

Thank you for your interest in my publications!

This article was downloaded from my personal website and for non-commercial purposes only.

If you have any question and/or comment, please contact with me.

Dr. Yang Xiao

Research Associate

Davidson School of Chemical Engineering, Purdue University

West Lafayette, IN 47907-2100, U.S.A

Office: 765-496-3787, Fax: 765-494-0805

E-mail: xiao63@purdue.edu, xiaohaiyi8080@gmail.com

Website: www.xiaohaiyi8080.com

Welcome to access more of my research at www.xiaohaiyi8080.com

Conversion of Glycerol to Hydrocarbon Fuels via Bifunctional Catalysts

Yang Xiao and Arvind Varma*

School of Chemical Engineering, Purdue University, 480 Stadium Mall Drive, West Lafayette, Indiana 47907, United States

Supporting Information

ABSTRACT: Utilization of byproduct glycerol improves biodiesel production in terms of both economics and sustainability. Conversion of glycerol to hydrocarbon (GTH) fuels is among the promising options, which provides additional renewable energy besides biodiesel and contributes further to independence from fossil fuels. In the present work, bifunctional catalysts (Pt/H-ZSM-5 and Pd/H-ZSM-5) were selected, prepared, characterized, and tested for GTH conversion. The addition of noble metals enhances aromatics' yield, and both catalysts convert GTH fuels effectively. On the basis of the experimental observations and prior literature, it is proposed that GTH conversion follows sequential hydrodeoxygenation and aromatization steps. Under optimized conditions, ~90% glycerol conversion and ~60% yield of aromatic hydrocarbons were achieved over the Pd/H-ZSM-5 catalyst.



As a potential substitute for fossil fuels, biodiesel, produced mainly from vegetable oil and alcohols via esterification and/or transesterification, has become increasingly attractive owing to its environmental benefits and renewable properties.^{1,2} In all cases, 10% (w/w) glycerol is generated as the main byproduct of biodiesel manufacture, resulting in its large surplus and low price. Thus, by utilization of glycerol, the biodiesel economy could be further improved.^{3–5} Besides the biodiesel area, as a polyol, glycerol is considered to be a representative model compound of biomass-derived oxygenates.^{6,7} Hence, fundamental studies of glycerol conversion additionally benefit the area of biomass conversion to biofuels. As a chemical, glycerol is utilized in animal feed, cosmetics, drugs, and as a feedstock for conversion to high-value chemicals. For these applications, not only chemistry but also separation processes must be developed.⁸ Fuel, rather than chemicals, is another choice for valorization of glycerol, which avoids purification of products because reaction mixtures could be used directly as fuels. Combined with biodiesel production, glycerol to hydrocarbon (GTH) conversion can provide additional renewable energy, which contributes further to independence from fossil fuels.

Owing to its high oxygen content (52 wt %), glycerol cannot be used directly as a fuel because the high oxygen content results in fuel degradation and poor combustion performance.⁹ It is, instead, preferable to convert glycerol to other fuels, for example, H₂, syngas,¹⁰ and fuel additives.¹¹ Because H₂ raises storage and safety concerns while syngas can be produced from alternative cheaper sources, glycerol-based H₂ and syngas routes are generally not followed. Glycerol-based fuel additives,

such as carbonate, propylene glycol, butanol, acrolein, and glyceryl acetal,¹² could increase the octane rating of fuels or serve as corrosion inhibitors or lubricants.¹³ Unfortunately, these various additives maintain either high oxygen content, high viscosity, or low heat value. Thus, current common ways of converting glycerol to fuels are unsatisfactory, owing to either low value product or insufficient combustion performance.

Shape-selective catalysis was first reported by Weisz and co-workers.¹⁴ As is well-known, by restricting undesired species, the topology of zeolites plays a key role in shape-selectivity.^{15–17} In addition, zeolite acidity is also a significant factor^{18,19} that influences activity, selectivity of reactions, and product distribution.^{20,21} The aromatization of C₅ and C₆ paraffins over ZSM-5 was discovered in the late 1960s,¹⁴ followed by that of ethane in the 1980s and that of methane in the 1990s.^{22,23} Aromatization of olefin and monohydric alcohols was also achieved,^{24,25} obtaining gasoline with a high content of aromatics. Among these, methanol to gasoline (MTG) and ethanol to gasoline (ETG) are two representative processes that convert short-chain alcohols to gasoline-range hydrocarbon fuels.^{26,27}

Hydrocarbon fuels play an essential part in the global energy chain, owing to their high energy density and ease of transportation. It is a recent idea to convert GTH fuels directly, as reported by a few publications. Hoang et al.²⁸ used a

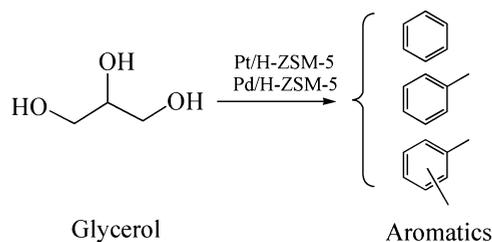
Received: September 8, 2016

Accepted: October 12, 2016

two-bed reactor, packed with Pd/ZnO and H-ZSM-5 sequentially, successfully converting glycerol to alkyl-aromatic hydrocarbons with a yield of ~60%. Instead, using a one-bed reactor packed with H-ZSM-5, Jang et al.²⁹ obtained a 30–40% yield of hydrocarbons from glycerol using alcohols as solvents, while Xiao et al.³⁰ reached a ~25% yield and 4 h catalyst life by NaOH pretreatment of H-ZSM-5. Recently, Tamiyakul et al.³¹ reported a ~50% yield of aromatics from glycerol via Zn/H-ZSM-5 catalyst, where both Zn and zeolite acidity effects were discussed. In addition to glycerol, oxygenates of polyol (ethylene glycol, 1,2-propanediol, and 1,4-butanediol^{32,33}) and sugar alcohol (glucose, sorbitol, and mannitol³⁴) are available from the fast pyrolysis of biomass. For use as motor fuels, these oxygenate mixtures need to be upgraded to hydrocarbons, typically employing zeolite and noble metals either separately^{35–38} or in a two-step process.³⁹

In the present work, as shown in Scheme 1, for the first time to our knowledge, bifunctional catalysts, which have both noble

Scheme 1. GTH Fuels via Bifunctional Catalysts



metal and acidic active sites, were investigated for GTH conversion. It is a novel concept to use such bifunctional catalysts for GTH conversion, although similar catalysts have been studied for other types of reactions.^{40,41} This work will not only benefit biodiesel manufacture by providing additional renewable high-octane hydrocarbon fuels derived from the byproduct glycerol but also offer potential applications of such bifunctional catalysts for the conversion of other biomass-derived oxygenates, especially polyols and sugar alcohols, to renewable high-octane hydrocarbon fuels.

