

Conversion of Glycerol to Alkyl-aromatics over Zeolites

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Catalytic conversion of glycerol to gasoline-range alkyl-aromatics has been investigated on a series of zeolites (HZSM-5, HY, Mordenite, and HZSM-22) at 300–400 °C and atmospheric pressure or 2 MPa. Although propenal (acrolein) is the major primary glycerol dehydration product over all zeolites, the pore structure of the zeolite plays a significant role on the final product distribution. The major products over one-dimensional zeolites Mordenite and HZSM-22 are oxygenates (propenal, acetol, and heavy oxygenates) without aromatic formation. HZSM-22 is suitable for the production of acrolein with 86% yield at 100% glycerol conversion. However, it is found that glycerol can be converted to high yields of alkyl-aromatics, mainly C₈–C₁₀ over three-dimensional HY and HZSM-5. A longer contact time, higher temperatures, and higher pressures favor the formation of aromatics, with a maximum yield of 60% over HZSM-5. A two-bed configuration with a deoxygenation/hydrogenation catalyst (Pd/ZnO) as the first bed and HZSM-5 as the second bed can further increase the alkyl-aromatic yield. The mono-functional oxygenates produced by the first bed were oligomerized and aromatized into gasoline-range alkyl-aromatics over the second bed.

Introduction

The worldwide increase in the production of biodiesel via the transesterification reaction from renewable natural oils and animal fats is leading to a continued increase in the glycerol supply to the market well beyond the need for chemical derivatives. In addition, glycerol is a model polyol compound that may be produced from fermentation and/or pyrolysis of the cellulosic content of biomass. For these reasons, there recently have been extensive studies on the conversion of glycerol to more valuable chemicals and fuel components.

Significant effort has been made to reform glycerol to synthesis gas (H₂ and CO),^{1–6} with follow-on Fischer–Tropsch synthesis for gasoline/diesel production or the water–gas shift reaction for the purpose of H₂ production. There seems to have been little research on the direct conversion of glycerol to gasoline-range hydrocarbon fuel molecules under relatively mild conditions. Closely related to glycerol conversion, Dumesic and co-workers demonstrated a dual-bed catalyst system for conversion of sorbitol into liquid fuels in

the liquid phase.⁷ Sorbitol is first converted to mono-functional intermediates (alcohols, ketones, and carboxylic acids) over a deoxygenation catalyst (10 wt % Pt–Re/C) at 18 bar pressure, and then these intermediates are condensed to higher C molecules over condensation catalysts (Ce₁Zr₁O_x, and Pd/ZrO₂) and finally fully deoxygenated to gasoline and diesel-range alkanes over Pt/SiO₂–Al₂O₃.

Methanol to gasoline (MTG) is an important acidic zeolite-catalyzed reaction that converts methanol to hydrocarbons.^{8–10} The preferred products obtained by this are principally aromatics in the gasoline boiling range (C₆–C₁₀). The conventional reaction pathway includes three main sequential steps: (i) the dehydration of methanol to dimethyl ether, (ii) the dehydration of dimethyl ether to olefins, and (iii) the oligomerization of olefins to mainly iso-paraffins and aromatics. The pore structure of the zeolite has a crucial effect on the product distributions. A 10-member ring (10-MR) medium-pore ZSM-5 produces aromatic-rich hydrocarbons, while an 8-MR small-pore SAPO-34 mainly produces light olefins.¹¹ This reaction could be extended to conversion of mono-functional oxygenates (alcohols, ketones, aldehydes, and carboxylic acids) into gasoline-range hydrocarbons.^{8,9,12–15} In our previous work, it has been demonstrated that propionaldehyde (propanal) could be effectively converted to aromatic-rich

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Table 1. Zeolite Structures and Properties

zeolite	topology code	channel structure	ring opening	pore diameter (Å)	Si/Al	S _{BET} (m ² /g)
HNaMOR ^a	MOR	1D	12-MR 8-MR	6.5 × 7.0 2.6 × 5.7	8	501
HZSM-22	TON	1D	10-MR	4.6 × 5.7	45	245
HY	FAU	3D	12-MR	7.4 × 7.4	40	780
HZSM-5	MFI	3D	10-MR	5.1 × 5.5 5.3 × 5.6	45	498

^a A total of 20% Na was exchanged, so that the resulting acid density is similar to the other zeolites.

gasoline-range molecules over HZSM-5,^{16–18} wherein an aldol condensation reaction pathway plays the predominant role.¹⁷

Zeolites have been identified as active catalysts for the production of propenal (acrolein) via dehydration of glycerol.^{19–23} For example, it is reported that a 73.6% acrolein yield has been achieved over HZSM-5 and an 80.3% acrolein yield has been achieved over zeolite β.¹⁹ Acrolein and propenal have the same active aldehyde functional group. It is expected that the acrolein-rich stream after glycerol dehydration over zeolites could be further converted to gasoline-range molecules over acidic zeolites.

