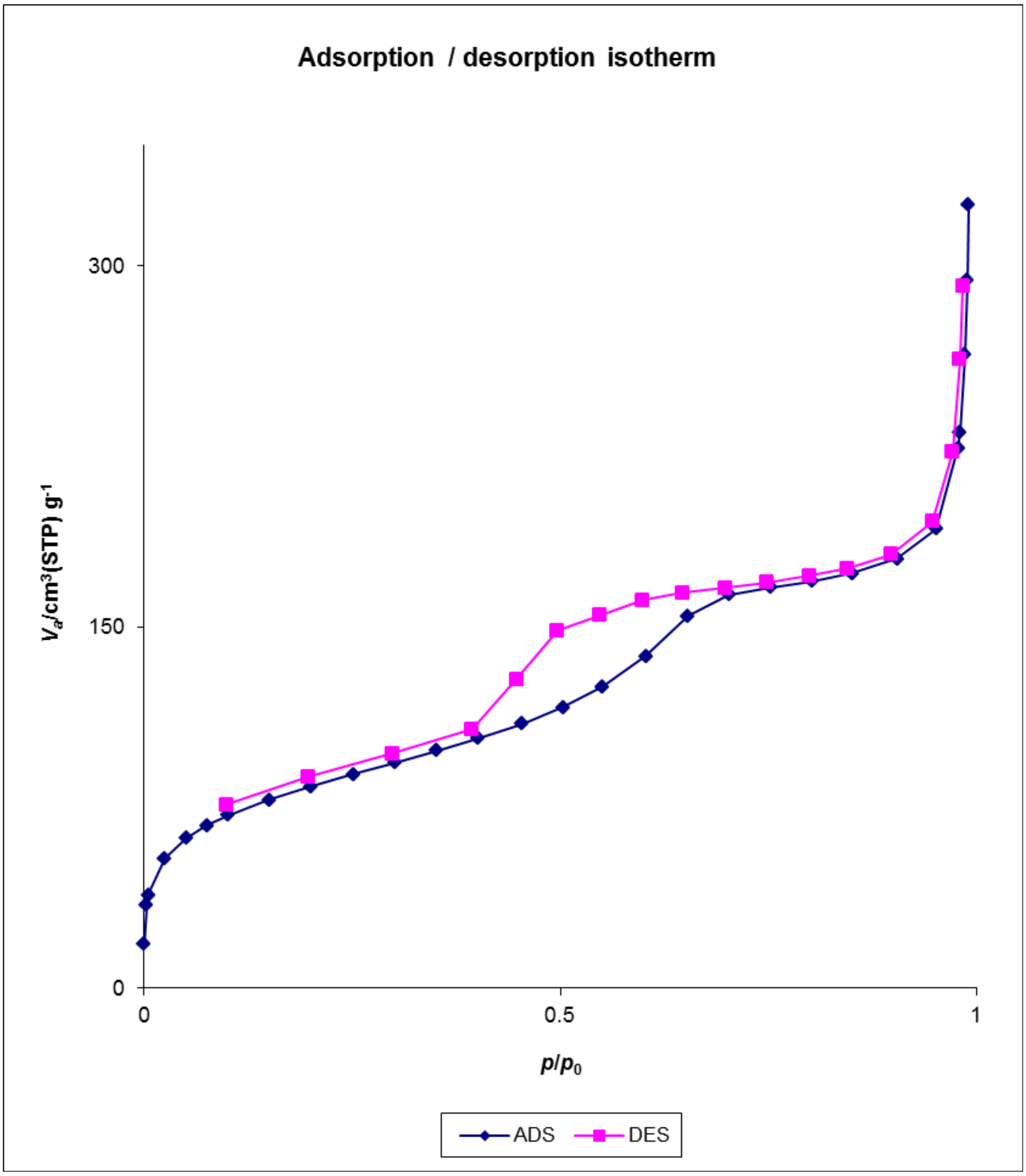


2.4.3 TEM image of SBA-15-$C_2H_4PhSO_3H$ (3a) catalyst

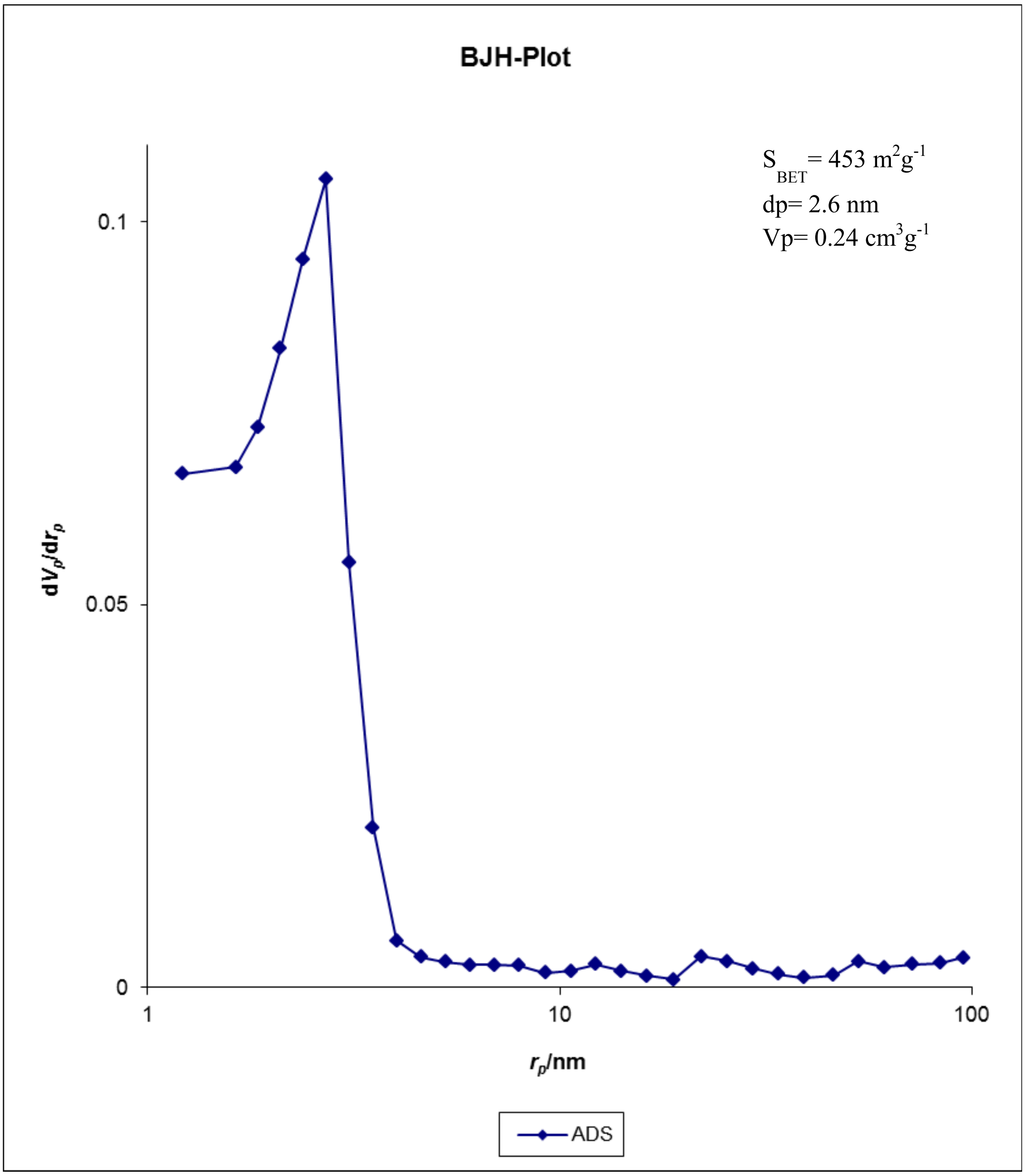


2.5 MCM-41-PrSO3H (1a)

2.5.1 Porosimetry data

