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RESEARCH ARTICLE

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COMPARISON OF NIOBIUM AND ZIRCONIUM OXIDES-BASED CATALYSTS AND SUPER ACIDIFIED ION EXCHANGE RESINS AS EFFICIENT CATALYSTS FOR DEHYDRATION OF FRUCTOSE TO HMF

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ABSTRACT

Background: The obtaining of HMF from fructose reaction was studied using a continuous packed bed tubular reactor (PBR) using catalysts based on niobium and zirconium compounds, as well as modified ion exchange resins (resins CT275 and SGC650H superacidified) and, using as solvents, DMSO and aqueous solutions of DMSO. Among all catalysts prepared, the superacidified ion exchange resins presented the best performance, followed by the catalysts based on zirconium compounds and those produced with niobium compounds. Sulfonating the acidic cationic has a positive effect on conversion and yield of HMF increasing at least 10% for the SGC650H maintaining the same residence time. The best results observed were for the feeding system consisting of DMSO and fructose. The presence of mesoporous seems to reduce the performance of supported zirconium materials studied as catalysts. For all catalysts used, it was observed that the presence of water in the solvent reactive promote a marked decrease in the conversion of fructose to HMF.

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INTRODUCTION

5-Hydroxymethyl-2-furfural (HMF) is a furanic derivative obtained from renewable sources that can replace petroleum derivatives. It is recognized as an important (chemical platform) building block because of its industrial potential to synthesize a wide variety of higher value-added chemical compounds such as biofuels, solvents, pharmaceuticals and other biopolymer precursors^[01, 02]. Selective hydrogenation of HMF produces 2,5-dimethylfuran (DMF) as an example of biofuel with ethanol-like properties and greater miscibility than diesel^[03]. Selective oxidation of HMF can form 2,5-furan dicarboxylic acid (FDCA), the latter with the potential to replace terephthalic acid as a monomer to produce polyesters^[04]. The hydrolysis of HMF forms levulinic acid^[05], another building block for synthesizing acrylate polymers and fuel additives, such as γ -valerolactone (GVL)^[06], 2-methyltetrahydrofuran and ethyl levulinate^[07]. HMF has been synthesized, mainly, by fructose dehydration using acid catalysts^[08, 09]. Several catalyst systems have been studied^[10-24] for HMF synthesis including homogeneous and heterogeneous catalysts, different solvent systems as aqueous organic or biphasic. Tacacima et al. ^[25] showed a high yield and selectivity in conversion of fructose to HMF over a gel-type strongly acidic resin (SGC650H) as catalyst and dimethylsulfoxide (DMSO) as solvent.

Moreover, comparison between batch reactor (PBR) and continuous packed bed reactor (PBR)^[25] showed that that PBR are more effective for this kind of study because the residence time (τ_{PBR}) is lower than the time of reaction spent in BTR (t_{BTR}) which reduces the contribution of homogenous reactions. The Eq. 1 shows the relation among catalyst concentration, rates of reaction and reaction time.

$$\frac{\tau_{PBR}}{t_{BTR}} = \frac{C_{BTR\ cat}}{C_{PBR\ cat}} = \frac{r_{Fruc}^{BTR}}{r_{Fruc}^{PBR}} \quad \text{Eq. 1}$$

The present work explores the use of PBR to test many acid catalysts in the conversion of fructose to HMF using dimethyl sulfoxide (DMSO) as solvent aiming to contribute to the state of art.

MATERIALS AND METHODS

Catalyst preparation

Preparation of superacidified ion exchange resins: This procedure was meant to increase the degree of sulfonation (DS), the acid strength (pKa) in order to enhance the activity. The catalysts were prepared using the commercial strong acidic ion-exchange macroreticular resin CT275 and a gel type resin SGC650H. The resins

individually were superacidified contacting them with fuming H_2SO_4 containing 65% of SO_3 in excess following literature indications [26, 27]. The acid was added dropwise until the presence of excess liquid be noticed. The flasks were kept in empty desiccator for a period of 48 h and after the end of this period they were washed with deionized water until the effluent be virtually free of acid and almost neutral (pH = 4.0). After the superacidified catalyst were kept in desiccator at least for 48 h before its use.

Preparation of catalyst based on niobium and/or zirconium compounds: Monofunctional (containing niobium or zirconium oxides) and bifunctional (containing niobium and zirconium oxides) nanoporous catalysts were prepared by mixing and hydrolyzing the compounds with colloidal silica sol Ludox 30 AM from Sigma-Aldrich, following the classical procedure of Derouane et. al. [28]. Niobium oxide (HS340 from CBMM) and ammoniacal niobium oxalate (ANO from CBMM) were the compounds used to prepare the catalysts containing niobium. To prepare the zirconium-containing catalysts, zirconyl nitrate (99.9% from Sigma-Aldrich) was hydrolyzed in Ludox 30 AM. All catalysts contained fixed niobium and/or zirconium contents equal to 5% by mass. The hydrolysis process occurred through the continuous mechanical and thermal actions provided by a heated magnetic stirrer maintained at a controlled temperature of 60 °C for a period of 48 h. All materials were then oven dried at 60 °C for 48 h. After drying, the materials were submitted to grinding and sieving, being particles ranging in size from 1 to 2 mm used in reaction.

Preparation of catalyst based on supported niobium and zirconium oxides on SBA-15 and MCM-41 mesoporous materials: SBA-15 [29] were synthesized with use of Pluronic® P123 ($\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$) with average molecular weight of 5800 g/mol) from Sigma-Aldrich brand. The synthesis was carried out using a homogeneous mixture containing 25.0 g of Pluronic® P123, 100 cm^3 of hydrochloric acid / HCl (35%) and 400 g of deionized water. The solution was heated to 45 °C with constant stirring and after 2 h, 30 g of tetraethyl orthosilicate (TEOS) was added until a gel was formed, which was maintained for a period of 24 h at a temperature of 45 °C. After that period, the obtained gel was filtered and repeatedly washed with distilled water, and finally dried in a ventilated oven at 60 for 48h. The product obtained was then calcined at a temperature of 500 °C for a period of 6 h in order to remove Pluronic® P123. MCM-41[30] was obtained using tetraethyl orthosilicate (TEOS) as a source of silica and cetyltrimethylammonium bromide (CTABr) as a template agent. The synthesized gel was prepared using 17.0 g of TEOS in an aqueous solution containing 2.0 g of CTABr and 0.5 g of sodium hydroxide. After stirring the solution for 2 h at 25 °C, the resulting homogeneous mixture was then crystallized under hydrothermal conditions at 110 °C in a Teflon coated autoclave for a period of 96 h. After this time, the solid obtained was filtered and washed with deionized water and dried in a ventilated oven at 80 °C. Finally, dried product was calcined at 600 °C for 24 h in order to remove the CTABr. Subsequently to this stage, the already calcined product was impregnated with salts of niobium (ammonia niobium oxalate) or zirconium nitrate (zirconium nitrate). The impregnation process occurred through the continuous mechanical and thermal actions provided by a heated magnetic stirrer maintained at a temperature of 60 °C for a period of 48 hours. Then, obtained materials were dried at 60 °C for 48 hours before use.

Catalyst characterizations: The catalyst was evaluated in relation to N_2 adsorption in Micromeritics Gemini VII. The FTIR-ATR was done in a Thermo Nicolet 6700. Scanning electronic microscopy was done in a JEOL JSM 5900 equipped with EDS/EDX. X-Ray diffractograms were obtained in a Shimadzu XRD-7000. The titrated acidity was obtained with NaOH (0.1 mol.L⁻¹).

Catalyst evaluation in continuous packed bed reactor (PBR): Initially, the feed solutions containing 4.5% (m/m) of fructose (Synth 98-102%) were prepared with the following solvents: anhydrous dimethyl sulfoxide (DMSO 99.9% Neon) and mixtures containing DMSO and deionized water (9:1) molar (mol/mol) and (9:1) in

mass(m/m). The catalysts evaluation was done in a tubular reactor made in 316 L SS (1/2" x 10 cm) with an internal volume of 8 mL (Figure 1), which is put in oil bath at 90 °C (Figure 2). This temperature is close to the isokinetic temperature for this process[25].



