

Zeolite-Catalyzed Formaldehyde–Propylene Prins Condensation

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Prins condensation of formaldehyde with propylene to form 3buten-1-ol is investigated using microporous solid acid catalysts. Zn/H-beta shows high conversion but leads to a broad product distribution composed primarily of pyrans. Mechanistic studies revealed that 3-buten-1-ol reacts via Prins cyclization or dehydrate to 1,3-butadiene that further reacts with formaldehyde via a hetero-Diels–Alder reaction. These secondary reactions are suppressed over ZSM-5 catalysts: 3-buten-1-ol is the predominant product over H-ZSM-5 zeolite under all conditions investigated. 3-Buten-1-ol selectivity of up to 75% is achieved. In a second step 3-buten-1-ol dehydrates at temperatures as low as 423 K, forming 1,3-butadiene. Although Brønsted acid sites are the primary catalytic sites, ion exchange of Zn^{II} increases the overall rate and 3-buten-1-ol selectivity. H-ZSM-5 showed significant differences in reactivity and selectivity as a function of the Si/Al ratio; optimal catalytic properties were observed within Si/Al = 40–140.

Introduction

A classical C–C bond forming reaction is the ene reaction, a six-electron pericyclic process occurring between an alkene possessing an allylic hydrogen atom (the ene) and an electron-deficient multiple bond co-reactant (the enophile). As a result of the ene reaction, two new σ bonds are formed and the π bond of the ene migrates. Scheme 1 illustrates the reaction with propylene as the ene and formaldehyde as the enophile.^[1]



Scheme 1. Representation of the ene reaction.

The Prins reaction is a specific example of the ene reaction referring to the condensation of formaldehyde with olefins.^[2,3] The reaction proceeds by electrophilic addition of the protonated formaldehyde to a nucleophilic center of the olefin to generate a carbocationic intermediate (Scheme 2).^[4] The primary products are unsaturated alcohols, diols, and alkyl diox-

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Scheme 2. Acid-catalyzed formaldehyde condensation with olefins.

anes (Scheme 2), depending on reaction conditions (such as temperature, solvent) and the catalyst. Under anhydrous conditions, for example, the cationic intermediate loses a proton to form an allylic alcohol. On the other hand, when water and a protic acid such as sulfuric acid are present, the reaction product is a 1,3-diol. With an excess of formaldehyde and lower reaction temperatures the favored pathway is an alkyl-dioxane.^[4] Compounds such as pyrans and dienes could be formed via consecutive reactions of the primary products.

The Prins reaction is of current interest because of the availability and low cost of lower olefins and because of the versatility of formaldehyde as a one-carbon electrophile. Shale gas production has reduced the cost of propane, a raw material for propylene manufacture, and has resulted in an increase in the production of methanol and formaldehyde.^[5,6] 3-Buten-1-ol, 1,3-butanediol, and *m*-dioxane are the expected products of the reaction. All of them are precursors to 1,3-butadiene although 3-buten-1-ol is the most desired product, since it affords the diene by a simple thermal dehydration.

Formaldehyde-propylene condensation is traditionally catalyzed by homogeneous mineral acids (such as sulfuric acid), or

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homogeneous Lewis acids such as SnCl₄, BF₃, and ZnCl₂.^[4,7,8] For example, using 1-5% H₂SO₄ at 353-398 K under pressure, the reaction forms *m*-dioxane, with 85% yield; 1,3-butanediol and oxan-4-ol were also observed.^[4] W. Fitzky described the reaction of formaldehyde (specifically paraformaldehyde) with propylene in the presence of zinc chloride in dichloromethane to obtain *m*-dioxane.^[7] Homogeneous acid catalysts, however, have significant drawbacks: they are corrosive, there are limits to reusability and they suffer from poor product selectivity control. 1,3-Butanediol has been reported to form in one-pot over a CeO₂ catalyst though hydrolysis of *m*-dioxane starting from formaldehyde and propylene.^[9] However, as the authors indicate, the coupling of these two reactions is not so efficient, as Prins condensation is favored under lower temperatures, and hydrolysis of *m*-dioxane is benefited by higher temperatures.^[9] Heterogeneous acidic catalysts and in particular catalysts which can enable selective formation of 3-buten-1-ol appear to have never been investigated experimentally. Recent theoretical studies on the Prins reaction identified zeolites as potential catalysts (for example, MgY, metal cation exchanged FAU).^[10-12] Fu et al. (using ONIOM2 B3LYP/6-31G(d,p):UFF and density functional theory) investigated this reaction and compared the MgY catalyzed and the uncatalyzed system.^[12] They found that the reaction barrier for the MgY was considerably lower than the uncatalyzed reaction, but despite these theoretical results, there is no experimental evidence for heterogeneous catalysis of the reaction between formaldehyde and propylene to 3-buten-1-ol and theoretical studies have mainly focused on this pathway without considering secondary reactions.

