ACS OMEGA

http://pubs.acs.org/journal/acsodf

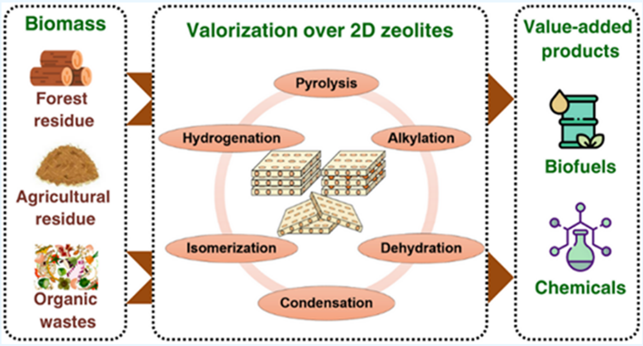
Mini-Review

Two-Dimensional Zeolites—Potential Catalysts for Biomass Valorization

Jino Mathew and Cheralathan Kanakkampalayam Krishnan*

Cite This: *ACS Omega* 2024, 9, 2048−2059

Read Online



ABSTRACT: Valorization of biomass and biomass-derived molecules has become a viable route to get fuels and useful chemicals as fossil feedstocks are dwindling and the demand for renewable feedstocks and sustainable energy sources are rising. Zeolites have been promising catalysts for biomass conversion owing to their structural features and active sites. However, the use of conventional zeolites was limited due to molecular diffusion constraints, which paved the way for the emergence of two-dimensional (2D) zeolites. The high external surface area, bimodal porosity (micropores and mesopores), and 2D structure of these zeolites envisage smooth diffusion of bulky molecules, enhanced accessibility to active sites, and slow deactivation, which are benefits in the valorization of biomass. In this brief review, current advancements in the use of layered 2D zeolites for biomass conversions are discussed. The relationship between the structural features and the catalytic potential of 2D zeolites in some of the major biomass conversion processes like pyrolysis, hydrodeoxygenation, alkylation, acetalization, condensation, and dehydration is discussed and multistep reactions that proceed via a cascade mechanism are highlighted.

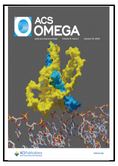
1. INTRODUCTION

It is imperative to find solutions to address the growing concerns on renewability and sustainability of sources used for producing energy and chemicals. For many decades, fossil feedstocks have been thought to be viable sources for energy and chemicals. The surge in human population and energy demand has led to increased dependence on fossil feedstocks. The resulting rapid depletion of fossil feedstocks and the growing environmental issues shift the focus on renewable and sustainable feedstocks. The quest for sustainability and environmentally friendly resources has directed researchers toward biomass, a renewable source of carbon produced from carbon dioxide and water through photosynthesis by plants and microbes. The use of biomass is a highly effective way to reduce greenhouse gas emissions, since the amount of carbon dioxide released is balanced out by the amount that is absorbed during the cultivation process. So, biomass, the largest available source of energy after crude oil, coal, and natural gas, has attracted much interest owing to its ability to provide a broad range of functionalized chemicals and fuels.[1]

Based on their origin, biomass feedstocks can be divided into three types: lignocellulosic, starch and sugar, and triglycerides. To eliminate the fuel vs food dilemma, nonedible lignocellulosic biomass could be chosen as a feasible feedstock, which is abundant in nature. The composition of lignocellulosic biomass is complex with 40−50% cellulose, 10−40% hemicellulose, and 15−30% lignin, making its valorization intricate and challenging.[2] The high-value utilization of lignocellulosic biomass can be accomplished using a variety of conversion methods, such as physical conversion to high-energy-density fuels, biological methods for the synthesis of bioethanol or biogas, and the biorefinery approach, which involves the production of biochemicals or chemical intermediates or biofuels through a chemo-catalytic approach.

The general approaches for lignocellulosic biomass conversion involve thermochemical and hydrolysis pathways. The thermochemical routes, i.e., pyrolysis, gasification, and liquefaction, employ high temperatures and pressures and yield a mixture of intermediates such as bio-oil which can be upgraded to hydrocarbon fuels. The hydrolysis pathway uses a fractionation strategy to isolate lignin and sugar fractions of biomass, which, in turn, could be processed selectively via chemical or biological methods. This selectivity achievable through hydrolysis pathway makes it a viable option for the

Received: November 1, 2023
Revised: December 8, 2023
Accepted: December 11, 2023
Published: January 2, 2024



https://doi.org/10.1021/acsomega.3c08645

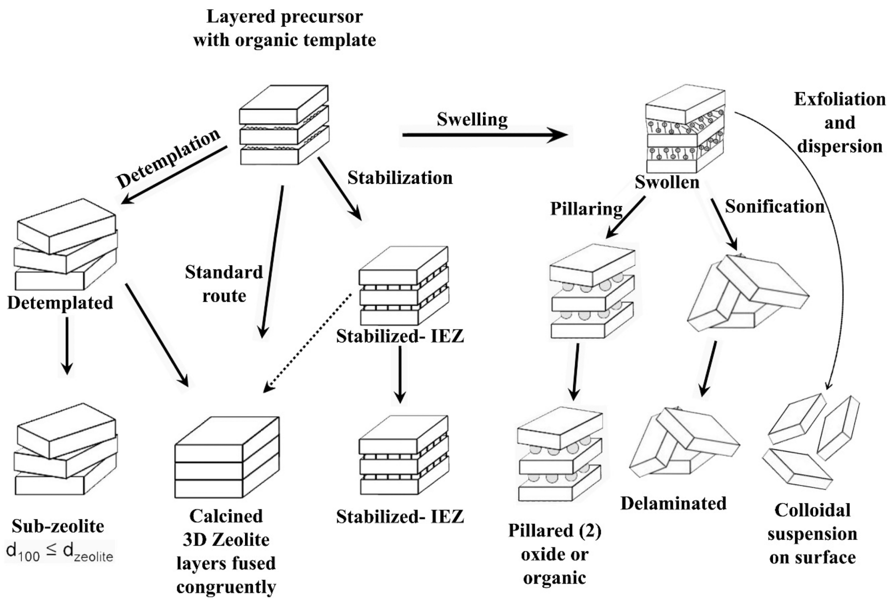


Figure 1. Schematic representation of possible manipulation in a layered zeolite precursor. Reprinted with permission from ref 8. Copyright 2014 American Chemical Society.

targeted synthesis of chemical intermediates or fuel-range hydrocarbons.[3]

Depolymerization of lignocellulosic biomass via hydrolysis-based methods is unique as they yield functionalized, targeted platform molecules which could be subsequently employed as building blocks for producing fine chemicals and chemical intermediates via catalytic processes. Heterogeneous catalysts with multiple functionalities are promising candidates for biomass conversion owing to their various advantages in terms of separation, catalyst recycling, and environmental friendliness. Catalysts having a combination of two or more functionalities, such as Lewis & Bronsted acid sites, basic sites and metallic sites, have replaced the conventional approach of using multiple monofunctional catalysts to catalyze a multistep reaction. This approach allows the complex multistep reactions to be integrated into a single pot, thereby simplifying the process involved, reducing the byproduct formation and ease the catalyst separation.[4] However, due to the limited catalyst stability, low product yields, and poor selectivity, they also pose obstacles, resulting in the production of intricate product mixtures. The downstream separation of these product mixtures is expensive and difficult. Hence, products made from biomass are often expensive, which restricts how broadly they can be used and incorporated into renewable energy cycles and sources.[2]

2. ZEOLITES: GENERAL OVERVIEW

Among various heterogeneous catalysts employed for valorization of biomass and biomass derived platform chemicals, zeolites are interesting candidates due to their structural and morphological features. Zeolites are crystalline microporous aluminosilicates with ordered micropores. They find applications as heterogeneous catalysts in a variety of processes, including petroleum refining, fine chemical synthesis, and biomass conversion. The appreciable catalytic properties of zeolites are linked to their structural features which stem up from interconnected one-, two-, or three-dimensional channels, tunable acidity, high thermal stability, and high surface area.[5] In zeolites, when protons neutralize the negative charge created by Al substitution in the Si−O−Si framework, Bronsted acid sites are formed, which are one of their key catalytically active sites. Lewis acid sites in zeolites are linked to framework or extra-framework Aluminum. The Lewis acid sites can also be created by introducing metal ions other than Al^{3+} into the zeolite framework. Moreover, metal functions, such as metallic nanoparticles, can be introduced into the zeolitic pores with varying degrees of dispersions. In addition to acid sites, basic sites can also be created by ion-exchanging/loading alkali metal ions. The different functionalities, which can be incorporated into a zeolite allow smooth interplay between them favoring reactions involving cascade mechanisms.[5] Despite all these advantages, the relatively small size of the zeolitic micropores limits the mass transport of bulky molecules and accessibility to active sites, leading to rapid coking and unwanted side reactions. There are efforts such as synthesis of zeolite with extra-large pores,[6a] introduction of secondary mesoporosity (hierarchical zeolites),[6b] creation of lamellar structures (2D zeolites),[6c] and preparation of zeolite nanocrystals (crystallite size <100 nm)[6d] to address these issues.