Figure 1. Packed bed reactor (PBR)

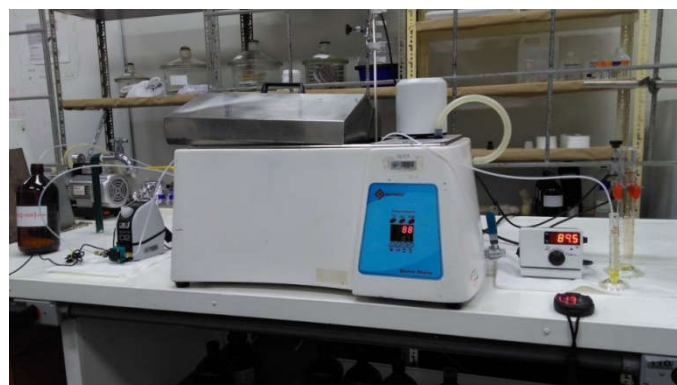


Figure 2. PBR System

The test begins filling the reactor with DMSO and pumping it with a flow of 2 mL/min for 30 minutes, time enough for conditioning the catalyst and stabilize the temperature (90 °C). After stabilization, the feed solution was modified, and the start of each test was considered after waiting a period equal four residence-time thus ensuring that the system was in a steady state. For each flow flows (2.0 mL.min⁻¹; 1.0 mL.min⁻¹; 0.50 mL.min⁻¹ and 0.25 mL.min⁻¹) corresponding to the residence time of 4, 8, 16 and 32 minutes the procedure is repeated. After that time samples with a fixed volume of 10 mL are collected to be analyzed. After sampling each feed solution, a new cleaning was performed in the pumping system using only pure DMSO. Subsequently, the feed solution was changed, and another test with the same reaction temperature was started. During the course of these reactions the feed sequence was maintained unchanged, maintaining the following sequence: anhydrous DMSO + 4.5% fructose; DMSO + deionized water (9:1, molar) + 4.5% fructose, and finally DMSO + deionized water (9:1, mass) + 4.5% fructose. The samples were stored under refrigeration at -6 °C. Analysis of HMF synthesized in DMSO was performed by HPLC using a reverse-phase Shimpack CLC-ODS(M)[®] column operating at 30 °C, binary eluent flow to 1.2 mL.min⁻¹ of acetonitrile and 1% acetic acid (m/m) at the ratio of 20:80. The 266 nm UV-Vis detector operating at 40 °C showed low sensitivity to the DMSO solvent and high to the HMF product, so that samples were diluted with water [25]. After removal from the refrigerator, the samples were naturally warmed to room temperature and, after this temperature stabilization, were filtered with a 0.20 μm syringe filter before being injected in the HPLC. The amount of fructose present in each sample was determined enzymatically using the D-Glucose / D-Fructose Enzytec[®] Produced by R-Biopharm AG, followed by UV-Vis spectrophotometry analysis at 340 nm. The conversion (X) was calculated by the Eq. 2 and the yield (Y) in HMF was calculated by Eq. 3. Selectivity could be calculated by Eq.4.

$$X(\%) = \left(1 - \frac{(\text{Fructose molar concentration})}{(\text{Fructose molar concentration feed})}\right) * 100 \quad \text{Eq. 2}$$

$$Y(\%) = \frac{\text{HMF molar concentration}}{\text{Fructose molar concentration feed}} * 100 \quad \text{Eq. 3}$$

$$S(\%) = \frac{Y}{X} * 100 \quad \text{Eq. 4}$$

RESULTS AND DISCUSSION

The characterization of prepared catalyst is presented in Supporting Information (SI). The procedure to remove the excess of acid used in the treatment of superacidified resin cause some neutralization of acid groups revealed by the sodium content in these materials according to EDS analysis. The titrated acidity of the samples showed that even with this partial neutralization, the acidic resins have the higher acidity of the prepared materials, followed by materials prepared with zirconium salt. The results of concentration of obtained HMF are presented in (SI) in diluted to perform the HPLC. The concentrations of fructose in samples obtained with anhydrous DMSO with the highest residence time are also presented in SI. The data obtained in quantitative analysis carried out allowed to characterize a relationship inversely proportional between the flow rate used and the production of HMF, i.e. the higher the flow rate used, implying a lower residence time, also lower the conversion of fructose in HMF as expected.

Table 2. Conversion of fructose and HMF yield for the materials tested as a catalyst

Catalyst	Fructose Conversion (%)	HMF Yield (%)
CT275 _{acidified}	95.96	~ 96
SGC650H _{acidified}	93.53	~ 93
Ludox [®] + ANO	18.6	0.92
Ludox [®] + Nb ₂ O ₅	12.7	0.19
Ludox [®] + Nb ₂ O ₅ + ANO	20.0	0.93
Ludox [®] + ZrO(NO ₃) ₂	83.4	39.8
Ludox [®] + ANO + Zr[(NO ₃) ₄]	35.6	4.77
MCM 41 + ANO	21.0	0.54
MCM 41 + ZrO(NO ₃) ₂	62.6	5.18
SBA + ANO	21.2	0.22
SBA + ZrO(NO ₃) ₂	67.1	9.24

The superacidified resins presented the highest conversions and yields among all tested catalyst. In both cases CT275 e SGC650H these values are 96.0% and 93.5% respectively with virtual selectivity of 100% as expected [25]. These values are superior and comparable to published data [7, 16, 20] obtained at higher temperature and reaction time. The regular SGC650H resin [25] at the same residence time showed an interpolated conversion of 85%. The acidification process has a positive influence on conversion of fructose probably cause by the increase of acid groups and the increase of acid strength (pKa) cause by further sulfonating of aromatic compounds. Moreover, recent papers are devoted to sulfonated catalysts revealing the importance of Brønsted acid sites in this reaction [26,27,31-35, 37]. It is possible to check the influence of the water in this process, once the conversion of fructose in HMF is also inversely proportional to the amount of water present in the solvent used. It is noticed mainly in materials with the highest acidity, i.e., ion exchange resins and zirconium-based catalysts. The niobium-based catalyst showed all the lowest conversion ranging from 18 to 21% and less than 1% of yield. These conversions are lower than other reported values pointed in literature [11,36,37]. One possible cause for this is the lack of thermal treatment i.e., hydrothermal[36] or any calcination. The group of materials prepared with ZrO(NO₃)₂ showed the second highest activity a conversion of 83.4% and a yield of almost 40%. These values are superior to that found in other studies [38,39]. It is possible to realize that the presence of mesoporous in zirconium supported on MCM-41 and on SBA-15 cause a reduction of yield probably promoting humins and/or oligomers formation [40]. This lower selectivity was observed in other studies [41, 42] even with sulfonated SBA-15 [43].

CONCLUSION

Superacidified resins produced by sulfonation of the commercial ion exchange resins CT275 and SGC650H showed a high efficiency in the conversion of D-fructose to HMF, using as a solvent the dimethyl sulfoxide (DMSO) under the test conditions. Both the activity as the selectivity shown by the high yield were superior to all other catalysts, confirming that the Brønsted acid sites are better suited to perform this reaction under the conditions studied. The acidification process has a positive influence on conversion of fructose probably caused by the increase of the number of acid groups and the increase of acid strength caused by further sulfonating of aromatic compounds. The catalysts based on zirconium presented a better performance when compared to those produced with niobium compounds, in particular the catalyst named Ludox[®] + ZrO(NO₃)₂. The oxide-based catalysts niobium and oxalate of niobium and ammonium (ANO) presented yield underwhelming when compared with the results extracted from scientific literature consulted. The mixed catalyst produced by mixing niobium and zirconium compounds also did not present a significant efficiency when compared to those consisting exclusively for niobium or zirconium compounds. The results obtained in the conversion of fructose using catalysts supported on MCM-41 as to those supported in SBA-15 obtained similar results, however those impregnated with zirconium showed superior results to impregnated with niobium. Overall, it was also possible to characterize that adding water to the reaction system substantially reduces the chemical conversion of fructose to HMF in all cases.

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Supplementary Information: Comparison of niobium and zirconium oxides-based catalysts and superacidified ion exchange resins as efficient catalysts for dehydration of fructose to HMF.