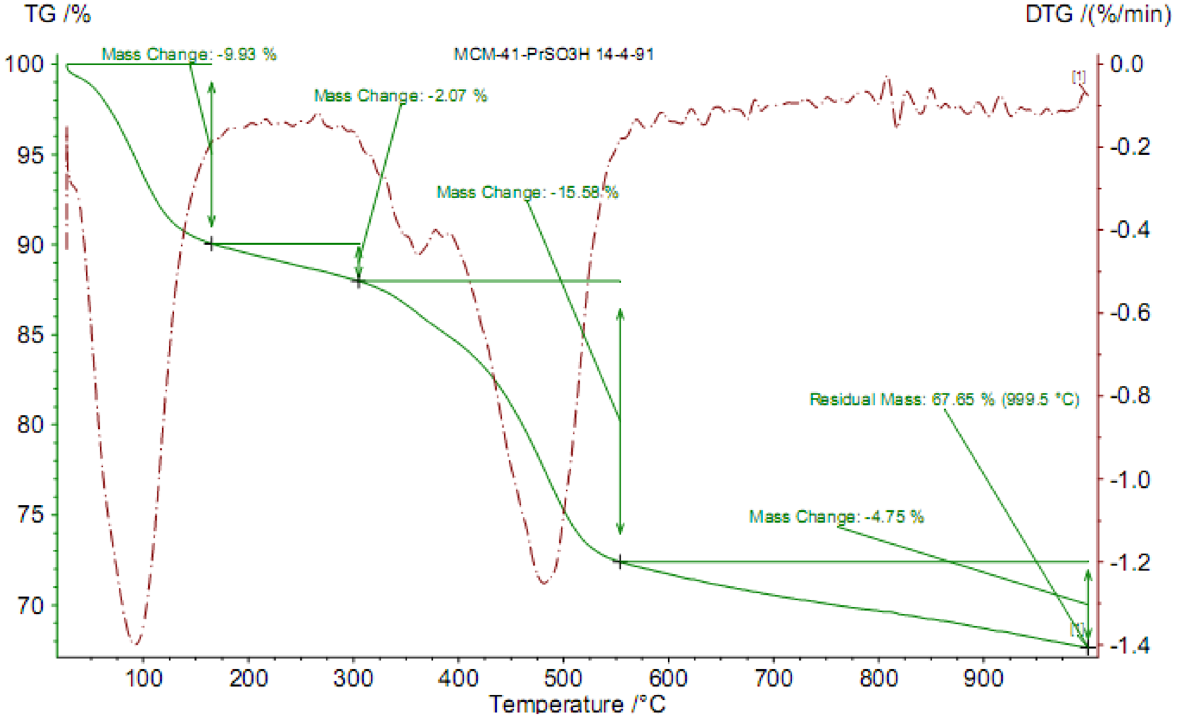


N_2 adsorption-desorption of MCM-41-PrSO3H (1a) catalyst



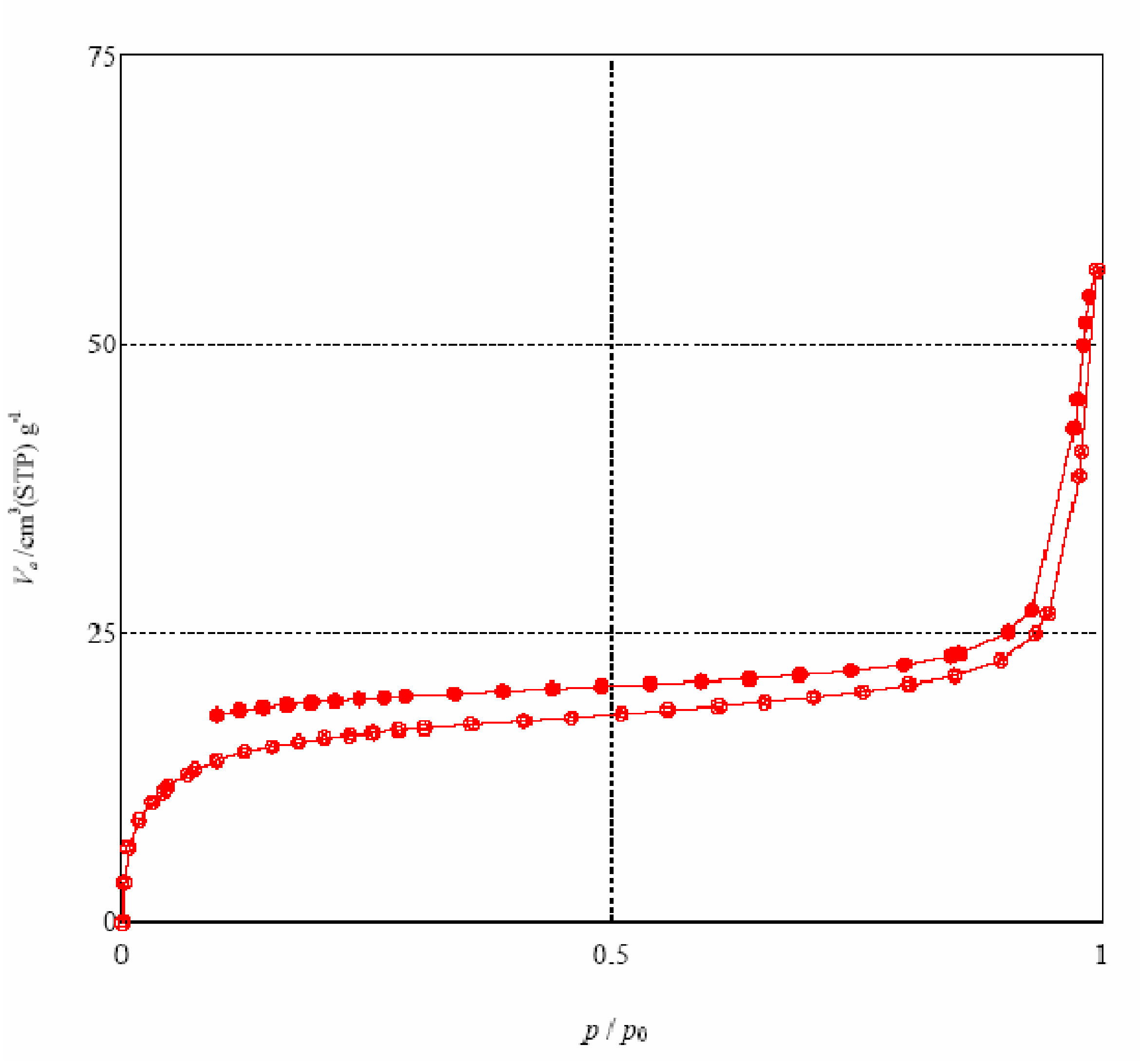
BJH analysis of MCM-41-PrSO3H (1a) catalyst