3. TWO-DIMENSIONAL ZEOLITES

Two-dimensional zeolites have gained wide recognition as heterogeneous catalysts in petrochemical refining and fine chemical synthesis. The 2D zeolites are generally obtained from lamellar precursors, which are made of crystalline zeolite nanolayers stacked in one specific direction by weak interlayer forces such as van der Waals forces or hydrogen bonding. So, the 2D zeolites are mesophase materials with one of their crystallographic dimensions being less than a few nanometers in size.

Only a few zeolite frameworks have been identified to adopt and yield 2D forms. Some notable zeolite frameworks that can adopt 2D forms are MWW, MFI, SOD, and FER. The key advantage of these zeolite frameworks is that they offer vast possibilities for modification while retaining the identity of the original layer. So, the topotactic condensation of the silanol groups between the layers of 2D zeolites can give rise to the corresponding 3D forms.[7] Some of the strategies used for achieving 2D zeolites are pillaring, delamination, interlayer expansion (swelling), detemplating, etc. (Figure 1). From a direct synthesis point of view, there are bottom-up and top-down approaches for achieving layered 2D zeolites, and there are three main approaches as depicted in Figure 2:

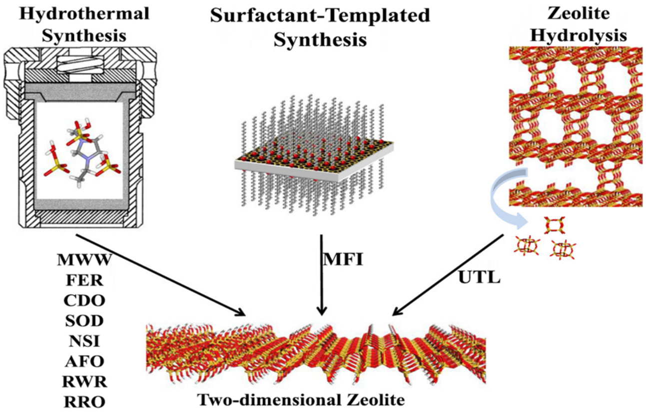


Figure 2. Schematic representation of possible routes leading to a two-dimensional zeolite. Reprinted with permission from ref 8. Copyright 2014 American Chemical Society.

(i) Some zeolites crystallize in lamellar structure under hydrothermal conditions, with structure-directing agents intercalated between the layers. The most studied 2D zeolite, MWW, is prepared via this method.

(ii) Synthesis of zeolite nanosheets using a specially designed surfactant or structure directing agent which restricts the growth of the crystal in one dimension. This method is adopted in the synthesis of MFI zeolite.

(iii) ADOR (Assembly−Disassembly−Organization−Reassembly) mechanism involving a transformation of a 3D zeolite to 2D form. This strategy is followed in germanosilicates with UTL, ITH, and IWW topologies.[8]

The microporous channels of conventional 3D zeolites pose severe limitations in catalytic applications due to hindrance to the diffusion of reactants and products. The remarkable performance of layered 2D zeolites in catalysis arises from their unique pore arrangements. For instance, MCM-22, a layered 3D zeolite of MWW framework topology, has two independent pore systems, one of which is formed by two-dimensional sinusoidal 10-membered ring (MR) channels and the other is formed by large cylindrical 12-ring supercages which are accessible by 10 membered ring windows.[7] The delaminated ITQ-2 formed from MCM-22(P), which has 2.5 nm thick sheets, does not contain these supercages. They contain 12 -MR "cups" or "pockets" on the external surface of each MWW layer. The nanosheets of the modified/synthesized 2D zeolites exhibit hierarchical micro- and mesoporosity between and within their layers. In conventional 3D zeolites, the catalytically active sites are found in the micropores, and the area surrounding these active sites is constrained, which restricts access to them. In contrast, 2D zeolites have better diffusion of molecules within their mesopores, and many of their active sites are exposed on external surfaces, which is a great advantage for catalysis. Some of the interesting properties of 2D zeolites are summarized in Figure 3.

Previously, some reviews have been published on the synthesis and structural features of 2D zeolites. For instance, Roth et al. reviewed the recent developments in the field of 2D zeolites giving a broad outlook on different 2D frameworks, their synthesis, characterization, and catalytic applications.[8] Přech et al. compared the catalytic performance of 3D zeolites, nanozeolites, hierarchical zeolites, and 2D zeolites including some biomass conversions.[9] To the best of our knowledge, there is no previous review that is entirely devoted to the applications of 2D zeolites for biomass valorization. This mini-review aims to establish the potential of 2D zeolites in the valorization of biomass and highlight the relationship between their structural properties and catalytic performance.

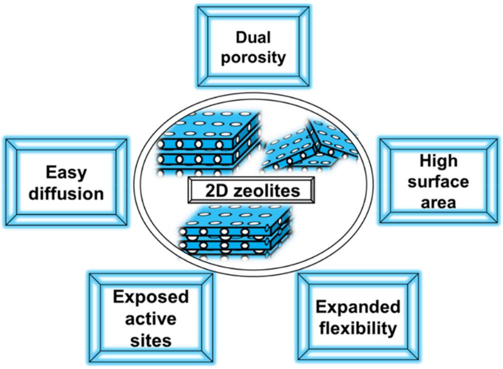


Figure 3. Properties of 2D zeolites.

4. 2D ZEOLITES IN BIOMASS TRANSFORMATIONS

Zeolites in general, due to their inherent and tunable acidity and shape selectivity, are excellent catalysts for biomass conversions. The enhanced diffusion of reactants and products in 2D zeolites, owing to their open structure, makes them better catalysts than conventional zeolites for the transformation of biomass feedstocks. Hence, 2D zeolites were investigated for a variety of biomass transformations, including pyrolysis, isomerization, hydrodeoxygenation, dehydration, transesterification, and hydrogenation, wherein single or multiple active sites are involved in the reactions. This section of the review tends to cover the potential of layered zeolites in some of the most important biomass conversions, including lignocellulosic feedstock and a few of the major triglyceride feedstock-based platform chemicals.

4.1. Catalytic Pyrolysis and Hydrodeoxygenation.

Pyrolysis is a widely used thermochemical conversion strategy to produce high-grade solids, bio-oils, and gaseous fuel from biomass feedstocks. Zeolites are among the most prevalent catalysts used for pyrolysis of biomass due to their shape-selective behavior and acidic nature. While typical 3D zeolites present an obstacle due to diffusion constraints, 2D zeolites facilitate the effective transport of bulky oxygenates generated during the early stages of pyrolysis. The potential of layered and delaminated MCM-22 and ITQ-2 zeolites was explored in the catalytic fast pyrolysis of paddy husk pyrolysis vapors by Naqvi et al.[10] The experiments were performed in a drop-type fixed-bed pyrolyzer at 450 °C. A surface area (546 m^2/g) for delaminated ITQ-2 zeolites higher than that of MCM-22 (226 m^2/g) offers more accessible active sites, resulting in a higher pyrolysis yield for the former. ITQ-2 showed a greater degree of deoxygenation than MCM-22 and favored considerable reduction of acids, ketones, and alcohols via cracking, oligomerization, or aromatization, leading to increased aromatics generation. This improved activity of ITQ-2 could be due to the larger number of accessible acid sites. Acidity plays a significant role in deciding the selectivity of deoxygenated products such as aromatics. Tuning the acid sites can change the degree of deoxygenation and as well as aromatization and change the selectivity. For example, Fermoso et al. modified lamellar and pillared ZSM-5 zeolites with MgO and ZnO which resulted in an overall decrease in surface area, a substantial reduction in Bronsted and Lewis acidic sites of the zeolites, and the generation of new Lewis acid sites of medium strength.[11] The lamellar and pillared ZSM-5 zeolites without MgO and ZnO gave large amounts of oxygenated aromatic compounds and aromatic hydrocarbons, whereas the metal oxide incorporated zeolites moderated the formation of aromatic hydrocarbons over oxygenated aromatics and inhibited the formation of undesirable polyaromatic hydrocarbons. Consequently, there was a significant reduction in the amount of coke formed on these catalysts.

Lee et al. compared the catalytic performance of unilamellar mesoporous MFI nanosheets (UMNs) as confirmed by the transmission electron microscopy image shown in Figure 4 with Al-SBA-15.[12]The UMNs showed comparatively stronger acid sites than Al-SBA-15 as evident from their NH_3 temperature-programmed desorption profiles.

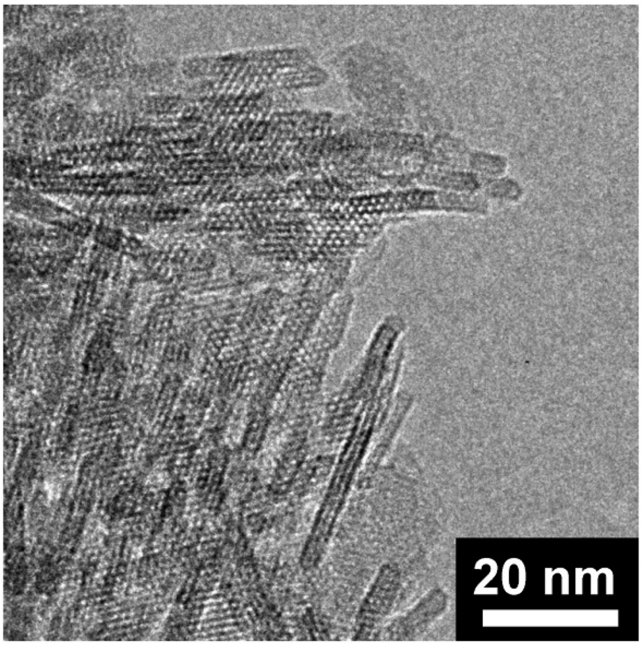


Figure 4. TEM image of unilamellar mesoporous MFI nanosheets. Reprinted with permission from ref 12. Copyright 2014 Elsevier.

