Glycerol Dehydration to Acrolein Catalyzed by ZSM-5 Zeolite in Supercritical Carbon Dioxide Medium

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Supercritical carbon dioxide (SC-CO_2) has been used for the first time as a reaction medium for the dehydration of glycerol to acrolein catalyzed by a solid acid. Unprecedented catalyst stability over 528 hours of time-on-stream was achieved and the rate of coke deposition on the zeolite catalyst was the lowest among extensive previous studies, showing potential for industrial application. Coking pathways in SC-CO_2 were also elucidated for future development. The results have potential implications for other dehydration reactions catalyzed by solid acids.

In light of the surplus of glycerol resulting from massive global biodiesel production, acrolein, the simplest unsaturated aldehyde that can be derived by glycerol dehydration, has received much research attention.[1] Conjugation of the carbonyl group with the vinyl group renders acrolein a versatile intermediate for the synthesis of an array of high-value chemicals such as methionine and acrylic acid.[1b] Commercially, acrolein is produced through the oxidation of propylene, based on fossil fuels. Shifting the raw material from propylene to glycerol would not only sustain commercial development for the biodiesel value chain, but also reduce net emissions from fossil fuels. Acrolein production from glycerol dehydration is thus a potential alternative to the currently established propylene oxidation.[1b]

Extensive efforts have been committed in recent years to improve glycerol dehydration to acrolein,[1b,2] including glycerol conversion in sub- and supercritical water,[3] as well as selective gas-phase conversion.[4] Although these different processes gave good glycerol conversion rates and selectivities to acrolein, a continuous process catalyzed by solid acids is desirable for industrial application. However, despite their initial good performance, few solid acid catalysts are known to maintain their catalytic activity long enough for practical application without need for regeneration, as the high functionality of glycerol leads to severe coking on the catalysts. Fast catalyst

deactivation remains a major technical problem for the commercial production of acrolein from glycerol.[1b,2]

The catalyst deactivation is mainly due to extensive coke deposition on the active sites of the catalyst.[5] Methods including adding O_2 to inhibit the rate of coking,[6] modifying catalysts by adjusting acid strength and distribution,[7] and amplifying catalyst pore size have slightly extended the catalyst life, but none has been convincingly successful.[8] Catalyst regeneration by coke combustion has also been attempted, but the catalyst was quickly deactivated again in a timeframe unsustainable for industrial applications.[9]

Although continuous development of better catalysts remains as one way to extend catalyst life, the potential of sustainable process engineering should be explored. In this work, a continuous fixed-bed reaction system was designed and constructed in which SC-CO_2 was used as a reaction medium for the catalytic glycerol dehydration to acrolein (see the Supporting Information, Figure SI1). Using a commercial ZSM-5 in its hydrogen form (HZSM-5), we conducted long-time runs of experiments, focusing on the catalytic stability. Efforts were also made to probe the coking mechanism on the zeolite performing in supercritical carbon dioxide (SC-CO_2) medium. For comparison, a considerable number of previous studies have used ZSM-5 or other solid acids as catalysts for gas-phase glycerol dehydration, showing quick deactivation. Therefore, we speculate that this SC-CO_2 system would further extend the life of better-designed catalysts.

We chose to test commercial HZSM-5 in our SC-CO_2 reaction system because of its well-documented performance (although it is not the best performer) in gas-phase glycerol dehydration (Table 1).[10] For further comparison, we also conducted a conventional gas-phase glycerol dehydration over 68 hours under similar conditions but with atmospheric CO_2 as the reaction medium instead of SC-CO_2. The glycerol dehydration in SC-CO_2 was repeated, including a preliminary run (Run-P) of 528 hours, Run-1 of 414 hours, and Run-2 of 506 hours, showing good repeatability for such a long time-on-stream (TOS). Evidently, the SC-CO_2 medium greatly prolonged the catalyst life compared to the quick deactivation of zeolite catalysts after much shorter TOS in the gas phase,[1b,10a,c] as corroborated by fact that the coke loading rate is one order of magnitude lower.

We further conducted another run under the same conditions except with the flow of SC-CO_2 having been cut off. However, a steady state flow of effluent could not be achieved for sample analysis after more than 12 hours of TOS, and the quickly rising pressure drop across the catalyst bed forced us to terminate the reaction.