The objective of this work is to investigate the conversion of glycerol to gasoline-range molecules over acidic zeolites with different pore geometries, including three important industrial zeolites: three-dimensional medium-pore ZSM-5, large-pore Y, and one-dimensional large-pore Mordenite (MOR). A one-dimensional medium-pore ZSM-22 is included because it has been reported that ZSM-22 is an active and stable catalyst for trimerization of propene to produce gasoline-range alkenes without aromatic formation.²⁴ To further increase the aromatic yields, a two-bed system (Pd/ZnO + HZSM-5) has been investigated to provide initial partial deoxygenation and hydrogenation before oligomerization and aromatization.

Experimental Section

Catalyst Preparation and Characterization. HZSM-5 (Si/Al = 45) and NaMOR (Si/Al = 8) were supplied by Süd-Chemie, Inc. HY (Si/Al = 40) was supplied by Zeolyst International. Na⁺ ions in the NaMOR zeolites were replaced with NH₄⁺ ions by ion exchange with a NH₄NO₃ solution at 80 °C for 10 h calculated to obtain 20% HNaMOR, so that the acid density obtained was similar to the other zeolites used in this study. ZSM-22 (Si/Al = 45) was synthesized by following a procedure in the literature.²⁵ X-ray diffraction (XRD) and scanning electron microscopy (SEM) confirmed that the structure was highly crystalline ZSM-22. HZSM-22 was obtained from a complete exchange with a 1 M solution of NH₄NO₃. The ammonium form of MOR and ZSM-22 were converted to the proton form by calcination at 550 °C. The

Brunauer–Emmett–Teller (BET) specific surface area (S_{BET}) of the zeolites was measured by nitrogen adsorption on an ASAP 2000 analyzer (Micromeritics). The properties of the zeolites used are shown in Table 1. The ZnO-supported Pd catalyst (Pd/ZnO) was prepared by incipient wetness impregnation (IWI) with palladium(II) nitrate solution (Aldrich), with an amount calculated to obtain a metal loading of 1 wt % Pd.

Catalytic Evaluation. The reactor was a 10 mm inner diameter, 316 stainless-steel, fixed-bed, continuous flow, tubular reactor. The reactor was heated by a split-tube furnace (Thermal Craft) with a digital feedback temperature controller (Omega). The catalyst (40–60 mesh) was treated *in situ* with He or N₂ for 1 h at 400 °C before each run. Glycerol was fed using a syringe pump or high-pressure piston pump, depending upon the reaction pressure. At elevated pressure, a back-pressure regulator was used, but at atmospheric pressure, this was removed. The reaction was carried out over a range of temperatures from 300 to 400 °C and at W/F from 0.1 to 1 h (mass of catalyst/mass flow rate of organic). During the reaction, glycerol was fed together with a H₂ carrier at a flow rate of 35 cc/min, giving a molar ratio of H₂/glycerol of 15:1.

When operating at higher pressure, liquid products, including water, were collected in a cold trap after accumulating for each hour of time on stream. Non-condensed products passed through the back-pressure regulator, went to vent, and were not quantified, but some samples were sent to an online gas chromatograph (GC) for product identification. After each run, the reactor was purged with dry carrier gas for 15 min to collect the residual products from the reactor. The collected liquid products were found to settle into two phases: a hydrocarbon phase containing aromatics and an aqueous phase containing oxygenates with product water. Each phase was then individually analyzed using a GC–flame ionization detector (FID) (HP 6980) equipped with a capillary HP-INNOWax column, and products were identified using a Shimadzu (Q2010) GC/MS. For some experiments at atmospheric pressure, where no back-pressure regulator was required, all products were directly sent to the GC for online analysis. This provided a consistent basis for determining yields of all products without having to estimate separately based on the collected phase volumes.