2.5.2 TGA-DTG analysis for MCM-41-PrSO3H (1a) catalyst

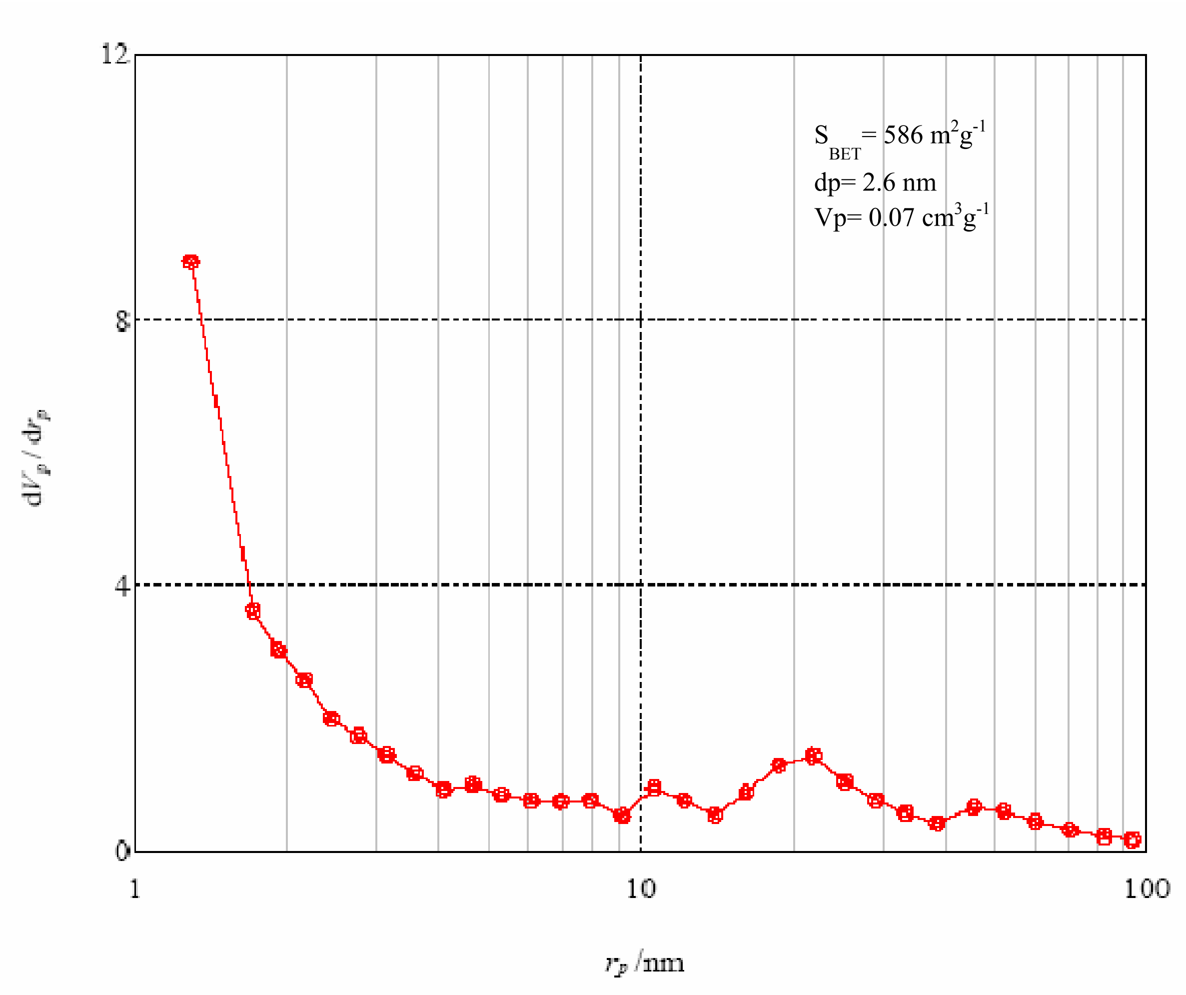


2.6 MCM-41-Ph-PrSO3H (1b)

2.6.1 Porosimetry data

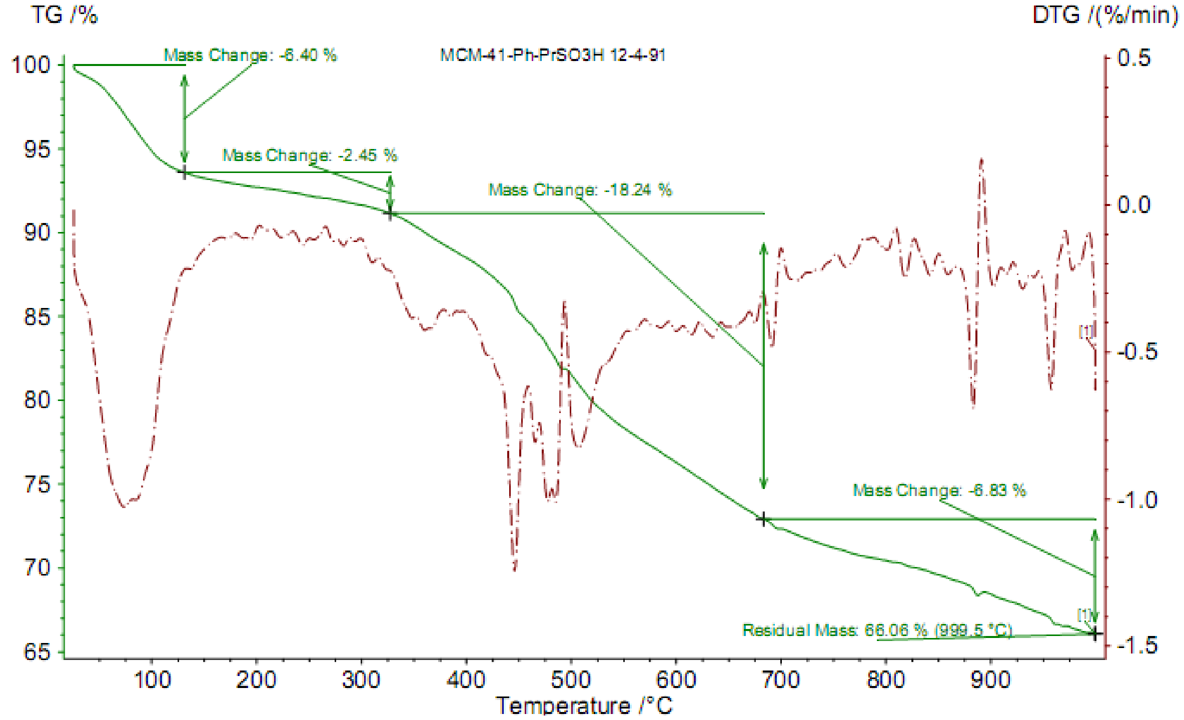


N_2 adsorption-desorption of MCM-41-Ph-PrSO3H (1b) catalyst

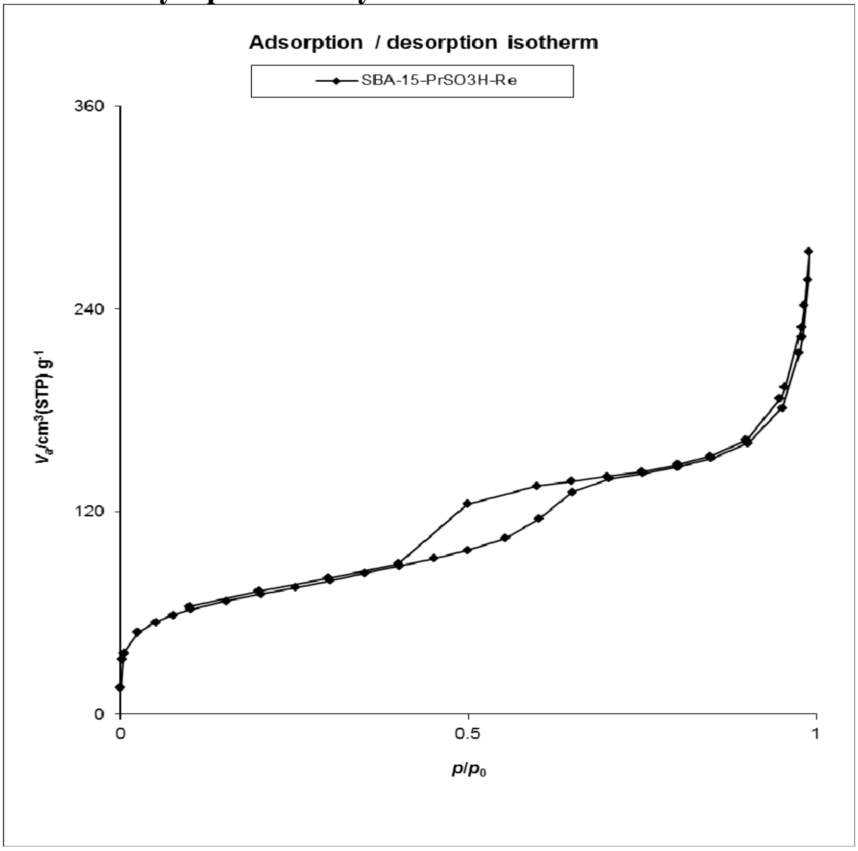