Herein we report an investigation of the selectivity control of the Prins reaction towards 3-buten-1-ol by minimizing subsequent undesired reactions. We envision a two-step process first reacting formaldehyde with propylene to form 3-buten-1ol, and second dehydrating this product to produce 1,3-butadiene. We have found that acid zeolites catalyze the Prins reaction between formaldehyde with propylene. We present the first experimental evidence of formaldehyde condensation with propylene using a heterogeneous catalyst to form the unsaturated alcohol, namely 3-buten-1-ol. Several large and medium pore size zeolites were tested and it was determined that H-ZSM-5 (MFI) is the optimal catalyst of the samples investigated. Further improvements in conversion and selectivity to 3-buten-1-ol can be achieved using Zn/H-ZSM-5. Large-pore Zn-exchanged zeolite beta was found to be very reactive but unselective towards the unsaturated alcohol, while FER and SSZ-13 showed no reactivity. It is shown that Brønsted acid sites are the catalytic sites of the primary and secondary reactions.

Results and Discussion

Catalyst characterization

Nitrogen physisorption, X-ray diffraction, X-ray fluorescence, SEM-EDX, and FTIR of adsorbed CD₃CN were used to characterize the catalyst samples used to investigate the Prins conden-



Table 1. Catalyst micropore volume and chemical composition.						
Catalyst	Micropore volume [cm ³ g ⁻¹]	Si/Al molar	Zn/Al molar	Si/Sn or Zr molar		
Zr-beta	0.22	_	-	166		
Sn-beta	0.24	-	-	96		
H-beta(12.5) ^[a]	0.17	12.0	-	-		
Zn/H-beta(12.5)	0.17	11.4	0.12	-		
Zn-FER(10)	0.13	7.1	0.004	-		
H-ZSM-5(25)	0.12	24.4	-	-		
Zn/H-ZSM-5(25)	0.11	25.5	0.22	-		
Zn/H-ZSM-5(11.5)	0.12	8.9	0.12	-		
Zn-SSZ-13(12)	0.25	7.4	0.09	-		
[a] Number in the p zeolite.	arenthesis indi	cate nominal v	values of t	he parent		

sation of formaldehyde with propylene. Basic catalyst characterization data are shown in Table 1.

Micropore volume measurements were consistent with the structure of the zeolites and it was found that Zn ion exchange does not have a significant impact on microporosity. X-ray diffraction patterns of Zn/H-beta(12.5) and Zn/H-ZSM-5(25) are similar before and after Zn exchange indicating that the structure of the samples is unaffected (Supporting Information, Figures S1 and S3); no impurities or additional crystal phases were identified in any of the diffraction patterns. Zinc content was measured by XRF (Table 1) and found to be 0.116 for Zn/ H-beta(12.5) (Si/Al = 11.4 from XRF) and 0.219 and 0.117 for Zn/H-ZSM-5(25) (Si/Al = 25.5 from XRF) and Zn-ZSM-5(11.5) (Si/ AI = 8.97 from XRF), respectively. On zeolites Zn-SSZ-13(12) and Zn-FER(10), the Zn/Al ratio was lower. Also note that the values measured by XRF for Zn/H-beta(12.5) and Zn-ZSM-5(25) are very close to those obtained by EDX (Supporting Information).

Prins condensation of formaldehyde with propylene

A variety of microporous solid acid catalysts, including Sn-, Zrbeta as well as ion-exchanged Zn/H-beta(12.5), Zn/H-ZSM-5(11.5) and (25), Zn-FER(10) and Zn-SSZ-13(12), were investigated to identify promising catalysts (Table 2). A control experiment showed that the uncatalyzed reaction at 423 K proceeds at a very slow rate. In this case, formaldehyde reacted to form a small amount of methanol and a small peak assigned to 3buten-1-ol was detected via gas chromatography (Table 2). Lewis acidic zeolite Sn-beta and Zr-beta were both inactive (Table 2). The reaction is clearly catalyzed by medium-pore Zn ion-exchanged H-ZSM-5(11.5) and (25) and by large-pore Zn/Hbeta(12.5). Furthermore, conversion over Zn-ion exchanged FER(10) and SSZ-13(12) was very low (Table 2) and the spent catalysts became dark brown after separation from the liquid. Side reactions forming heavier products are probably taking place or the formed products cannot easily diffuse out. Zn/H-ZSM-5(11.5) and (25), unlike Zn/H-beta, proved to be a very efficient catalyst, showing high activity and high selectivity towards 3-butene-1-ol, the desired product. In contrast, over Zn/



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Catalyst	CH ₂ O Conversion			Carbon-based Selectivity [%]			04	
	[%]		HO	0	-	C ^o		
None ^[a]	5.5	_	100.0	_	_	-	-	
Zr-beta ^[b]	-	-	-	-	-	-	-	
Sn-beta ^[b]	-	-	-	-	-	-	-	
Zn/H-beta(12.5) ^[c]	46.6	10.2	0.9	-	1.8	82.4	4.6	
Zn/H-FER(10)	0.2	14.8	85.2	-	-	-	-	
Zn/H-ZSM-5(25)	38.9	3.1	57.7	11.8	6.7	6.3	14.4	
Zn/H-ZSM-5(11.5)	20.5	1.4	62.5	15.9	-	12.8	7.3	
Zn/H-SSZ-13(12)	0.06	-	100.0	-	-	-	-	

H-beta(12.5) five-carbon species dominated the product distribution and the major product was 2H-pyran with 82.4% carbon selectivity.