Results and Discussion

Effect of the Pore Structure on Glycerol Conversion. The effect of the pore structure on product distribution during glycerol conversion was first tested. These experiments were performed on HZSM-5, HY, HNaMOR, and HZSM-22 at a W/F of 0.5 h, with reaction temperature varied from 300 to 400 °C and pressure at either atmospheric or 2 MPa.

For the one-dimensional zeolites (HNaMOR and HZSM-22), the condensed products obtained from the conversion of glycerol are all oxygenates, irrespective of the temperature and pressure in the tested range. The oxygenates contained propenal, 1-hydroxyactone (acetol), acetaldehyde, and heavier oxygenates. No hydrocarbon phase was observed. The heavier oxygenates were identified by the GC/MS as a number of molecules, such as 3-methyl-2-butanone, 2-cyclopenten-1-one,

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Table 2. Product Distribution (Yield) of Glycerol Conversion on Different Zeolites^a

catalyst	HZSM-5	HY	HNaMOR	HZSM-22
conversion (%)	95.1	95.2	92.9	100
oxygenate (mol _{carbon} %)	76.1	85.2	92.9	100
acetaldehyde	5.4	13.6	14.2	14.1
propanal	4.7	13.7	8.9	1.1
propenal	59.4	30.7	27.4	80.4
acetol	1	8.2	7	2.5
large oxygenates C ₄₊	5.6	19	35.4	1.9
hydrocarbon (mol _{carbon} %)	20.9	10.1		
benzene	1.2	0.3		
toluene	2.6	0.9		
C ₈ aromatics	3.6	1.9		
C ₉ aromatics	3.9	3.3		
C ₁₀ aromatics	4.5	3.1		
C ₁₁ aromatics	2	0.6		
C ₁₂ aromatics	3.1	0		

^a Reaction conditions: *T*, 400 °C; TOS, 3 h; W/F, 0.5 h; *P*, 2 MPa.

4-hydroxy-4-methyl-2-pentanone, 3-hepten-1-one, and 5-ethyl-4-methyl-3-heptanone.

For the three-dimensional zeolites (HZSM-5 and HY), only oxygenates were produced at 300 °C, irrespective of the pressure. The oxygenates consisted of acetaldehyde, formaldehyde, propenal, acetol, and small amounts of heavier oxygenates. Once the temperature was increased to 400 °C, a hydrocarbon phase formed and aromatics were identified, irrespective of the pressure. The results show that the aromatization reactions are favored at higher temperatures. The fact that the aromatization reaction happened over the three-dimensional zeolites and not over the one-dimensional zeolites at the same reaction conditions suggests that the intersection of the pore channels may play an important role for aromatic formation.

Table 2 compares the product distribution over the different zeolites at 400 °C and 2 MPa. A high propenal yield (80.3%) was achieved over the one-dimensional medium-pore HZSM-22. A significantly higher large oxygenate yield, at the expense of the propenal yield, was observed for the one-dimensional large-pore HNaMOR. The results may show that the larger pore size allows the condensation reactions of small oxygenates produced from glycerol dehydration. A similar trend was observed when comparing the oxygenate distribution over the three-dimensional medium-pore HZSM-5 and large-pore HY. The total oxygenate yield was lower for three-dimensional zeolites, but gasoline-range aromatics (C_{6–12}) were observed for these zeolites (HZSM-5 and HY). It should be pointed out that fewer aromatics were produced on HY because deactivation has already occurred to a significant extent at time on stream (TOS) = 3 h. The faster deactivation of HY could be explained by its larger pore size leading to more coke deposition inside the pores. These results indicate that the medium-pore HZSM-5 and HZSM-22 are more suitable than the large-pore HY and HNaMOR for the production of gasoline-range molecules (aromatics) and acrolein, respectively.

