Conversion of Monosaccharides into 5-Hydroxymethylfurfural and Furfural Using Acidic Templated Mesoporous Carbons

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Resumo/Abstract

RESUMO – As moléculas plataforma 5-hidroximetilfurfural (HMF) e furfural podem ser obtidas pela desidratação da frutose e xilose, respectivamente, em catálise ácida de Brønsted. Preparamos 10 Carbonos Mesoporosos Modelados de Brønsted para essas reações. As caracterizações mostraram que eles apresentam 2 diferentes grupos de sítios ácidos, assim como as Amberlysts 45 e 15, sendo os mais fortes relacionados a espécies de ácido sulfônico ou fenilssulfônico. Um *volcano plot* foi encontrado na correlação de TONPlataforma com porcentagem de sítios mais fortes, indicando que o maior TONPlataforma ocorre na faixa de 70-80 % de sítios mais fortes, pertencentes aos catalisadores CMK-3-PSA, CMK-5- PSA, CMK-8-PSA e S-CMK-8-PSA. Na segunda parte deste trabalho, Carbonos Mesoporosos Modelados Bifuncionais foram preparados pela troca iônica parcial do CMK-8-PSA e Amb-45 com Al(III), Sc(III), Fe(III), Cu(II), Sn(IV) e Yb(III). Eles foram usados na conversão de glicose em HMF, uma reação mais econômica que ocorre por catálise ácida de Lewis e Brønsted. Os melhores resultados foram obtidos para os catalisadores com Sn(IV), que tiveram a melhor combinação de sítios ácidos de Lewis e Brønsted para produzir HMF.

*Palavras-chave: HMF, Furfural, Carbono Ácido, Brønsted, Lewis*

ABSTRACT – The platform molecules 5-hydroxymethylfurfural (HMF) and furfural can be obtained by the dehydration of fructose and xylose, respectively, in Brønsted acid catalysis. We prepared 10 Brønsted Templated Mesoporous Carbons (BTMC) for these reactions. The characterizations showed that they present 2 different groups of acid sites, as well the Amberlysts 45 and 15, being the stronger sites related to sulfonic or phenylsulfonic acid species. A volcano plot was found in the correlation of TONPlatform with their percentage of stronger sites, indicating that the highest TONPlatform happens in the range of 70-80 % of stronger acid sites, belonging to the catalysts CMK-3-PSA, CMK-5-PSA, CMK-8-PSA and S-CMK-8-PSA. In the second part of this work, Bifunctional Templated Mesoporous Carbons (BiTMC) were prepared by the partial ion exchange of the CMK-8-PSA and Amb-45 with Al(III), Sc(III), Fe(III), Cu(II), Sn(IV) and Yb(III). They were used in the conversion of glucose into HMF, a more economically reaction that occurs by Lewis and Brønsted acid catalysis. The best results were obtained for the catalysts with Sn(IV), which had the best combination of Lewis and Brønsted acid sites to produce HMF.

*Keywords: HMF, Furfural, Acidic Carbon, Brønsted, Lewis*

## Introduction

5-Hydroxymethylfurfural (HMF) and furfural are bio-based products considered platform molecules for being intermediates in the production of chemicals and fuels (1). They can be obtained in good yields by the dehydration of the monosaccharides fructose and xylose, respectively, in Brønsted acid catalysis. Many solid catalysts have been studied in these reactions, such as zeolites, metal oxides, heteropolyacids, phosphates, acidic silicas and sulfonic acid resins (2). However, they present low active site availability, poor mechanical and thermal stability, and inferior durability and reusability.

A class of catalysts that has been presenting good results in acidic catalytic reactions, overcoming practically all the previous drawbacks, and has few studies in the conversion of monosaccharides is the Brønsted Templated Mesoporous Carbons (BTMC) (3,4). These catalysts are prepared by a step-by-step method, which starts with the synthesis of Templated Mesoporous Carbon Supports (TMCS) using mesoporous silica as hard template. After removing the silica template with NaOH or HF, the acidic species, usually sulfonic acid groups, are grafted on their surface by post-grafting methods. Therefore, herein, we firstly propose the synthesis of different Brønsted Templated Mesoporous Carbons (BTMC) for the conversion of fructose and xylose into respectively HMF and furfural.