The stronger acidity of UMNs resulted in extensive deoxygenation of bio-oil obtained from different constituents from biomass, thereby improving the bio-oil quality with a high yield of monoaromatics. For instance, as shown in Figure. 5, in the catalytic pyrolysis of cellulose, the stronger Bronsted acidic sites of UMN promoted the conversion of levoglucosan to monoaromatics via furans, while for Al-SBA-15, conversion from furans to monoaromatics was less,[12] indicating the importance of strong acid sites for deoxygenation leading to monoaromatics.[12]

Hydrodeoxygenation (HDO) reactions are also considered as one of the most efficient strategies to remove oxygen from bio-oil to produce saturated hydrocarbons under mild conditions. HDO has been employed for oxygen removal in various bio-oil model compounds. HDO activity is known as a combined effect of metal dispersion, acid sites, and diffusion of reactants and products. So, obviously, 2D zeolites are the suitable candidates as catalysts for HDO due to their favorable properties. Yoon et al. studied the catalytic activity of Rh nanoparticles supported on various layered MWW zeolites like MCM-22(C: calcined), MCM-22(SC; swollen and calcined), and MCM-36 (pillared derivative) for the HDO of f 1,3,5-trimethoxybenzene (1,3,5-TMB), a bulky lignin model compound, and guaiacol.[13] For comparison purposes, amorphous mesoporous materials such as MCM-41 and silica−alumina-aerogel (SAA) were also studied. Due to the high metal dispersion and excellent mass transfer of reactants and products, Rh-MCM-36 demonstrated superior performance for the conversion of both 1,3,5-TMB, and guaiacol and better selectivity toward the desired products as compared to Rh-loaded mesoporous materials as presented in Figure 6 and Figure 7. The complementary effects of metals, acid sites, and accessibility were evident when Gutiérrez-Rubio et al. used Ni_2P supported on 2D zeolites for guaiacol HDO.[14] The introduction of Ni_2P on MCM-22, lamellar ZSM-5 (L-ZSM-5), and pillared ZSM-5 (PI-ZSM-5) generated new Lewis acid sites ($Ni^{\delta+}$) apart from the Bronsted acid sites. Ni_2P/PI-ZSM-5 with a higher number of active sites and greater accessibility for these active sites showed higher HDO activity with 78% conversion and more than 95% selectivity to cyclohexane, a most important deoxygenated product.[14]

4.2. Alkylation, Condensation, and Acetalization Reaction. The delaminated 2D zeolites are studied for the transformation of biomass-derived platform chemicals into fuels and other molecules. HMF is one of the most important platform chemicals obtained from C-6 sugars via dehydration because, owing to the presence of highly reactive functional groups, it can be converted to value-added bioproducts via organic transformations by catalytic methods. One example is that when HMF is alkylated and followed by hydrodeoxygenation, kerosene can be produced.[15] Alkylation of aromatics with HMF using large pore (H-Beta, USY, and Mordenite), delaminated zeolites (2D ITQ-2), and mesoporous aluminosilicates can produce 5- benzyl HMF derivatives.[15] Among these catalysts, 2D-ITQ-2 zeolites exhibited excellent performance in alkylation by giving 99% selectivity to alkylated products and particularly 76% selectivity toward p-alkylated product at 99% conversion as presented in Table 1. This impressive catalytic activity of 2D-ITQ-2 is primarily due to its optimal acidity and the huge exterior surface area created by "cup-like" cavities which are also shape-selective.[15]

Employing condensation reaction, for example aldol condensation, is a potent way to unleash the potential of biomass-derived compounds like furfural, HMF, glycerol, etc. and exploit them as sources of fuels and chemicals. Though homogeneous acid and base catalysts can facilitate condensation reactions, heterogeneous catalysts would be advantageous, as they can be separated easily and reused. Though delaminated 2D zeolites were studied for condensation reactions, mixed results were obtained based on whether the zeolite has "cup-like" cavities or not. For example, Kikhtyanin et al. exploited the highly accessible acid sites of layered zeolites for aldol condensation of furfural with acetone.[16] MWW zeolites such as MCM-22 (3D), MCM-49 (an analogue of MCM-22), MCM-36(pillared zeolite), and MCM-56 (delaminated zeolite) were used for the study. All of the catalysts produced FAc (4-(2-furyl)-3-buten-on) as the main product dimerized and condensed to form further products. Compared to wide-pore beta zeolite, the MWW zeolites performed better in terms of conversion.

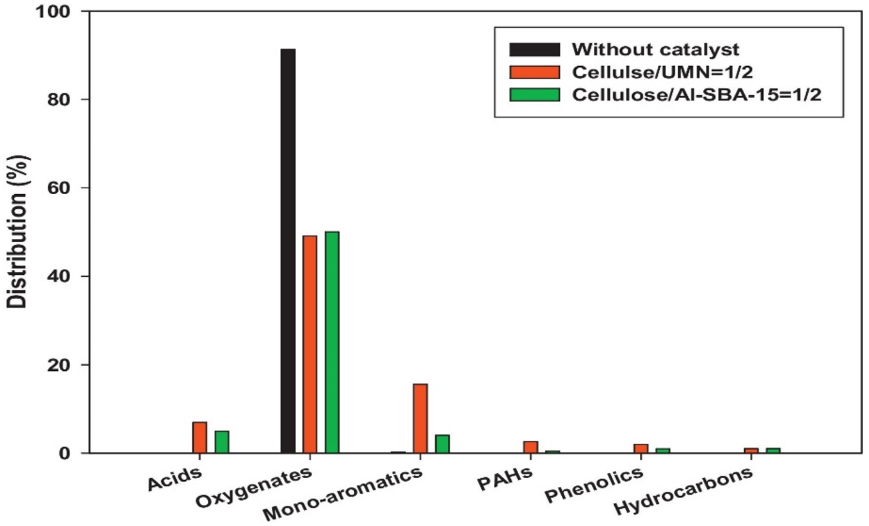


Figure 5. Product distribution of the catalytic pyrolysis of cellulose. Reprinted with permission from ref 12. Copyright 2014 Elsevier.

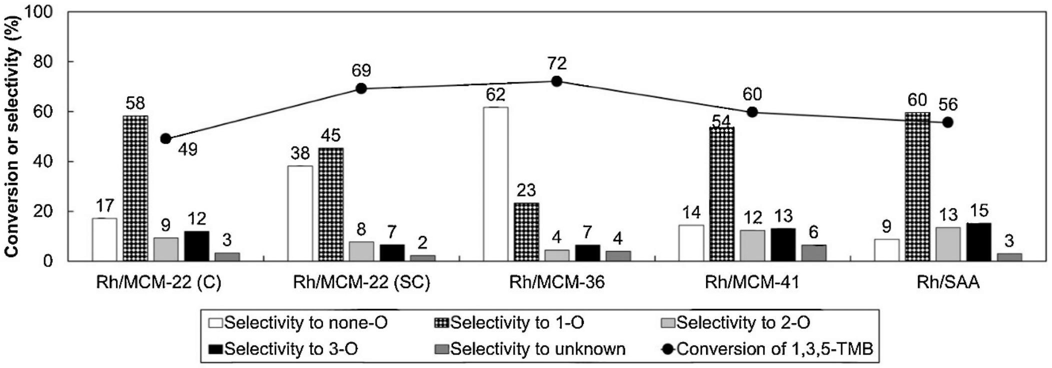


Figure 6. HDO reaction results for 1,3,5-TMB on different catalysts. Reprinted with permission from ref 13. Copyright 2017 Elsevier.

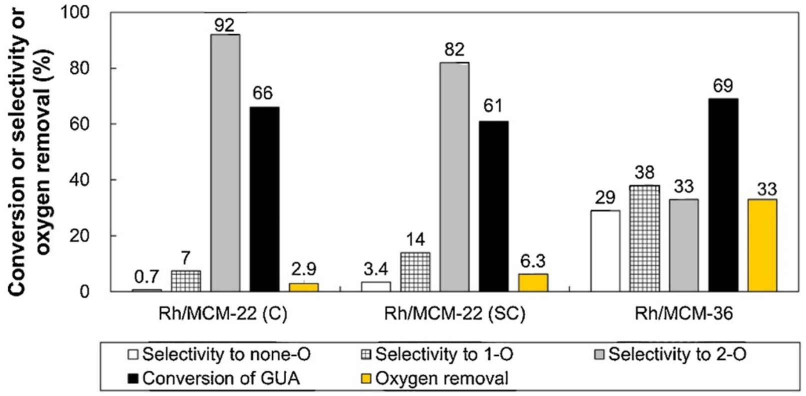


Figure 7. HDO reaction results of guaiacol on different catalysts. Reprinted with permission from ref 13. Copyright 2017 Elsevier.