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1 - Surface area (m²/g), pore volume (mL/g) mean pore diameter (nm)

Catalyst	Surface area (m ² .g ⁻¹)	Pore diameter (nm)	Pore volume (mL.g ⁻¹)
CT275 _{acidificated}	22	26.285	0.151
SGC650H _{acidificated}	(*)	(*)	(*)
Ludox [®] + ANO	93	10.479	0.244
Ludox [®] + Nb ₂ O ₅	184	5.041	0.232
Ludox [®] + Nb ₂ O ₅ + ANO	83	7.342	0.152
Ludox [®] + ZrO(NO ₃) ₂	75	9.662	0.224
Ludox [®] + ANO + ZrO(NO ₃) ₂	110	6.352	0.175
MCM 41 + ANO	553	3.757	0.520
MCM 41 + ZrO(NO ₃) ₂	521	3.886	0.506
SBA + ANO	394	4.034	0.398
SBA + ZrO(NO ₃) ₂	402	4.086	0.411

2- Results of enzymatic determination of fructose for diluted samples in spectrometer UV-Vis

Sample	Absorbance(-)			C _{D-fructose initial} (g.L ⁻¹ sample)	C _{D-fructose final} (g.L ⁻¹ sample)	C _{D-fructose converted} (g.L ⁻¹ sample)	Conversion X (%)
	A ₂	A ₃	ΔA				
blanck	0.182	0.237	0.084	n/a	n/a	n/a	n/a
CT275 _{acidificated}	0.189	0.265	0.022	0.495	0.020	0.475	96.0
SGC650H _{acidificated}	0.191	0.280	0.036	0.495	0.032	0.463	93.5
Ludox [®] + ANO	0.183	0.693	0.455	0.495	0.403	0.092	18.6
Ludox [®] + Nb ₂ O ₅	0.178	0.665	0.487	0.495	0.432	0.063	12.7
Ludox [®] + Nb ₂ O ₅ + ANO	0.189	0.635	0.446	0.495	0.396	0.099	20.0
Ludox [®] + ZrO(NO ₃) ₂	0.199	0.344	0.093	0.495	0.082	0.413	83.4
Ludox [®] + ANO + ZrO(NO ₃) ₂	0.182	0.597	0.360	0.495	0.319	0.176	35.6
MCM 41 + ANO	0.179	0.675	0.441	0.495	0.391	0.104	21.0
MCM 41 + ZrO(NO ₃) ₂	0.184	0.447	0.209	0.495	0.185	0.310	62.6
SBA 15 + ANO	0.182	0.622	0.440	0.495	0.390	0.105	21.2
SBA 15 + ZrO(NO ₃) ₂	0.186	0.340	0.184	0.495	0.163	0.332	67.1

A₂, A₃ and ΔA are intermediate values in the enzymatic method for fructose determination

Source: Author

Item 3 – HPLC results

C_{fructose} in feed = 0.279 mmol/mL or mol/L

3.1. Ion Exchangeresin CT275 superacidificated.

Flow/residence time	DMSO anhydrous + 4.5% fructose		DMSO+H ₂ O (9:1 molar) + 4.5% fructose		DMSO+H ₂ O (9:1 massa) + 4.5% fructose	
	Concentration					
Q (mL.min ⁻¹)	µg·mL ⁻¹	mmol·L ⁻¹	µg·mL ⁻¹	mmol·L ⁻¹	µg·mL ⁻¹	mmol·L ⁻¹
2.00 (space time: 4 min)	16705	132.43	4200	33.30	1522	12.07
1.00 (space time: 8 min)	25281	200.45	14036	111.28	3208	25.43
0.50 (space time: 16min)	34586	274.24	13816	109.55	10664	84.56
0.25 (space time: 32 min)	38139	302.41	20250	160.57	14051	111.41

3.2. Ion Exchange resin SGC650H superacidificated.

DMSO anhydrous + 4.5% fructose		
Flow/residence time		
Q (mL.min ⁻¹)	µg·mL ⁻¹	mmol·L ⁻¹
2.00 (space time: 4 min)	16108.9	127.73
1.00 (space time: 8 min)	23436.9	184.84
0.50 (space time: 16 min)	25562.9	202.70
0.25 (space time: 32 min)	33370.2	264.60

3.3. Ludox[®] + ANO.

Flow/residence time	DMSO anhydrous + 4.5% fructose		DMSO+H ₂ O (9:1 molar) + 4.5% fructose		DMSO+H ₂ O (9:1 massa) + 4.5% fructose	
	Concentration					
Q (mL.min ⁻¹)	µg·mL ⁻¹	mmol·L ⁻¹	µg·mL ⁻¹	mmol·L ⁻¹	µg·mL ⁻¹	mmol·L ⁻¹
2.00 (space time: 4 min)	205	1.63	14	0.11	6	0.04
1.00 (space time: 8 min)	387	3.07	8	0.06	32	0.26
0.50 (space time: 16 min)	296	2.34	12	0.10	10	0.17
0.25 (space time: 32 min)	321	2.54	9	0.07	157	1.24

3.4. Ludox[®] + Nb₂O₅

Flow/residence time	DMSO anhydrous + 4.5% fructose		DMSO+H ₂ O (9:1 molar) + 4.5% fructose		DMSO+H ₂ O (9:1 massa) + 4.5% fructose	
	Concentration					
Q (mL.min ⁻¹)	µg·mL ⁻¹	mmol·L ⁻¹	µg·mL ⁻¹	mmol·L ⁻¹	µg·mL ⁻¹	mmol·L ⁻¹
2.00 (space time: 4 min)	52	0.41	54	0.43	8	0.06
1.00 (space time: 8 min)	31	0.24	68	0.54	80	0.63
0.50 (space time: 16 min)	38	0.30	62	0.49	555	4.40
0.25 (space time: 32 min)	65	0.51	15	0.11	71	0.56

3.5. Ludox[®] + Nb₂O₅ + ANO

Flow/residence time	DMSO anhydrous + 4.5% fructose		DMSO+H ₂ O (9:1 molar) + 4.5% fructose		DMSO+H ₂ O (9:1 massa) + 4.5% fructose	
	Concentration					
Q (mL.min ⁻¹)	µg·mL ⁻¹	mmol·L ⁻¹	µg·mL ⁻¹	mmol·L ⁻¹	µg·mL ⁻¹	mmol·L ⁻¹
2.00 (space time: 4 min)	51	0.40	43	0.34	45	0.36
1.00 (space time: 8 min)	61	0.48	16	0.13	71	0.56
0.50 (space time: 16 min)	138	1.08	21	0.17	30	0.24
0.25 (space time: 32 min)	323	2.56	28	0.23	15	0.11

3.6. Ludox[®] + ZrO(NO₃)₂

Flow/residence time	DMSO anhydrous + 4.5% fructose		DMSO+H ₂ O (9:1 molar) + 4.5% fructose		DMSO+H ₂ O (9:1 massa) + 4.5% fructose	
	Concentration					
Q (mL.min ⁻¹)	µg·mL ⁻¹	mmol·L ⁻¹	µg·mL ⁻¹	mmol·L ⁻¹	µg·mL ⁻¹	mmol·L ⁻¹
2.00 (space time: 4 min)	1989	15.77	163	1.28	54	0.43
1.00 (space time: 8 min)	3458	27.41	208	1.64	61	0.48
0.50 (space time: 16 min)	11654	92.41	569	4.51	240	1.90
0.25 (space time: 32 min)	14316	109.23	1054	8.36	365	2.88

3.7. Ludox[®] + ANO + ZrO(NO₃)₂

	DMSO anhydrous + 4.5% fructose		DMSO+H ₂ O (9:1 molar) + 4.5% fructose		DMSO+H ₂ O (9:1 massa) + 4.5% fructose	
	μg·mL ⁻¹	mmol·L ⁻¹	μg·mL ⁻¹	mmol·mL ⁻¹	μg·mL ⁻¹	mmol·mL ⁻¹
Flow/residence time	Concentration					
Q (mL·min ⁻¹)						
2.00 (space time: 4 min)	275	2.18	83	0.66	107	0.84
1.00 (space time: 8 min)	855	6.77	278	2.20	75	0.60
0.50 (space time: 16 min)	644	5.10	47	0.37	49	0.38
0.25 (space time: 32 min)	1653	13.10	40	0.31	199	1.57