Even though the production of HMF and furfural from fructose and xylose presents high yields, they have some commercial drawbacks. Fructose is commercially produced by the enzymatic isomerization of glucose, a cheaper monosaccharide, which makes the direct conversion of glucose into HMF more desirable (1). The production of furfural from xylose, in turn, occurs at high temperatures and reaction times, then, it would be desirable to decrease these parameters to make this reaction more economically viable (1). A promising solution for both problems is to use bifunctional catalysts with Lewis and Brønsted acidity to convert glucose and xylose into HMF and furfural. Thus, the Lewis acid sites firstly isomerizes the precursors into the reactive intermediates fructose and xylulose, which are subsequently dehydrated by Brønsted acid sites into their respective platform molecules (5).

A very interesting bifunctional catalyst for the conversion of glucose into HMF was obtained by the partial ion exchange of the Brønsted acid sites of the resin sulfonic Amberlyst-15 with cations Fe(III), achieving HMF yields close to 60 % (6). Therefore, in the second part of this work, we propose a partial ion exchange of the Brønsted acid sites of the best BTMC prepared in the first part with promising metallic cations for the isomerization of monosaccharides, such as Al(III), Sc(III), Fe(III), Cu(II), Sn(IV) and Yb(III) (6–9). The Bifunctional Templated Mesoporous Carbons (BiTMC) produced were then used in the conversion of glucose and xylose into HMF and furfural, respectively.

Furthermore, in both parts of this work, we selected tetrahydrofuran containing 20 wt. % of water as solvent for the catalytic reactions, which is known to increase the reaction rates and selectivities to platform molecules from monosaccharides (10).

## Materials and Methods

*Synthesis of the TMCS and BTMC*

Ten TMCS and BTMC were prepared. For the synthesis of the carbon supports, the silica hard template, the carbon source and the pyrolysis temperature were varied (**Table 1**). To remove the silica template, HF concentrated was used. The nomenclature of these materials is “Carbon-Pyrolysis temperature”.

After that, two different post-grafting methods were selected to functionalize with Brønsted acid species. For the carbon supports pyrolyzed at 550 °C, which theoretically present a surface functionalized with oxygen groups, it was selected the fuming sulfuric acid method (11), in order to graft sulfonic acid species (catalyst “Carbon-SA”). For the supports pyrolyzed at 1000 °C, which present a more hydrophobic surface, the diazonium salt method (12) was selected to graft phenylsulfonic acid species (catalyst “Carbon-PSA”) (**Table 1**).

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| *TMCS* | *Silica*  *Template* | *Carbon*  *Source* | *TPyrolysis*  *(°C)* | *Post-*  *Grafting* | *BTMC* |
| C-Chi-550 | Ludox  AS-40 | Chitosan | 550 | Fuming H2SO4 | **C-Chi-SA** |
| CMK-3-550 | SBA-15 | Sucrose | **CMK-3-SA** |
| CMK-5-550 | Al-SBA-15 | Furfuryl Alcohol | **CMK-5-SA** |
| CMK-8-550 | KIT-6 | Sucrose | **CMK-8-SA** |
| S-CMK-8-550 | KIT-6 | 2-Thiophene Methanol | **S-CMK-8-SA** |
| C-Chi-1000 | Ludox  AS-40 | Chitosan | 1000 | Diazonium Salt | **C-Chi-PSA** |
| CMK-3-1000 | SBA-15 | Sucrose | **CMK-3-PSA** |
| CMK-5-1000 | Al-SBA-15 | Furfuryl Alcohol | **CMK-5-PSA** |
| CMK-8-1000 | KIT-6 | Sucrose | **CMK-8-PSA** |
| S-CMK-8-1000 | KIT-6 | 2-Thiophene Methanol | **S-CMK-8-PSA** |

**Table 1.** Synthetic parameters of the TMCS and BTMC.

*Characterization of the TMCS and BTMC*

Powder X-Ray Diffraction (XRD) analysis was performed using a Rikagu Multiflex diffractometer. Nitrogen physisorption was recorded at 77 K using a Micro 100 series Surface Area and Pore Size Analyzer instrument from JWGB Sci & Tech. Scanning Electron Microscopy (SEM) was performed using a model S-3400N equipment from Hitachi. Thermogravimetric Analysis (TGA) was performed in a TGA Q500 V20.13 Build 39, with air flow. RAMAN spectra were obtained using a Renishaw inVia spectrometer with a 633 nm excitation wavelength. Infrared spectroscopy (FTIR) was performed in a Prestige-21 infrared spectrometer. X-Ray Photoelectron Spectroscopy (XPS) was made in a Thermo Fisher Scientific K-alpha photoelectron spectrometer. Potentiometric titration was performed in a pH meter Metrohm 827 pH Lab. In this experiment, 40 mg of the samples were added in 35 mL of a solution of NaNO3 0.1 mol L−1, stirring for 10 min. After that, the mixture was titrated with a standard solution of NaOH 0.01 mol L-1/NaNO3 0.1 mol L−1.