Although not the target product of this study, 2H-pyran is a useful starting chemical to form pentanediols and can be used to synthesize aliphatic α,β -unsaturated olefinic dicarboxylic acid esters useful as plasticizers in vinyl chloride polymers among others.^[13, 14] Side reactions of formaldehyde and of propylene were also observed with Zn/H-beta(12.5): methyl formate was detected by GC-MS suggesting that formaldehyde undergoes Cannizzaro-type reactions forming methanol and formic acid since methyl formate is formed by the condensation of methanol with formic acid.^[15] At the same time, propylene hydrates to form 2-propanol in high yield (29%). The water molecules needed for this reaction are formed during dehydration reactions and from paraformaldehyde decomposition into formaldehyde. The extent of dehydration reactions over Zn/H-beta(12.5) is higher compared to Zn/H-ZSM-5(11.5) and (25) and this can explain the higher propylene hydration extent in the former case. Finally, to verify that product distribution over Zn/H-beta is not a result of lower propylene/formaldehyde ratios (since propylene is in parallel consumed in hydration to 2-propanol), we performed an experiment under C_3H_6/CH_2O molar ratio = 4.8. We found the same product distribution confirming that Zn/H-beta is not a selective catalyst to 3-buten-1-ol formation.

These undesired reactions were not favored over Zn/H-ZSM-5(11.5) and (25) under any of the experimental conditions investigated (2-propanol yield was, as a maximum 1.3% over Zn/ H-ZSM-5(25)). This is important because with H-ZSM-5 the olefin to formaldehyde ratio remains high throughout the reaction because propylene is not consumed by side reactions. Zn/ H-ZSM-5 samples with two different Si/Al ratios (Si/Al=25 and Si/Al = 11.5) produce 3-buten-1-ol with selectivity of 57.7-62.5%, while 1,3-butadiene (1.4-3.1% selectivity) and butanal (11.8-15.9%) were also observed. The overall selectivity to C-4 products can be as high as 80% and much higher than with Zn/H-beta(12.5) (less than 11% for both 3-buten-1-ol and 1,3butadiene). The C-5 products (m-dioxane, 2H-pyran, and oxan4-ol) are still formed using Zn/H-ZSM-5(11.5) and (25) catalysts, but the extent of these reactions decreases considerably. The Si/Al ratio was found to have an important effect for Zn/H-ZSM-5: higher Si/Al ratio results in higher conversion and only slightly lower 3-buten-1-ol selectivity. Zn/H-ZSM-5(11.5) and (25) shows that both pore size and three-dimensional channels facilitate selective formation of 3-buten-1-ol and C-4 products as compared to C-5 compounds.

Reaction pathway studies

To better understand the product distribution over both Zn/H-ZSM-5(25) and Zn/H-beta(12.5), the reaction was monitored at three different times: 1, 2.5, and 4 h (Figure 1). Figure 1 a displays the changes in selectivity as a function of reaction time on Zn/H-ZSM-5(25). 3-Buten-1-ol is the predominant product clearly showing that Zn/H-ZSM-5(25) does not catalyze many of the secondary reactions observed on Zn/H-beta(12.5). Selectivity increases rapidly from 1 to 2.5 h reaction time and then reaches a plateau (experiments at longer reaction times (6 h) verified the latter). Butanal selectivity decreases monotonically with time; this molecule may be produced via 3-buten-1-ol isomerization. 1,3-butadiene is only observed after 4 h reaction time, indicating slow 3-buten-1-ol dehydration rates. m-Dioxane forms in low selectivity after 4 h of reaction time as well. Finally, oxan-4-ol selectivity slightly increases with time, while that of 2H-pyran decreases. The former could form from the 2H-pyran, since water is generated through paraformaldehyde decomposition and dehydration reactions (3-buten-1-ol dehydration to 1,3-butadiene).

In the case of Zn/H-beta(12.5) (Figure 1b), selectivity to 2Hpyran, the predominant product, increases monotonically with reaction time, while that of oxan-4-ol decreases as the latter can dehydrate to form 2H-pyran. However, 2H-pyran selectivity increases at a faster rate than expected if oxan-4-ol dehydration was the only formation pathway. 3-Buten-1-ol selectivity also decreases accompanied with an increase in 1,3-butadiene, suggesting that 3-buten-1-ol can form the diene via dehydration under these reaction conditions. Compared with Zn/H-

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Figure 1. Product selectivity versus time over a) Zn/H-ZSM-5(25) and b) Zn/ H-beta(12.5). T = 423 K, C₃H₆/CH₂O molar ratio = 2.4.