For all three catalytic materials (H-ZSM-5, Pt/H-ZSM-5, and Pd/H-ZSM-5) studied in the present work, BET, TEM, XRD, and chemisorption measurements were conducted to obtain their physical and chemical properties. The BET results show that specific surface areas are in the range of 400–500 m²/g (Table S1), while the pore diameters are 0.5–0.6 nm, which are both consistent with those reported in the literature.^{42–44} As compared with H-ZSM-5, after metals (Pt and Pd) are loaded on the support, specific surface areas and average pore diameters decrease somewhat. The metal dispersions (24.3% for Pt, 29.7% for Pd) and particle sizes (3.6 nm for Pt, 3.2 nm for Pd) obtained from chemisorption³³ are consistent with the results from TEM (Figure S2; 4.2 nm for Pt, 3.8 nm for Pd).⁴⁵ The XRD patterns (Figure S3) for H-ZSM-5 are compared to diffraction patterns for MFI (ZSM-5) reported in the International Zeolite Association (IZA) structure database.⁴⁶ Pt/H-ZSM-5 and Pd/H-ZSM-5 are similar to unsupported H-ZSM-5, and no Pt or Pd peaks are identified, likely due to low metal content (5 wt %) and high metal dispersions (20–30%).⁴⁷

Before a detailed discussion of conditions that affect the GTH process, a few preliminary experiments, using Pd/H-ZSM-5 as the catalyst, were conducted to investigate the effects of contact time (W/F), total pressure, H₂/glycerol ratio, and temperature on glycerol conversion and liquid hydrocarbon yield. It was found that long W/F and high temperature are preferred to obtain higher glycerol conversion and liquid hydrocarbon yield, while high pressure and high H₂/glycerol ratio are not as important. Thus, standard conditions, as follows, W/F = 6 g cat-h/g glycerol, T = 400 °C, p_{total} = 1 atm, and H₂/glycerol molar ratio = 10, were used to obtain the effects of the above operating conditions.

For both Pt/H-ZSM-5 and Pd/H-ZSM-5 catalysts, three 8 h runs were conducted and no significant deactivation was found. As the element analysis in Table S2 of the Supporting Information shows, three 8 h runs result in a relatively small ~4–7% metal leaching. This loss is unavoidable and is consistent with prior works.^{48,49}

Under the standard conditions, product distributions over H-ZSM-5, Pt/H-ZSM-5, and Pd/H-ZSM-5 are shown in Table 1,

Table 1. Typical Product Distributions for H-ZSM-5, Pt/H-ZSM-5, and Pd/H-ZSM-5 Catalysts at 1 atm, 10 H₂/Glycerol Molar Ratio, 400 °C, and 6 g cat-h/g Glycerol

name	General			chemical species	molecular formula	Details		
	mole fraction, %					molar fraction %		
	H-ZSM-5	Pt/H-ZSM-5	Pd/H-ZSM-5			H-ZSM-5	Pt/H-ZSM-5	Pd/H-ZSM-5
glycerol	9.78	6.75	8.01	glycerol	C ₃ H ₈ O ₃	9.78	6.75	8.01
oxygenates	58.32	32.46	23.23	acetaldehyde	C ₂ H ₄ O	0.32	1.32	2.31
				propanal	C ₃ H ₆ O	3.22	2.37	4.92
				propenal (acrolein)	C ₃ H ₄ O	54.21	27.73	13.84
				hydroxyacetone (acetol)	C ₂ H ₆ O ₂	0.57	1.04	2.16
				gases	8.73	11.87	7.43	methane
aromatics	23.17	48.92	61.33	ethylene	C ₂ H ₄	3.25	4.11	2.29
				propylene	C ₃ H ₆	4.83	6.76	3.81
				benzene (C ₆)	C ₆ H ₆	0.00	2.20	2.52
				toluene (C ₇)	C ₇ H ₈	0.75	5.41	6.31
				<i>p</i> -xylene (C ₈)	C ₈ H ₁₀	6.74	9.46	16.28
				<i>m</i> -xylene (C ₈)	C ₈ H ₁₀	0.98	14.57	11.55
				<i>o</i> -xylene (C ₈)	C ₈ H ₁₀	1.27	3.85	6.24
				cumene (C ₉)	C ₉ H ₁₂	1.58	8.16	12.32
				C ₉ +		11.85	5.27	6.11

which describes that there are always more than 10 components in products, including unreacted glycerol, oxygenates, gases, and aromatics, where aromatics are the target products as hydrocarbon fuels. Without loading metals, H-ZSM-5 alone converts glycerol primarily to oxygenates (mainly acrolein), while the C₆–C₈ aromatics' yield is ~11%. This is consistent with the literature.^{12,13} High oxygenate content implies a low glycerol hydrodeoxygenation (HDO) ability of H-ZSM-5. In contrast, metal (Pt or Pd)-supported H-ZSM-5 produces lower oxygenates' yields and higher aromatics' yields.

Catalysts with the same metal (Pd and Pd) types and amounts, but supported on amorphous SiO₂, were also tested. Both Pd/SiO₂ and Pt/SiO₂ gave low aromatics' yields (<5%), with conversions of 15–25%, while the main liquid products were short-chain oxygenates such as acrolein and acetol. These experimental observations demonstrate that the design of bifunctional catalysts, with both noble metal and acidic ZSM-5 support, is necessary for GTH conversion.

HDO of glycerol via either dehydration/hydrogenation or hydrogenation/dehydration pathways includes two or three consecutive reactions of C–O bond cleavages, producing monohydric alcohols or short-chain hydrocarbons, respectively. The XPS results (Table S4) show the presence of Pt and Pd on the surface of Pt/H-ZSM-5 and Pd/H-ZSM-5, respectively, as compared to the unsupported H-ZSM-5. Because the contents of oxygenates decrease by ~20–30% with metal addition, it is thus deduced that addition of noble metals (Pt and Pd) to H-ZSM-5 enhances C–O bond cleavages of glycerol. In the presence of metals, more aromatic hydrocarbons, instead of HDO products such as monohydric alcohols or short-chain hydrocarbons, are found in Table 1, which implies that the HDO products are converted to aromatic hydrocarbons over H-ZSM-5 through a shape selectivity mechanism.^{14,17}

All three catalyst samples were found to be acidic by NH₃-TPD measurements, as shown in Table S3 and Figure S4, because ammonia desorption peaks from Brønsted acid were observed at ~600–700 K.⁵⁰ The higher aromatics' yield obtained over Pd/H-ZSM-5 catalyst likely owes to its higher H/metal site ratio (0.63), as compared to Pt/H-ZSM-5 (0.13).

Thus, it is assumed that in the present experiments, two main reactions occur sequentially in the GTH process: HDO and aromatization. Specifically, bifunctional catalysts, containing both noble metals (Pt or Pd) and acidic support (H-ZSM-5), deoxygenate glycerol to oxygenates and other intermediates such as short-chain hydrocarbons (both paraffins and olefins) and/or monohydric alcohols. Then, aromatics are generated by combining short-chain species in the channel (diameter similar to the kinetic diameter of aromatics) or on the acidic sites of H-ZSM-5 zeolite. In the results described below, only data for Pd/H-ZSM-5 are reported. Similar results were obtained for Pt/H-ZSM-5 as well but are not reported because Pd/H-ZSM-5 was always superior.

The effects of total pressure and H₂/glycerol molar ratio on glycerol conversion and the product distribution are shown in Figure 1. Under atmospheric pressure, when the H₂/glycerol molar ratio increases above 10, glycerol conversion and product distributions do not change significantly. Similarly, the total pressure in the range of 1–20 atm does not influence the glycerol conversion and product distribution.