*Synthesis of the BiTMC*

The calculation of Brønsted acid sites exchanged was based on the concentration of stronger acid sites by potentiometric titration. The synthesis was performed in a boiling flask containing a mixture of metallic salt, BTMC and ethanol (1g of BTMC:125mL of ethanol) under stirring and reflux for 24 h. The final product was then filtered, washed with ethanol and water, and dried at 80 °C for 1.5 h. The nomenclature of the BiTMC is: “Percentage of Brønsted acid sites exchanged-Metallic cation-BTMC”.

*Catalytic Tests*

The catalytic tests were performed in thick-glass reactors of 15 mL, containing 2.00 g of a solution of 2 wt. % of monosaccharides in tetrahydrofuran containing 20 wt. % of water (THF/H2O = 4/1), and the catalyst. For the reactions, the reactors were placed in an oil bath already heated at 130 °C or 160 °C for the dehydration of glucose/fructose or xylose, respectively, and remained in different reaction times at 300 rpm. The reactions were stopped by cooling down the reactors in ice bath.

Identification and quantification of the products were performed by High Performance Liquid Chromatography (HPLC) using standards. For the catalytic reactions using BTMC, a Shimadzu HPLC LC-10AD was coupled to a Bio-rad Aminex HPX-87H column of 300.0 mm x 7.8 mm (0.005 mol L−1 H2SO4 as mobile phase). For the catalytic reactions using BiTMC, in turn, the same HPLC was coupled to a Rezex RCM-Monosaccharide column of 300.0 mm x 7.8 mm (pure water as mobile phase). In both systems, the detectors used were a refraction index (Shimadzu RID-20A) and a diode array (Shimadzu SPD-10A).

## Results and Discussion

*Characterization of the TMCS and BTMC*

The XRD analysis (not shown) confirmed that the TMCS present the same long-range pore organization of their respective silica template (SBA-15, CMK-3 and CMK-5 = hexagonal pores array in the *P6mm* symmetry; and KIT- 6, CMK-8 and S-CMK-8 = cubic pores array in the *Ia3d* symmetry). Nitrogen physisorption analysis (not shown) confirmed that all the TMCS are mesoporous (pore diameter higher than 3.20 nm) and present high surface area (between 300-1900 m2 g-1). SEM analysis (not shown) exhibited that the carbons C-Chi present roughness surface with honeycomb-like morphology; CMK-3 and CMK-5 aggregates of worm-like morphology, and CMK-8 and S-CMK-8 aggregates without well-defined morphology. The TGA analysis (not shown) confirmed low content of Silicon (< 5 wt. %) in all TMCS.



**Figure 1.** RAMAN deconvoluted spectra of the TMSC sulfonated with SA (A) and PSA (B) species. D\*-band: defect-rich short carbon layers; D-band: defective graphene layers; D#-band: oxidized functional groups on the carbon surface; G-band: ordered graphene layers.



**Figure 2.**High-resolution XPS spectra of S 2p for the TMSC sulfonated with SA (A) and PSA (B) species. Poly-Th: polythiophene-type chains; -C-(S=O)-C-: sulfoxide groups; -C-(O=S=O)-C-: sulfone groups; -SO3H: sulfonic acid groups.

After the post-grafting methods, the XRD, SEM and nitrogen physisorption analysis (not shown) exhibited that the long-range pore organization and morphology of the BTMC were collapsed, and their surface area decreased; however, they are still mesoporous. In addition, the RAMAN analysis (**Figure 1**) showed that the functionalization favored the aromatization of their carbon layers, producing longer defective graphene layers; and increased the amount of oxidized functional groups on their carbon matrix surfaces. The presence of the sulfonic and phenylsulfonic acid species were confirmed by FTIR and by S 2p XPS (**Figure 2**). Moreover, the latter analysis showed that the contribution of -SO3H signal is higher for the BTMC functionalized with phenylsulfonic acid species than sulfonic acid species.