However, among the MWW zeolites, MCM-22 and MCM-49 were found to be more active than MCM-36 and MCM-56. The oddly decreased activity of MCM-36 and MCM-56 compared to the 3D zeolites (MCM-22 and MCM-49) was explained by the fact that the reaction in MCM-22 and MCM-49 is taking place in super cages in addition to the cup-like cavities on the external surface, but in MCM-36 and MCM-56 it takes place only on the cup-like cavities. Despite the higher conversion of furfural over MWW catalysts, they deactivated rapidly due to coke formation. This was more severe in MCM-36 due to the easily accessible "cups" on the external surface.[16] Vieira et al. studied the condensation of glycerol, a byproduct of biodiesel production, with acetone to form cyclic ketals like solketal using vanadium oxides supported on lamellar ferrierite zeolites.[17] The purely siliceous delaminated zeolite ITQ-6 (micro/mesoporous zeolite) and FER, a microporous zeolite, employed in this study were obtained from the same lamellar PreFER precursors via postsynthetic modifications as represented in Figure 8. 1,5 and 10 wt % vanadium-impregnated on ITQ-6 and FER supports were investigated for the acid-catalyzed acetalization of glycerol and acetone. The mechanism and possible products are shown in Scheme 1. Not so surprisingly, the micro/mesoporous

Table 1. Results Obtained in the Alkylation of Toluene with HMF by Different Acid Catalysts[a]

Catalyst (Si/Al)	$r°_{Alk}$ ($\times 10^5$ mol min^{-1})	$r°_{OBMF}$ ($\times 10^5$ mol min^{-1})	Time (h)	Conv (%)	Yield (%) OBMF	Yield (%) alk	Sel (%) alk	Sel. (%) alk (o:p:m)
Mordenite(10)	0.16	0.14	8	20	9	11	55	27:73:0
USY-720(12.2)	2.56	0.57	6	100	5	95	95	46:52:2
HBeta(12.5)	0.57	0.14	6	69	15	54	78	24:72:4
ITQ-2(15)	1.54	—	8	99	1	98	99	22:76:2
MCM-41(12)	0.97	0.38	8	99	15	84	85	40:56:4
PTSA[b]	1.01	6.1	8	100	14	86	86	45:48:7
			24	100	5	95	95	45:48:7

[a] Reprinted with permission from ref 15. Copyright 2015 Royal Society of Chemistry. Reaction conditions: HMF (0.5 mmol), toluene (25 mL), catalysts 15.75 mg (25 wt %), reflux temperature, nitrogen atmosphere. [b] 12 mg of PTSA was added.

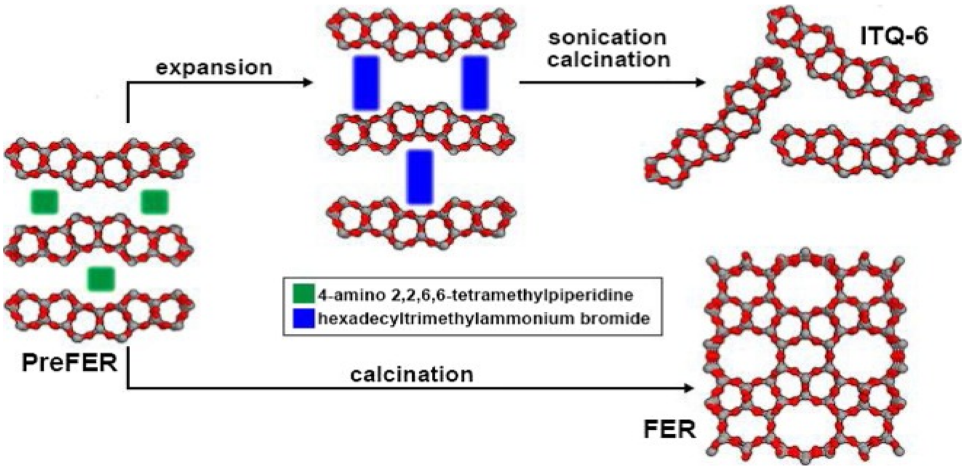
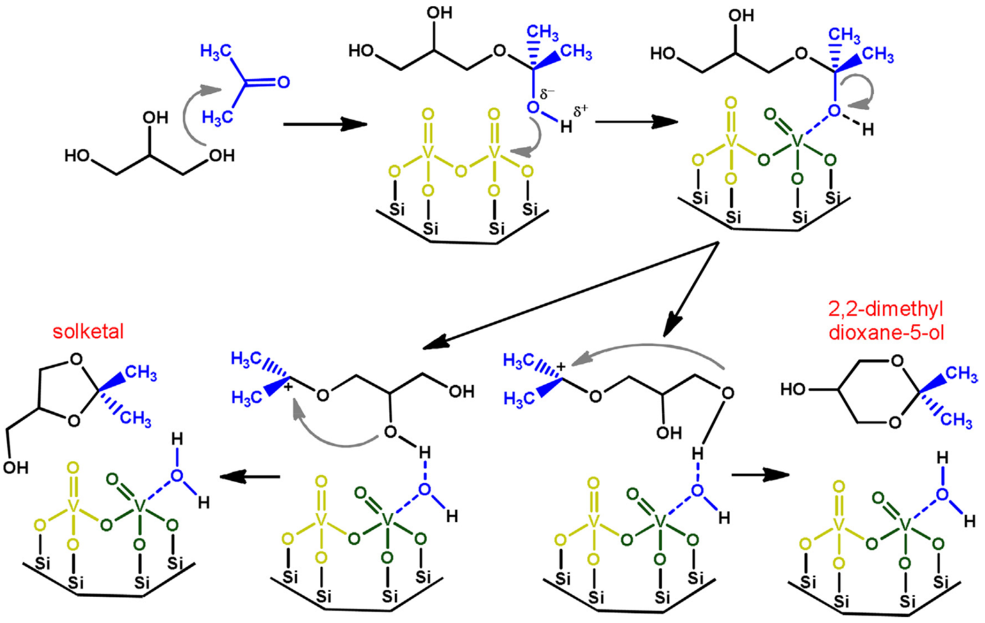


Figure 8. A schematic of postsynthesis treatments used for preparing ITQ-6 and FER, from PreFER lamellar precursor. Reprinted with permission from the ref 17. Copyright 2018 Elsevier.

Scheme 1. Mechanism for Condensation of Glycerol with Acetone over Vanadium Loaded Si-FER and Si-ITQ-6 Catalysts[a]

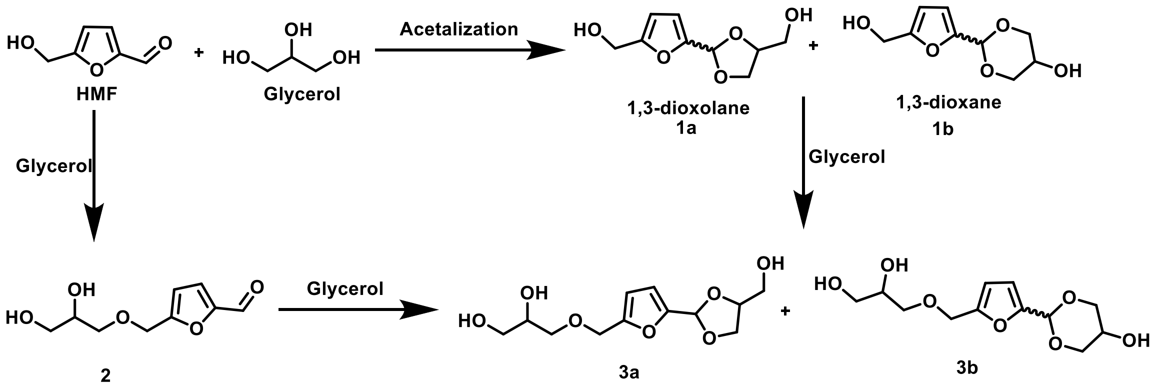


[a] Reprinted with permission from ref 17. Copyright 2018 Elsevier.