BJH analysis of MCM-41-Ph-PrSO3H (1b) catalyst

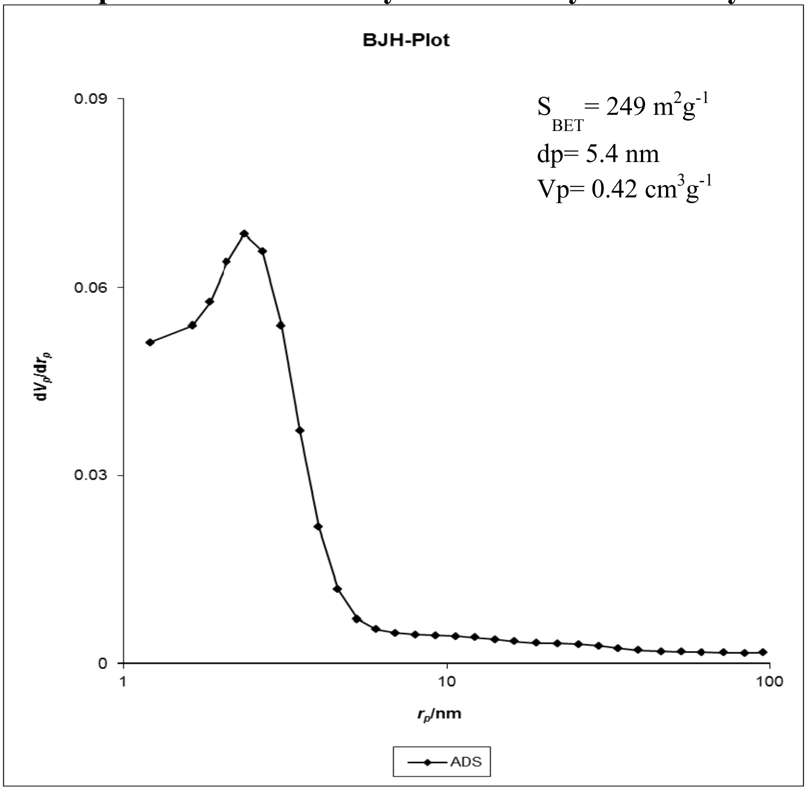
2.6.2 TGA-DTA analysis for MCM-41-Ph-PrSO3H (1b) catalyst



2.7 Recycled 2a catalyst porosimetry data



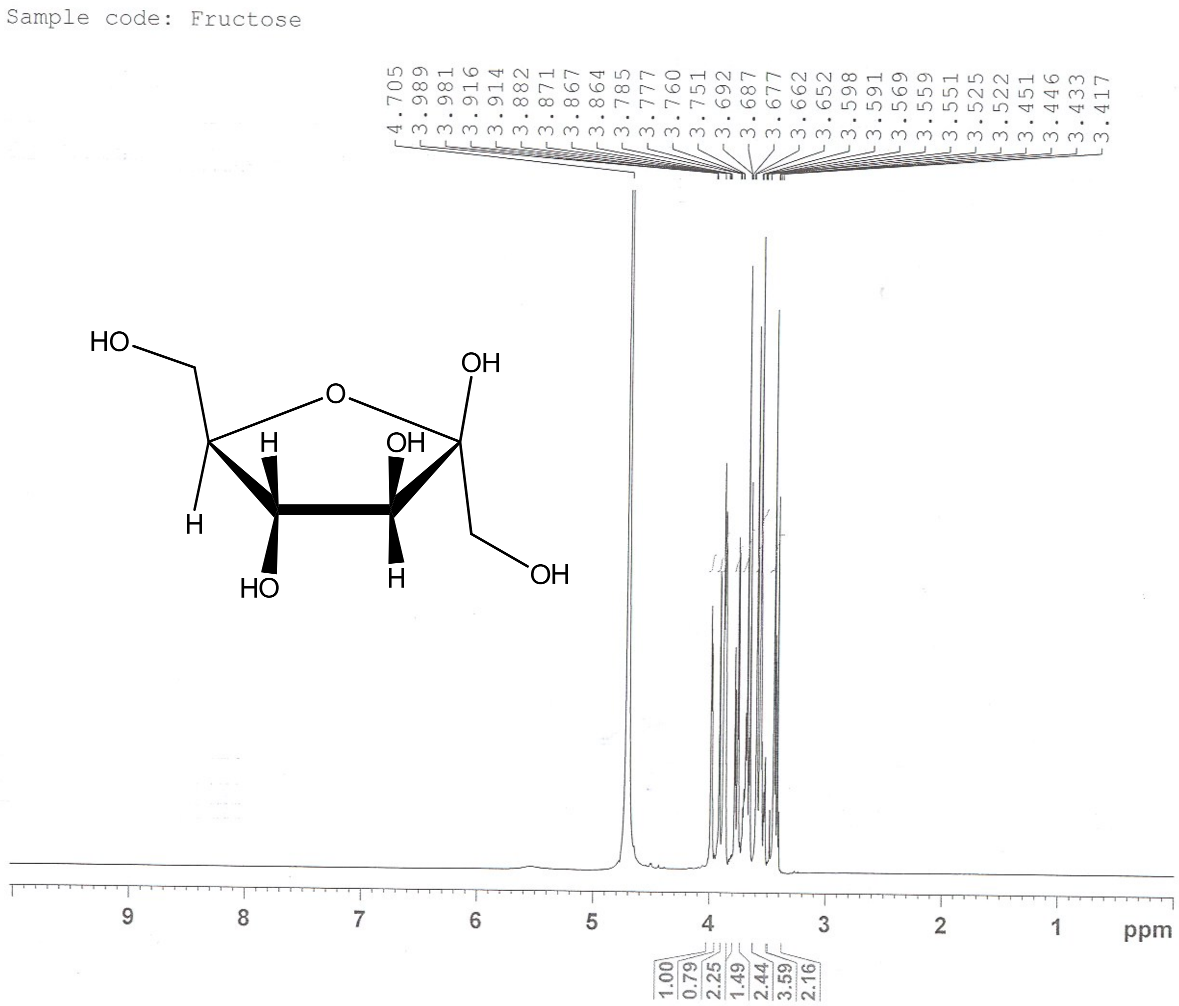
N2-sorption isotherm of recycled 2a catalyst after 3 cycles.