3.8. MCM41 – ANO

	DMSO anhydrous + 4.5% fructose		DMSO+H ₂ O (9:1 molar) + 4.5% fructose		DMSO+H ₂ O (9:1 massa) + 4.5% fructose	
	μg·L ⁻¹	mmol·L ⁻¹	μg·L ⁻¹	mmol·L ⁻¹	μg·L ⁻¹	mmol·L ⁻¹
Flow/residence time	Concentration					
Q (mL·min ⁻¹)						
2.00 (space time: 4 min)	37.4	0.30	5.9	0.04	7.7	0.06
1.00 (space time: 8 min)	47.6	0.37	13.8	0.11	11.7	0.08
0.50 (space time: 16 min)	68.2	0.54	39.1	0.31	14.3	0.11
0.25 (space time: 32 min)	186.9	1.48	52.1	0.41	30.6	0.24

3.9. MCM41 - + ZrO(NO₃)₂

	DMSO anhydrous + 4.5% fructose		DMSO+H ₂ O (9:1 molar) + 4.5% fructose		DMSO+H ₂ O (9:1 massa) + 4.5% fructose	
	μg·mL ⁻¹	mmol·L ⁻¹	μg·mL ⁻¹	mmol·L ⁻¹	μg·mL ⁻¹	mmol·L ⁻¹
Flow/residence time	Concentration					
Q (mL·min ⁻¹)						
2.00 (space time: 4 min)	1.8	0.01	258.5	2.04	94.8	0.76
1.00 (space time: 8 min)	232.7	1.84	281.9	2.23	179.4	1.41
0.50 (space time: 16 min)	616.8	4.88	1171.6	9.28	727.5	5.76
0.25 (space time: 32 min)	1794.4	14.23	1421.8	11.27	995.9	7.90

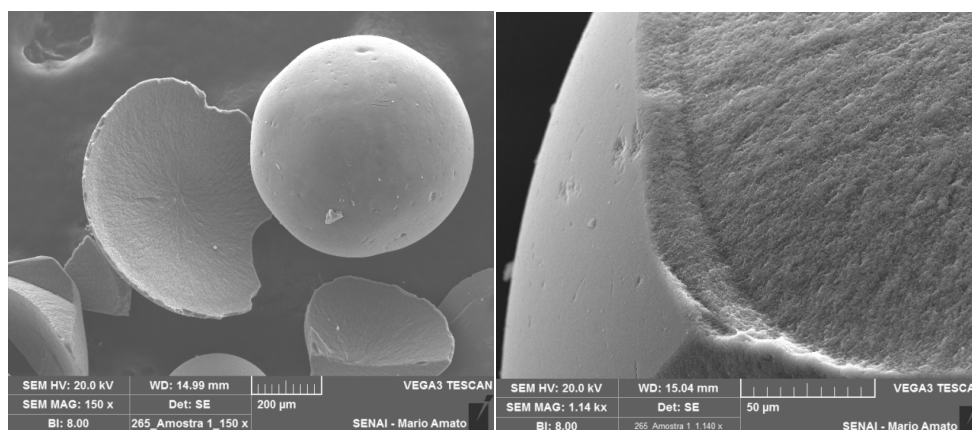
3.10. SBA – ANO.

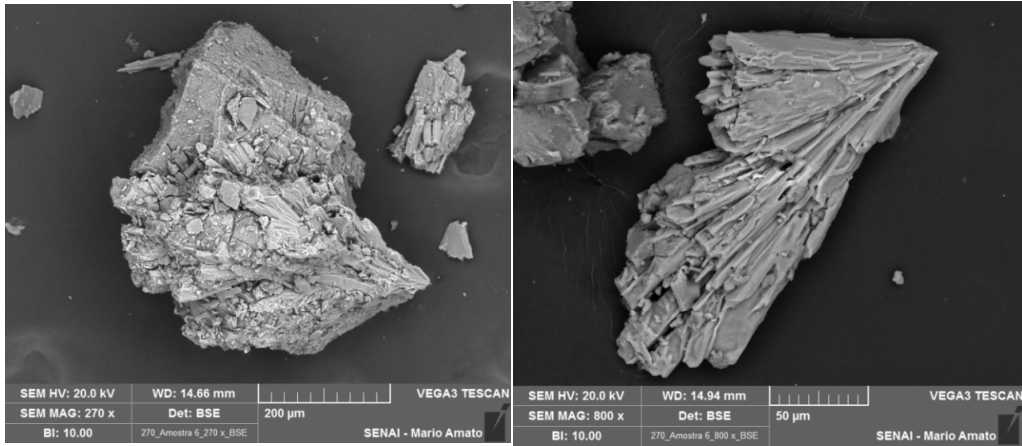
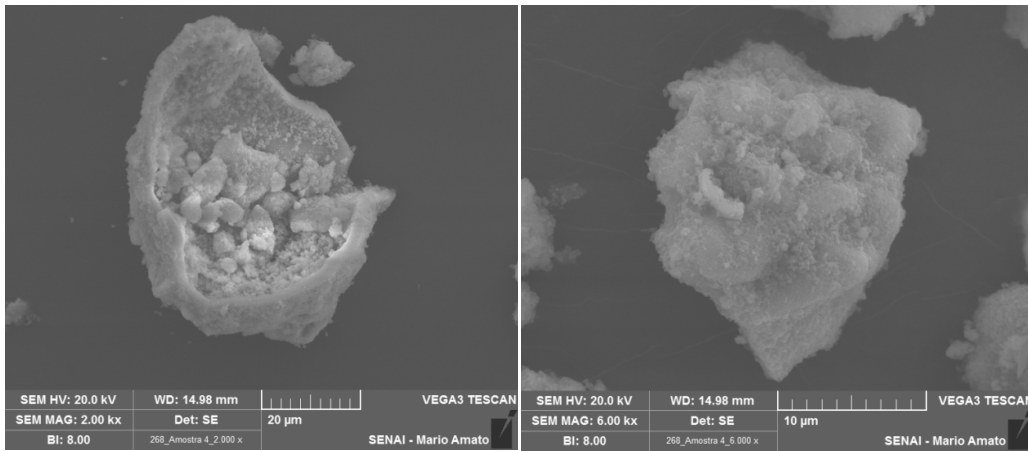
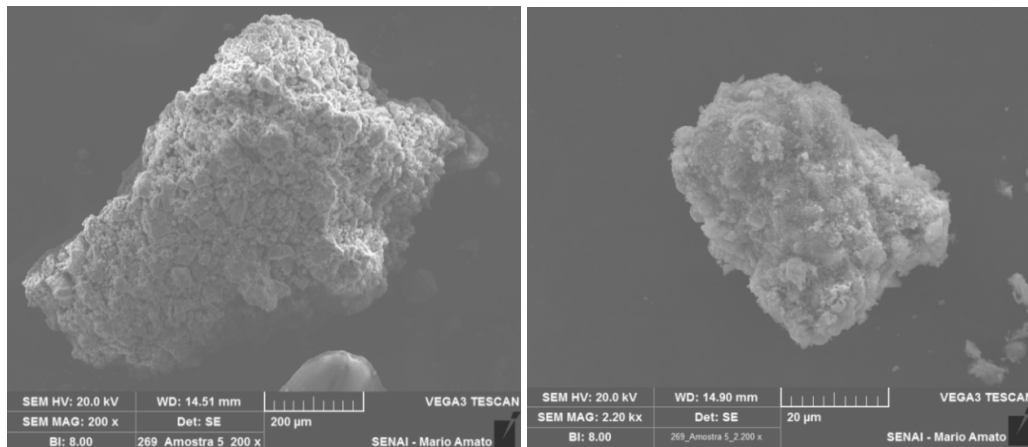
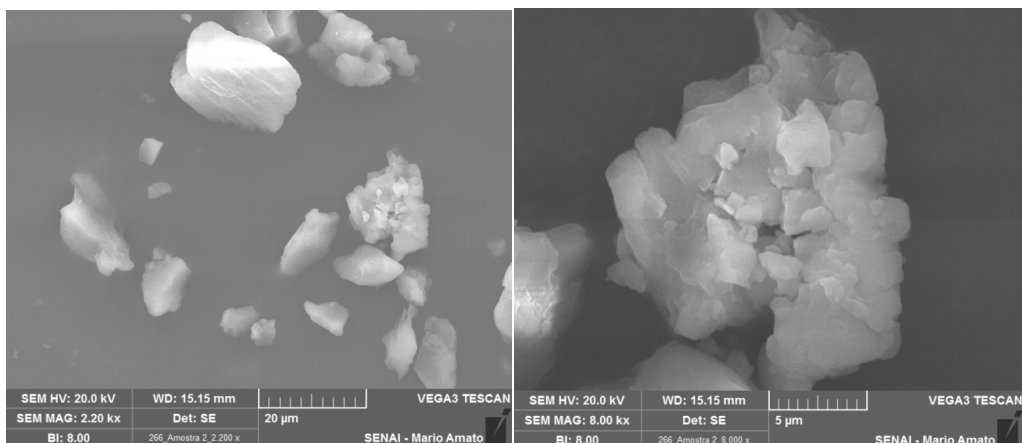
	DMSO anhydrous + 4.5% fructose		DMSO+H ₂ O (9:1 molar) + 4.5% fructose		DMSO+H ₂ O (9:1 massa) + 4.5% fructose	
	μg·mL ⁻¹	mmol·L ⁻¹	μg·mL ⁻¹	mmol·L ⁻¹	μg·mL ⁻¹	mmol·L ⁻¹
Flow/residence time	Concentration					
Q (mL·min ⁻¹)						
2.00 (space time: 4 min)	21.8	0.17	12.5	0.10	5.9	0.04
1.00 (space time: 8 min)	24.6	0.20	19.2	0.16	7.3	0.06
0.50 (space time: 16 min)	37.6	0.30	24.3	0.18	12.7	0.10
0.25 (space time: 32 min)	76.8	0.61	24.8	0.20	22.2	0.17