ITQ-6 with surface area >600 m^2/g showed superior performance in the reaction due to the high dispersion and accessibility of active sites. Among the vanadium-impregnated ITQ-6 zeolites, [5V]Si-ITQ-6 (5 wt % Vanadium) gave 100% conversion and 99% selectivity to solketal. [10V]Si-ITQ-6 exhibited a lower activity due to the formation of V_2O_5 agglomerates on the surface.[17]

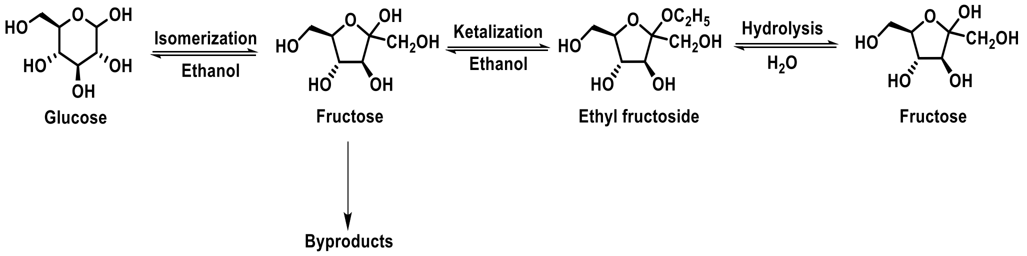
Acetalization of glycerol with HMF is an important reaction to produce valuable diol monomers like HMF glyceryl acetal which find tremendous applications in industry.[18] Since both HMF

Scheme 2. Pathways for Acetalization Reaction of HMF with Glycerol[a]



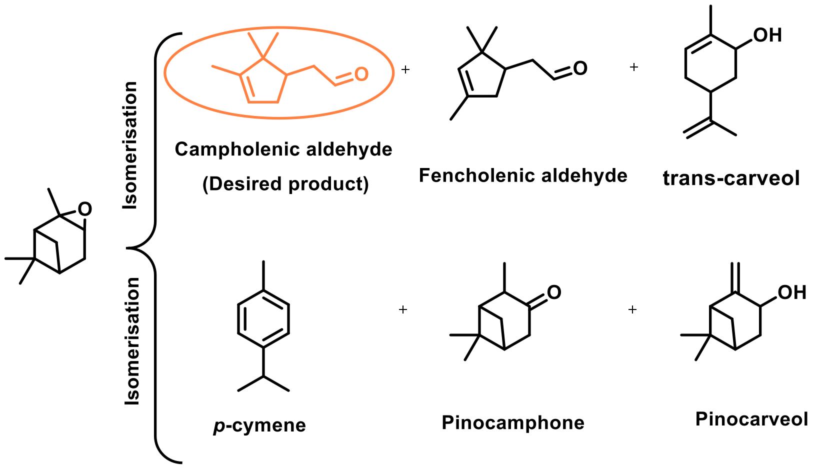
[a]Adapted with permission from ref 18. Copyright 2018 American Chemical Society.

Scheme 3. Reaction Pathway for Converting Glucose to Fructose[a]



[a]Adapted with permission from ref 20b. Copyright 2015 John Wiley and Sons.

Scheme 4. Possible Products of α-Pinene Oxide Isomerization[a]



[a]Adapted with permission from ref 21. Copyright 2018 Royal Society of Chemistry.

and glycerol are highly functionalized, there are possibilities for various side reactions like self-polymerization, cross etherification, etc., as illustrated in Scheme 2.

2D zeolites show excellent selectivity for the acetalization reaction with glycerol. For example, Arias et al. examined the efficiency of various solid acid catalysts like Beta zeolite, HY zeolite, ITQ-2, MCM-41, and p-toluenesulfonic acid for the acetalization of glycerol with HMF and among the catalysts, ITQ-2 gave 98% yield of acetals (1) with 100% selectivity owing to its mild Bronsted acidic sites, accessibility to the acid sites and enhanced diffusion of reactants and products.[18] The acetalization reaction between many other furan-based derivatives, such as furfural, 2 methyl furfural, and 5-benzylfurfural with glycerol was also explored using the ITQ-2 catalyst, and cyclic acetals was produced with good yield and selectivity.[18]

4.3. Isomerization. Glucose to fructose isomerization is considered as one of the important steps in the production of HMF and lactic acid from glucose. Due to their structure and dimensionality, 2D zeolites could be efficient catalysts. Using periodic DFT calculations, Li et al. theoretically studied the synergistic effects between Lewis acidic Sn sites and hydroxyl groups of MOR, BEA, MFI, and MWW zeolites for isomerization of glucose.[19] Among the studied framework types, MWW zeolites are expected to have higher glucose isomerization reaction activity due to the lower barrier for the hydride shift caused by the presence of strongly acidic bridging silanol

https://doi.org/10.1021/acsomega.3c08645
ACS Omega 2024, 9, 2048−2059

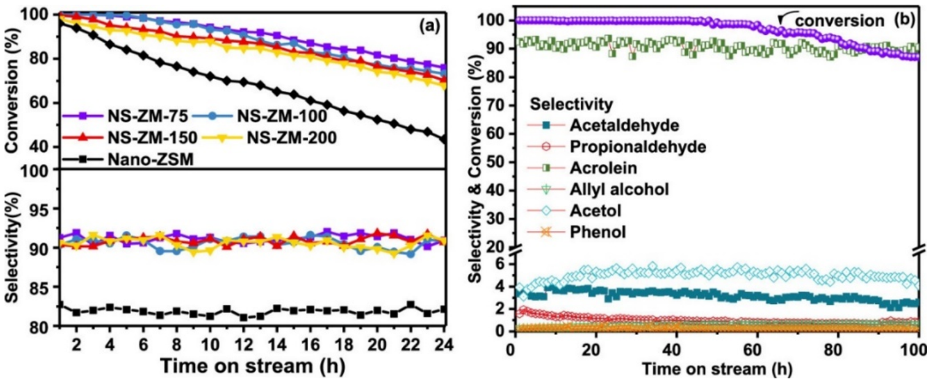


Figure 9. (a) Catalytic performance of different catalysts at $T = 320$ °C, WHSV = 4 h^{-1}, and 1 atm; (b) catalytic performance of NS-ZM-75 at $T = 320$ °C, WHSV = 2 h^{-1}, and 5% glycerol feed. Reprinted with permission from ref 26. Copyright 2020 American Chemical Society.

groups next to the Sn site. Ren et al. compared isomerization of glucose and maltose on pillared Sn − MWW, a 2D zeolite with its 3D analogue, Sn-MWW.[20a] The conversion of glucose and fructose selectivity on pillared Sn-MWW and Sn-MWW were comparable. However, in the case of maltose isomerization, the pillared Sn-MWW catalyst showed higher conversion (79%) than Sn-MWW (40%) with comparable selectivity for maltulose due to better accessibility to the active sites in the pillared Sn−MWW. Similarly, the facile accessibility of Lewis and Bronsted acidic sites in Sn-containing self-pillared pentasil (Sn-SPP) zeolites was exploited for glucose isomerization (Scheme 3). Sn-SPP with Si/Sn ratio of 186 gave the best performance with 85% glucose conversion and 65% yield of fructose with 74% selectivity.[20b]

Apart from the isomerization of sugars, 2D zeolites have also been explored for the isomerization of terpenes such as α-pinene oxide, and one of the products of this reaction, campholenic aldehyde, is a highly valuable chemical. The selectivity of campholenic aldehyde is related to Lewis acid sites as Bronsted acid sites cause the formation of undesirable side products as shown in Scheme 4. For this reason, between Ti-MCM-36 and Al-MCM-36, the former was found to be the better catalyst.[21]

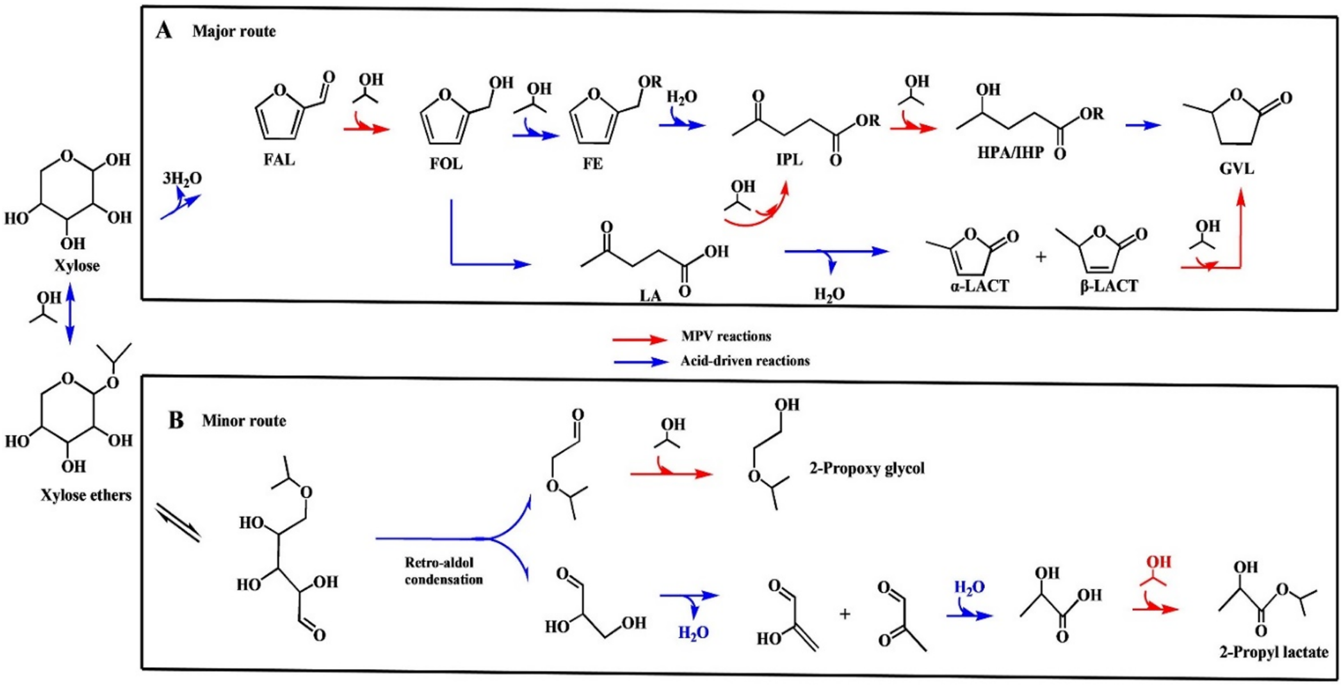
However, in contrast to this, when Ti-MCM-36 was compared with Ti-MCM-22, the latter was found to be the better catalyst in terms of campholenic aldehyde yield due to more number of tetrahedrally coordinated Lewis acidic Ti species that are located on the outer surface of Ti-MCM 22 as well as lack of Bronsted acidic sites.[21] So, Ti-MCM-22 gave a campholenic aldehyde yield of 96% at 100% conversion of α-pinene oxide, whereas Ti-MCM-36 yielded 91% campholenic aldehyde at 99% conversion of α-pinene oxide.