BJH pore size distribution of recycled 2a catalyst after 3 cycles.

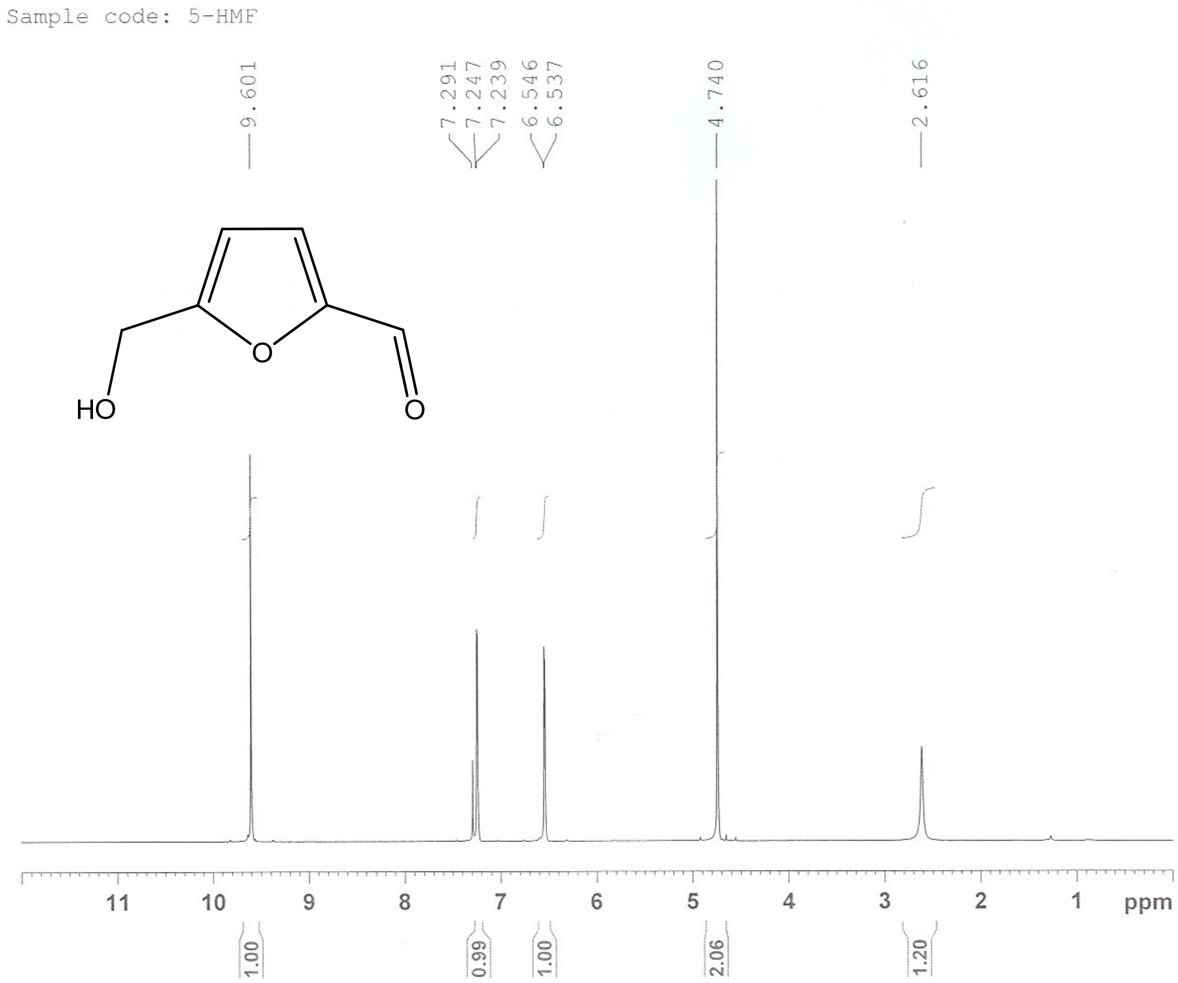
3 NMR analysis

3.1 Fructose

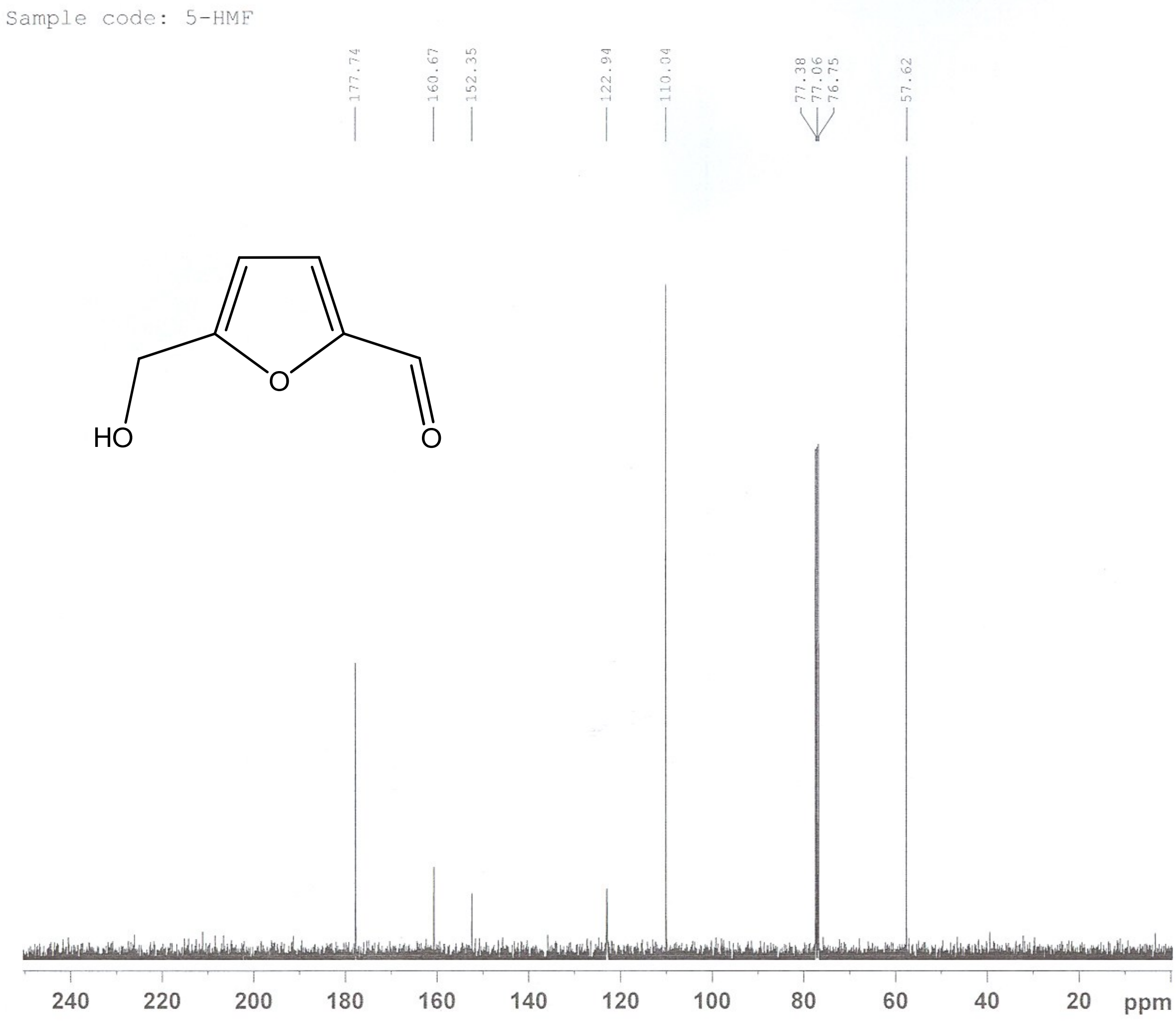


^{1}HNMR of Fructose in D_2O

3.2 5-Hydroxymethylfurfural (5-HMF)