Details of the glycerol conversion and yields of acrolein and acetol against TOS are given in Figure 1. In Run-P, we had to

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Table 1. Results of glycerol dehydration in SC-CO$_2$ and gas-phase CO$_2$ catalyzed by HZSM-5 in comparison with previously reported data.

HZSM-5	Run-P		Run-1		Run-2		Gas phase		HZSM-5 in ref. [10a]	
Mass [g]	3.08 (5 mL)		3.08 (5 mL)		3.08 (5 mL)		3.08 (5 mL)		1.00	
TOS [h]	51	528	51	414	51	506	8	50	2	8
Conversion [mol %]	96.4	78.7	97.4	85.8	96.7	82.6	98.5	67.9	99.0	72.6
Yield [mol %]										
acrolein	58.1	39.2	53.8	45.1	53.3	47.4	51.2	30.6	59.0	45.3
acetol	10.7	10.5	9.8	10.1	9.2	10.1	9.0	7.1	8.7	7.4
acetaldehyde	3.6	3.9	5.4	4.4	4.4	3.4	8.1	6.7	5.5	5.2
propionaldehyde	2.4	4.4	3.2	3.3	2.2	3.9	1.4	0.9	6.2	4.4
Coke loading[a]	–	0.16	–	0.17	–	0.15	–	1.99	–	2.81
Carbon balance [mol %]	82.3	83.7	80.5	85.3	79.8	81.6	77.6	87.8	78.6	88.0

[a] For fair comparison, this is normalized based on per 10 g of glycerol input over the entire TOS (wt% per 10 g glycerol), determined by thermogravimetric analysis (Figure SI3).
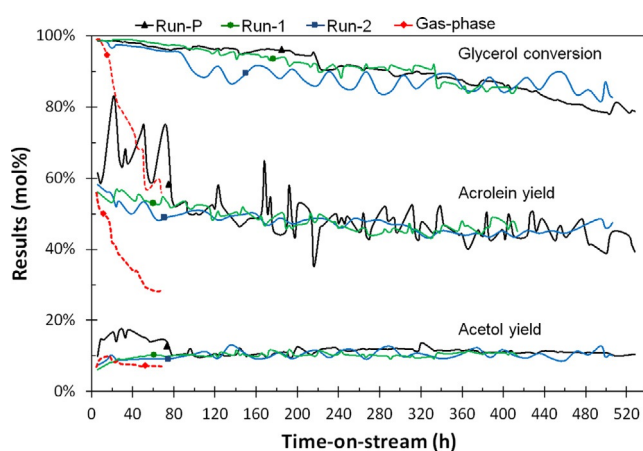
Figure 1. Glycerol conversion and yields of acrolein and acetol with TOS over HZSM-5 in SC-CO$_2$ reaction system in comparison with those in gas-phase CO$_2$.

stop the CO$_2$ flow and the feed of glycerol solution (but not the heaters) around every 200 h of TOS for roughly 5 minutes to change an exhausted CO$_2$ cylinder. This brief interruption might have accelerated the coking. Nonetheless, no obvious pressure drop across the catalyst bed was observed over the 528 h of TOS. In Run-1 and Run-2, we improved the CO$_2$ supply by connecting two CO$_2$ cylinders in parallel to the CO$_2$ pump, enabling continuous runs without interruption. These repeated runs showed reproducible results with our SC-CO$_2$ reaction system. Importantly, the contrast with dehydration in gas-phase CO$_2$ clearly demonstrated the advantages of using SC-CO$_2$ as the reaction medium. The gas-phase reaction was terminated after 68 h of TOS due to a significant pressure drop across the catalyst bed. This contrast indicates the essential roles of SC-CO$_2$ in our reaction, as discussed further in the following sections.