3.11. SBA - + ZrO(NO₃)₂

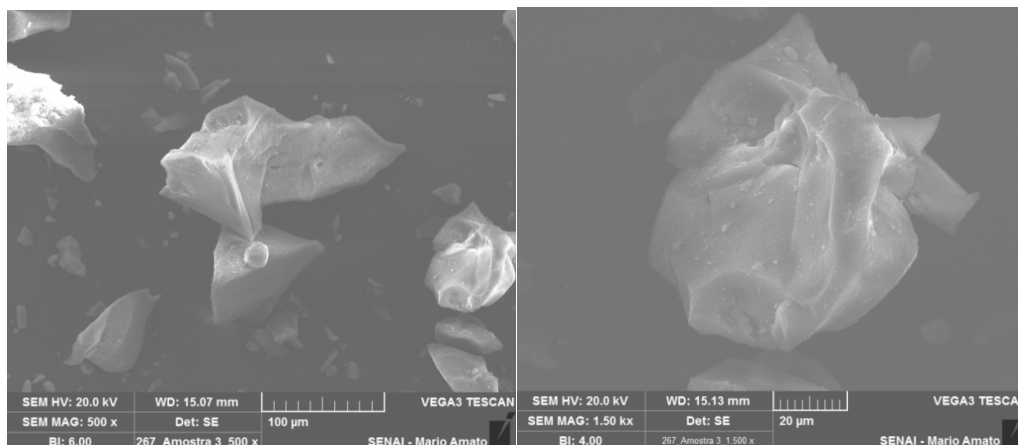
	DMSO anhydrous + 4.5% fructose		DMSO+H ₂ O (9:1 molar) + 4.5% fructose		DMSO+H ₂ O (9:1 massa) + 4.5% fructose	
	μg·mL ⁻¹	mmol·L ⁻¹	μg·mL ⁻¹	mmol·L ⁻¹	μg·mL ⁻¹	mmol·L ⁻¹
Flow/residence time	Concentration					
Q (mL·min ⁻¹)						
2.00 (space time: 4 min)	5.7	0.04	64.6	0.51	59.7	0.47
1.00 (space time: 8 min)	287.6	2.28	2744.7	21.76	105.0	0.83
0.50 (space time: 16 min)	465.7	3.68	2918.3	23.14	151.5	1.20
0.25 (space time: 32 min)	3203.8	25.40	2970.6	23.54	266.4	2.11