It has been proposed that propenal and acetol are the primary products from glycerol dehydration over acidic catalysts, depending upon which –OH is first removed.^{19–21} Dehydration involving the central –OH and terminal –OH of glycerol results in two intermediate enols, which are tautomerized to 3-hydroxypropionaldehyde and 1-hydroxyacetone (acetol), respectively.²¹ Further dehydration of 3-hydroxypropionaldehyde leads to the formation of propenal (acrolein).^{19–21} Acetone, 1,2-propanediol, acetaldehyde,

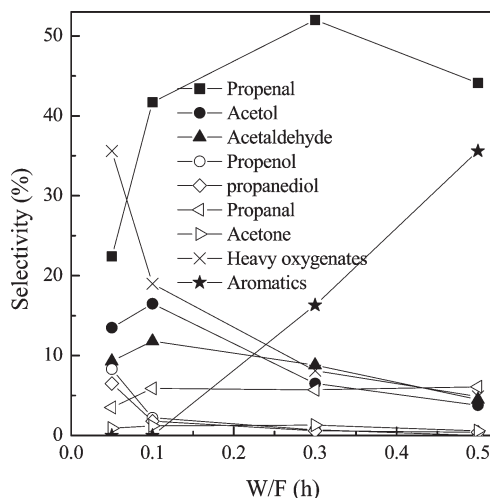


Figure 1. Product selectivities of glycerol conversion over HZSM-5 as a function of W/F. Reaction conditions: *T*, 400 °C; *P*, 2 MPa (data taken offline).

and formaldehyde may be generated from acetol and/or 3-hydroxypropionaldehyde by hydrogenation, dehydrogenation, dehydration, cracking, and decarbonylation reactions.^{19–21} Acid-catalyzed aldol condensation of these formed aldehydes and ketones plays an important role for carbon chain growth in the formation of heavy oxygenates and aromatics. Because the zeolites used have a similar acid density (by varying the Si/Al ratio for HZSM-5 and HY and HZSM-5 and by exchange degree for MOR), the observed differences in product distribution appear to be a result of the pore structure.

Although H₂ was used as a carrier gas in this study, the amount of H₂ involved in the reactions is estimated to be quite small. First, the major reactions (glycerol dehydration, aldol condensation, and aromatization) that occur over acidic zeolites do not require hydrogen. Hydrogenation is a minor reaction over acidic zeolites. H₂ required for hydrogenation could be supplied from hydrogen-transfer reactions from the reactants or from carbonaceous surface species.²⁰ Second, the activation and dissociation of H₂ is believed to occur only to a small extent because of the lack of a typical H₂-activating transition metal (such as Cu or Pt) over acidic zeolites. In our recent work, it has been demonstrated that the type of carrier gas (H₂ or He) has no effect on the initial activity of oxygenate conversion over an acidic zeolite (HZSM-5)²⁶ and catalytic stability is only slightly improved when He was replaced by H₂, further confirming that the involvement of gas-phase H₂ is limited in these reactions over acidic zeolites.

Glycerol Conversion over HZSM-5 and HZSM-22. HZSM-5 and HZSM-22 were further studied in detail because HZSM-5 showed a high gasoline-range aromatic yield and HZSM-22 showed a high acrolein yield. Figure 1 shows the product distribution of glycerol conversion over HZSM-5 as a function of space time (W/F) at 2 MPa and 400 °C. Only an aqueous phase was obtained for W/F < 0.1 h. The product mixture mainly contained propenal, with smaller amounts of acetol, acetaldehyde, propanal, propanediol, propenal, acetone, and other heavier oxygenates. As W/F was increased to greater than 0.1 h, the liquid products separated into two phases (aqueous and hydrocarbon). The

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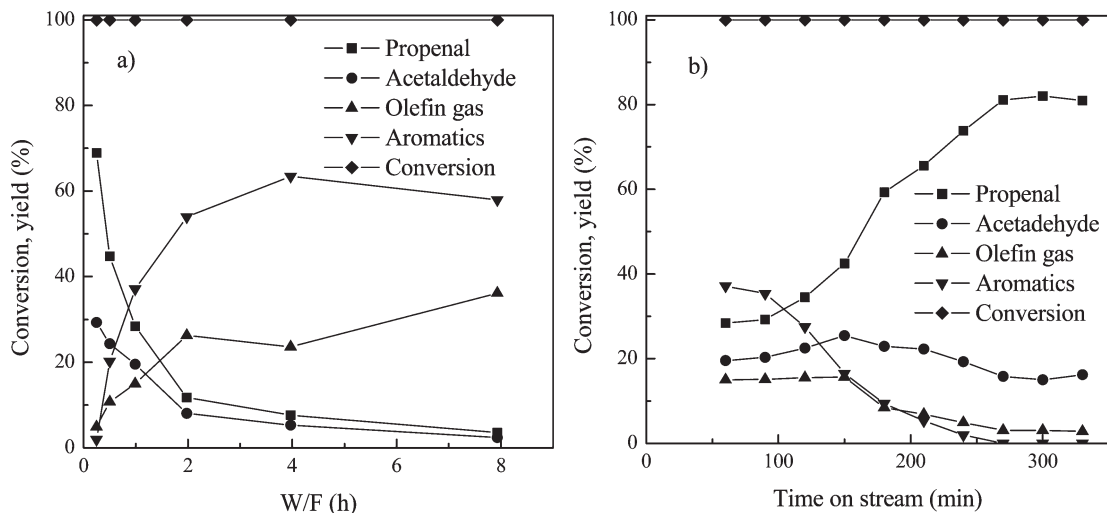