ZSM-5(25), over Zn/H-beta(12.5) dehydration rates are higher. 1,3-butadiene selectivity initially grows at a faster rate suggesting that the product is consumed in another reaction. *m*-Dioxane selectivity decreases with reaction time, but this compound is not sequentially converted into any other products.

The reaction network was investigated using reaction intermediates and by-products as reactants over both Zn/H-ZSM-5(25) and Zn/H-beta(12.5). The findings over Zn/H-beta(12.5) will be discussed first to better understand the sequential reactions forming C-5 species. Reacting 3-buten-1-ol with formaldehyde (formaldehyde in excess) showed that 3-buten-1-ol reacts to completion and that oxan-4-ol (7.5%) and 2H-pyran (92.5%) were the only products detected (Scheme 3). In the absence of catalysts, these species are not formed. Oxan-4-ol reacted via dehydration (39% conversion) to form 2H-pyran when used as reactant. Moreover, when 2H-pyran is used in the feed no reaction was observed indicating that it is a final stable compound. This reaction is among the expected byproducts because formation of homoallylic alcohols (such as 3-



-H₂C

Scheme 3. Reaction network of formaldehyde reaction with propylene.

CH₂O

+CH₂C

buten-1-ol) in Prins condensations induce Prins cyclization chemistry forming compounds with the pyran skeleton.^[16]

Product evolution versus time (Figure 1b) and an experiment using oxan-4-ol as reactant indicate that there is a second pathway leading to 2H-pyran (besides Prins cyclization). Indeed, reaction of 1,3-butadiene with formaldehyde showed selective formation of 2H-pyran (93% selectivity). Formaldehyde properties as a dienophile were reported by Gresham and Steadman who demonstrated the first reaction of formaldehyde with methylpentadiene forming 2,4-dimethyl-5,6-dihydro-1,2-pyran.^[17] Evidence of 1,3-butadiene and formaldehyde reaction forming 2H-pyran in the presence of AlCl₃, BF₃, and ZnCl₂ is observed in a patent filed in 1972.^[18] This reaction is a Hetero-Diels-Alder reaction where formaldehyde acts as the dienophile (Scheme 3). Additional information about the transition state structures of the hetero-Diels-Alder reaction between 1,3-butadiene and formaldehyde catalyzed by AICl₃ was recently reported in a theoretical investigation.^[1]

1,3-Butadiene is formed from the dehydration of 3-buten-1ol, as confirmed using 3-buten-1-ol as reactant. 1,3-Butadiene could potentially form from *m*-dioxane (obtained from Prins condensation of formaldehyde with propylene) decomposition; this reaction produces 1,3-butadiene, formaldehyde, and water. However, *m*-dioxane seems to be a stable compound under our experimental conditions. The decrease of selectivity with reaction time may be related to the reverse reaction, as propylene was detected in the gas phase when *m*-dioxane was used as reactant.

The reactivity of stable reaction intermediates was investigated with and without formaldehyde in the feed over Zn/H-ZSM-5(25). Using 3-buten-1-ol and formaldehyde as reactants, oxan-4-ol (58.5%) and 2H-pyran (41.5%) were observed, that is, dehydration of oxan-4-ol is slower over Zn/H-ZSM-5(25) compared to Zn/H-beta(12.5) (oxan-4-ol=7.5% and 2Hpyran = 92.5%). This was verified using oxan-4-ol as reactant; the conversion was lower than 5%. When reacting pure 3buten-1-ol, 1,3-butadiene was formed selectively (74% selectivity at 61% conversion) followed by 2H-pyran. With 3-buten-1ol as reactant is possible that the reverse Prins reaction occurs forming formaldehyde and propylene, and thus 2H-pyran can form either by Prins cyclization (3-buten-1-ol reaction with formaldehyde) or Hetero-Diels-Alder of 1,3-butadiene with formaldehyde. These experiments demonstrate that 3-buten-1ol dehydration will selectively form 1,3-butadiene, but that this

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reaction is inhibited by the presence of other species such as formaldehyde. However, these results are encouraging as even under the low temperature investigated (423 K), 3-buten-1-ol dehydration to 1,3-butadiene, as a second step, affords the diene at about 46% yield. Finally, when reacting 1,3-butadiene with formaldehyde a very small amount of 2H-pyran is observed. In conclusion, over Zn/H-ZSM-5(25), sequential reactions of 3-buten-1-ol such as Prins cyclization and Diels–Alder of 1,3-butadiene with formaldehyde are inhibited. These findings explain the high selectivity towards 3-buten-1-ol obtained with Zn/H-ZSM-5(25). Overall these data lead to the reaction network shown in Scheme 3.