The molecular formula of glycerol is C₃H₈O₃. Thus, theoretically, three moles of H₂ are needed to fully deoxygenate glycerol. From Figure 1, a H₂/glycerol molar ratio of 6 gives a lower conversion of glycerol, while ratios larger than 10 present

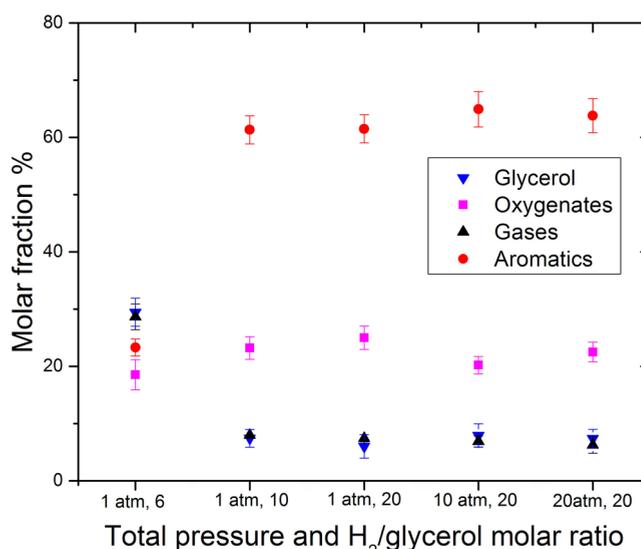


Figure 1. Effects of total pressure and H₂/glycerol ratio at 400 °C and 6 cat·h/g glycerol for Pd/H-ZSM-5 catalyst.

steady glycerol conversion and product distribution. It is thus concluded that a H₂/glycerol molar ratio of 10 provides excess H₂ and does not need to be further increased. This is likely due to the ease of H₂ dissociative adsorption over Pt and Pd surfaces. High H₂ pressure is generally preferred to have better HDO performance.⁵¹ Figure 1, however, does not support this trend, which may be explained by the aliphatic, rather than aryl, properties of glycerol.^{51–53} In summary, when Pt/H-ZSM-5 and Pd/H-ZSM-5 were used in GTH conversion, a moderate H₂/glycerol ratio and atmospheric pressure provided good glycerol conversion and aromatic hydrocarbon yield.

The effects of temperature on glycerol conversion and product distribution are shown in Figure 2. With increasing temperature, glycerol conversion also increases. At 300 °C, which is slightly higher than the boiling point of glycerol (290 °C), glycerol conversion is only ~15%, where almost all products are oxygenates and no gas/aromatics products are found. At 350–400 °C, conversion of glycerol and the yield of

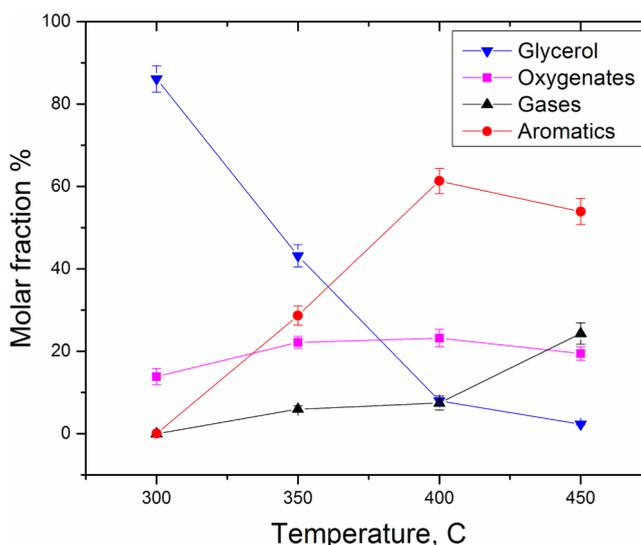


Figure 2. Effect of temperature at 1 atm, 10 H₂/glycerol molar ratio, and 6 g cat·h/g glycerol for Pd/H-ZSM-5 catalyst.

aromatics keep increasing, while the molar fraction of the oxygenates stays essentially the same, which indicates that oxygenates are converted to aromatics, as also noted above in the context of Table 1. At 450 °C, however, the yields of oxygenates and aromatics both decrease because more gases are produced due to the high temperature that results in glycerol decomposition.

Along with C–O bond cleavages, three other types of glycerol bond cleavages may also occur in the presence of noble metal catalysts: C–H, O–H, and C–C bonds. Noble metals are preferred for both activating glycerol binding and hydrogen dissociative adsorption.⁵⁴ At lower temperature (up to ~200 °C), C–H and O–H bonds are easily broken due to their lower reaction barriers,⁵⁵ which could be prevented by high H₂ content via possible hydrogenation. At higher temperature (300–400 °C), both C–C and C–O bond cleavages can occur simultaneously because their reaction barriers are higher than C–H/O–H bond cleavages and close to each other. For example, both C–O and C–C bonds of glycerol are cleaved on the Pt surface at 350 °C, forming ethanol, ethylene glycol, and 1,2-propanediol.⁵⁶ To obtain high aromatic hydrocarbons in GTH conversion, the key issue is how to break the C–O bond while keeping the C–C bond intact. Appropriate noble metals, such as Pt, Pd, and Rh, favor the cleavage of C–O bonds in glycerol rather than other bonds because these metals promote the formation of hydrocarbons from polyols instead of CO and H₂.⁵⁷

The kinetic behavior of GTH is shown in Figure 3. It is found that if the contact time (W/F) is smaller than 0.1 g cat-

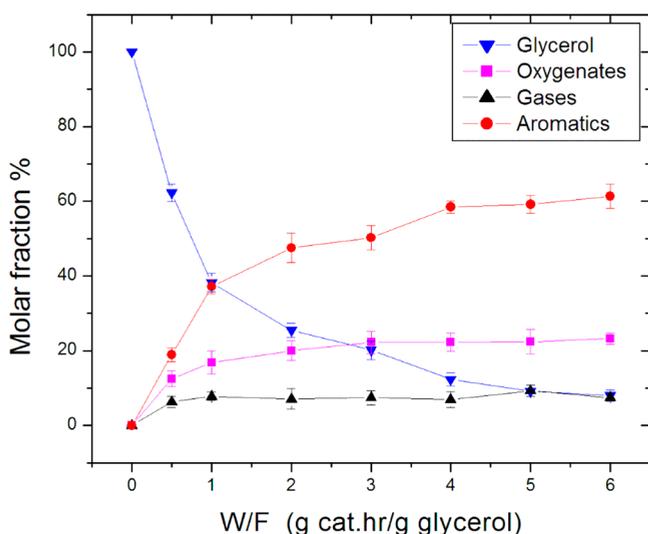


Figure 3. Kinetic behavior at 1 atm, a H₂/glycerol molar ratio of 10, and 400 °C for Pd/H-ZSM-5 catalyst.

h/g glycerol, no hydrocarbons exist in the liquid products. As shown in Figure 3, when W/F is 0.5 g cat-h/g glycerol, ~20% aromatics are found in the liquid products. With an increase of W/F, both glycerol conversion and aromatics' yields increase, while for W/F greater than about 2 g cat-h/g glycerol, gas and oxygenate contents remain essentially constant. This indicates that the latter two types of chemical species are converted to aromatics as contact time increases.