Figure 2. Glycerol conversion on HZSM-5 as a function of (a) W/F at TOS = 60 min and (b) TOS at W/F = 1 h. Reaction conditions: T , 400 °C; atmospheric pressure (data taken online).

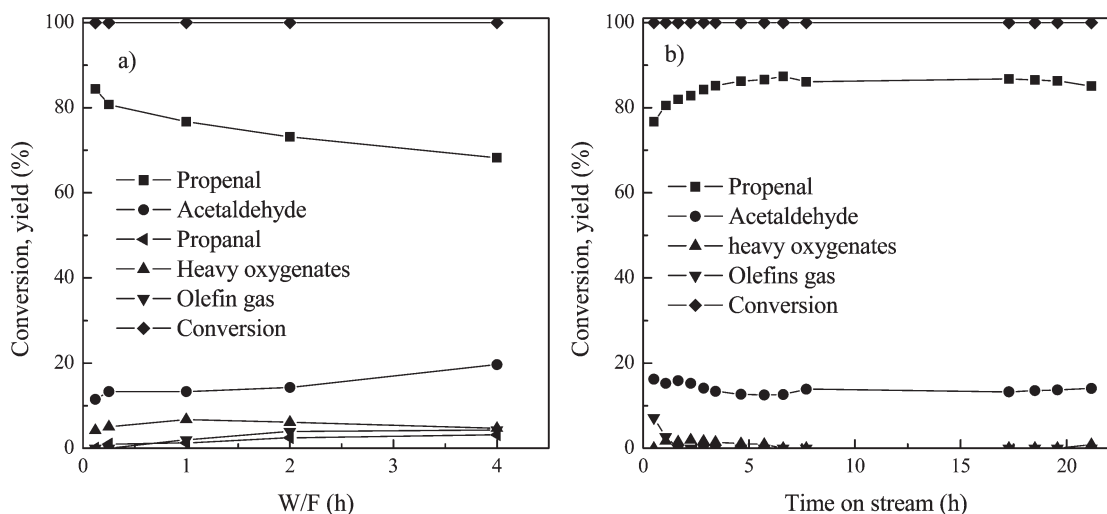


Figure 3. Glycerol conversion on HZSM-22 as a function of (a) W/F at TOS = 1 h and (b) TOS at W/F = 1 h. Reaction conditions: T , 400 °C; atmospheric pressure (data taken online).

hydrocarbon phase consisted of C_9 – C_{12} aromatics, with smaller amounts of xylene, toluene, and benzene. The volume of aromatics increased with increasing W/F, up to a yield of about 35% (carbon molar basis of liquid products) at a W/F of 0.5 h.

Figure 2a shows the product distribution for glycerol conversion over HZSM-5 as a function of W/F at atmospheric pressure and 400 °C with otherwise the same conditions as above (analyzed by online GC). A similar product distribution was observed as those at 2 MPa, with oxygenate products containing propenal and acetaldehyde and aromatic products consisting of C_6 – C_9 . The olefin gas is comprised mainly of propene, with a smaller amount of ethene. Experiments at much longer W/F, up to 8 h, were conducted to observe the change in product distribution, even though glycerol conversion was 100% for all experiments. Propenal is a predominant product appearing at very low W/F, similar to the results at high pressure. Aromatics appeared beginning at W/F = 0.25 h and increased with increasing W/F. Aromatics appeared at higher W/F for atmospheric pressure than that at 2 MPa, indicating that the aromatization reaction is more favored at higher pressure. The increase in aromatic yield is accompanied by the decrease in propenal and acetaldehyde yields, implying

that propenal and acetaldehyde are the intermediates for aromatic formation. The maximum aromatic yield (60%) is achieved at a W/F of 4 h and decreased at the longest W/F because of cracking, with a concomitant increase in the olefin gas yield.

