Conversion of glucose to lactic acid derivatives with mesoporous Sn-MCM-41 and microporous titanosilicates

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Manuscripts

1 **Conversion of glucose to lactic acid derivatives with mesoporous Sn-**

2 **MCM-41 and microporous titanosilicates**

3

4 **Short title: Glucose to lactic acid with different catalysts**

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1

1   **Abstract**

2   <u>Background:</u> The production of value-added products from biomass has acquired

3   increasing importance due to the high worldwide demand for chemicals and energy,

4   uncertain petroleum availability and the necessity of finding environmentally friendly

5   processes. In this work we present the synthesis of several catalysts for the conversion

6   of glucose to methyl lactate.

7   <u>Results:</u> A MCM-41 type mesoporous material containing tin (Si/Sn= 55) was

8   developed with a uniform ordered mesoporous structure, high specific surface area and

9   high pore volume. Sn-MCM-41 was tested in three consecutive catalytic cycles to

10   evaluate its reusability giving methyl lactate yields of 43 %, 41 % and 39 %, in each

11   cycle. The slightly reduction in activity could be explained by the reduction in the

12   accessibility of active centers due to the adsorption of reaction products and structural

13   changes. Microporous titanosilicates and MFI-type zeolite ZSM-5 showed a lower

14   catalytic performance, but exfoliated materials give higher yields to methyl lactate and

15   pyruvaldehyde dimethyl acetal than their respective layered precursors.

16   <u>Conclusions:</u> Sn-MCM-41 material showed good results in the conversion of glucose to

17   methyl lactate even in three catalytic cycles and exfoliated materials facilitated the

18   access of glucose to the catalytic sites and fast desorption of products.

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20

21   **Keywords**: Glucose conversion; Lactic acid; Sn-MCM-41; Porous titanosilicates;

22   exfoliated materials

23

Introduction

Nowadays, there is a growing interest in developing alternatives for replacing fossil sources due to unknown petroleum availability, high worldwide demand for chemicals and energy and concern about climate change. Besides, there is a need to develop methods to decrease global greenhouse gas emissions by consuming feedstock produced by plant growth photosynthesis, neutral in terms of CO_2 balance. [1] In fact, at the beginning of the 20th century, many industrial materials such as dyes, solvents and synthetic fibers were made from trees and agricultural crops [2]. Later, after the discovery of inexpensive fossil fuels, our society became dependent on petroleum derivatives. Nowadays, the new concept of biorefinery [3] has emerged pursuing the integration of the production of fuels (biofuels), heat and electricity (biopower) and platform molecules from biomass. A clear pathway to producing such platform molecules is the catalytic transformation of sugars. For example, Fig. 1 shows a tentative representation of the production of sugars from biorenewable resources and their transformation into some bioproducts of interest.

However, biochemical processes are more applicable due to the thermal instability of carbohydrates. Nowadays fermentation processes dominate the production of biofuels and value-added compounds from carbohydrates. Currently, few products are directly obtained from carbohydrates by catalysis such as gluconic acid, sorbitol and hydroxymethylfurfural. [4]

Lactic acid is the most widely occurring hydroxycarboxylic acid and has several applications in food industry, chemical sector and polymer market. [5,6] Even though there is a chemical synthesis route from petrochemical resources (acetaldehyde), [7] about 90 % of lactic acid is commercially produced by the microbial fermentation of aqueous

3

1   glucose. [8] However, biological processes in general have various drawbacks including

2   low reaction rates causing long reaction times and the need for huge reactors, and low

3   concentrations of products usually in water solutions requiring high energy

4   consumption for their purification. In addition, biological processes are quite sensitive

5   to pH and temperature parameters. [9]

6   Homogeneous catalysts have been tested as an alternative to fermentation processes

7   and some compounds have been found to be efficient in the catalytic transformation of

8   sugars, for example NaOH, [10] H_2SO_4 [11] and $ZnSO_4$. [12] However, these reactions are

9   carried out under extreme conditions of temperature and pressure, and the catalysts are

10 toxic or corrosive. Their recovery can therefore be a difficult process.