Item 4 –SEM images of the materials utilized as catalysts

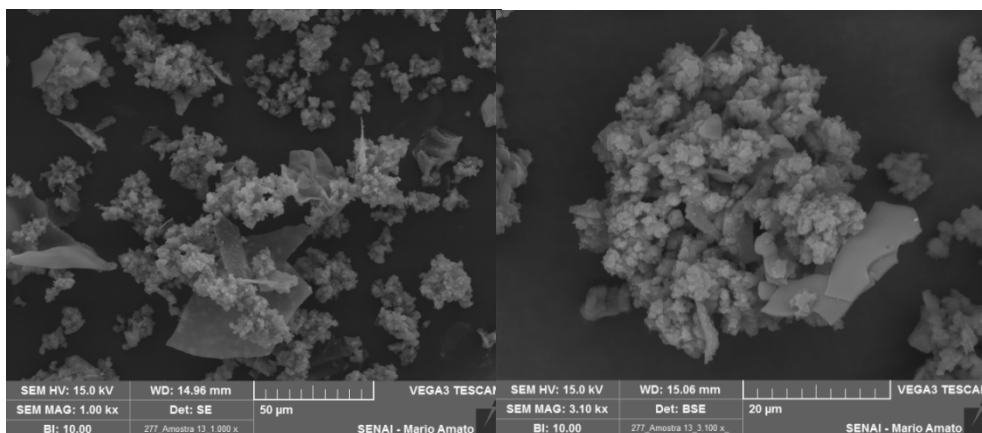
4.1. SEM of CT275_{acidified}

4.2. SEM of Ludox[®] + ANO4.3. SEM of Ludox[®] + Nb₂O₅4.5. SEM of Ludox[®] + Nb₂O₅ + ANO4.6. SEM of Ludox[®] + ZrO(NO₃)₂

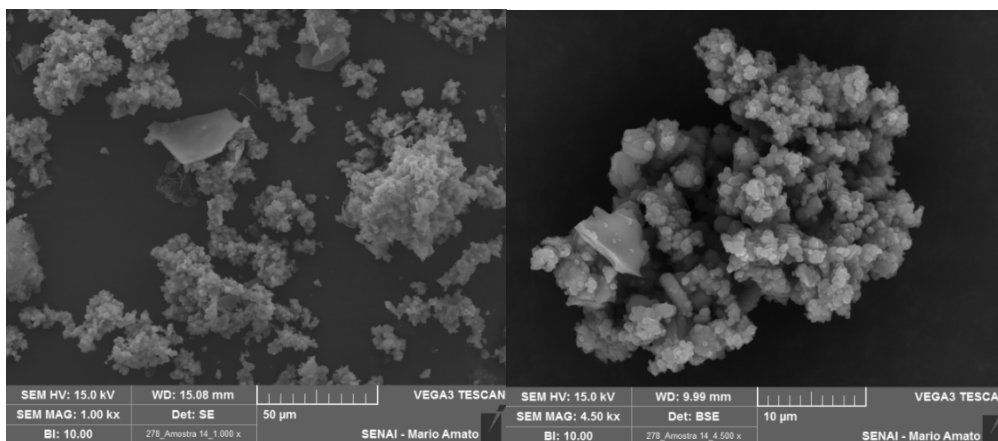
4.7. SEM of Ludox® + ANO + ZrO(NO₃)₂



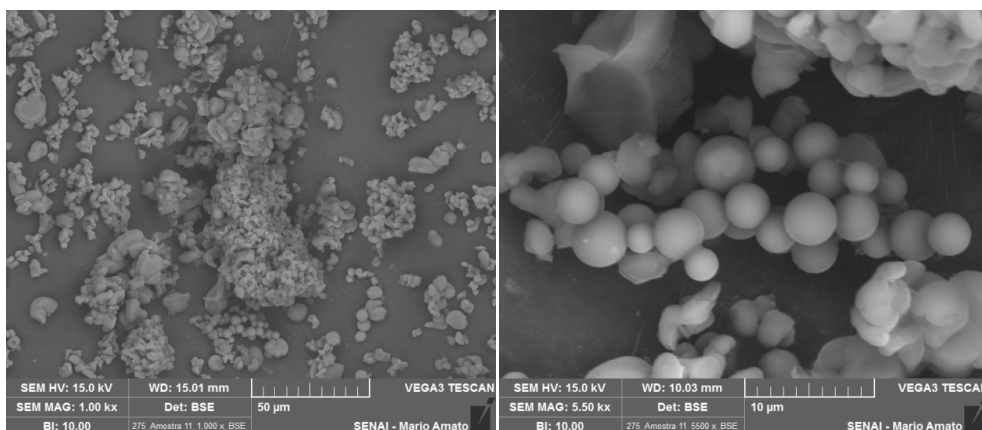
4.7. SEM of MCM 41 + ANO



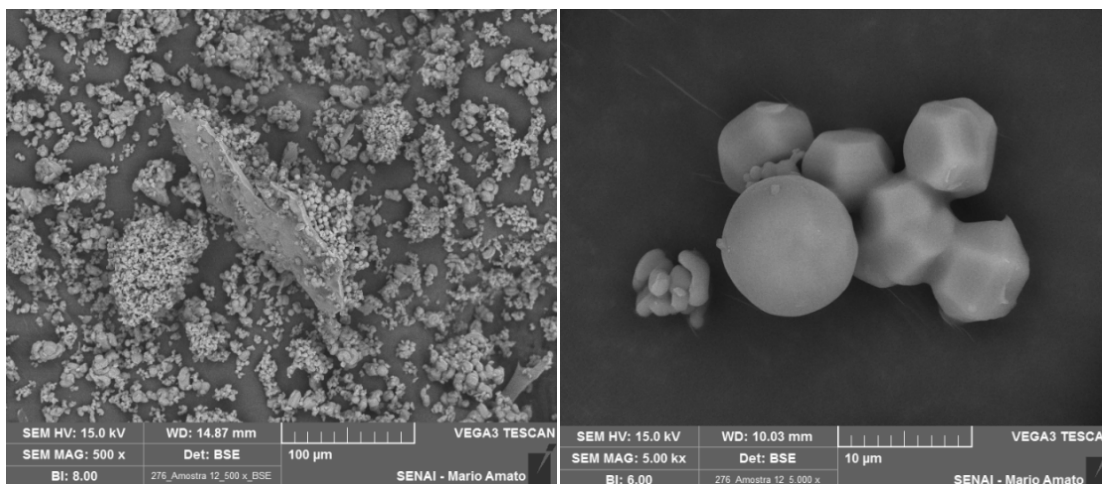
4.8. SEM of MCM 41 + ZrO(NO₃)₂



4.9. SEM of SBA + ANO

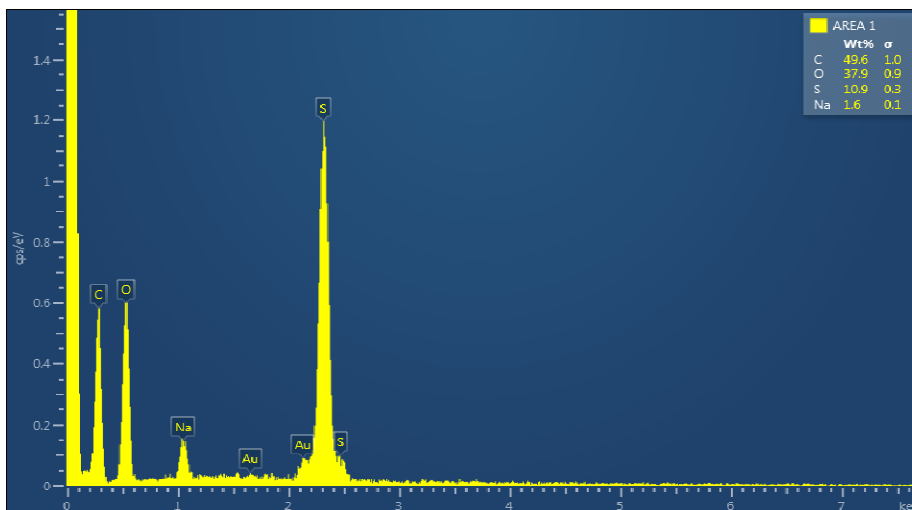


4.10. SEM of SBA + ZrO(NO₃)₂

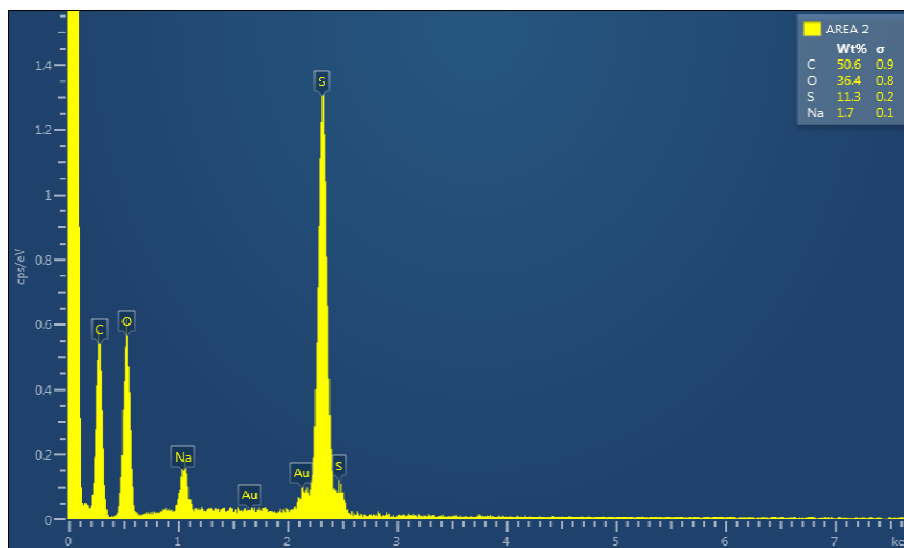


Item 5.EDS catalyst composition

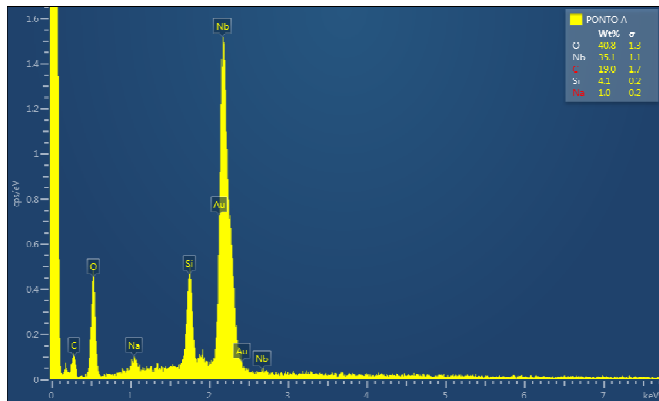
5.1. CT 275 superacidified.



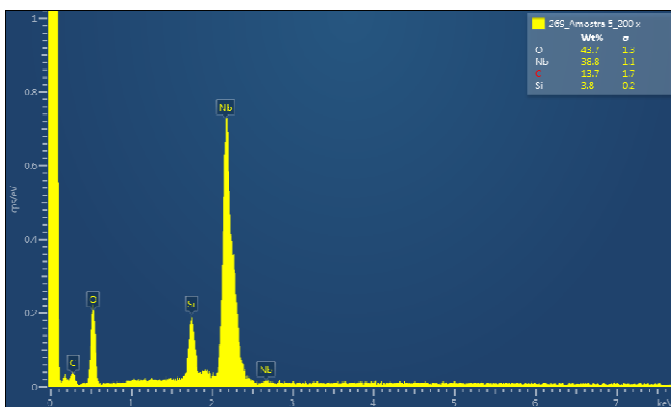
5.2. SGC650H superacidified



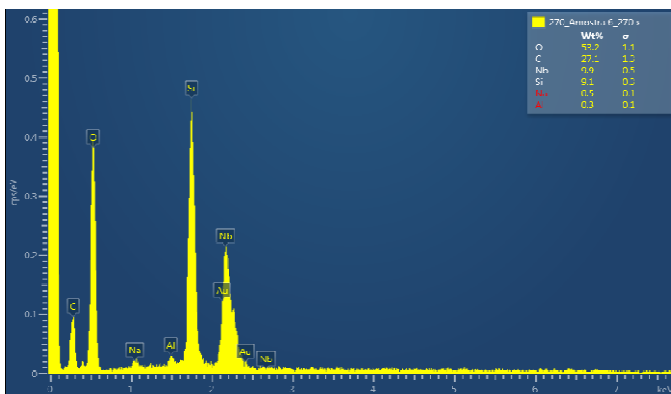
5.3. Oxalate of niobium and ammonium agglomerated with colloidal silica Ludox® + ANO.