Figure 2b shows the results for glycerol conversion as a function of TOS at a W/F of 1 h and 400 °C. With increasing TOS, a significant reduction of the aromatic yield is observed after about 2 h, while propenal increases with continued 100% glycerol conversion. The results indicate that the sites for aromatization are gradually reduced, while the sites for glycerol dehydration are less affected. Aromatics require the internal pore configuration of HZSM-5 to form, and as deactivation and coking in the pores increases, this serial pathway is reduced.²⁷

In comparison to HZSM-5, glycerol conversion on HZSM-22 was performed as a function of W/F at 400 °C and atmospheric pressure (Figure 3a). The major products are propenal and acetaldehyde. Increasing W/F from 0.12 to 4 h decreased the propenal yield from 84.4 to 68.2%, while

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the acetaldehyde yield increased from 11.5 to 19.6% and the olefin gas yield increased from 0 to 4.3%. The online samples at the shortest TOS did show peaks for non-aromatic hydrocarbon oligomers; however, no higher hydrocarbon products were observed after the first sample, even at $W/F = 4$ h. The results imply that the sites for the formation of hydrocarbon oligomers deactivated quickly, while the sites for glycerol dehydration to propenal appear less affected.

Figure 3b shows the effect of TOS on the product distribution over HZSM-22. The yield to propenal increased to 86% at the expense of acetaldehyde and olefin gas in the first several hours. The propenal yield was maintained at 86% up to the tested maximum of 20 h with 100% glycerol conversion. The propenal yield over HZSM-22 is comparable to the highest propenal yield over $H_4SiW_{12}O_{40}$ (87% yield) reported in the literature and higher than other zeolites (such as 73.6% for ZSM-5 and 80.1% for zeolite β) reported in the literature.¹⁹ Thus, HZSM-22 is a good candidate for acrolein production.

Over both HZSM-5 and HZSM-22, propenal is the major primary product. Over HZSM-5, propenal can be further converted to aromatics via oligomerization (aldol condensation) and aromatization reactions, while over HZSM-22, it can only be converted to non-aromatic hydrocarbon oligomers without aromatization observed. The pore intersection sites present for HZSM-5 but absent for HZSM-22 are important for aromatization reactions. The pore intersection has a space larger than both pore channels, providing the room for aromatization.²⁷

It has been demonstrated that propenal (formed via selective hydrogenation of the $C=C$ double bond of propenal) is readily converted to aromatic-rich hydrocarbons over HZSM-5^{16–18} and to gasoline-range isoalkanes (with rapid deactivation) over HZSM-22²⁸ at low W/F . In both cases, acid-catalyzed aldol condensation plays an important role. An aldol trimer of propenal can directly form a C_9 aromatic over HZSM-5.¹⁷ However, aromatics appeared at longer W/F over HZSM-5, and isoalkanes appeared at much longer W/F over HZSM-22, during glycerol conversion. This difference may be explained by two reasons. First, in comparison to propenal, propenal is less active for aldol condensation because of the relatively less active α -H as a consequence of the influence of the conjugated $C=C$ bond. Second, the significant amount of water produced from glycerol dehydration may compete for the active sites, with propenal limiting further reactions.

Figure 4 shows the temperature-programmed oxidation (TPO) profiles of spent HZSM-5 and HZSM-22 after 6 h TOS. It is seen that double the amount of carbon is observed over HZSM-5 compared to HZSM-22. A small shoulder peak at >800 °C is present for HZSM-22 but absent for HZSM-5, indicating some more refractory coke on HZSM-22. This could be interpreted in terms of the shape and size of the crystallites for HZSM-5 and HZSM-22. HZSM-5 has a cubic shape, with a primary crystallite size less than 100 nm,¹⁸ while HZSM-22 has a needle shape, with the needle length of several micrometers.^{25,28} In addition, the BET surface area is double for HZSM-5 compared to HZSM-22. The one-dimensional pore with openings at the ends of the needle-shaped crystals suggests that a relatively