11 Recent research has focused on heterogeneous catalysis due to the growing industrial

12 interest in processes for the conversion of sugars to value-added products and the

13 drawbacks of the other alternatives. [13,14] In 2005, Hayashi et al. [15] found that Ti-based

14 Lewis acids such as $SnCl_4$ and $SnCl_2$ were efficient catalysts for sugar transformation.

15 A few years later, Taarning et al. [16] applied Beta zeolite containing Al, Zr, Ti and Sn,

16 achieving interesting results with Sn-Beta zeolite in the conversion of triose

17 dihydroxyacetone to methyl lactate. An interesting research study carried out by Holm

18 et al. [17] in 2010 reported high conversion of common sugars (such as glucose, fructose

19 and sucrose) catalyzed with Lewis acidic zeotypes for the direct formation of methyl

20 lactate, achieving high selectivity. West et al. [18] made a study of liquid-phase

21 isomerization of trioses to methyl lactate using commercially available zeolite H-USY

22 as a catalyst, obtaining effective results. In 2011, Li et al. [19] used ordered mesoporous

23 substituted silicates with MCM-41 type structure (such as Al-, Ga- and Sn-MCM-41)

24 obtaining high catalytic performance in the complete conversion of trioses to the desired

4

1 lactate. In the same year, Wang et al. [20] demonstrated that tin ion-exchanged

2 montmorillonite, which is a Brønsted acid, shows a high catalytic activity and

3 selectivity for the conversion of trioses into methyl lactate. In recent research,

4 Osmundsen et al. [21] tested different microporous and mesoporous stannosilicates such

5 as Sn-BEA, Sn-MFI, Sn-MCM-41 and Sn-SBA-15, observing their potential as

6 catalysts for the conversion of trioses and sucrose to methyl lactate with high activity

7 and selectivity. Recent reports have demonstrated that tin-containing compounds [21-23]

8 exhibit a high catalytic activity in the aqueous isomerization of sugars.

9   In the present work, MCM-41 modified with tin was synthesized. Sn-MCM-41 was

10 tested as catalyst in the transformation of glucose to methyl lactate. Other catalysts such

11 as zeolite ZSM-5 and microporous titanosilicate materials (ETS-10) [24] and layered

12 materials (JDF-L1 [25] and AM-4 [26,27]) were chosen for the comparison of their catalytic

13 results with those of Sn-MCM-41. Besides, zeolites offer a strong limitation to

14 molecular diffusion, and the accessibility to catalytic sites in layered materials can be

15 drastically enhanced by their exfoliation. [28] For this reason, UZAR-S1 [29] and UZAR-S2,

16 [30] which are exfoliated materials obtained from JDF-L1 and AM-4, respectively, were

17 also tested.

18

19 **Materials and methods**

20 **Catalyst preparation**

21   MCM-41 with a nominal atomic Si/Sn ratio of 75 was prepared by dissolving 1.015

22 g hexadecyltrimethyl-ammonium bromide (CTABr) (98 %, Sigma) in 45 mL of

23 deionized water with 0.417 g of NaOH (98 %, pellets (anhydrous), Sigma-Aldrich).

24 Then 0.05 g of SnCl$_2$ dihydrate (98 %, Sigma-Aldrich) was added to this solution as the

5

1   Sn source. Finally, 3.41 g of tetraethyl orthosilicate (TEOS) (98 %, Aldrich) was also

2   added. The mixture gave rise to a gel with a molar composition of 6 TEOS: 1 CTABr:

3   900 H_2O: 4 NaOH: 0.08 $SnCl_2$ which was heated under reflux at 80 ºC for 8 h. The solid

4   product was recovered by filtration, washed with deionized water and dried at 70 ºC

5   overnight. The dried Sn-MCM-41 was calcined for activation in still air at 650 ºC for 8

6   h. For the purposes of comparison, MCM-41 was synthetized in the same way but

7   without the addition of a tin source.

8   Commercial zeolite ZSM-5 (Zeolyst International, Si/Al=25) and microporous

9   titanosilicate materials (JDF-L1, AM-4, ETS-10, UZAR-S1 and UZAR-S2) were also

10   used. JDF-L1 and AM-4 were synthesized at 230 °C for 24 h by a seeded secondary

11   growth procedure using the following molar compositions: SiO_2:TiO_2:Na_2O:H_2O

12   4.2:1:2.9:101 and 4.2:1:2.9:68, respectively. To obtain UZAR-S1 and UZAR-S2, the

13   layered materials were protonated in the presence of acetic acid and swollen using

14   nonylamine. For exfoliation, the swollen materials were mixed with an $HCl/H_2O/EtOH$

15   solution at 55 °C for 8 h under reflux. More details of these procedures can be found

16   elsewhere. [28,29]

17   Besides, ETS-10 crystals of about 400 nm in size were prepared according to

18   previously reported procedures [24] by hydrothermal synthesis at 230 ºC for 24 h, using

19   TiO_2-anatase (nanopowder, <25 nm particle size, 99.7 %, Aldrich) with a gel of molar

20   composition 5.5 SiO_2: 1 TiO_2: 4.6 Na_2O: 1.9 K_2O: 147 H_2O.