The surface acidity of the BTMC was evaluated by potentiometric titration with the strong base NaOH. The potentiometric titration curves (not shown) exhibited two different groups of acid sites, a stronger and a total, which considers the stronger and the less acidic species. From those curves, the concentration of stronger acid sites (NS), total acid sites (NT) and the percentage of stronger acid sites were calculated (**Figure 3**).



**Figure 3.** Concentration of stronger acid sites (NS), total acid sites (NT), and percentage of stronger acid sites of the BTMC and Amberlysts, by potentiometric titration with NaOH.



**Figure 4.** Correlation between -SO3H signal contribution, by S 2p XPS; and percentage of stronger sites, by potentiometric titration, of the BTMC.

The results pointed out that the less acidic BTMC are the chitosan-based ones. The acidity of the CMK catalysts, in turn, can be divided in 2 groups: CMK-SA group (CMK-3-SA, CMK-5-SA, CMK-8-SA and S-CMK-8-SA), with the highest concentration of total acid sites of the BTMC (between 1650 – 2250 µmol g-1) and a percentage of stronger sites close to 50 %; and the CMK-PSA group (CMK-3-PSA, CMK-5-PSA, CMK-8-PSA and S-CMK-8-PSA), with a concentration of total acid sites between 880 – 1370 µmol g-1 and the highest percentage of stronger acid sites of the BTMC (between 70 – 80 %). Interestingly, the percentage of stronger acid sites of the BTMC functionalized with phenylsulfonic acid species are higher than those with sulfonic acid species. Thus, a linear correlation was found between the -SO3H signal, by S 2p XPS; and the percentage of stronger acid sites, by potentiometric titration (**Figure 4**), suggesting that the higher the -SO3H signal contribution of the BTMC, the higher is their percentage of stronger sites. From this, it can be concluded that the stronger acid sites of the BTMC are prevenient of the sulfonic and phenylsulfonic acid species. The less acidic species, in turn, might be related to carboxylic acid species and hydroxyl of alcohols and phenols (13).

For the sake of comparison, two sulfonic acid resins were also studied, the Amberlyst-15 (Amb-15) and Amberlyst-45 (Amb-45). Their potentiometric titration results showed they present the highest concentration of stronger, total and percentage of stronger acid sites of this study.

*Catalytic Studies of the BTMC and Amberlysts*

The catalytic screening of the BTMC and Amberlysts for the conversion of fructose and xylose into respectively HMF and furfural is presented in **Figure 5**. It is firstly observed that all catalysts produced platform molecules, confirming that they present active Brønsted acid sites to convert fructose and xylose into HMF and furfural, respectively.

Comparing now the catalytic performance of the BTMC, a pattern is observed in both reactions: the worst catalyst is C-Chi-SA (HMF and furfural yield of 2 %); followed by C-Chi-PSA (HMF and furfural yield of 19 % and 14 %, respectively), the CMK-SA group (HMF and furfural yield between 32-50 % and 16-27 %, respectively), and, with the best results, CMK-PSA group (HMF and furfural yield between 65-68 % and 41-45 %, respectively). These results show that the BTMC functionalized with phenylsulfonic acid species exhibit better results than those with sulfonic acid species, even the latter presenting higher concentration of stronger and total acid sites than the former (**Figure 3**). This trend indicates that the concentration of acid sites is not the main factor to improve the production of platform molecules from monosaccharides.

Lastly, the Amberlysts presented different catalytic results depending on the reaction. For the conversion of fructose into HMF, they presented practically the same results of the CMK-PSA group. On the other hand, for the conversion of xylose into furfural, they presented 10 % higher furfural yield than the CMK-PSA group.

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**Figure 5.** Catalytic screening of the BTMC and Amberlysts in the conversion of fructose into HMF and xylose into furfural, at 130 °C and 160 °C, respectively, in THF/H2O = 4/1, 1 h of reaction and 50 mg of catalyst.

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**Figure 6.** Correlation between TONPlatform with the percentage of stronger acid sites of the BTMC and Amberlysts.