Role of acid sites and Zn cations

Spectroscopic studies of [D₃]acetonitrile (CD₃CN) adsorbed on H-ZSM-5(25) and Zn/H-ZSM-5(25) as well as on H-beta(12.5) and Zn/H-beta(12.5) were used to investigate the interaction of this molecule with the acid sites and the Zn sites after ionexchange (Figure 2; Supporting Information, Figure S5). The IR spectra were collected at different temperatures starting from about 323 K and ending at 723 K. On the parent H-ZSM-5(25) zeolite four bands at 2326, 2299, 2281, and 2249 cm⁻¹ were observed. These are attributed to interactions of the nitrile group with AI^{3+} Lewis acid sites (LAS), Brønsted acid sites (BAS), Si-OH groups, and the asymmetric stretching vibration of physisorbed [D₃]acetonitrile, respectively.^[19] An additional band at 2313 cm⁻¹ was observed for Zn/H-ZSM-5(25). This band is attributed to Zn²⁺ cations incorporated in the vicinity of two framework AI atoms for low Zn concentrations (Zn/AI <0.15).^[19] Isolated zinc species located at exchange sites as Zn²⁺ cations interacting with two Al sites have been previously suggested.^[20] However, as the Zn/Al for the Zn/H-ZSM-5(25) increases to 0.22 (see Table 1), additional sites at nearby framework AI pairs having two zinc cations bridged by an oxygen atom cannot be excluded. Brønsted acid sites are still present on Zn/H-ZSM-5(25) as not all the protons are exchanged by Zn^{2+} (Zn/Al ratio = 0.22), that is, this catalyst has both Brønsted acid and Lewis acid properties. This is in accordance with isotopic titration of Brønsted sites with deuterium which indicated that Zn replaces most protons, but some zeolitic acid protons are always present in the samples.^[20] Similar observations were made for H-beta and Zn/H-beta(12.5) (Supporting Information, Figure S5). Overall, CD₃CN IR spectra show that zinc ion-exchanged H-ZSM-5(25) and H-beta(12.5) are hybrid materials, possessing both Brønsted and Lewis acid sites.

Figure 3 compares H-ZSM-5 and Zn/H-ZSM-5 for two Si/Al ratios (25 and 11.5). Zn incorporation has a clear effect on conversion and product distribution for both Si/Al ratios and the effect is more pronounced for the sample with a Si/Al = 25. Not only the reaction rate increases when Zn cations are exchanged into H-ZSM-5, but selectivity towards 3-buten-1-ol is also higher when Zn is present. Comparison at iso-conversion (Supporting Information, Figure S6) for the Zn/H-ZSM-5(25) shows higher selectivity compared with H-ZSM-5(25) (60.5 versus 45.7%). Oxan-4-ol selectivity is slightly higher on Zn/H-ZSM-5, while 2H-pyran (primarily formed via dehydration of

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2400 2380 2360 2340 2320 2300 2280 2260 2240 2220 2200 Wavenumber, cm⁻¹



Figure 2. IR spectra of $[D_3]$ acetonitrile adsorbed on H-ZSM-5(25) and Zn/H-ZSM-5(25). Data are shown at low temperature and higher temperature close to reaction conditions.

the former) selectivity is lower (Zn/H-ZSM-5(25): oxan-4-ol = 14.5%, 2H-pyran = 6.3%, Zn/H-ZSM-5(11.5): oxan-4-ol = 7.3%, 2H-pyran = 12.9%, H-ZSM-5(25): oxan-4-ol = 6.1%, 2H-pyran = 18.8%, H-ZSM-5(11.5): oxan-4-ol = 7.2%, 2H-pyran = 24.9%). It is concluded that dehydration rates are higher when the concentration of Brønsted acid sites is higher (no Zn incorporation). Similarly, reactions requiring excess formaldehyde, forming C-5 compounds, are favored on H-ZSM-5 over Zn/H-ZSM-5. For example, if we compare C-4 versus C-5 selectivity over H-ZSM-5(11.5) and Zn/H-ZSM-5(11.5), total selectivity to C-4 compounds in the presence of the Zn containing catalyst is 79.8% as opposed to 67.8% for the H-ZSM-5(11.5). The molecular origin of this effect is not clear: it may be that Zn blocks those unselective sites and also induces confinement effects. These data clearly show that Brønsted acid sites are the catalytically active sites for Prins condensation of formaldehyde with propylene.





Figure 3. Prins reaction conversion and product selectivity: effect of Zn content, T = 423 K, reaction time = 4 h, C_3H_e/CH_2O molar ratio = 2.4, a) Si/Al = 25, b) Si/Al = 11.5, black: H-ZSM-5, gray: Zn/H-ZSM-5.