21

Catalyst characterization

23   Powder low angle X-ray diffraction (LA-XRD) patterns were recorded on a Siemens

24   D5000 X-ray diffractometer using Cu-Kα_1 radiation (λ = 1.5418 Å) over a 2θ range of

6

1   1-8º at a step size of 0.01º. Also, some materials were characterized by conventional X-

2   ray diffraction (XRD) using a D-Max Rigaku System with a Cu-Kα_1 radiation (λ =

3   1.5418 Å) over a 2θ range of 2.5-40º.

4   Elemental analysis was performed to determine the Si/Sn ratio in Sn-MCM-41

5   samples using a Thermo Electron ARL ADVATXP X-ray fluorescence (XRF)

6   sequential spectrometer equipped with an X-ray tube Be window and a Rh anode.

7   Nitrogen adsorption/desorption isotherms were obtained using a Micromeritics

8   Tristar 3000 surface area and porosity analyzer, after previously degassing the samples

9   at 200 ºC for 8 h under vacuum. The specific surface area was calculated by the BET

10   (Brunauer-Emmett-Teller) method.

11   TEM pictures were taken with a FEI TECNAI T20 transmission electron

12   microscope at 200 kV.

13   Thermogravimetric analyses (TGA) were performed in air from room temperature to

14   750 ºC with a heating rate of 10 ºC/min using Mettler Toledo TGA/SDTA 851$^\text{e}$

15   equipment.

16

17   **Catalytic reaction**

18   The conversion of sugars to methyl lactate was performed by dissolving 225 mg of

19   D-(+)-glucose (99 %, Alfa Aesar) in 8.0 g of methanol (HPLC, Scharlau). 30 mg of

20   naphthalene (99 %, Aldrich) was added as internal standard. The catalyst (160 mg) was

21   dispersed in the methanol solution. The mixture was then sealed in a 35 mL-Teflon-line

22   autoclave and heated to 160 ºC for different times in a rotary oven.

23   After the reaction time, the catalyst was recovered by centrifugation and the reaction

24   products were quantitatively measured by mass detector gas chromatography (GC-MS).

7

1   The equipment used was an Agilent 6850 GC system with a capillary column HP-5MS

2   (30 m x 0.250 mm x 0.25 μm), coupled with an Agilent 5975C MSD.

3   The yields of the different products were determined based on the internal standard

4   of naphthalene using calibration curves made with the commercial compounds methyl-

5   S-(-)-colate (98 %, Aldrich), methyl glycolate (98 %, Alfa Aesar), methylglyoxal 1,1-

6   dimethylacetal, also called pyruvaldehyde dimethyl acetal (97 %, Aldrich), and 1,1,2,2–

7   tetramethoxypropane (99 %, Aldrich). Unidentified compounds detectable by GC-MS

8   were calculated from the response factor of the methyl lactate. Yields were calculated

9   on a carbon basis. Glucose conversion was determined using an analytical method,

10   which consists of an enzymatic quantitative determination of glucose (Glucose (HK)

11   Assay Kit, Sigma).

12   In the reusability experiments, the recovered catalyst was washed with methanol at

13   room temperature and dried in an oven at 60 ºC overnight prior to reuse.

14

15   **Results and discussion**

16   **Catalyst characterization**

17   XRF analysis showed that the Sn-MCM-41 samples had a Si/Sn atomic ratio in the

18   range of 50-60 (mean=55; standard deviation=11; samples=3), lower than the nominal

19   ratio (Si/Sn=75) and thus indicating a high degree of tin incorporation in the catalysts.