^{1}HNMR of 5-Hydroxymethylfurfural (5-HMF) in $CDCl_3$



^{13}CNMR of 5-Hydroxymethylfurfural (5-HMF) in $CDCl_3$

4 Calculation based on Mixture ^{1}HNMR

After completion of the reaction, 2 ml water and 3 ml acetone were added to the mixture. The catalyst was recovered by centrifuge and solvent was evaporated under rotary evaporator. Finally, the product was dissolved in 0.5 ml D_2O for NMR analysis. The conversion and selectivity was calculated based on NMR by standard addition of fructose.

$$Remaining\ fructose\ equivalant\ hydrogen = A = \frac{\int_{3.4\,ppm}^{4.1\,ppm} HNMR}{7}$$

$$Remaining\ fructose\ equivalant\ hydrogen\ after\ STD\ addition\ of\ fructose = B = \frac{\int_{3.4\,ppm}^{4.1\,ppm} HNMR}{7}$$

$$A - B \ldots (mmol, Fructose\ STD)$$

$$A \ldots\ldots\ldots x(remained\ \ Fructose\ in\ the\ mixture)$$

$$x = \frac{A \times [STD\ Fructose\ (mmol)]}{B - A}$$

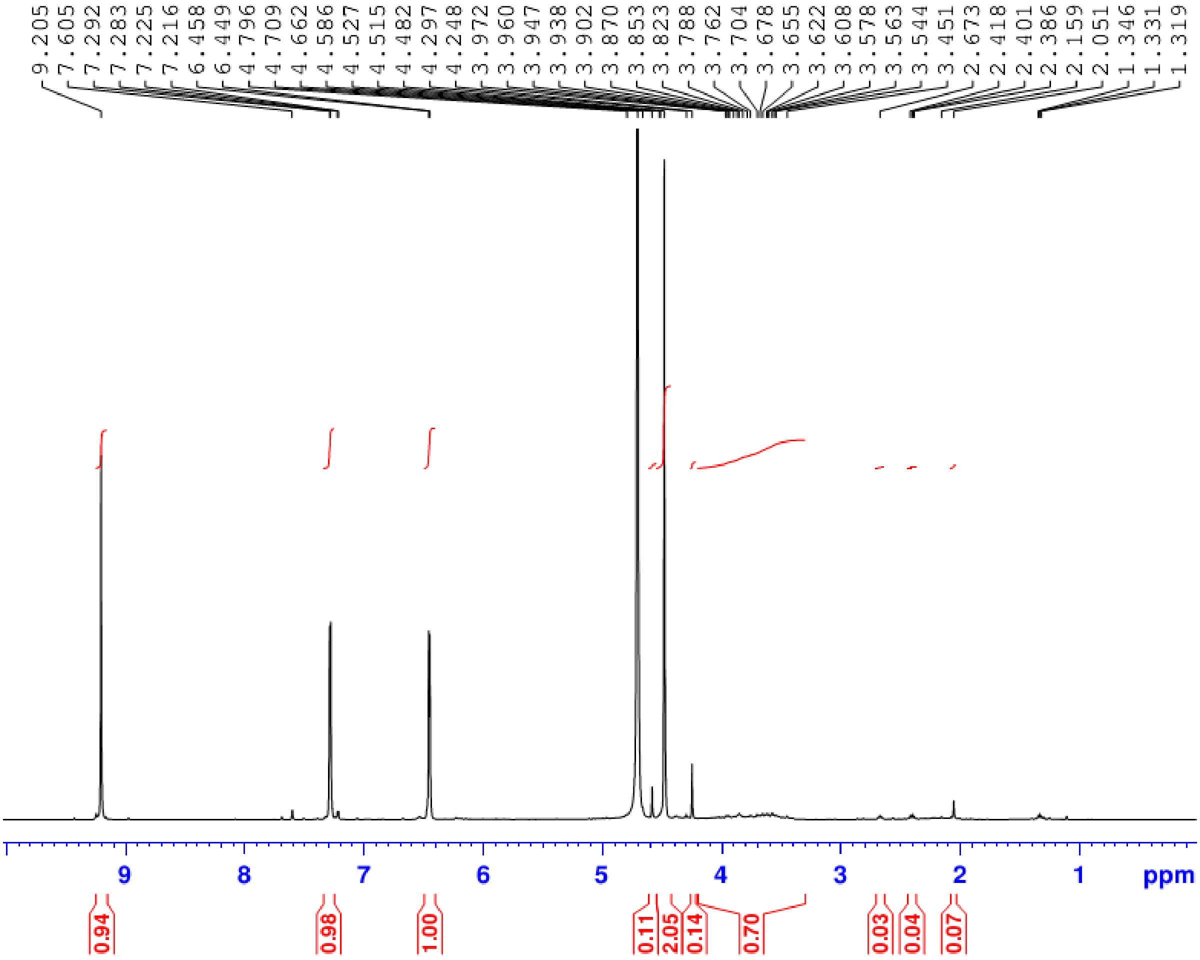
$$Conversion(\%) = (1 - x) \times 100$$

$$5 - HMF(equivalent\ Hydrogen) = \int_{6.45\,ppm}^{6.5\,ppm} HNMR$$

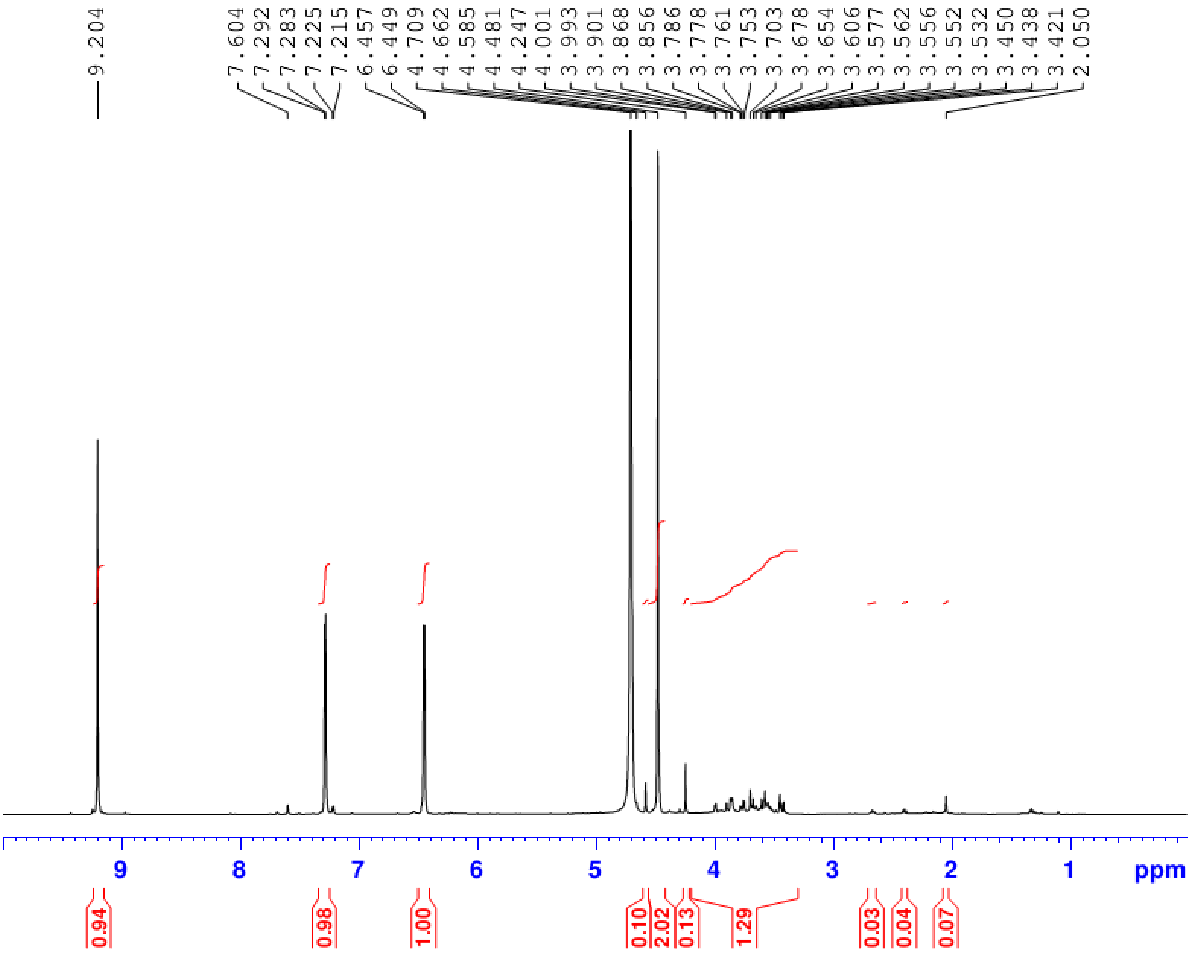
$$y\ (HMF\ Yield) = \frac{\int_{6.45\,ppm}^{6.5\,ppm} HNMR}{A} \times x \times 100$$