To understand better the effect of zinc, two samples having higher Zn/Al ratio (Zn/Al=0.47 and Zn/Al=1.10, measured by XRF) were synthesized using dry impregnation and compared with the ion-exchanged sample (Zn/Al=0.12 for Zn/H-ZSM-5(11.5)). Dry impregnation is an example where acidic protons are replaced by both ion-exchange and chemical reaction with

ZnO particles formed from decomposition of Zn nitrate.^[21] Conversion significantly decreases for both impregnated samples (0.5% for Zn/Al=0.47 and 0.1% for Zn/Al=1.10). Under these conditions, it is assumed that Brønsted acid sites are exchanged by Zn^{II} leading to the observed conversion decrease. This finding further supports a key catalytic role for Brønsted acid sites.

The role of the acid sites was investigated using sodium cations to poison the acid sites. The sodium containing sample was prepared by impregnation of Zn/H-ZSM-5(11.5) with NaNO₃ (Zn/Al = 0.09 and Na/Al = 2.44 based on XRF analysis). We found the Na-containing sample is a poor catalyst and has very low reaction rates (conversion = 1.7%), that is, the experiments verify that the Brønsted acid site is necessary for high catalytic activity. Furthermore to that, we also observed zinc leaching (Supporting Information, Table S5) for both Si/Al 11.5 and 25. 3-Buten-1-ol and butanal are the only products formed over the Zn/Na-ZSM-5(11.5) impregnated catalyst. The present observations are in accordance with the effect of zinc discussed above and presented in Figure 3.

We have also evaluated the effect of Si/Al ratio on a series of H-ZSM-5 samples using a standard set of reaction conditions (423 K, 4h; Supporting Information, Table S1), lower reaction temperatures (353, 373, 393 K) and shorter reaction times (1 and 2.5 h). Detailed results at 393 K and 2.5 h are presented in Table 3, but similar trends were observed under other reaction conditions. Conversion and product selectivity are strongly correlated with Si/Al ratio. Conversion increases up to Si/Al=40.0 and then starts decreasing as the Si/Al ratio increases. Analogous catalytic behavior has been shown for condensation of isobutyl-aldehyde with tert-butyl alcohol to form 2,5-dimethyl-2,4-hexadiene over H-ZSM-5 for Si/Al ranging between 25 and 89.^[22,23] Although at lower Si/Al ratios Al content and thus acid site density is higher, conversion follows the opposite trend. That is, competing reactions may be favored by lower Si/Al ratios leading to higher deactivation rates and pore/active site blocking. These reactions include olefins and diolefins oligomerization, since it is known that Brønsted acid sites catalyze these reactions, even at room temperature.^[24] Catalyst fouling was evident by the darkening (coking) of the spent solids and confirmed by thermogravimetric analysis of the spent catalysts under air flow (Figure 4) shows the differential weight profiles

N CH ₂ O COnver	sion	Carbon-based Selectivity [%]			
[%]	HO			€	
7 8.5	54.6	16.0	5.8	9.8	8.8
9 18.6	57.6	13.0	5.3	10.5	10.3
5 26.9	59.0	11.6	2.9	15.5	8.3
30.8	60.6	8.3	2.3	20.3	6.5
2 22.9	74.5	6.7	4.4	6.2	4.5
3 6.1	68.9	12.5	7.7	2.5	1.7
	[%] 7 8.5 9 18.6 5 26.9 0 30.8 2 22.9 8 6.1	[%] HO 7 8.5 54.6 9 18.6 57.6 5 26.9 59.0 0 30.8 60.6 2 22.9 74.5 8 6.1 68.9	[%] Ho of 7 8.5 54.6 16.0 9 18.6 57.6 13.0 5 26.9 59.0 11.6 0 30.8 60.6 8.3 2 22.9 74.5 6.7 8 6.1 68.9 12.5	$[\%] \qquad \qquad$	$[\%] \qquad \qquad$

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Figure 4. Derivative weight versus temperature, analysis conditions: air flow = 50 mL min⁻¹, rate = 10° min⁻¹, room temperature to 1073 K, Reaction conditions: T = 393 K, reaction time = 2.5 h, C₃H₆/CH₂O molar ratio = 2.4.

while weight loss profiles are presented in the Supporting Information, Figure S7. Note the similar activity but very different differential weight profiles of the Si/Al = 11.5 and 500 samples. On the former spent sample, formation of higher molecular weight oligomers is clear by the higher temperature peak (Supporting Information, Figure S7), while on the latter sample only low temperature peaks attributed to water or other physically adsorbed species is present. H-ZSM-5(11.5) having the highest density of acid sites and Si/Al = 500 with the lowest density of acid sites both show low activity under all the conditions of temperature and time studied; however, the reason for that behavior is different for each case. Higher acid site density (lower Si/Al ratios) will favor competing reactions limiting activity towards Prins condensation, while samples with lower acid site densities (higher Si/Al ratios) are not effective catalysts because the number density of acid sites is low. These two phenomena result in maximum activity (at Si/Al = 40) as indicated by the catalytic results. Furthermore, hydrophilicity/hydrophobicity, which is changing as Si/Al ratio changes, may also play a role in catalytic rates as the adsorption of polar compared to non-polar species will be affected. An optimal Si/Al ratio is needed to achieve the most efficient adsorption stoichiometry for isobutylene and isobutylaldehyde condensation over H-ZSM-5, as previously reported.^[22,23] Moreover, Si/Al ratio also affects product selectivity; catalytic data show that 3-buten-1-ol selectivity is favored as the Si/Al ratio increases. For selective isoprene synthesis from formaldehyde and isobutene over different zeolites including H-ZSM-5, it has been shown that high selectivity can be obtained only in the presence of weakly acidic Brønsted sites, as the protonation of formaldehyde should be more favorable compared with the protonation of the olefin.^[24] 3-Buten-1-ol selectivity up to 74.5% can be obtained at Si/Al=140, as selectivity to butanal and C-5 compounds decreases when Si/Al increases.