20   Fig. 2a shows the LA-XRD pattern of MCM-41 and Sn-MCM-41. The highest peak

21   observed for both samples (2.48º and 2.33º for MCM-41 and Sn-MCM-41, respectively)

22   indicates the order of the mesopores, as expected in MCM-41 type ordered mesoporous

23   structures. In agreement with previous reports, the Sn-MCM-41 sample shows (100),

24   (110), (200) and (210) reflections, characteristic of hexagonal channel arrays. No

8

diffraction bands were observed at angles higher than 6º, thus demonstrating the amorphous nature of the samples. The values of the unit cell parameter ($a_0 = 2 \cdot d_{100}/3^{0.5}$) are 4.11 and 4.38 nm for MCM-41 and Sn-MCM-41, respectively. These values, within the range reported by other authors for Sn-MCM-41, [31,32] suggest that tin is incorporated in the framework of the MCM-41. The differences would be due to the larger size of Sn^{4+} (ionic radius 0.55 Å) compared with that of Si^{4+} (ionic radius 0.26 Å) as well as Sn-O having a longer bond length than that of Si-O. Both effects produce an increase in the unit cell parameter of Sn-MCM-41. The incorporation of tin in tetrahedral coordination within the MCM-41 framework can generate Lewis acidity. [19]

Fig. 2b presents the XRD patterns of the other catalysts used in the transformation of glucose. The XRD patterns of ETS-10, JDF-L1, AM-4 and ZSM-5 show high angle diffraction lines which indicate that the materials are crystalline. UZAR-S1 and UZAR-S2, as for other delaminated porous materials, are XRD-amorphous exhibiting broad reflections of the parent materials JDF-L1 and AM-4, respectively. [28,29]

Calcination was used to remove the organic surfactant from as-synthesized Sn-MCM-41. The TGA curve (not shown) revealed that the weight loss of as-synthetized Sn-MCM-41 is around 40 %, corresponding to the surfactant. However, the activated Sn-MCM-41 curve did not show this weight loss, showing that the calcination process was done properly.

The TEM images in Figs. 3a and 3b correspond to as-synthesiszed Sn-MCM-41. The homogeneity of these images suggests a good dispersion of tin atoms in the MCM-41 structure. The TEM images of activated Sn-MCM-41 reveal the presence of pores (Figs. 3c and 3d) where no morphological changes are observed with respect to the as-synthesized sample.

9

1   The BET surface area for Sn-MCM-41 is 801 m^2/g (Table 1), which is very close to

2   that of MCM-41 synthesized in the same way. The Sn-MCM-41 pore volume is lower

3   than that of MCM-41; this could be owing to tin atoms inserted into the structure. ZSM-

4   5 and ETS-10 give BET surface areas of 367 and 253 m^2/g, typical values for these

5   microporous materials. JDF-L1 and AM-4 scarcely adsorb N_2 and this is reflected by

6   BET specific surface areas of 30 and 13 m^2/g, respectively. The exfoliation process

7   increases the BET surface area with respect to the as-synthesized materials, attaining

8   BET specific surface areas of 159 and 112 m^2/g for UZAR-S1 and UZAR-S2,

9   respectively.

10

11   **Catalytic results**

12   Different catalysts were used in the transformation of glucose in methanol to obtain

13   methyl lactate (ML) as the desired product. However, other side-products were detected

14   by GC-MS. In this work only three of these side-products were quantified: methyl

15   glycolate (MG), pyruvaldehyde dimethyl acetal (PADA) and 1,1,2,2-

16   tetramethoxypropane (TMP). Based on previous reports [16,17,20] and the different

17   products identified by GC-MS, a possible reaction pathway has been developed (Fig. 4).

18   In an alcohol medium (methanol), hexoses such as glucose suffer retro-aldol reactions

19   to form carbohydrate products with lower numbers of carbon atoms. On the one hand, a

20   compound with four carbon atoms such as erythroxe is formed, which undergoes

21   different transformations until obtaining methyl glycolate (MG) as the final product. On

22   the other hand, compounds with three carbon atoms are formed such as glyceraldehyde

23   and dihydroxyacetone which are lactic acid isomers. These products lose water

24   molecules and form pyruvaldehyde, which in methanol suffers a reversible reaction to

10

obtain pyruvaldehyde dimethyl acetal (PADA) and another reaction to form methyl

lactate (ML), our desired product. However, PADA could undergo changes to form

1,1,2,2-tetramethoxypropane (TMP), another reaction product.