Selectivity (%)= [(y/{(1-x)*100}]*100

4.1 Mixture and calculations:



(Mixture ^{1}HNMR)



(Mixture+ 10 mg STD Fructose) ^{1}HNMR

$$A = \frac{\int_{3.4\,ppm}^{4.4\,ppm} HNMR}{7} = \frac{0.7}{7} = 0.10$$

B=1.29/7=0.18

mmol fructose STD added=10 mg/180mgmol^{-1}=0.055

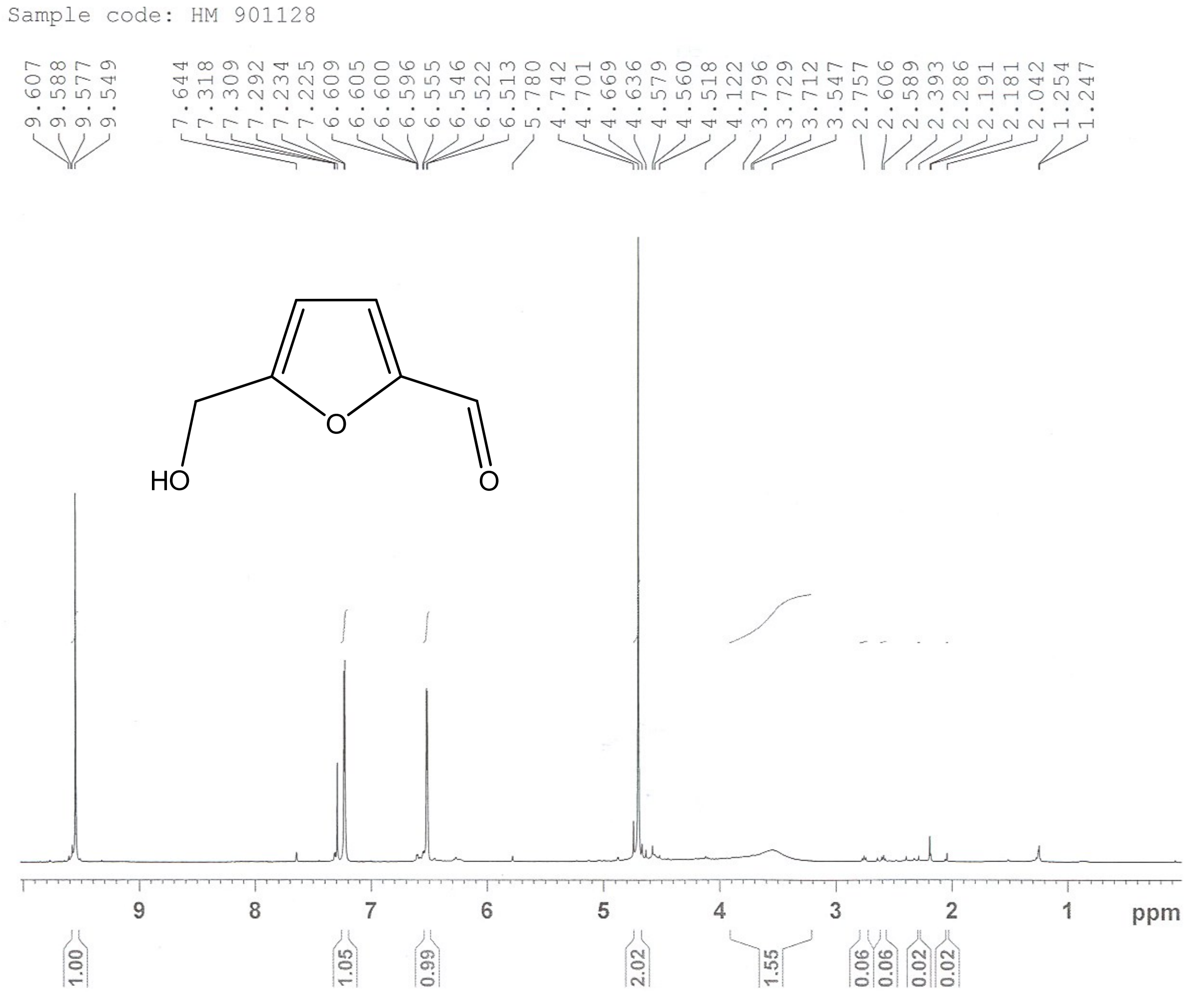
x=0.1*0.055/0.08=0.07

$$Conversion(\%) = (1 - x) \times 100 = \mathbf{93\%}$$

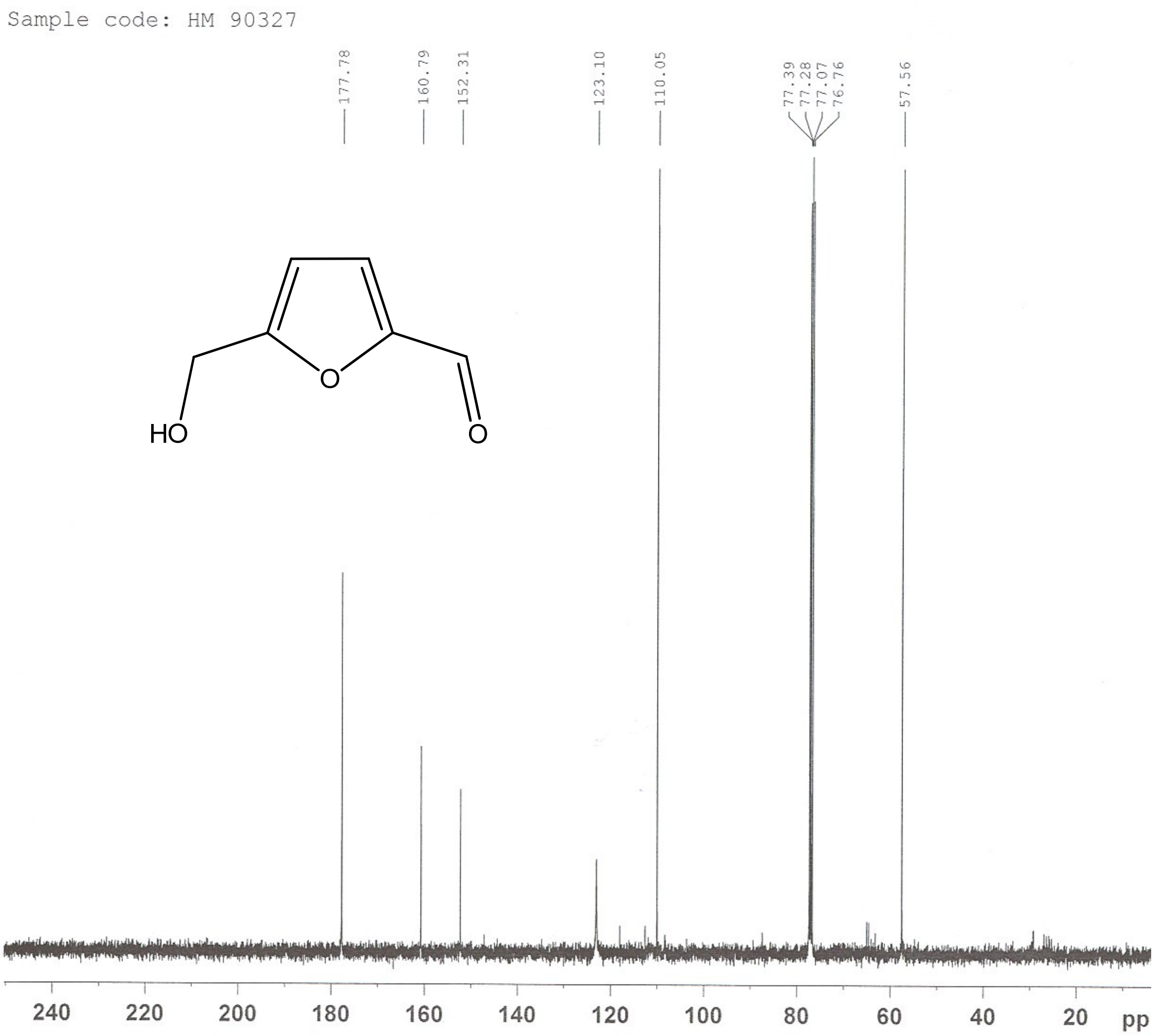
$$y\,(HMF\ Yield) = \frac{\int_{6.45\,ppm}^{6.5\,ppm} HNMR}{A} \times x \times 100 = 1/0.1*0.07*100 = \mathbf{70\%}$$

Selectivity (%)= y/[(1-x)*100]*100=70/93)*100=**75.3%**

Isolated 5-HMF from reaction mixture by column chromatography (solvent=Ethyl acetate)