4.4. Dehydration Reactions.

Another interesting application of 2D zeolites is the dehydration of sugars and glycerol. Sugars obtained by the hydrolysis of biomass fractions can be dehydrated to produce highly functionalized platform chemicals, such as HMF and furfural. These dehydration reactions are acid-catalyzed reactions; hence, solid acid catalysts like zeolites can be used. Lima et al. studied the protonic form of 3D zeolite (Nu-6(2)) and layered 2D zeolite (del-Nu-6(1)) obtained from a common precursor, Nu-6(1) for dehydration of D-xylose to furfural.[22] The 2D zeolite, delaminated Nu-6(1) (del-Nu-6(1)) with a high BET surface area (151 m^2/g) was the better catalyst than 3D zeolite (Nu-6(2)). The del-Nu-6(1) catalyst gave a reaction rate that is twice that of Nu-6(2). The improved catalytic performance of del-Nu-6(1) could be correlated to better accessibility to the acid sites compared with Nu-6(2). The del-Nu-6(1) was proven as an economically viable catalyst because of its stability in continuous runs, even though exfoliated niobates outperform it in terms of catalytic activity.[22] Superior dehydration performances were observed when MCM-22 and its delaminated form were used for aqueous phase dehydration of xylose to furfural. Although delaminated ITQ-2 had a higher external surface area than MCM-22, comparable catalytic performances were observed due to the similar concentrations of acidic sites. Moreover, no leaching was observed for both catalysts during recycling studies.[23] Though the reason for the difference in the activity between Nu-6(2) and MCM-22-based catalysts is not explained, the reason can be understood based on the difference in their framework type and surface area. Nu-6(2) is an NSI framework-type zeolite containing small pore pentasil units, whereas MCM-22 is an MWW framework-type zeolite having 10MR pore openings and a layered structure with two independent pore channels. Apart from this, both MCM-22 and ITQ-2 exhibit much higher surface areas (333, 623 m^2/g, respectively) compared to Nu-6(2) and del-Nu-6(1) (20, 151 m^2/g respectively). The higher surface area of MWW-based zeolites favors better accessibility of acid sites compared to the catalysts based on NSI. The 2D nanosheets of MWW were also found to be efficient catalysts for the dehydration of fructose to HMF.[24] The catalytic activity was correlated to the accessibility of acid sites in the prepared MWW nanosheets using disorder index (DI) which was governed by wt % of the CTAB used for their preparation. The $HMWW_{4.0}$ sample prepared using 4 wt % of CTAB with the highest external surface area (234 m^2/g) compared to other HMWW samples gave HMF selectivity of 90% at fructose conversion of 93% due to its optimum DI, and accessible acid sites.[24] This example shows the importance of the accessibility of acid sites in the dehydration of sugars and the advantage of utilizing 2D zeolites for the same.

In addition to converting carbohydrates into platform chemicals, 2D zeolites are also useful for converting glycerol into acrolein via dehydration. Acrolein is an important chemical with added value that is utilized in the manufacture of acrylic acid necessary for the manufacturing of polymers. The major limitation of the catalytic dehydration of glycerol is catalyst deactivation due to coke deposition. MCM-36 and ITQ-2 showed superior performance over MCM-22 in the production of acrolein from glycerol.[25] This superior performance of the 2D zeolites compared to their 3D counterpart is attributed to their higher exterior surface area and mesopores, which lead to lesser pore obstruction due to coke. Coke formation takes place mainly

Scheme 5. Reaction Pathway for (A) Conversion of Xylose and Furfural into γ-Valerolactone through Acid Catalyzed (red) and MPV (blue) Reactions; (B) Retro-Aldol Condensation of Xylose into 2-Propoxy Glycol and 2-Propyl Lactate[a]



[a] Reprinted with permission from ref 29. Copyright 2020 Elsevier. ABbreviations: FAL, furfural; FOL, furfuryl alcohol; FE, isopropyl furfuryl ether; IPL, isopropyl levulinate; LA, levulinic acid; LACT, a/b-angelica lactones; GVL, c-valerolactone.

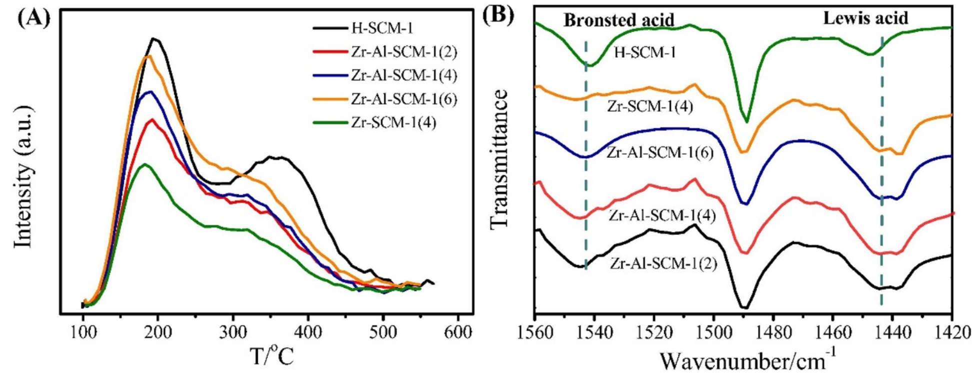


Figure 10. (A) NH_3-TPD profiles and (B) pyridine-FTIR spectra collected after treatment at 100 °C under vacuum. Reprinted with permission from ref 29. Copyright 2020 Elsevier Inc.

in the mesopores of the 2D zeolites, and hence, it is possible to access interior channels and active sites in the micropores without hindrance. Also, the compositions of the coke formed in the pores differ based on the types of pores; polyglycols formed on the exposed surfaces of MCM-36 and ITQ-2, whereas polyaromatics formed in the micropores of MCM-22.[25] Similar observations were made when self-pillared MFI nanosheets are used for glycerol dehydration.[26] The mesoporous self-pillared nanosheets (NS-ZM-75) showed impressive catalytic performance with 100% conversion of glycerol and 92% acrolein selectivity at a WHSV of 4 h^{-1}. Further, the same self-pillared MFI (NS-ZM-75) showed a lower rate of deactivation compared to the conventional nano-ZSM-5 zeolite as shown in Figure 9.[26]

4.5. Downstream Processing via Cascade Reactions.

Multifunctional catalysts possessing more than one active component can circumvent the difficulties associated with using multiple catalysts with different active sites and their separation after each step during the reaction. The multifunctional catalysts facilitate a multistep reaction to proceed in tandem or cascade mode, producing a range of products with different levels of selectivity. To achieve a certain product of interest with a higher selectivity, the active sites must be properly balanced and tuned. For example, Bronsted-Lewis acid bifunctional materials, acid−base bifunctional materials, acid/base-metal bifunctional materials and metals dispersed on nanomaterials are known to catalyze variety of biomass conversions.[4] Layered 2D zeolites can be suitable catalysts in cascade reactions owing to their ability to bear different active components with high dispersion and enhanced accessibility. For instance, ferrierite (FER) type layered 3D ECNU-35 and delaminated DECNU-35 2D zeolites, modified with Pd were employed for the reductive etherification of furfural with ethanol which is a two-step cascade reaction.[27] In this reaction, the first step is the acid-catalyzed acetalization of furfural to form a diacetal, which is followed by conversion of the diacetal to furfuryl ethyl ether over Pd sites. DECNU-35 showed exceptional catalytic activity compared to ECNU-35 and other reference catalysts like bulk FER, MCM-22, ITQ-1, and Al_2O_3. The superior performance of DECNU-35 was attributed to its higher specific surface area ($511 m^2/g$), optimum concentration of Pd species and acid sites, and enhanced diffusion of molecules due to its mesoporosity.[27]

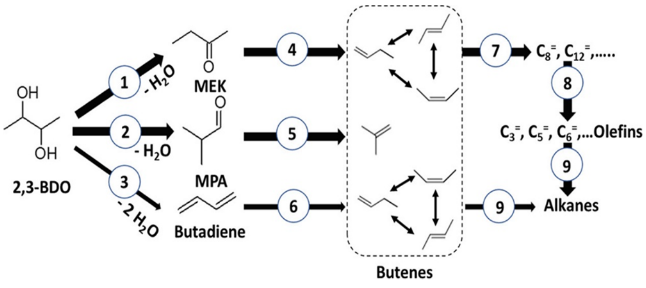
γ-Valerolactone (GVL) is one of the most important value-added chemicals that finds application as fuel additives and solvents. The production of GVL from sugars or other platform chemicals like furfural or levulinic acid involves a series of steps and different active sites.[28a,b] Li et al. explored the catalytic efficiency of bifunctional Zr–Al–SCM-1 catalysts possessing both Lewis and Bronsted acidic sites for the production of GVL from xylose.[29] The Zr–Al–SCM-1 is basically a delaminated double-layered 2D zeolite having both Zr and Al in the framework, which are responsible for Lewis and Brosted acid sites, respectively. Xylose to GVL conversion of the catalyst takes place in two different routes as shown in Scheme 5.