In the present work, bifunctional metal-supported catalysts (Pt/H-ZSM-5 and Pd/H-ZSM-5) were prepared by an incipient wetness impregnation method and tested for

converting GTH fuels. On the basis of the experimental observations and prior literature, it is proposed that GTH conversion follows sequential HDO and aromatization steps. The operating conditions, including the H₂/glycerol ratio, total pressure, temperature, and contact time were investigated and discussed. It was found that the presence of Pt or Pd enhances the yield of aromatics, and for this purpose, Pd is superior to Pt. The Pd/H-ZSM-5 catalyst exhibits ~90% glycerol conversion and a ~60% yield of aromatic hydrocarbons at 400 °C temperature, 1 atm pressure, and 6 g cat-h/g glycerol contact time. This work provides a potential attractive way to convert glycerol, a byproduct of biodiesel production, to hydrocarbon fuels.

EXPERIMENTAL METHODS

Chloroplatinic acid hydrate and palladium(II) nitrate hydrate were used as metal precursors, while H-ZSM-5 was obtained by calcining ammonium form ZSM-5 (Si/Al = 40) in air at 500 °C for 4 h.^{50,58} Pt and Pd were loaded on H-ZSM-5 by incipient wetness impregnation (IWI) method to obtain 5 wt % Pt/H-ZSM-5 and 5 wt % Pd/H-ZSM-5 catalysts, respectively. In other sections, metal loadings and details of H-ZSM-5 are not noted explicitly when describing the catalysts. Thus, for example, Pt/H-ZSM-5 refers to 5 wt % Pt placed on H-form ZSM-5 with a Si/Al ratio of 40. These catalysts were characterized by BET, chemisorption, TEM, XRD, AES-ICP, XPS, and NH₃-TPD techniques. The catalyst testing experiments were conducted in a continuous flow reactor, as shown in Figure S1. The standard reactor operating conditions were 400 °C, 1 atm total pressure, 2.25 g of catalyst, mixed gas of N₂ and H₂ at flow rates of 100 and 15–200 mL/min, respectively, and a pure glycerol feed rate of 0.3 mL/h (liquid, at room temperature). All experiments were conducted under excess hydrogen flow (feed molar ratio of H₂ to glycerol of ~10). Detailed information about materials, catalyst characterization, catalyst preparation, activity tests, and composition analysis is provided in the Supporting Information.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acseenergylett.6b00421.

Detailed information about materials, catalyst characterization, catalyst preparation, activity tests, and composition analysis (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: avarma@purdue.edu. Tel.: +1-(765) 494-8484. Fax: +1-(765) 494-0805.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the R. Games Slayter Fund. The authors thank Mr. John R. Di Iorio for help with the NH₃-TPD measurements.