The key role of Brønsted acid sites was verified by titrating the sites during catalysis using 2,6-di-tert-butylpyridine and

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pyridine. Both species interact with Brønsted sites forming pyridinium ions and as the kinetic diameter of the former is 7 Å while of the latter is 5.4 Å, 2,6-di-tert-butylpyridine will selectively titrate outer surface acid sites and pore mouths while pyridine will be able to titrate all sites. Pre-determined amounts of both species (based on proton site density of the H-ZSM-5(40)) were added in the reaction solution. These experiments were performed at 373 K and 1 h reaction time, while the rest reaction parameters were kept constant. Adding 2,6-di-*tert*-butylpyridine (so as to have complete theoretical coverage of all Brønsted acid sites) had no effect on catalytic results (Supporting Information, Table S2); that is, formaldehyde-propylene condensation occurs in the pores of H-ZSM-5(40). In contrast, when pyridine was in the reaction solution there is a clear effect (Figure 5). Conversion decreased with in-



Figure 5. Pyridine addition influence on CH_2O conversion and product selectivity. Reaction conditions: T=373 K, reaction time = 1 h, C_3H_6/CH_2O molar ratio = 2.4.

creasing pyridine amount; the reaction is almost completely inhibited when the amount of pyridine equals to amount of acid sites. Furthermore, 3-buten-1-ol was the only product detected. When the amount of pyridine is half the amount needed for complete coverage, 3-buten-1-ol and butanal were the two products formed, while only a small amount of C5 products is observed. As the amount of pyridine decreases and more Brønsted acid sites become available, 3-buten-1-ol selectivity decreases, while that of C5 compounds increases. These findings support the conclusion that Brønsted acid sites play a crucial role for both activity and product distribution.

Conclusions

We have reported the first experimental evidence of Prins condensation between formaldehyde and propylene selectively forming 3-buten-1-ol using heterogeneous catalysis. This product can dehydrate upon heating to form 1,3-butadiene; an im-



portant monomer for the production of synthetic rubber. We explored a number of Lewis acidic (Sn- and Zr-Beta) and hybrid (containing both Lewis and Brønsted acid sites) Zn containing zeolites and found that the hybrid materials are more active and selective. Zn containing H-ZSM-5 was the optimal catalyst of those investigated exhibiting high activity and selectivity to the target product; 3-buten-1-ol. Zn containing Hbeta is active but not selective, since it catalyzes a series of undesired reaction steps, mainly involving 3-buten-1-ol sequential reactions to form C-5 compounds. Zn addition favors both activity and 3-buten-1-ol selectivity however, the catalytically active site is the Brønsted acid sites. An optimum Brønsted acid site density is essential to achieve high activity and 3buten-1-ol selectivity and to suppress undesired side reactions.

Experimental Section

Catalyst Preparation

Zn containing zeolites: A series of zinc-containing zeolites were prepared by ion exchange from commercially available samples. The parent zeolites were: ferrierite (CP914C, Si/Al=10, Zeolyst International, H⁺ form obtained after calcination at 773 K for 20 h under 100 mL min $^{-1}$ air flow), H-SSZ-13 (Si/Al = 12) synthesized using a protocol reported elsewhere, H^+ form of the zeolite used for ion-exchange,^[25] ZSM-5 (CBV 2314 and CBV 5524G, Si/Al=11.5 and 25, Zeolyst International, H⁺ form obtained after calcination at 773 K for 20 h under 100 mL min⁻¹ air flow), and beta (CP814E*, Si/ Al=12.5, Zeolyst International H^+ form obtained after calcination at 773 K for 20 h under 100 mLmin⁻¹ air flow,). Ion-exchange was performed at 343 K for 5.5 h using an aqueous solution of 0.005 м Zn(NO₃)₂·6H₂O (Sigma Aldrich), the ratio of zeolite mass per volume of solution was 1 g per 100 mL. The exchanged sample was then dried overnight at 383 K and finally calcined at 773 K under 100 mL min $^{-1}$ air for 20 h. One sodium-containing sample was prepared by impregnation of the ion-exchanged Zn/H-ZSM-5 (H-ZSM-5 Si/Al = 11.5 nominal) with an aqueous solution of NaNO₃ (Sigma Aldrich). Two samples of zinc-containing H-ZSM-5 (Si/Al = 11.5) were prepared using the dry impregnation method. Theoretical Zn/Al ratios were 0.5 and 1.0. For 1 g of zeolite, 0.4 mL of DI H_2O was used to dissolve the required amount of $Zn(NO_3)_2 \cdot 6H_2O$. The zinc precursor was dropwise added to H-ZSM-5. The samples were dried overnight at 383 K and finally calcined at 773 K under 100 mLmin^{-1} air for 20 h.