Another very interesting strategy to compare the catalytic performance of the catalysts is by the turnover number of HMF and furfural production, which considers the production of those products per catalytic site. Considering that the stronger acid site is the active one, the turnover number of platform molecule production (TONPlatform) can be easily calculated. In addition, observing the **Figures 3** and **5**, one can see that the yield of platform molecules of all catalysts seems to follow their percentage of stronger acid sites, suggesting that this parameter may be important for these reactions. For this reason, the TONPlatform of all catalysts were correlated with their percentage of stronger acid sites (**Figure 6**). Interestingly, it is noticed a volcano plot with the best results in the range of 70-80 % of stronger acid sites, belonging to the CMK-PSA group. In this case, this group produced between 2.5-5.0 mols of HMF and 2.0-4.0 mols of furfural per mol of stronger acid site; whereas the Amberlysts, the best catalysts according to the **Figure 5**, only 0.5-1.5 mols of platform molecules per mol of stronger acid site. Therefore, it can be concluded that the really important parameter for those reactions is the percentage of stronger acid sites, which is optimum for the CMK-PSA group.

*Preliminary Catalytic Studies of the BiTMC*

So far, we have only synthesized some BiTMC and performed their catalytic screening in the conversion of glucose into HMF. Initially, for the sake of comparison, we selected the BTMC CMK-8-PSA and the resin sulfonic Amb-45 to make the partial ion exchange. Considering that our goal is to produce catalysts with Brønsted and Lewis acidity, we firstly decided to perform the partial ion exchange of 40 % of the Brønsted acid sites of those catalysts. Their catalytic screening in the conversion of glucose into HMF is presented in **Figure 7**. The catalysts converted 15-30 % of glucose and produced fructose and HMF, as expected; and mannose, an epimer of glucose that is produced by Lewis acid catalysis and is undesired for producing HMF in low yields (7).

Observing the effect of the metallic cations, it is clear that the catalysts containing Cu(II) and Yb(III) exhibited results worse than the blank (pure Brønsted acid catalyst). On the other hand, the cation Al(III) favored only the isomerization of glucose into fructose; with selectivities of 44 % and 22 % for 40%-Al(III)-CMK-8-PSA and 40%-Al(III)-Amb-45, respectively. The cation Fe(III), in turn, was active only for 40%-Fe(III)-CMK-8-PSA in the isomerization of glucose into fructose (selectivity of 12 %). The catalysts with Sc(III) were well active, producing fructose and HMF; however, with more selectivity for the isomer. Lastly, the catalysts with Sn(IV) were the best for the production of HMF, achieving selectivities of 12 % and 21 % for 40%-Al(III)-CMK-8-PSA and 40%-Al(III)-Amb-45, respectively. This result indicates that these materials present good combination of Lewis and Brønsted acid sites to first isomerize glucose into fructose, and subsequently convert fructose into HMF.

As some cations did not have effect in the reaction with 40 % of Brønsted acid sites exchanged, we decided to exchange 100 % of these sites. So far, this experiment was performed just for M-Amb-45 (**Figure 8**). Interestingly, the increase of the percentage of Brønsted acid sites exchanged did not change the conversion of glucose (with the exception of 100%-Sc(III)-Amb-45, achieving 47 % of conversion). It was also observed that the production of fructose was increased for the catalysts with Al(III), Cu(II) and Yb(III) (41%, 26 % and 39 %, respectively), which was expected due to the complete exchange of Brønsted sites for Lewis acid sites. However, the catalysts with Sc(III), Fe(III) and Sn(IV) practically had the same distribution of products of their respective catalysts with 40 % of Brønsted acid sites exchanged (**Figure 7B**), indicating no effect for the further Lewis acid sites added.

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**Figure 7.** Catalytic screening of the BiTMC 40%-M-CMK-8-PSA (A) and 40%-M-Amb-45 (B) in the conversion of glucose into HMF, at 130 °C, in THF/H2O = 4/1, 2 h of reaction and 20 mg of catalyst.

From those preliminary results, we can conclude that the catalysts with the cations Al(III), Cu(II) and Yb(III) are promising Lewis acid catalysts for producing fructose as the main product. The catalysts with Sc(III), in turn, have active Lewis and Brønsted acid sites; however, the later sites were not able to convert all the fructose produced in the former sites, which decreased their HMF selectivity. This problem was not observed for the catalysts with Sn(IV), which had the best combination of Lewis and Brønsted acid sites to produce HMF as the main product.



**Figure 8.** Catalytic screening of the 100%-M-Amb-45 in the conversion of glucose into HMF, at 130 °C, in THF/H2O = 4/1, 2 h of reaction and 20 mg of catalyst.