REFERENCES

- (1) Di Serio, M.; Tesser, R.; Pengmei, L.; Santacesaria, E. Heterogeneous catalysts for biodiesel production. *Energy Fuels* **2008**, *22*, 207–217.
- (2) Aransiola, E. F.; Ojumu, T. V.; Oyekola, O. O.; Madzimbamuto, T. F.; Ikhu-Omoregbe, D. I. O. A review of current technology for biodiesel production: State of the art. *Biomass Bioenergy* **2014**, *61*, 276–297.
- (3) Johnson, D. T.; Taconi, K. A. The glycerin glut: Options for the value-added conversion of crude glycerol resulting from biodiesel production. *Environ. Prog.* **2007**, *26*, 338–348.
- (4) Fan, X.; Burton, R.; Zhou, Y. Glycerol (byproduct of biodiesel production) as a source for fuels and chemicals – mini review. *Open Fuels Energy Sci. J.* **2010**, *3*, 17–22.
- (5) Thanh, L. T.; Okitsu, K.; Boi, L. V.; Maeda, Y. Catalytic technologies for biodiesel fuel production and utilization of glycerol: a review. *Catalysts* **2012**, *2*, 191–222.
- (6) Corma, A.; Huber, G. W.; Sauvanaud, L.; O'Connor, P. Processing biomass-derived oxygenates in the oil refinery: Catalytic cracking (FCC) reaction pathways and role of catalyst. *J. Catal.* **2007**, *247*, 307–327.
- (7) Watanabe, M.; Iida, T.; Aizawa, Y.; Aida, T. M.; Inomata, H. Acrolein synthesis from glycerol in hot-compressed water. *Bioresour. Technol.* **2007**, *98*, 1285–1290.
- (8) Ayoub, M.; Abdullah, A. Z. Critical review on the current scenario and significance of crude glycerol resulting from biodiesel industry towards more sustainable renewable energy industry. *Renewable Sustainable Energy Rev.* **2012**, *16*, 2671–2686.
- (9) Quispe, C. A. G.; Coronado, C. J. R.; Carvalho, J. A., Jr. Glycerol: production, consumption, prices, characterization and new trends in combustion. *Renewable Sustainable Energy Rev.* **2013**, *27*, 475–493.
- (10) Hirai, T.; Ikenaga, N.; Miyake, T.; Suzuki, T. Production of hydrogen by steam reforming of glycerin on ruthenium catalyst. *Energy Fuels* **2005**, *19*, 1761–1762.
- (11) Pagliaro, M.; Ciriminna, R.; Kimura, H.; Rossi, M.; Della Pina, C. From glycerol to value-added products. *Angew. Chem., Int. Ed.* **2007**, *46*, 4434–4440.
- (12) Climent, M. J.; Corma, A.; Iborra, S. Conversion of biomass platform molecules into fuel additives and liquid hydrocarbon fuels. *Green Chem.* **2014**, *16*, 516–547.
- (13) Karinen, R. S.; Krause, A. O. I. New biocomponents from glycerol. *Appl. Catal., A* **2006**, *306*, 128–133.
- (14) Weisz, P. B.; Frilette, V. J. Intracrystalline and molecular-shape-selective catalysis by zeolite salts. *J. Phys. Chem.* **1960**, *64*, 382–382.
- (15) Fraenkel, D. Role of external surface sites in shape-selective catalysis over zeolites. *Ind. Eng. Chem. Res.* **1990**, *29*, 1814–1821.
- (16) Song, C. Recent advance in shape-selective catalysis over zeolites for synthesis of specialty chemicals. *Stud. Surf. Sci. Catal.* **1998**, *113*, 163–186.
- (17) Csicsery, S. M. Shape-selective catalysis in zeolites. *Zeolites* **1984**, *4*, 202–213.
- (18) Alvaro-Munoz, T.; Marquez-Alvarez, C.; Sastre, E. Use of different templates on SAPO-34 synthesis: Effect on the acidity and catalytic activity in the MTO reaction. *Catal. Today* **2012**, *179*, 27–34.
- (19) Ono, Y. Transformation of lower alkanes into aromatic-hydrocarbons over ZSM-5 zeolites. *Catal. Rev.: Sci. Eng.* **1992**, *34*, 179–226.
- (20) Corma, A.; Martinez, A.; Martinez, C. Isobutane 2-butene alkylation on MCM-22 catalyst - influence of zeolite structure and acidity on activity and selectivity. *Catal. Lett.* **1994**, *28*, 187–201.
- (21) Roldan, R.; Romero, F. J.; Jimenez-Sanchidrian, C.; Marinas, J. M.; Gomez, J. P. Influence of acidity and pore geometry on the product distribution in the hydroisomerization of light paraffins on zeolites. *Appl. Catal., A* **2005**, *288*, 104–115.
- (22) Chen, N. Y.; Yan, T. Y. M2 forming - a process for aromatization of light-hydrocarbons. *Ind. Eng. Chem. Process Des. Dev.* **1986**, *25*, 151–155.
- (23) Wang, L. S.; Tao, L. X.; Xie, M. S.; Xu, G. F.; Huang, J. S.; Xu, Y. D. Dehydrogenation and aromatization of methane under nonoxidizing conditions. *Catal. Lett.* **1993**, *21*, 35–41.
- (24) Harandi, M. N.; Owen, H. Integrated staged conversion of methanol to gasoline and distillate. U.S. Patent US4899002 A, 1990.
- (25) Olsbye, U.; Svelle, S.; Bjorgen, M.; Beato, P.; Janssens, T. V. W.; Joensen, F.; Bordiga, S.; Lillerud, K. P. Conversion of methanol to hydrocarbons: how zeolite cavity and pore size controls product selectivity. *Angew. Chem., Int. Ed.* **2012**, *51*, 5810–5831.
- (26) Széchenyi, A.; Barthos, R.; Polymosi, F. Aromatization of ethanol on Mo2C/ZSM catalysts. *Catal. Lett.* **2006**, *110*, 85–89.
- (27) Derouane, E. G.; Nagy, J. B.; Dejaifve, P.; van Hooff, J. H. C.; Spekman, B. P.; Védrine, J. C.; Naccache, C. Elucidation of the mechanism of conversion of methanol and ethanol to hydrocarbons on a new type of synthetic zeolite. *J. Catal.* **1978**, *53*, 40–55.
- (28) Hoang, T. Q.; Zhu, X. L.; Danuthai, T.; Lobban, L. L.; Resasco, D. E.; Mallinson, R. G. Conversion of glycerol to alkyl-aromatics over zeolites. *Energy Fuels* **2010**, *24*, 3804–3809.
- (29) Jang, H. S.; Bae, K.; Shin, M.; Kim, S. M.; Kim, C. U.; Suh, Y. W. Aromatization of glycerol/alcohol mixtures over zeolite H-ZSM-5. *Fuel* **2014**, *134*, 439–447.
- (30) Xiao, W. Y.; Wang, F.; Xiao, G. M. Performance of hierarchical HZSM-5 zeolites prepared by NaOH treatments in the aromatization of glycerol. *RSC Adv.* **2015**, *5*, 63697–63704.
- (31) Tamiyakul, S.; Ubolcharoen, W.; Tungasmita, D. N.; Jongpatiwut, S. Conversion of glycerol to aromatic hydrocarbons over Zn-promoted HZSM-5 catalysts. *Catal. Today* **2015**, *256*, 325–335.
- (32) Vispute, T. P.; Huber, G. W. Production of hydrogen, alkanes and polyols by aqueous phase processing of wood-derived pyrolysis oils. *Green Chem.* **2009**, *11*, 1433–1445.
- (33) Besson, M.; Gallezot, P.; Pinel, C. Conversion of biomass into chemicals over metal catalysts. *Chem. Rev.* **2014**, *114*, 1827–1870.
- (34) Fukuoka, A.; Dhepe, P. L. Catalytic conversion of cellulose into sugar alcohols. *Angew. Chem., Int. Ed.* **2006**, *45*, 5161–5163.
- (35) Taher, D.; Thibault, M. E.; Di Mondo, D.; Jennings, M.; Schlaf, M. Acid-, water- and high-temperature-stable ruthenium complexes for the total catalytic deoxygenation of glycerol to propane. *Chem. - Eur. J.* **2009**, *15*, 10132–10143.
- (36) Qin, L. Z.; Song, M. J.; Chen, C. L. Aqueous-phase deoxygenation of glycerol to 1,3-propanediol over Pt/WO₃/ZrO₂ catalysts in a fixed-bed reactor. *Green Chem.* **2010**, *12*, 1466–1472.
- (37) Mentzel, U. V.; Holm, M. S. Utilization of biomass: Conversion of model compounds to hydrocarbons over zeolite H-ZSM-5. *Appl. Catal., A* **2011**, *396*, 59–67.
- (38) Xiong, K.; Yu, W.; Vlachos, D. G.; Chen, J. G. Reaction pathways of biomass-derived oxygenates over metals and carbides: from model surfaces to supported catalysts. *ChemCatChem* **2015**, *7*, 1402–1421.
- (39) Vispute, T. P.; Zhang, H.; Sanna, A.; Xiao, R.; Huber, G. W. Renewable chemical commodity feedstocks from integrated catalytic processing of pyrolysis oils. *Science* **2010**, *330*, 1222.
- (40) Resende, F. L. P. Recent advances on fast hydrolysis of biomass. *Catal. Today* **2016**, *269*, 148–155.
- (41) Thangalazhy-Gopakumar, S.; Adhikari, S.; Gupta, R. B. Catalytic pyrolysis of biomass over H+ZSM-5 under hydrogen pressure. *Energy Fuels* **2012**, *26*, 5300–5306.
- (42) Serrano-Ruiz, J. C.; Dumesic, J. A. Catalytic routes for the conversion of biomass into liquid hydrocarbon transportation fuels. *Energy Environ. Sci.* **2011**, *4*, 83–99.
- (43) Olson, D. H.; Kokotailo, G. T.; Lawton, S. L.; Meier, W. M. Crystal-structure and structure-related properties of ZSM-5. *J. Phys. Chem.* **1981**, *85*, 2238–2243.