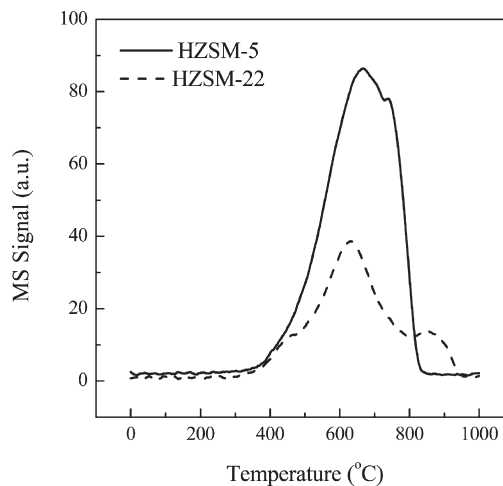


Figure 4. CO_2 evolution profiles from TPO of spent HZSM-5 and HZSM-22. Reaction conditions: T , 400 °C; P , 1 atm; W/F , 1 h; TOS, 6 h.

Table 3. Effect of the Catalyst (Pd/ZnO, HZSM-5, and Pd/ZnO + HZSM-5) on Glycerol Conversion and Product Distribution (Yield)^a

catalyst	Pd/ZnO	HZSM-5	Pd/ZnO + HZSM-5
conversion (%)	91.7	96.9	99.0
oxygenate (mol_{carbon} %)			
acetaldehyde	10.4	7.8	22.4
propenal	13.0	6.1	0.8
propenal	2.9	59.4	5.0
alcohols	24.7	0.2	33.0
acetol	10.3	1.0	1.5
ketones	24.9	1.1	0.8
propandiol	5.4	0.4	0.0
total (mol_{carbon} %)	91.7	76.0	63.5
hydrocarbon (mol_{carbon} %)			
benzene	0	1.2	0.7
toluene	0	2.6	5.6
C_8 aromatics	0	3.6	11.8
C_9 aromatics	0	3.9	11.1
C_{10} aromatics	0	4.5	4.4
C_{11} aromatics	0	2.0	0.7
C_{12} aromatics	0	3.1	1.2
total (mol_{carbon} %)	0	20.9	35.5

^a Reaction conditions: T , 400 °C; P , 2 MPa; W/F , 0.5 h; TOS, 3 h.

small amount of coke can cause significant pore blockage that leads to significant reduction in the accessibility of the active sites in this channel system, and this limits the formation and removal of oligomers. Thus, the oligomeric hydrocarbons are only observed for very short TOS during glycerol conversion over HZSM-22.

Glycerol Conversion on a Two-Bed System (Pd/ZnO Followed by HZSM-5). To separate the catalytic activity for deoxygenation from oligomerization and to increase the gasoline-range aromatic yield, glycerol conversion was carried out on a two-bed system. A deoxygenation catalyst (Pd/ZnO) was placed as the first bed to partially deoxygenate the glycerol to mono-functional oxygenate intermediates, followed by the acidic zeolite bed to oligomerize these intermediates to the final products. Table 3 reports the results of glycerol conversion over Pd/ZnO, HZSM-5, and Pd/ZnO + HZSM-5, at 400 °C and 2 MPa.

In contrast to propenal formed as the major oxygenate on HZSM-5, the Pd/ZnO deoxygenates glycerol to mono-functional compounds, such as acetaldehyde, propenal, acetone, and alcohols, without the formation of a hydrocarbon phase. The propenal yield is much lower on Pd/ZnO than that on

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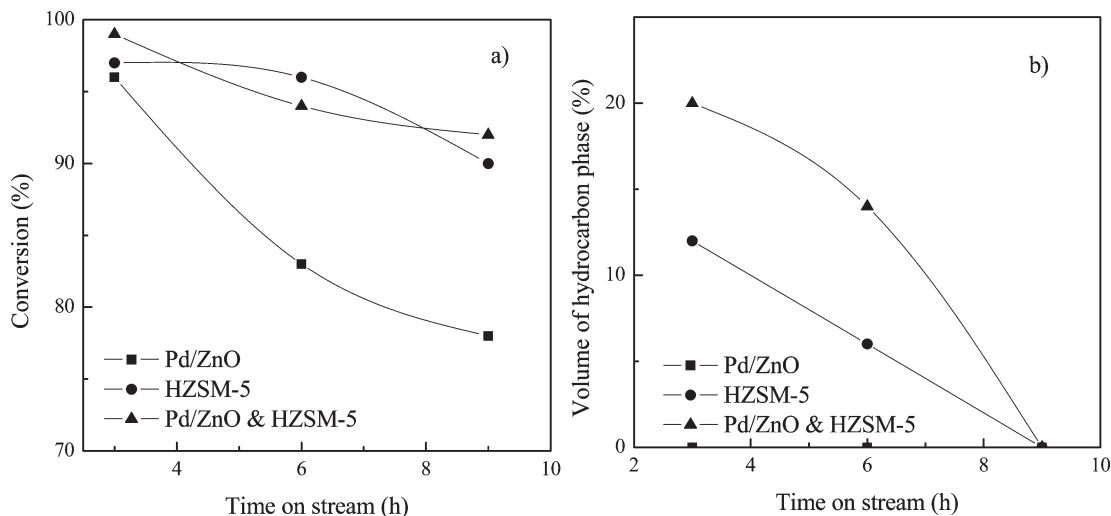