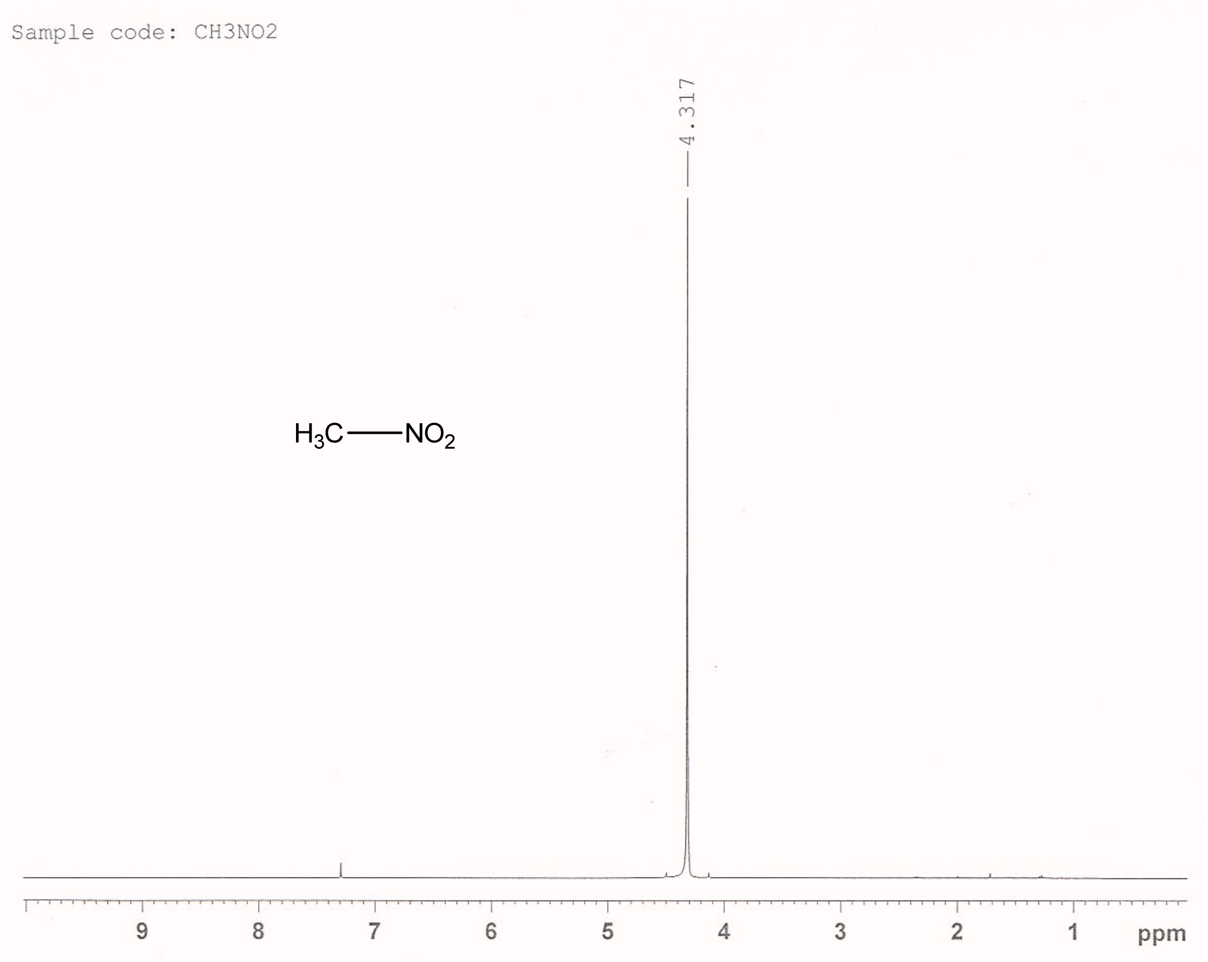


^{1}HNMR of isolated HMF (CDCl$_3$)



^{13}CNMR of isolated 5-hydroxymethylfurfural in $CDCl_3$

CH_3NO_2



^{1}HNMR of nitromethane in $CDCl_3$

5 References

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[1] M. H. Lim, C. F. Blanford and A. Stein, *Chem. Mater.*, 1998, **10**, 467.

[2] D. Margolese, J. A. Melero, S. C. Christiansen, B. F. Chmelka and G. D. Stucky, *Chem. Mater,*. 2000, **12**, 2448.

[3] B. Karimi and D. Zareyee, *Org. Lett.*, 2008, **10**, 3989-3992.

[4] J. A. Melero, G. D. Stucky, R. van Grieken, G. Morales, *J. Mater. Chem.,* 2002, **12**, 1664.