In this work, different solid catalysts have been used in the transformation of

glucose to methyl lactate. The yields of the quantified products are presented in Table 2.

Sn-MCM-41 provides the highest methyl lactate and total yields of 43 % and 59 %,

respectively, demonstrating that Sn-MCM-41 has a pore system sufficiently large for

glucose to enter. Conventional MCM-41 is considerably less active for the reaction than

Sn-MCM-41, which is encouraging. Additionally, it should be noted that for Sn-MCM-

41, the catalytic experiments were repeated 4 times in the same conditions with an

average methyl lactate yield value of 42.7 % and standard deviation of 5.1 %,

highlighting the reproducibility of the results. Similar to the case of zeolites, the

catalytic behavior is related to the Lewis acidity ascribed to Sn incorporated in the

MCM-41. [17] The Lewis acid sites can favor the retro-aldol reactions with the cleavage

of C-C bonds of glucose (Fig. 4) to form trioses. [33] Moreover, it has been demonstrated

that Sn-MCM-41 could have the combination of acid sites leading to the conversion of

trioses to lactates. [19] Other reaction pathways are possible such as polymerization that

products have not been analyzed. This can explain the lower total yield in comparison to

the conversion of glucose.

The methyl lactate yield obtained with Sn-MCM-41 is comparable to that obtained

in similar operating conditions (160 ºC and 20 h) by Holm et al. [17] using Sn-Beta zeolite

as catalyst (methyl lactate yield, 43 %) and higher than the yields obtained by the same

authors using other metal containing zeolites: Ti-Beta (methyl lactate yield, 31 %) and

Zr-Beta (methyl lactate yield, 33 %). In the conversion of sucrose (disaccharide

11

1   composed of glucose and fructose) at 160 ºC for 16 h, Osmundsen et al. [21] achieved a

2   methyl lactate yield of 25 % using Sn-MCM-41. Using Sn-Beta zeolite with Si/Sn=200,

3   these authors achieved a methyl lactate yield close to 60 %. Also using Sn-MCM-41, Li

4   et al. [19] converted trioses (dihydroxiacetone) in ethanol to ethyl lactate with a yield of 98

5   % after 6 h at a lower temperature (90 ºC) than the temperature used here. It has been

6   pointed out [21] that the use of hexose sugars is significantly more interesting, due to their

7   lower cost compared to trioses, but more challenging, due the possibility of other

8   reaction pathways occurring that may decrease the yield to lactate compounds. Finally,

9   Sn-MCM-41 has been used as catalyst in the isomerization of glucose into fructose and

10 mannose. Moliner et. al. [22] obtained about 30 % of glucose conversion with 40 %

11 fructose selectivity at 140 ºC and 90 min of reaction in an aqueous medium. These

12 operating conditions are different from those used here (methanol, 160 ºC and optimum

13 time 20 h), but it cannot be ruled out that these reactions could occur. In fact,

14 Osmundsen et al. [21] found a fructose yield of about 80 % at much lower temperatures

15 (80 ºC) for 48 h in methanol.

16   For the layered materials (JDF-L1 and AM-4) and for microporous titanosilicate

17 ETS-10 and zeolite ZSM-5, the methyl lactate yields are very low, under 4%. The

18 exfoliated materials UZAR-S1 and UZAR-S2 give higher yields to the total products

19 and to methyl lactate than their respective layered precursors. This behavior is in

20 agreement with the observed role of delayered zeolitic materials (ITQ-2, ITQ-6 and

21 ITQ-18), with good access of the reactants to their catalytic sites as well as fast

22 desorption of the products, for example in the synthesis of bulky diamino diphenyl

23 methane. [34] It should be noted that UZAR-S2, which is protonated, gave the highest

24 yields to PADA, indicating that the conversion of pyruvaldehyde to PADA was favored

12

1   with Brønsted acidic catalysts against the parallel route to methyl lactate (see scheme in

2   Fig. 4).

3   The evolution with time of the catalytic performance of Sn-MCM-41 was also

4   studied (Fig. 5). At short times, the yield of methyl lactate increased with time.