Sn-beta and Zr-Beta: Zr-beta and Sn-beta were synthesized according to protocols described previously.^[26,27]

Analytical Section

Nitrogen physisorption was performed in a Micromeritics 3Flex system at 77 K to determine the micropore volume using the tplot method. Samples were degassed overnight at 523 K and backfilled with dry nitrogen prior to analysis. Scanning electron microscopy images were recorded on a JEOL JSM 7400F at 10 μ A. X-ray diffraction (XRD) patterns were collected using a Bruker D8 diffractometer with Cu_{ka} radiation. The diffraction pattern was collected for 2 s at each increment of 0.02° between 5 and 50°. X-ray fluorescence (XRF) using a Rigaku WDXRF was used for elemental analysis of the Zn containing samples. Coupled plasma-atomic emission spectroscopy (ICP-AES) analysis was performed by Galbraith Laboratories (Knoxville, TN) to determine Zr and Sn content of the final beta samples. In situ Fourier transform infrared (FTIR) spectra were obtained on an Agilent Cary 660 FTIR Spectrometer equipped with a MCT detector (128 scans at a spectral resolution of 2 cm^{-1}) with a homemade in situ transmission cell. A vacuum level of $< 1.3 \times 10^{-9}$ MPa in the transmission cell was reached through a vacuum manifold, which is connected to a mechanical pump and a diffusion pump. A self-standing zeolite wafer was loaded to a custommade sample holder, followed by annealing at 723 K under vacuum to completely remove adsorbed water. After cooling to 323 K, ca. 1.3×10^{-5} MPa of deuterated acetonitrile (CD₃CN) was introduced to the transmission cell via the vacuum manifold, and IR spectra were collected in the process of heating the zeolite wafer to 723 K.

Catalyst evaluation

The reaction of formaldehyde with propylene was carried out in a 50 mL batch reactor (Parr Instrument Company) under magnetic stirring. Temperature controlled with a band heater and a controller (Dwyer Instruments, Inc.). In a typical experiment, the reactor was loaded with required amounts of the reactants (propylene = 0.75 MPa and paraformaldehyde = 0.1 g) in the presence of a solvent (1,4-dioxane = 20 mL) and an appropriate amount of catalyst (0.25 g). Reaction temperature was set constant at 423 K unless otherwise stated. After reaction, the reactor was cooled down using an ice bath. The gas phase was collected using a gas bag and liquid phase was collected after catalyst separation using filtration. The gas phase was analyzed using an Agilent 7890A gas chromatographer equipped with an HP-PLOT Q column (30 m length and 0.53 mm diameter) and an FID detector. The liquid phase was analyzed using an Agilent 7890B gas chromatographer equipped with an Innowax column (30 m length and 0.25 mm diameter) and an FID detector as well. Liquid products were also identified with gas chromatography (GC)-mass spectroscopy (MS) with a Shimadzu GC-2010 having the same Innowax column and being coupled with a GC-MS-QP2010 PLUS. Reaction products were quantified using multi-point calibration curves. Conversion of formaldehyde was calculated based on products and reaction stoichiometry using the equation:

 $Conv. = \frac{moles \text{ of } CH_2O \text{ converted to all products}}{moles \text{ of } CH_2O \text{ initially loaded}}$

Selectivity was carbon-based excluding side products such as methanol and 2-propanol formed via formaldehyde and propylene through independent side reactions; these reactions were however only observed with beta zeolite (see Results and Discussion for more details).

C-based selectivity = $\frac{\text{moles of C in product }i}{\text{moles of C in all products}}$

The heterocycle compounds are abbreviated as follows: 1,3-Dioxane, 4-methyl- is abbreviated as *m*-dioxane, tetrahydro-4*H*-pyran-4ol is abbreviated as oxan-4-ol and 5,6-dihydro-2*H*-pyran is abbreviated as 2H-pyran.

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Conflict of interest

The authors declare no conflict of interest.

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FULL PAPERS

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Zeolite-Catalyzed Formaldehyde-Propylene Prins Condensation



Substituting homogenous acids: Prins condensation between formaldehyde and propylene is traditionally catalyzed by homogeneous acids. The first experimental evidence is reported of the reaction over microporous solid acid catalysts. It was determined that H-ZSM-5 (MFI) is the optimal catalyst favoring selective formation of 3-buten-1-ol. In a second step, 3-buten-1-ol easily dehydrates to 1,3-butadiene.