Figure 5. Conversion of glycerol on Pd/ZnO, HZSM-5, and Pd/ZnO and HZSM-5: (a) conversion as a function of TOS and (b) percentage by volume of the hydrocarbon phase as a function of TOS. Reaction conditions: T , 400 °C; P , 2 MPa; W/F , 0.5 h (data taken offline).

369 HZSM-5, as a result of it being readily hydrogenated by
 370 propanal over the Pd. When HZSM-5 was present as a
 371 second bed, the oxygenate products from the Pd/ZnO further
 372 reacted to form aromatic compounds. The aldehydes and
 373 ketones may follow an aldol-condensation pathway with
 374 cyclization and aromatization to form the alkyl-aromatics,
 375 as described previously.¹⁷ The alcohols may also follow a
 376 similar path as with methanol to hydrocarbon.^{8–10} While
 377 the aromatics are evenly distributed from C_6 to C_{12} on
 378 HZSM-5 only, the C_8 – C_9 aromatics were found as the
 379 predominant compounds in the hydrocarbon phase over
 380 Pd/ZnO + HZSM-5. The aromatic (gasoline-range) yields
 381 are significantly increased for Pd/ZnO + HZSM-5 com-
 382 pared to HZSM-5 only.

383 The conversion of glycerol and the percentages of the
 384 hydrocarbon volume obtained on Pd/ZnO, HZSM-5, and
 385 Pd/ZnO with HZSM-5 as a function of time on stream are
 F5 386 shown in panels a and b of Figure 5. In comparison to the
 387 single Pd/ZnO bed, glycerol conversion on HZSM-5 and Pd/
 388 ZnO with HZSM-5 did not decrease significantly with TOS.
 389 As shown in Figure 5b, the hydrocarbon-phase yield from
 390 the two-bed experiments accounted for 20% by volume (note
 391 that a maximum 35% volume hydrocarbon phase could be
 392 formed assuming that glycerol could be completely dehy-
 393 drated to benzene and water), while from the HZSM-5 only,
 394 12% by volume was obtained over the first 3 h. The two-bed
 395 experiments still provided a higher volume of hydrocarbons
 396 up to 6 h. However, no aromatics were produced after 6 h. It
 397 should be noted that H_2 consumed in the first bed (Pd/ZnO)

could be supplied by glycerol reforming and the water–gas
 shift reaction.

Conclusions

400 We have demonstrated a zeolite-based route for the con-
 401 version of glycerol to gasoline-range fuels (alkyl-aromatics).
 402 Although propanal (acrolein) is the major primary glycerol
 403 dehydration product over all zeolites, the pore structure of the
 404 zeolite plays a crucial role in the final product distribution.
 405 One-dimensional medium-pore HZSM-22 is suitable for acro-
 406 lein production, with 86% yield at 100% glycerol conversion.
 407 Three-dimensional medium-pore HZSM-5 shows a high alkyl-
 408 aromatic yield. Longer contact times, higher temperatures,
 409 and higher pressures favor the formation of aromatics, with
 410 a maximum 60% yield over HZSM-5. The presence of a
 411 deoxygenation catalyst (Pd/ZnO) before the HZSM-5 results
 412 in a significant enhancement of the liquid hydrocarbon yield
 413 by partially deoxygenating and hydrogenating the feed to
 414 HZSM-5. These results suggest a strategy for developing an
 415 active, stable, and selective catalyst for glycerol conversion to
 416 fungible fuels.
 417

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