5   However, at long times the yield reached a constant value of around 43 %; therefore, 20

6   h is considered as the optimum time. The rest of the products gave lower yields, below

7   10 %. The PADA yield decreased with time because it reacted to give TMP. Also, at

8   high conversion it could be converted into methyl lactate with the back reaction shown

9   in Fig. 4 (18). TMP produced from PADA appeared when the PADA diminished. As

10 expected for a final product, there was an increase in the MG yield with time to reach an

11 optimum at 20 h.

12   Sn-MCM-41 was tested in three consecutive catalytic cycles to evaluate its

13 reusability (Fig. 6). The methyl lactate yield was slightly reduced, the first, second and

14 third cycles giving methyl lactate yields of 43 %, 41 % and 39 %, respectively. This

15 lower activity could be explained by the reduction in the accessibility of active centers

16 due to the adsorption of reaction products or structural changes. In any event, the use of

17 methanol instead of water as solvent avoids coke deposition and structural damage, as

18 has been shown in the conversion of trioses in H-USY zeolite. The yield to MG (Fig. 6)

19 has low values and decreased in consecutive cycles from 3.4 % to 2.0 %. The PADA

20 yields vary from 4.6 % in the first cycle to 7.5 % in the second and 6.4 % in third. This

21 indicates that some properties of the catalysts could change to favor the production of

22 PADA instead of methyl lactate. Finally, the yield to TMP in the three cycles is

23 insignificant, being around 1.5 % in all cases.

13

1   It is well known that MCM-41 type catalysts have limited hydrothermal stability, so

2   the catalyst was characterized after its use in glucose conversion. The BET surface area

3   and pore volume decreased after use (Table 1), consistent with the slight activity

4   decrease. The TEM of the used catalysts (Fig. 3e) shows the pore structure of MCM-41

5   with no appreciable changes in the morphology.

6   The thermal behavior of the catalyst was also studied (not shown). TGA of the as-

7   synthetized Sn-MCM-41 indicates that the CTABr surfactant was completely removed,

8   as indicated above. The solid after reaction has a total weight loss of around 13 %. A

9   first weight loss below 100 ºC (around 2 %) is due to the adsorbed methanol. After 100

10   ºC, there are several weight losses up to 600 ºC which could be related to absorbed

11   compounds and, at the highest temperatures, to carbonaceous species that would be

12   responsible for catalyst deactivation.

13   In their reusability study, Holm et al. (17) regenerated the catalysts (Sn, Ti, Zr- Beta

14   zeolites) by calcination after each cycle. The catalysts were stable but in a fixed bed

15   reactor the Sn-Beta zeolite deactivated gradually with time. There is a similarity

16   between the fixed bed reactor and our operating conditions, where the catalyst is only

17   washed with methanol and not regenerated by calcination after each cycle to remove the

18   carbonaceous deposits observed by TGA. In fact, for a Sn-MCM-41 catalyst,

19   Osmundsen et al. [21] and Li et al., [19] using sucrose and trioses as reactants, respectively,

20   found that the deposition of carbon species deactivated the catalysts and that washing

21   with solvent was not enough to regenerate them.

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1 ## Conclusions

2   Sn-MCM-41 material with an atomic ratio Si/Sn=55 showed good results in the

3 conversion of glucose to methyl lactate with yields of around 43 %. Regarding its

4 stability, similar yields to methyl lactate were obtained in three consecutive reaction

5 cycles with only a slight reduction that can be explained by the surface area reduction

6 and/or carbonaceous deposits. Other microporous materials tested exhibited lower

7 yields to methyl lactate. Exfoliated materials (UZAR-S1 and UZAR-S2) allowed better

8 accessibility of glucose to the catalytic sites and fast desorption of the products,

9 increasing the reaction yield in comparison with their corresponding precursor layered

10 materials (JDF-L1 and AM-4).

11

12 ## Acknowledgements

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1 **FIGURE CAPTIONS**

2 **Fig. 1** Sugars: from biorenewable resources to platform molecules.

3 **Fig. 2** a) LA-XRD diffractograms of as-synthesized Sn-MCM-41 and MCM-41. b) XRD

4 diffractograms of microporous catalysts.

5 **Fig. 3** TEM images of: a) and b) as-synthesized Sn-MCM-41; c) and d) Sn-MCM-41

6 activated by calcination at 650 ºC in still air; e) Sn-MCM-41 catalyst after 20 h of reaction.

7 **Fig. 4** Possible reaction pathway for the transformation of glucose using Sn-MCM-41 as

8 catalyst.