- (44) Huang, L. M.; Guo, W. P.; Deng, P.; Xue, Z. Y.; Li, Q. Z. Investigation of synthesizing MCM-41/ZSM-5 composites. *J. Phys. Chem. B* **2000**, *104*, 2817–2823.
- (45) Ertl, G.; Knözinger, H.; Schüth, F.; Weitkamp, J. *Handbook of heterogeneous catalysis*; John Wiley & Sons: New York, 2008.
- (46) Baerlocher, C.; McCusker, L. B.; Olson, D. H. MFI - Pnma. *Atlas of zeolite framework types* 6th ed.; Elsevier Science B.V.: Amsterdam, The Netherlands, 2007; pp 212–213.
- (47) Zhu, Z. Z.; Lu, G. Z.; Guo, Y.; Guo, Y. L.; Zhang, Z. G.; Wang, Y. Q.; Gong, X. Q. High performance and stability of the Pt-W/ZSM-5 catalyst for the total oxidation of propane: the role of tungsten. *ChemCatChem* **2013**, *5*, 2495–2503.
- (48) Hyde, P. J.; Maggiore, C. J.; Srinivasan, S. Use of a nuclear microprobe in the study of fuel cell electrodes. *J. Electroanal. Chem. Interfacial Electrochem.* **1984**, *168*, 383–394.
- (49) Antolini, E.; Salgado, J. R. C.; Gonzalez, E. R. The stability of Pt–M (M = first row transition metal) alloy catalysts and its effect on the activity in low temperature fuel cells: A literature review and tests on a Pt–Co catalyst. *J. Power Sources* **2006**, *160*, 957–968.
- (50) Di Iorio, J. R.; Bates, S. A.; Verma, A. A.; Delgass, W. N.; Ribeiro, F. H.; Miller, J. T.; Gounder, R. The dynamic nature of bronsted acid sites in Cu-zeolites during NOx selective catalytic reduction: quantification by gas-phase ammonia titration. *Top. Catal.* **2015**, *58*, 424–434.
- (51) Nimmanwudipong, T.; Runnebaum, R. C.; Block, D. E.; Gates, B. C. Catalytic conversion of guaiacol catalyzed by platinum supported on alumina: reaction network including hydrodeoxygenation reactions. *Energy Fuels* **2011**, *25*, 3417–3427.
- (52) Gao, D.; Schweitzer, C.; Hwang, H. T.; Varma, A. Conversion of Guaiacol on Noble Metal Catalysts: Reaction Performance and Deactivation Studies. *Ind. Eng. Chem. Res.* **2014**, *53*, 18658–18667.
- (53) Gao, D.; Xiao, Y.; Varma, A. Guaiacol hydrodeoxygenation over platinum catalyst: reaction pathways and kinetics. *Ind. Eng. Chem. Res.* **2015**, *54*, 10638–10644.
- (54) Harris, J.; Andersson, S. H-2 Dissociation at Metal-Surfaces. *Phys. Rev. Lett.* **1985**, *55*, 1583–1586.
- (55) Liu, B.; Greeley, J. Decomposition pathways of glycerol via C-H, O-H, and C-C bond scission on Pt(111): a density functional theory study. *J. Phys. Chem. C* **2011**, *115*, 19702–19709.
- (56) Dasari, M. A.; Kiatsimkul, P. P.; Sutterlin, W. R.; Suppes, G. J. Low-pressure hydrogenolysis of glycerol to propylene glycol. *Appl. Catal., A* **2005**, *281*, 225–231.
- (57) Lara, P.; Paneque, M.; Poveda, M. L.; Salazar, V.; Santos, L. L.; Carmona, E. Formation and cleavage of C-H, C-C, and C-O bonds of ortho-methyl-substituted anisoles by late transition metals. *J. Am. Chem. Soc.* **2006**, *128*, 3512–3513.
- (58) Chiang, H.; Bhan, A. Catalytic consequences of hydroxyl group location on the rate and mechanism of parallel dehydration reactions of ethanol over acidic zeolites. *J. Catal.* **2010**, *271*, 251–261.

Electronic Supplementary Information

Conversion of Glycerol to Hydrocarbon Fuels via Bifunctional Catalysts

Yang Xiao and Arvind Varma*

School of Chemical Engineering, Purdue University, 480 Stadium Mall Drive, West Lafayette,
Indiana 47907, United States

☐ Tel.: +1-(765) 494-4075. Fax: +1-(765) 494-0805. E-mail: avarma@purdue.edu.

Experimental

Materials

Chloroplatinic acid hydrate (99.9% metal basis) and palladium (II) nitrate hydrate (99.8% metals basis) were used as metal precursors, both from Alfa Aesar. ZSM-5 (Si/Al=40) of ammonium form was supplied by Zeolyst International. The following chemicals, all ACS grade, were obtained from Mallinckrodt Chemicals: pure glycerol, 37 wt% HCl and NaOH pellets. The following chemical standards were from Sigma-Aldrich: acetaldehyde, benzene, cumene, ethylene, hydroxyacetone (acetol), methane, propanal, propenal (acrolein), propylene, toluene, m-xylene, o-xylene, p-xylene. Ultra-high purity grade gases (H_2 , He, O_2 , CH_4 , C_2H_6 and C_3H_8) were purchased from Indiana Oxygen. The 0.5%Pt/ Al_2O_3 (metal dispersion= $31\pm 0.5\%$) standard used for calibration of chemisorption measurements was obtained from Micromeritics.

Catalyst Preparation

ZSM-5 (Si/Al=40) of ammonium form was converted to its H-form (H-ZSM-5) by calcining in air at 500 °C for 4 h^{2, 3}. Pt and Pd were loaded on H-ZSM-5 by the impregnation method, to obtain 5 wt% Pt/H-ZSM-5 and 5 wt% Pd/H-ZSM-5 catalysts, respectively. Briefly, Pt and Pd precursors were dissolved separately in deionized water, and then added dropwise to the well-stirred H-ZSM-5 slurry, with pH=5-6 and stirring continued for at least 8 hrs at room temperature for each metal loading. The slurry was then rinsed, dried in air at 100 °C. As noted above, the Pt and Pd loadings were both 5 wt%, while H-ZSM-5 was the H-form ZSM-5 with a Si/Al ratio of 40. For this reason, in

later sections the metal loadings and details of H-ZSM-5 are not noted explicitly when describing the catalysts. Thus, e.g., Pt/H-ZSM-5 refers to 5 wt% Pt placed on H-form ZSM-5 with a Si/Al ratio of 40.

Catalyst characterization

The physisorption properties of the catalysts, including BET surface area, pore size distribution, average pore volume and pore diameter, were measured using a Micromeritics ASAP 2000 apparatus, where nitrogen was used as adsorbent gas. Degassing was performed at 280 °C for 6 hrs before measurements. The Pt dispersion was obtained using the H₂-O₂ titration approach¹, where the calibration was done using the 0.5%Pt/Al₂O₃ standard described in Materials section. The surface morphology of catalyst samples was obtained using a FEI-Tecnaï transmission electron microscope (TEM), operated at 200 kV with LaB₆ source. The samples were prepared by suspending the catalyst particles in water, collecting the fines, and placing them on a 200 copper mesh with lacey carbon film coating, followed by drying in air. The powder X-ray diffraction (XRD) was performed on a Rigaku SmartLab X-ray diffractometer with a Cu K α radiation source. Elemental analysis of fresh 5%Pd/H-ZSM-5, 3-times used 5%Pd/H-ZSM-5, fresh 5%Pt/H-ZSM-5, and 3-times used 5%Pt/H-ZSM-5 was carried out by ICP-AES method.

TPD experiments were performed using a Micromeritics Autochem II 2920 Chemisorption analyzer equipped with an Agilent 5975C mass selective detector (MSD)

to identify the gaseous species evolved from the catalyst samples. The samples were placed between two quartz wool plugs inside a U-shaped quartz cell held within a clam-shell furnace, with $50 \text{ cm}^3 \text{ min}^{-1}$ flowing UHP helium at ambient temperature for 1 h, and heated to 873 K (0.167 K s^{-1}).