Between the two routes, dehydration of xylose to furfural and its further conversion to GVL are found to be the major one. The catalytic activity of Zr–Al–SCM-1 was compared with that of Zr-SCM-1 and Zr–Al-MCM-22, a 3D layered zeolite solely possessing micropores. Determination of acid sites of the catalysts using TPD of NH_3 and pyridine-FTIR spectroscopy has been done and the results are shown in Figure 10.

The TPD of NH_3 indicated a higher number of acid sites of medium strength in Zr–Al–SCM-1 than in Zr-SCM-1. Further, when Zr-SCM-1 solely contains Lewis acidic sites, Zr–Al-MCM-22 and Zr–Al–SCM-1 catalysts exhibited presence of both Lewis and Bronsted acid sites. Zr–Al–SCM-1 having 4 wt % Zr, Zr–Al–SCM-1 (4) exhibited superior catalytic activity than Zr-SCM-1 and Zr–Al-MCM-22 due to its optimal Lewis to Brosted acid site ratio and double-layered delaminated structure, which increases surface area and improves accessibility to active sites and helps smooth diffusion of reactants and products.[29]

Another example of the application of 2D zeolites in the cascade process is in the production of butene-rich C_{3+} olefins from 2,3- Butanediol (2,3-BDO) over copper-modified pillared MFI zeolite. The conversion of 2,3-BDO involves hydrogenation and dehydration steps, and different products are possible as shown in Scheme 6. The cascade reactions involved were catalyzed by different Cu species and Lewis & Bronsted acidic sites present on the multifunctional Cu/PMFI zeolite.[30]

Scheme 6. Different Reactions Involved in Conversion of 2,3-Butanediol to Butene-Rich C3+ Olefins[a]



[a]Reprinted with permission from ref 30. Copyright 2022 American Chemical Society.

The reaction was performed in a hydrogen environment at 573 K and Cu/PMFI showed notable activity with 38% selectivity to butenes at >96% conversion, along with various other products like C_2–C_4 alkanes, ethylene, propene, and methyl ethyl ketone. The mesoporous channels present in pillared MFI zeolites facilitate the diffusion of butenes from the micropores, thereby eliminating further oligomerization, hydrogenation, or cracking reactions that produce nonbutene olefins. The reduced diffusion length also limits the coke formation in the pores.[30]

5. RECOMMENDATIONS AND FUTURE OUTLOOK

Though 2D zeolites offer great flexibility and efficient catalytic performance, there are many challenges ahead. The complexity involved in the 2D zeolite chemistry and synthesis methods has been a major factor limiting their use. Poor understanding of the formation mechanism of 2D zeolites, lack of adequate characterization techniques to confirm the layered nature of zeolites without any ambiguity, lack of understanding of the reaction mechanism in catalytic reactions, lack of knowledge of the location of active sites in the 2D zeolites, etc. are some of the hurdles for the usage of these materials as catalysts for biomass conversion.

To fully utilize the potential of 2D zeolites in valorization of biomass, more active research is required in the following areas: (i) exploring cost-effective, direct, and green methods for the preparation of 2D zeolites, (ii) ways to introduce multifunctionalities in 2D zeolites, (iii) extending the catalytic studies on more 2D zeolite frameworks, and (iv) in situ characterization methods to establish the role of 2D structure and active sites in deciding the reaction pathways and product selectivity.

6. CONCLUSIONS

Conventionally, 3D zeolites have been utilized for biomass conversion. However, the microporous structure of typical 3D zeolites has limited their applicability as it prevents the transport of bulky molecules inside the pores, presents low accessibility to active sites, and supports coke deposition and quick catalyst deactivation. The emerging 2D zeolites, due to their micro/meso dual porosity, which enables quick diffusion of large molecules, high exterior surface area and improved accessibility to active sites and less deactivation, can outperform 3D zeolites. This has been evidenced from recent studies on the efficient catalytic performance of 2D zeolites in some of the most significant biomass transformations such as pyrolysis, alkylation, isomerization, dehydration, condensation, acetalization, and cascade reactions. However, the potential of multifunctional 2D zeolites has not been fully utilized for cascade reactions. The complexity of multistep catalytic reactions in batches could be overcome by using a multifunctional catalyst with all the necessary active sites on a single catalyst. The multifunctionalities could be introduced onto 2D zeolites during the structural modifications of their layered precursors, which in turn will reduce the time and cost, thereby producing efficient catalysts for cascade reactions.

■ AUTHOR INFORMATION

Corresponding Author

Cheralathan Kanakkampalayam Krishnan – *Department of Chemistry, School of Advanced Sciences, Vellore Institute of Technology, Vellore 632014, India;* orcid.org/0000-0001-9988-6486; Email: cheralathan.k@vit.ac.in

Author

Jino Mathew − *Department of Chemistry, School of Advanced Sciences, Vellore Institute of Technology, Vellore 632014, India*

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.3c08645

Notes

The authors declare no competing financial interest.

Biographies

Jino Mathew received his B.Sc. in chemistry in 2019 from Payyanur College, Kannur University, Kerala, India. He obtained his M.Sc. in Chemistry from Central University of Kerala, India, in 2021. In 2022, he joined the Department of Chemistry, Vellore Institute of Technology, India, as a Ph.D. student under the supervision of Dr. Cheralathan K K. He has been selected for an "Innovation in Science Pursuit for Inspired Research (INSPIRE)" fellowship by Department of Science and Technology, India. His current research involves development of multifunctional zeolites for biomass conversions.

Cheralathan Kanakkampalayam Krishnan (Cheralathan K K) received his M.Sc. in chemistry from School of Chemistry, Madurai Kamaraj University, Madurai, India, in 1998. He obtained his Ph.D in 2003 from Anna University, Chennai, India, for his thesis on zeolite based catalytic reactions for fine chemical synthesis. He had postdoctoral stints in Chonbuk National University, Republic of Korea, Korea Research Institute of Chemical Technology, Republic of Korea, and Institute of Industrial Science, The University of Tokyo, Japan. Currently, he is a Professor of Chemistry at Vellore Institute of Technology, Vellore, India. His research interests include heterogeneous catalysis, zeolites and other porous materials, nanomaterials, valorization of biomass platform chemicals, methanol reformation for hydrogen production, and carbon materials for electrode applications.

■ ACKNOWLEDGMENTS

The authors thank VIT for providing a SEED Grant (Sanction order No: SG20220044) and a DST-INSPIRE Fellowship (File no: DST/INSPIRE Fellowship/2021/IF210338) for carrying out this research work.

■ REFERENCES

(1) Sudarsanam, P.; Peeters, E.; Makshina, E. V.; Parvulescu, V. I.; Sels, B. F. Advances in Porous and Nanoscale Catalysts for Viable Biomass Conversion. *Chem. Soc. Rev.* **2019**, *48*, 2366−2421.

(2) Lin, L.; Han, X.; Han, B.; Yang, S. Emerging Heterogeneous Catalysts for Biomass Conversion: Studies of the Reaction Mechanism. *Chem. Soc. Rev.* **2021**, *50*, 11270−11292.

(3) Alonso, D. M.; Bond, J. Q.; Dumesic, J. A. Catalytic Conversion of Biomass to Biofuels. *Green Chem.* **2010**, *12*, 1493−1513.

(4) Li, H.; Fang, Z.; Smith, R. L.; Yang, S. Efficient Valorization of Biomass to Biofuels with Bifunctional Solid Catalytic Materials. *Prog. Energy Combust. Sci.* **2016**, *55*, 98−194.

(5) Ennaert, T.; Van Aelst, J.; Dijkmans, J.; De Clercq, R.; Schutyser, W.; Dusselier, M.; Verboekend, D.; Sels, B. F. Potential and Challenges of Zeolite Chemistry in the Catalytic Conversion of Biomass. *Chem. Soc. Rev.* **2016**, *45*, 584−611.