9 **Fig. 5** Product yields as a function of reaction time for the conversion of glucose at 160 ºC

10 with Sn-MCM-41. The data at 20 h correspond to the average values with standard deviations.

11 Acronyms are the same as in Table 2.

12 **Fig. 6** Product yields as a function of reuse cycle of Sn-MCM-41 catalyst at 160 ºC during 20

13 h. Acronyms are the same as in Table 2.

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TABLES

Table 1 BET specific surface area and pore volume measured at $p/p_0 = 0.97$ by nitrogen
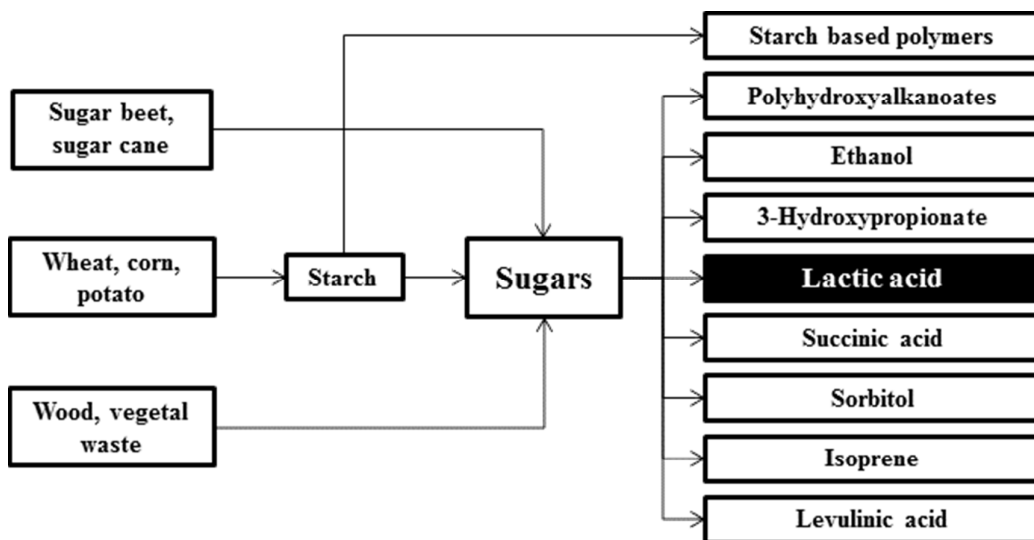
adsorption of the catalysts used in this work.

Catalyst	Surface area (m^2/g)	Pore volume (cm^3/g)
MCM-41	1199	0.80
Sn-MCM-41	801	0.44
JDF-L1	30	0.08
UZAR-S1	159	0.17
AM-4	13	0.05
UZAR-S2	112	0.18
ZSM-5	367	0.55
ETS-10	253	0.14
Used Sn-MCM-41 (after 20 h of reaction)	710	0.34
Used Sn-MCM-41 (after 3rd reaction cycle)	689	0.31

Table 2. Catalytic results after 20 h at 160 ºC (*MG: methyl glycolate; ML: methyl lactate;*

PADA: pyruvaldehyde dimethyl acetal; TMP: 1,1,2,2-tetramethoxypropane).

Catalyst	Analyzed yields (%)					*Total yield*	**Glucose conversion** (%)
	MG	**ML**	**PADA**	**TMP**	**Un-indentified products**		
Sn-MCM-41[1]	3.4±0.1	42.7±5.1	4.6±1.2	1.8±0.8	6.5±2.6	*59.0*	100
MCM-41	0.7	0.7	2.8	0.1	5.1	*9.4*	68
JDF-L1	3.9	1.8	1.2	0.2	1.7	*8.8*	85
UZAR-S1	2.1	3.9	4.4	0.1	6.6	*17.1*	93
AM-4	2.5	1.2	0.6	0.1	0.7	*5.1*	72
UZAR-S2	3.6	5.2	19.1	0.2	12.1	*40.2*	79
ETS-10	4.8	1.9	1.5	0.2	1.4	*9.8*	85
ZSM-5	1.1	3.5	0.5	0.2	9.4	*14.7*	89

[1] The average values and standard deviation correspond to four experiments.

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FIGURE 1

FIGURE 2

FIGURE 3

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FIGURE 4
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FIGURE 5

FIGURE 6