Catalyst activity testing

The experiments were conducted in a continuous flow system as shown in Figure S1. The catalysts were packed in a stainless steel fixed-bed reactor with OD = 12.7 mm and ID = 10.2 mm, where stainless steel meshes and quartz wool plugs were inserted at both ends. Prior to the GTH reaction, the catalysts were activated at 400°C , 1 atm for 4 h under a gas mixture (H_2 -25%, N_2 -75%) flow. Pure glycerol was heated to 300°C to ensure its evaporation prior to being pumped (by an IP 25 Isocratic pump from Dionex) into the reactor. The product mixture was condensed in a glass condenser, cooled down by propanediol circulation (to -20°C) controlled by a circulator (Thermo Haake C10). The liquid products were collected every 10 min and the compositions were analyzed, while the gaseous products were analyzed on-line every 5 min. The standard reactor operating conditions were 400°C , 1 atm total pressure, 2.25 g catalyst, mixed gas of N_2 and H_2 at flow rates 100 mL/min and 15-200 mL/min respectively, and pure glycerol feed rate 0.3 mL/h (liquid, at room temperature). All experiments were conducted under excess hydrogen flow (feed molar ratio of H_2 to glycerol ~ 10). A blank test with packing inert materials, instead of the catalyst, was conducted under the standard reaction conditions. It was found that glycerol conversion was $< 2\%$. All experiments have mass

balances of $90 \pm 3\%$. Possible factors affecting mass balance include liquid or solid hold-up in the system, including the reactor and condenser, and possible coke deposit on the catalysts.

Composition analysis

Since typical products split into three phases: gaseous phase, organic liquid phase (upper phase) and aqueous liquid phase (lower phase), these three phases were analyzed separately. Both liquid product samples were analyzed by a GC-MS (LECO Pegasus 4D GCxGC-TOF), coupled with an auto sampler (CTC, GC-xt) and equipped with a DB-WAX column (30 m \times 0.32 mm). For routine analysis, the organic liquid samples were analyzed by a gas chromatograph (Agilent GC 6890) equipped with flame ionization detector and a DB-WAX (30 m \times 0.32 mm) column, while the aqueous liquid samples were analyzed by a gas chromatograph (Agilent GC 5890) equipped with flame ionization detector and a Select Biodiesel for glycerides uliMetal Column (15m*0.32 mm, ID=0.10 μ m) with a retention gap. The gaseous product was analyzed by a micro-GC (Agilent 3000A Micro GC) equipped with a Mol-Sieve 5A column and a Plot U column. Calibration was performed for all the components.

Table S1. BET and chemisorption results

Materials	BET results		Chemisorption results	
	Specific surface area (m ² /g)	Average pore diameter (nm)	Metal dispersion (%)	Metal particle size (nm)
H-ZSM-5	476	0.58	-	-
Pt/H-ZSM-5	421	0.52	24.3	3.6
Pd/H-ZSM-5	437	0.53	29.7	3.2

Table S2. Catalyst AES-ICP element analysis results

Materials	Fresh	3-times Used	Fresh	3-times Used
	5% Pd/H-ZSM-5	5% Pd/H-ZSM-5	5% Pt/H-ZSM-5	5% Pt/H-ZSM-5
Metal content, %	4.73	4.39	5.04	4.82

Table S3. Catalyst NH₃-TPD results

Materials	H-ZSM-5	Pd/H-ZSM-5	Pt/H-ZSM-5
H/Al ratio	0.88	0.78	0.17
H/Metal ratio	-	0.63	0.13

Table S4. Catalyst XPS results

Elements, atomic %	Si	O	Pt	Pd
H-ZSM-5	33.26	66.14	0	0
Pt/H-ZSM-5	33.39	66.08	0.53	0
Pd/H-ZSM-5	31.98	66.95	0	1.06