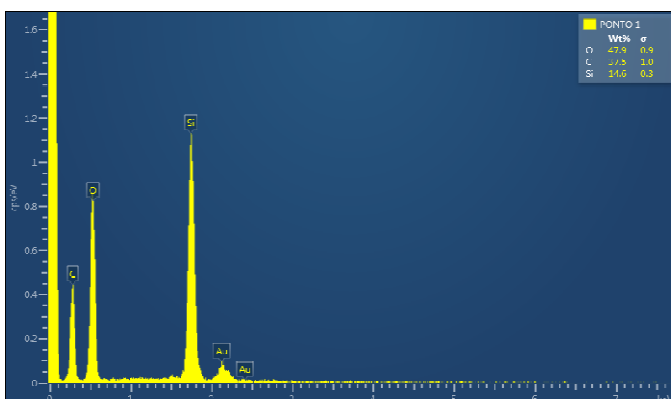
5.4. Niobium oxide agglomerated with colloidal silica Ludox® + Nb₂O₅



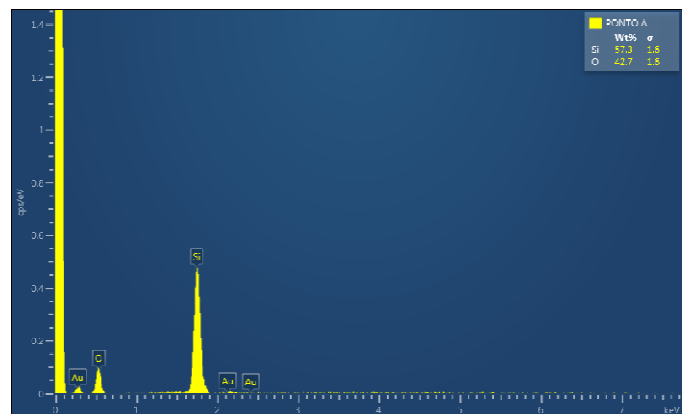
5.5. Niobium oxide and oxalate of niobium and ammonium agglomerated with colloidal silica Ludox® + Nb₂O₅ + ANO



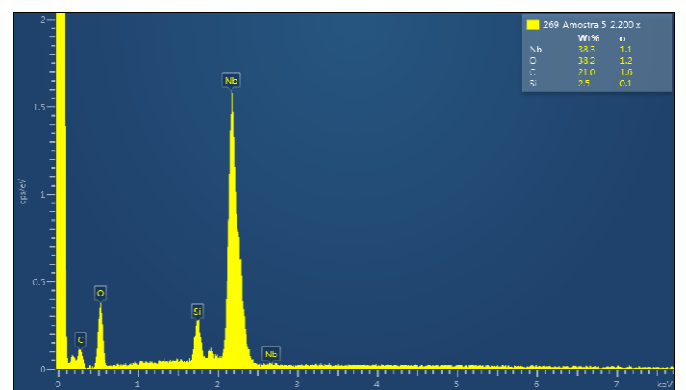
5.6. Zirconium nitrate agglomerated with colloidal silica Ludox® + ZrO(NO₃)₂.



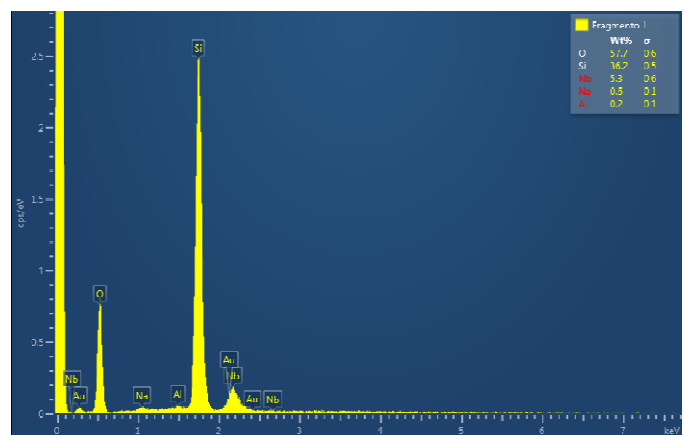
5.7. Zirconium nitrate + oxalate of niobium and ammonium agglomerated with colloidal silica Ludox® + ANO + ZrO(NO₃)₂



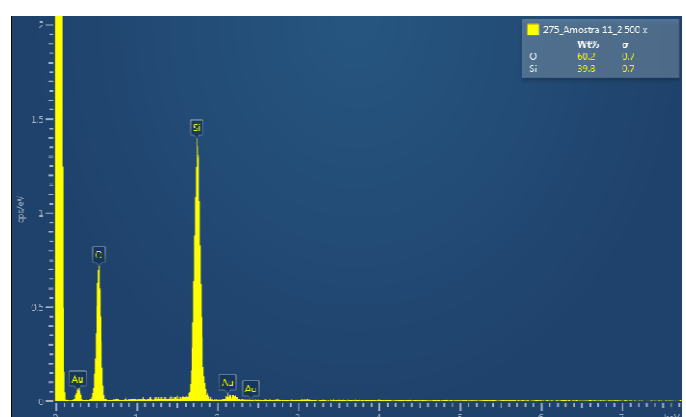
5.8. Oxalate of niobium and ammonium impregnated in MCM-41 MCM41 – ANO.



5.9. Oxalate of niobium and ammonium impregnated in SBA-15 SBA – ANO

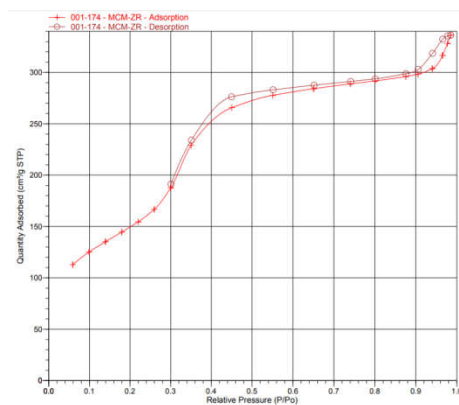
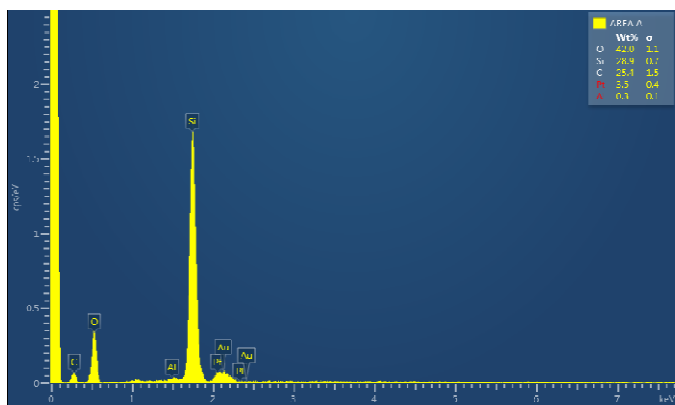