(6) (a) Paillaud, J. L.; Harbuzaru, B.; Patarin, J.; Bats, N. Extra-Large-Pore Zeolites with Two-Dimensional Channels Formed by 14 and 12 Rings. *Science* **2004**, *304*, 990−992. (b) Feliczak-Guzik, A. Hierarchical Zeolites: Synthesis and Catalytic Properties. *Microporous Mesoporous Mater.* **2018**, *259*, 33−45. (c) Sardar, M.; Maharana, M.; Manna, M.; Sen, S. 2D Zeolites. *Layered2D Advanced Materials and Their Allied Applications* **2020**, 193−210. (d) Tago, T.; Konno, H.; Nakasaka, Y.; Masuda, T. Size-Controlled Synthesis of Nano-Zeolites and Their Application to Light Olefin Synthesis. *Catal. Surv. Asia.* **2012**, *16*, 148−163.

(7) Díaz, U.; Corma, A. Layered Zeolitic Materials: An Approach to Designing Versatile Functional Solids. *Dalton Trans.* **2014**, *43*, 10292−10316.

(8) Roth, W. J.; Nachtigall, P.; Morris, R. E.; Čejka, J. Two-Dimensional Zeolites: Current Status and Perspectives. *Chem. Rev.* **2014**, *114*, 4807−4837.

(9) Přech, J.; Pizarro, P.; Serrano, D. P.;´Cejka, J. From 3D to 2D Zeolite Catalytic Materials. *Chem. Soc. Rev.* **2018**, *47*, 8263−8306.

(10) Naqvi, S. R.; Uemura, Y.; Yusup, S.; Sugiura, Y.; Nishiyama, N. In Situ Catalytic Fast Pyrolysis of Paddy Husk Pyrolysis Vapors over MCM-22 and ITQ-2 Zeolites. *J. Anal. Appl. Pyrolysis* **2015**, *114*, 32−39.

(11) Fermoso, J.; Hernando, H.; Jana, P.; Moreno, I.; Přech, J.; Ochoa-Hernández, C.; Pizarro, P.; Coronado, J. M.; Čejka, J.; Serrano, D. P. Lamellar and Pillared ZSM-5 Zeolites Modified with MgO and ZnO for Catalytic Fast-Pyrolysis of Eucalyptus Woodchips. *Catal. Today* **2016**, *277*, 171−181.

(12) Lee, H. W.; Park, S. H.; Jeon, J. K.; Ryoo, R.; Kim, W.; Suh, D. J.; Park, Y. K. Upgrading of Bio-Oil Derived from Biomass Constituents over Hierarchical Unilamellar Mesoporous MFI Nanosheets. *Catal. Today* **2014**, *232*, 119−126.

(13) Yoon, J. S.; Lee, T.; Choi, J. W.; Suh, D. J.; Lee, K.; Ha, J. M.; Choi, J. Layered MWW Zeolite-Supported Rh Catalysts for the Hydrodeoxygenation of Lignin Model Compounds. *Catal. Today* **2017**, *293*−*294*, 142−150.

(14) Gutiérrez-Rubio, S.; Berenguer, A.; Přech, J.; Opanasenko, M.; Ochoa-Hernández, C.; Pizarro, P.; Čejka, J.; Serrano, D. P.; Coronado, J. M.; Moreno, I. Guaiacol Hydrodeoxygenation over Ni2P Supported on 2D-Zeolites. *Catal. Today* **2020**, *345*, 48−58.

(15) Arias, K. S.; Climent, M. J.; Corma, A.; Iborra, S. Synthesis of High-Quality Alkyl Naphthenic Kerosene by Reacting an Oil Refinery with a Biomass Refinery Stream. *Energy Environ. Sci.* **2015**, *8*, 317−331.

(16) Kikhtyanin, O.; Chlubná, P.; Jindrová, T.; Kubička, D. Peculiar Behavior of MWW Materials in Aldol Condensation of Furfural and Acetone. *Dalton Trans.* **2014**, *43*, 10628−10641.

(17) Vieira, L. H.; Possato, L. G.; Chaves, T. F.; Pulcinelli, S. H.; Santilli, C. V.; Martins, L. Studies on Dispersion and Reactivity of

Vanadium Oxides Deposited on Lamellar Ferrierite Zeolites for Condensation of Glycerol into Bulky Products. *Mol. Catal.* **2018**, *458*, 161−170.

(18) Arias, K. S.; Garcia-Ortiz, A.; Climent, M. J.; Corma, A.; Iborra, S. Mutual Valorization of 5-Hydroxymethylfurfural and Glycerol into Valuable Diol Monomers with Solid Acid Catalysts. *ACS Sustainable Chem. Eng.* **2018**, *6*, 4239−4245.

(19) Li, G.; Pidko, E. A.; Hensen, E. J. M. Synergy between Lewis Acid Sites and Hydroxyl Groups for the Isomerization of Glucose to Fructose over Sn-Containing Zeolites: A Theoretical Perspective. *Catal. Sci. Technol.* **2014**, *4*, 2241−2250.

(20) (a) Ren, L.; Guo, Q.; Orazov, M.; Xu, D.; Politi, D.; Kumar, P.; Alhassan, S. M.; Mkhoyan, K. A.; Sidiras, D.; Davis, M. E.; Tsapatsis, M. Pillared Sn-MWW Prepared by a Solid-State-Exchange Method and Its Use as a Lewis Acid Catalyst. *ChemCatChem.* **2016**, *8*, 1274−1278. (b) Ren, L.; Guo, Q.; Kumar, P.; Orazov, M.; Xu, D.; Alhassan, S. M.; Mkhoyan, K. A.; Davis, M. E.; Tsapatsis, M. Self-Pillared, Single-Unit-Cell Sn-MFI Zeolite Nanosheets and Their Use for Glucose and Lactose Isomerization. *Angew. Chem., Int. Ed.* **2015**, *54*, 10848−10851.

(21) Pitinova-Stekrova, M.; Eliášová, P.; Weissenberger, T.; Shamzhy, M.; Musilová, Z.; Čejka, J. Highly Selective Synthesis of Campholenic Aldehyde over Ti-MWW Catalysts by α-Pinene Oxide Isomerization. *Catal. Sci. Technol.* **2018**, *8*, 4690−4701.

(22) Lima, S.; Pillinger, M.; Valente, A. A. Dehydration of D-Xylose into Furfural Catalysed by Solid Acids Derived from the Layered Zeolite Nu-6(1). *Catal. Commun.* **2008**, *9*, 2144−2148.

(23) Antunes, M. M.; Lima, S.; Fernandes, A.; Pillinger, M.; Ribeiro, M. F.; Valente, A. A. Aqueous-Phase Dehydration of Xylose to Furfural in the Presence of MCM-22 and ITQ-2 Solid Acid Catalysts. *Appl. Catal., A* **2012**, *417*−*418*, 243−252.

(24) Hao, R.; Du, A.; Zhu, Q.; Wu, X.; Liu, S.; Wang, K.; Wang, Y. Disordered HMWW Zeolite Nanosheets Catalyzing Fructose to 5-Hydroxymethylfurfural. *Catal. Lett.* **2023**, 1−10.

(25) Rodrigues, M. V.; Vignatti, C.; Garetto, T.; Pulcinelli, S. H.; Santilli, C. V.; Martins, L. Glycerol Dehydration Catalyzed by MWW Zeolites and the Changes in the Catalyst Deactivation Caused by Porosity Modification. *Appl. Catal., A* **2015**, *495*, 84−91.

(26) Ali, B.; Lan, X.; Arslan, M. T.; Wang, H.; Gilani, S. Z. A.; Wang, S.; Wang, T. Self-Pillared MFI-Type Zeolite Nanosheets as Selective Catalysts for Glycerol Dehydration to Acrolein. *ACS Appl. Nano Mater.* **2020**, *3*, 10966−10977.

(27) Wang, J.; Fan, Y.; Guo, X.; Gu, Q.; Jiang, J.; Guan, Y.; He, X.; Ma, Y.; Xu, H.; Wu, P. Direct Synthesis and Delamination of Swollen Layered Ferrierite for the Reductive Etherification of furfural. *ChemCatChem.* **2022**, *14*, e202200535.

(28) (a) Jayakumari, M. T.; Kanakkampalayam Krishnan, C. Tuning Al Sites in Y-Zeolite for Selective Production of ϒ-Valerolactone from Levulinic Acid. *Appl. Catal., A* **2023**, *663*, 119318. (b) Malu, T. J.; Manikandan, K.; Cheralathan, K. K. Levulinic Acid−A Potential Keto Acid for Producing Biofuels and Chemicals. In *Biomass, Biofuels, Biochemicals: Recent Advances in Development of Platform Chemicals*; Elsevier, 2019; pp 171−197.

(29) Li, X.; Yuan, X.; Xia, G.; Liang, J.; Liu, C.; Wang, Z.; Yang, W. Catalytic Production of γ-Valerolactone from Xylose over Delaminated Zr-Al-SCM-1 Zeolite via a Cascade Process. *J. Catal.* **2020**, *392*, 175−185.

(30) Adhikari, S.; Zhang, J.; Unocic, K.; Wegener, E. C.; Kunal, P.; Deka, D. J.; Toops, T.; Sinha Majumdar, S.; Krause, T. R.; Liu, D.; Li, Z. Direct 2,3-Butanediol Conversion to Butene-Rich C3+Olefins over Copper-Modified 2D Pillared MFI: Consequence of Reduced Diffusion Length. *ACS Sustainable Chem. Eng.* **2022**, *10*, 1664−1674.