## Conclusions

In the first part of this work, different TMCS were prepared varying the silica hard template, the carbon source, and the pyrolysis temperature. These materials indeed are mesoporous and present high surface area. From them, BTMC were synthetized by 2 different post-grafting methods, grafting sulfonic or phenylsulfonic acid species on their surface. The characterizations showed that these catalysts still are mesoporous and contain high surface areas, although they lost their long-range pore organization and morphology after the functionalization. In addition, they present 2 different groups of acid sites, being the stronger one related to the sulfonic or phenylsulfonic acid species. They were active for the conversion of fructose and xylose into HMF and furfural, respectively, as well the Amberlysts 45 and 15, which were studied for the sake of comparison. Lastly, a volcano plot was found in the correlation of TONPlatform with their percentage of stronger sites, indicating that the highest production of platform molecules per stronger acid site happens in the range of 70-80 % of stronger acid sites, belonging to the catalysts of the CMK-PSA group (CMK-3-PSA, CMK-5-PSA, CMK-8-PSA and S-CMK-8-PSA). With this study, we can also conclude that the really important parameter for a catalyst convert fructose and xylose into platform molecules is its percentage of stronger acid sites.

In the second part, different bifunctional catalysts were prepared by the partial ion exchange of the Brønsted acid sites of the CMK-8-PSA and Amb-45 with Al(III), Sc(III), Fe(III), Cu(II), Sn(IV) and Yb(III). The preliminary catalytic studies in the conversion of glucose into HMF showed that the catalysts with the metallic cations Al(III), Cu(II) and Yb(III) are promising Lewis acid catalysts for producing fructose as the main product. The catalysts with Sc(III), in turn, have active Lewis and Brønsted acid sites; however, they produced HMF in low selectivities. This problem was not observed for the catalysts with Sn(IV), which had the best combination of Lewis and Brønsted acid sites to produce HMF as the main product.

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## References

1. J.M.R. Gallo, M.A. Trapp, *J. Braz. Chem. Soc.* *28* (**2017**) 1586–1607.

2. P. Zhou, Z. Zhang, *Catal. Sci. Technol.* *6* (**2016**) 3694–3712.

3. B. Chang, J. Fu, Y. Tian, X. Dong, *J. Phys. Chem. C* *117* (**2013**) 6252–6258.

4. L. Geng, G. Yu, Y. Wang, Y. Zhu, *Appl. Catal. A Gen.* *427*–*428* (**2012**) 137–144.

5. J.L. Vieira, G. Paul, G.D. Iga, N.M. Cabral, J.M.C. Bueno, C. Bisio, J.M.R. Gallo, *Appl. Catal. A Gen.* *617* (**2021**) 1–16.

6. S. Xu, C. Yin, D. Pan, F. Hu, Y. Wu, Y. Miao, L. Gao, G. Xiao, *Sustain. Energy Fuels* *3* (**2019**) 390–395.

7. J. Pimenta Lorenti, E. Scolari, N.M. Cabral, C. Bisio, J.M.R. Gallo, *Ind. Eng. Chem. Res.* *60* (**2021**) 12821–12833.

8. J. Liu, B.B. Yang, X.Q. Wang, C.L. Liu, R.Z. Yang, W.S. Dong, *Appl. Clay Sci.* *141* (**2017**) 118–124.

9. S. Luo, L. Zhu, A. Talukdar, G. Zhang, X. Mi, J.P. Cheng, P.G. Wang, *Mini. Rev. Org. Chem.* *2* (**2005**) 177–202.

10. M.A.A. Mellmer, C. Sener, J.M.R.M.R. Gallo, J.S.S. Luterbacher, D.M.M. Alonso, J.A.A. Dumesic, *Angew. Chemie - Int. Ed.* *53* (**2014**) 11872–11875.

11. A. Takagaki, M. Toda, M. Okamura, J.N. Kondo, S. Hayashi, K. Domen, M. Hara, *Catal. Today* *116* (**2006**) 157–161.

12. X. Wang, R. Liu, M.M. Waje, Z. Chen, Y. Yan, K.N. Bozhilov, P. Feng, *Chem. Mater.* *19* (**2007**) 2395–2397.

13. Z. Zhang, D.W. Flaherty, *Carbon N. Y.* *166* (**2020**) 436–445.