5. 10. Zirconium nitrate impregnated in MCM-41 MCM41 - ZrO(NO₃)₂



5.11.Zirconium nitrate impregnated in SBA-15 SBA - ZrO(NO₃)₂

MCM41 - ZrO(NO₃)₂

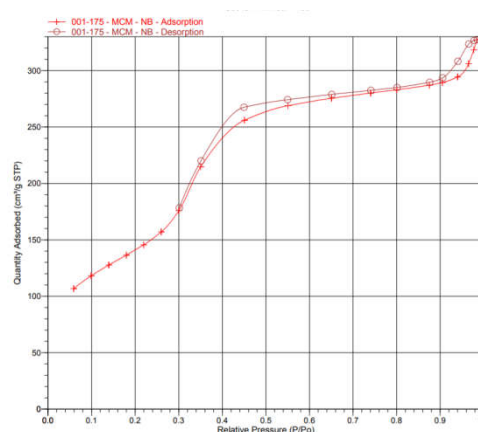


6 – Porosity and surface area

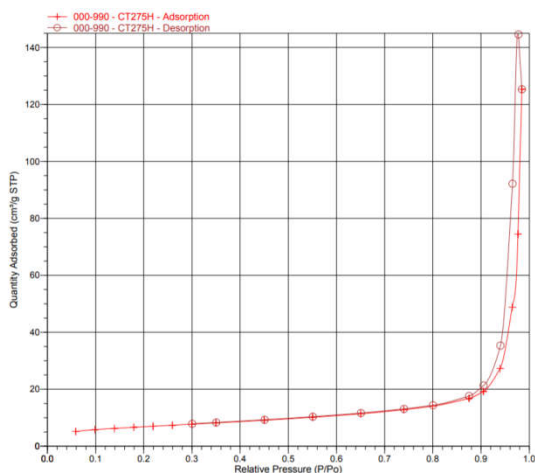
Catalyst	Specific area (m ² .g ⁻¹)	Average diameter (nm)	Porous volume (mL.g ⁻¹)
CT275 regular			
CT275 _{acidificated}	22	26.285	0.151
SG650H _{acidificated}		-	~0.00 (*)
Ludox [®] + ANO	93	10.479	0.244
Ludox [®] + Nb ₂ O ₅	184	5.041	0.232
Ludox [®] + Nb ₂ O ₅ + ANO	83	7.342	0.152
Ludox [®] + ZrO(NO ₃) ₂	93	9.662	0.224
Ludox [®] + ANO + ZrO(NO ₃) ₂	110	6.352	0.175
MCM 41 + ANO	521	3.886	0.506
MCM 41 + ZrO(NO ₃) ₂	553	3.757	0.520
SBA + ANO	402	4.086	0.411
SBA + ZrO(NO ₃) ₂	394	4.034	0.398

(*) atequipmentconditions

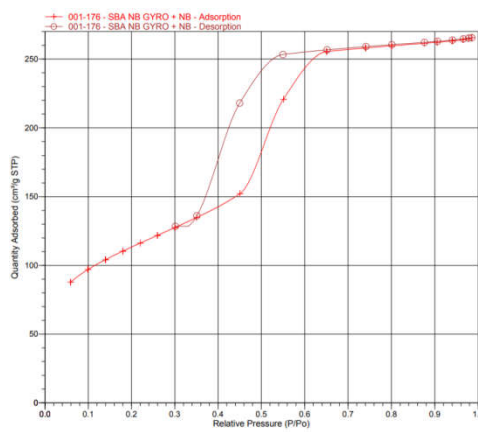
MCM41 - ANO



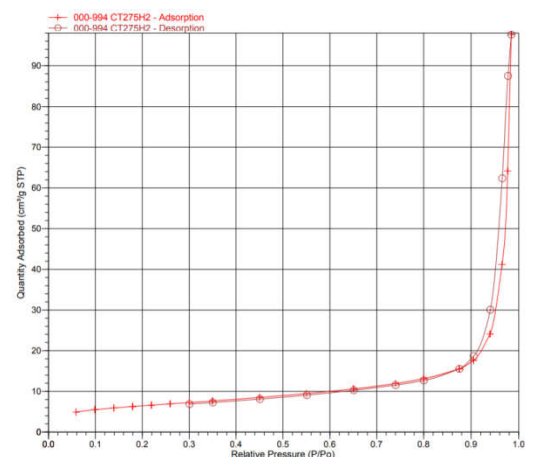
CT275 superacidificated before sulfonation



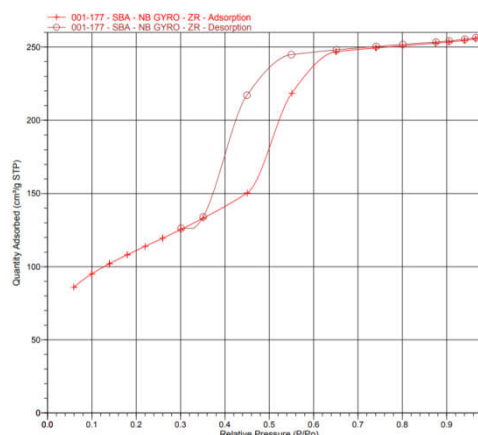
SBA – ANO



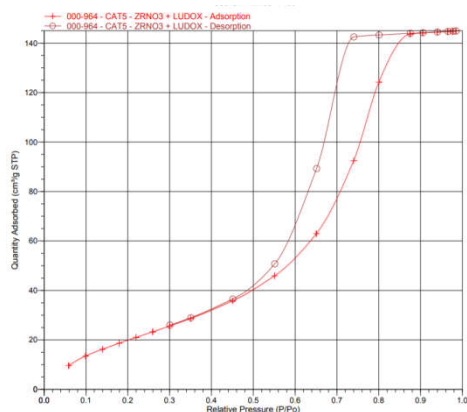
CT275 superacidificated after sulfonation



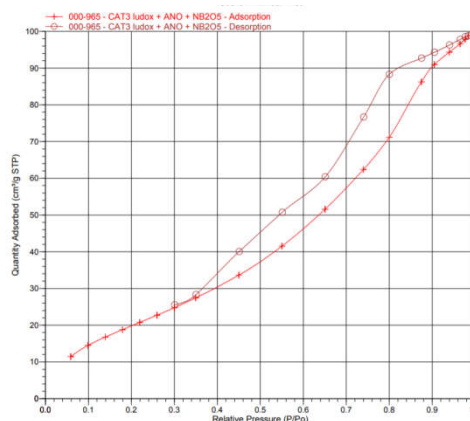
SBA - ZrO(NO₃)₂



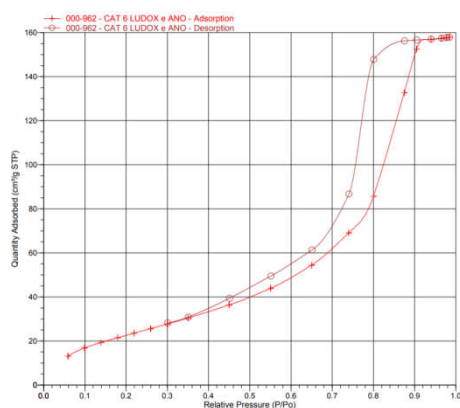
Ludox[®] + ZrO(NO₃)₂



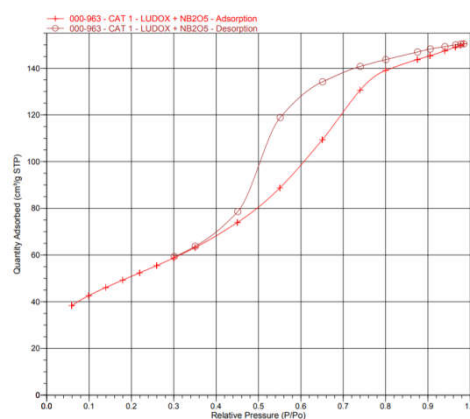
Ludox[®] + ANO + Nb₂O₅



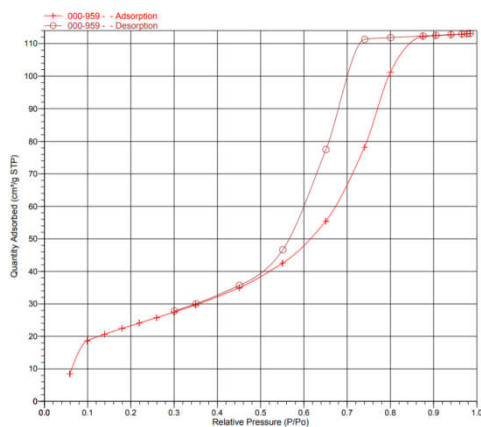
Ludox[®] + Nb₂O₅



Ludox[®] + Nb₂O₅



Ludox[®] + ANO + ZrO(NO₃)₂



7 – Titrated acidity (mmol H⁺/gcat)

Catalyst	Acidity (mmol de H ⁺ .g ⁻¹ catalyst)
CT275 _{acidificated}	1.79
SGC650H _{acidificated}	1.63
Ludox [®] + ANO	1.25
Ludox [®] + Nb ₂ O ₅	1.07
Ludox [®] + Nb ₂ O ₅ + ANO	1.13
Ludox [®] + ZrO(NO ₃) ₂	1.42
Ludox [®] + ANO + ZrO(NO ₃) ₂	1.24
MCM 41 + ANO	1.18
MCM 41 + ZrO(NO ₃) ₂	1.45
SBA + ANO	1.22
SBA + ZrO(NO ₃) ₂	1.37