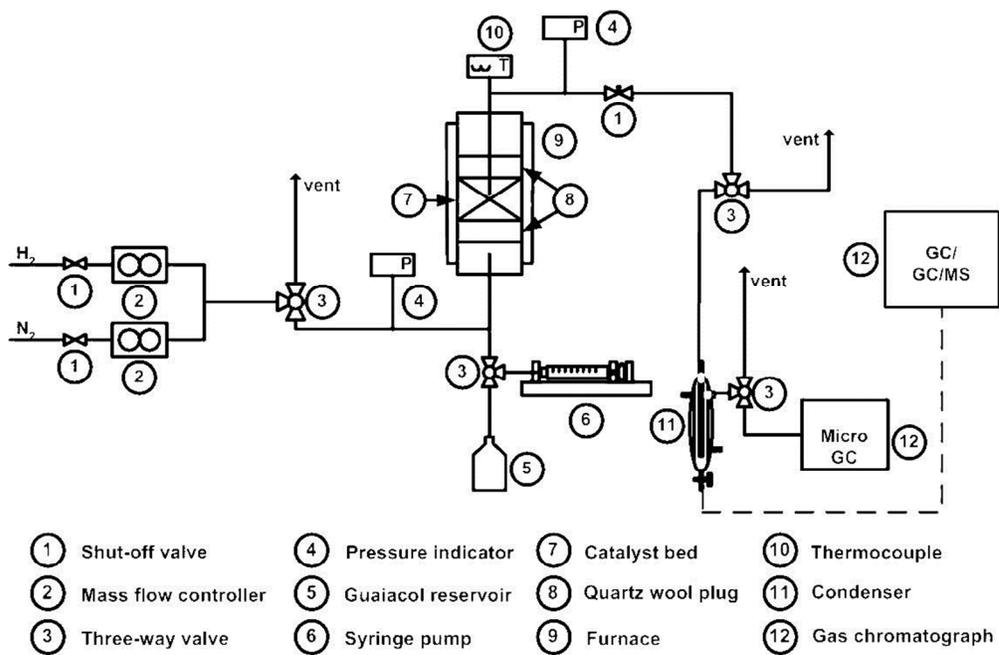


Figure S1. Schematic diagram of the experimental setup

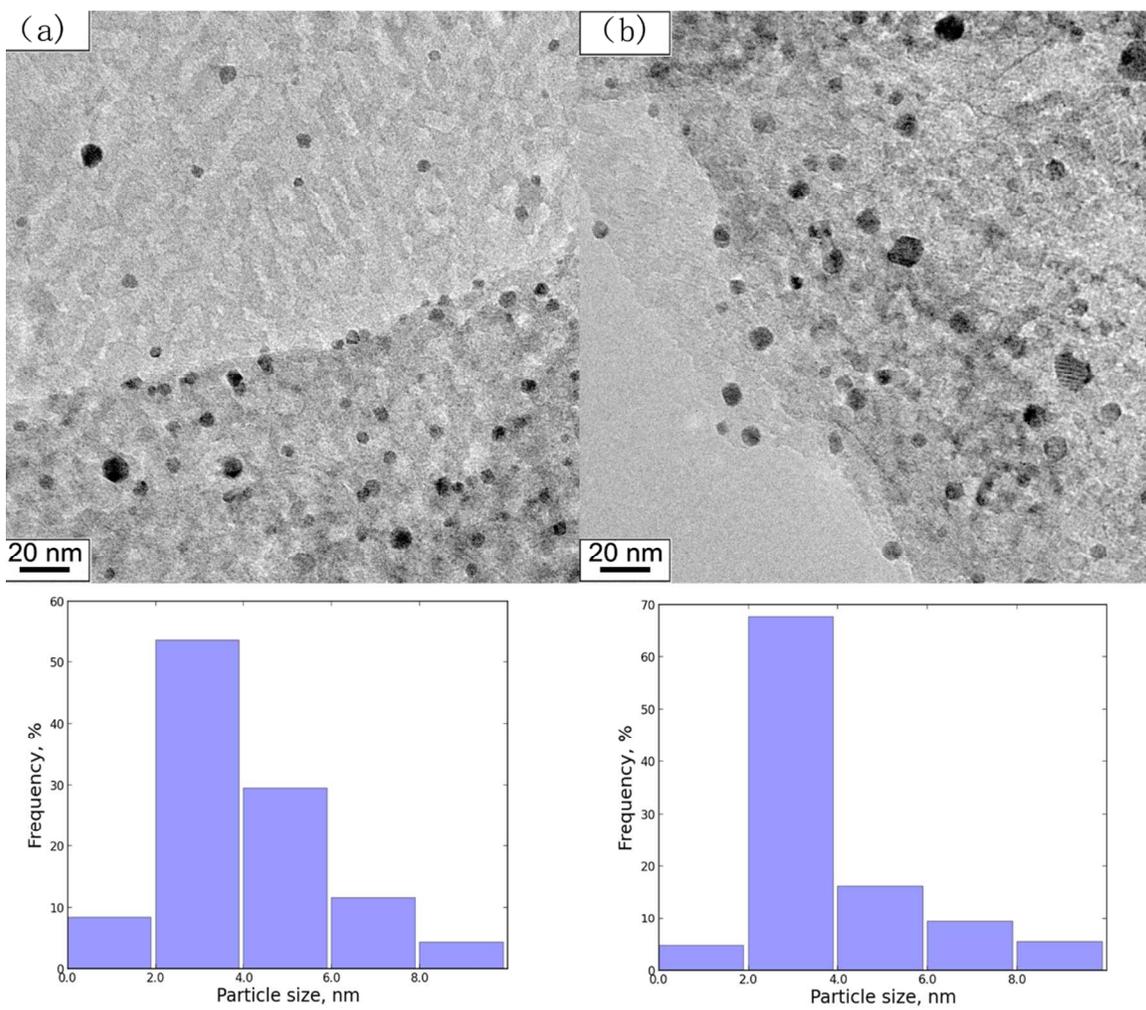


Figure S2. TEM scans and particle size distributions for a) Pt/H-ZSM-5 and b) Pd/H-ZSM-5

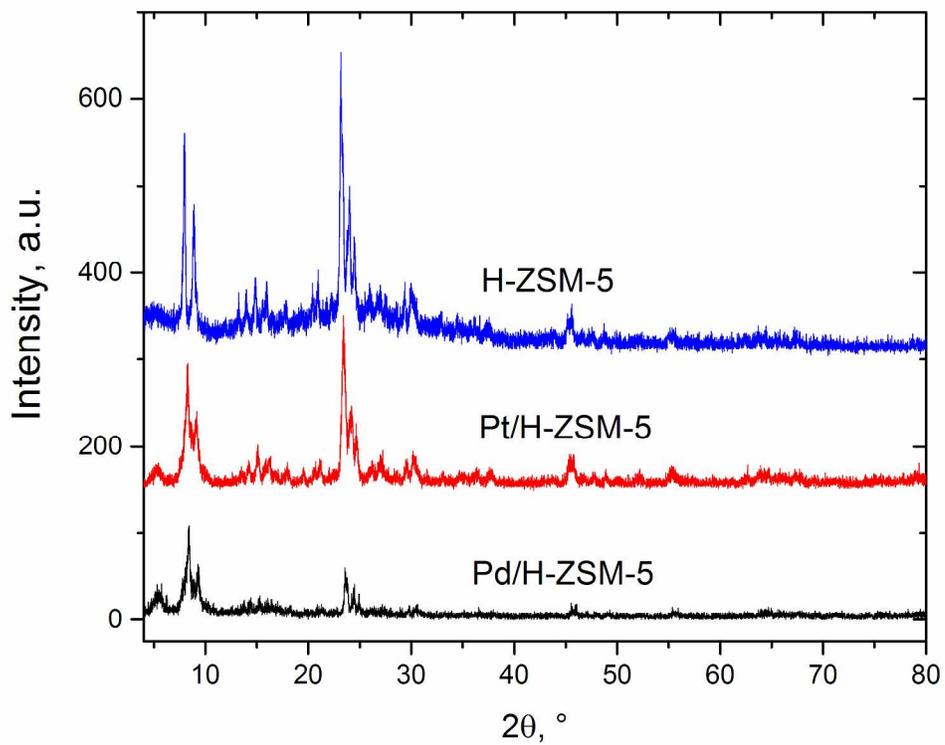


Figure S3. XRD patterns of H-ZSM-5, Pt/H-ZSM-5 and Pd/H-ZSM-5

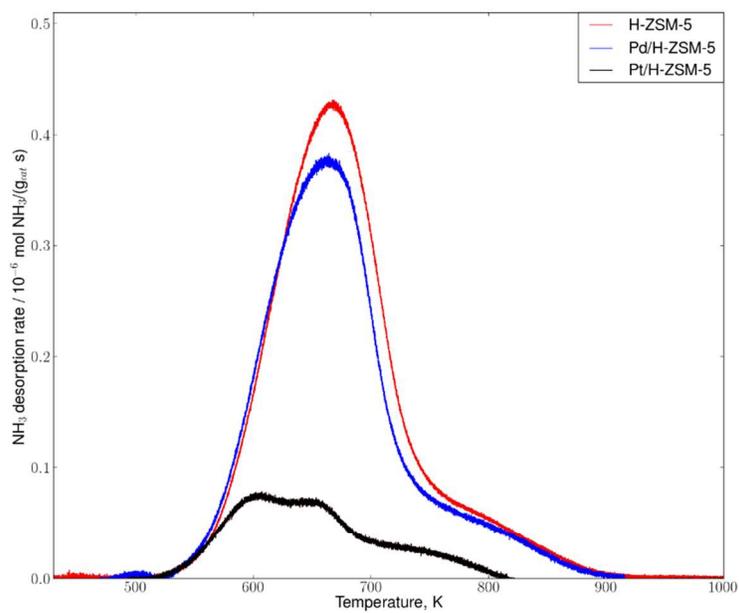


Figure S4. Catalyst NH₃-TPD rate plot

References

1. Benson, J. E.; Boudart, M. Hydrogen-Oxygen Titration Method for the Measurement of Supported Platinum Surface Areas. *J Catal* 1965, 4, 704-710.
2. Chiang, H.; Bhan, A. Catalytic consequences of hydroxyl group location on the rate and mechanism of parallel dehydration reactions of ethanol over acidic zeolites. *J Catal* 2010, 271, 251-261.
3. Di Iorio, J. R.; Bates, S. A.; Verma, A. A.; Delgass, W. N.; Ribeiro, F. H.; Miller, J. T.; Gounder, R. The Dynamic Nature of Bronsted Acid Sites in Cu-Zeolites During NO_x Selective Catalytic Reduction: Quantification by Gas-Phase Ammonia Titration. *Top Catal* 2015, 58, 424-434.