Fluid phase equilibria offer insight into the reaction mechanism and kinetics, but, to our knowledge, neither theoretical modeling nor experimentally verified equilibrium data concerning the ternary mixture C$_3$H$_8$O$_3$/H$_2$O/CO$_2$ have been reported to date. There have been investigations on the binary mixtures

C$_3$H$_8$O$_3$/CO$_2$,[11] C$_3$H$_8$O$_3$/H$_2$O,[12] and H$_2$O/CO$_2$,[13] showing that the binary mixture of C$_3$H$_8$O$_3$/CO$_2$ has very limited miscibility in a wide range of temperature and pressure. From these reports and the fact that the boiling points of the pure components of C$_3$H$_8$O$_3$/H$_2$O/CO$_2$ at 8 MPa are 582.1, 293.5, and 31.1 °C, respectively, we may deduce that vapor–liquid equilibrium or even the more complex liquid–liquid–vapor equilibrium formed in our reaction system. The reactant glycerol could be in both the vapor and liquid phases at 320 °C and 8 MPa. Although glycerol does not dissolve well in SC-CO$_2$,[11a] the major reaction product of acrolein, which is also considered as a coke precursor,[1b] is soluble in the highly diffusive SC-CO$_2$,[14] and is thus quickly moved out of the catalyst bed, preventing it from further secondary reactions that lead to decomposition and coking. Other coke precursors might be dissolved through the combination of water polarity and CO$_2$ nonpolarity, washing out both the hydrophilic and hydrophobic coke precursors and thus enabling long catalyst life.

We speculate that our SC-CO$_2$ reaction system is a classical multiphase trickle-bed reactor and that glycerol conversion mainly occurred in the liquid phase. Therefore, the theory proposed by Hulteberg et al.[15] that glycerol vapor condensed in catalyst pore channels accelerates coke formation needs to be reconsidered for our SC-CO$_2$ system, because our system significantly prolonged catalyst life. Reaction kinetics should be further studied, focusing on the hydrodynamic parameters of the trickle-bed reactor, such as liquid holdup, flowing state, and wetting characteristics between the liquid and the catalyst.

In comparison to reported data (Table 1),[10a] the yield of acrolein declined very slowly while that of acetol maintained relatively stable over the long TOS. Concerning the reaction mechanism for the formation of acrolein vs. acetol, it is well accepted that acrolein is mainly catalyzed at the Brønsted acid sites whereas the Lewis acid sites (extra-framework Al species) favor the formation of acetol.[1, 10d, 16] However, other reports have contradicted this,[10a,c] attributing the higher acetol yield to the larger amount of weak acid sites in zeolites desorbed at <300 °C as characterized by temperature-programmed desorption of ammonia (NH$_3$-TPD). Our characterization of the catalyst by using infrared pyridine adsorption (Py-FTIR, Figure 2a) and
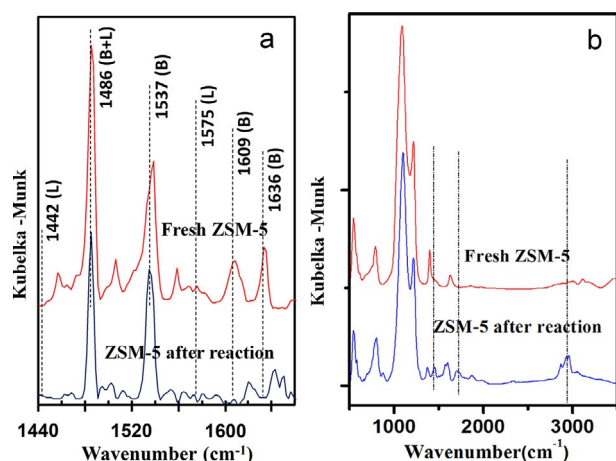
Figure 2. Characterization of fresh vs. spent HZSM-5 after reaction in SC-CO_2: a) Py-FTIR spectroscopy; b) DRIFTS (L = Lewis acid site, B = Brønsted acid site).

NH_3-TPD (Table SI1 and Figure SI2) revealed that the HZSM-5 had predominantly Brønsted acid sites (except for the non-distinguishable region of B + L acid sites at 1486 cm^{-1}) and moderate distribution of each of weak, medium, and strong acid sites. After reaction, the amount of Brønsted acid sites decreased due to coking, as reflected prominently in peaks at 1636 and 1609 cm^{-1} (Figure 2 a). It is reasoned that the Brønsted acid sites, which favored acrolein formation, also led to faster coking kinetics, whereas the coking and decoking by SC-CO_2 at Lewis acid sites reached equilibrium.

Analyzing the reaction products offered more insights into the SC-CO_2 system. The gas product mainly consisted of acetaldehyde, propionaldehyde, and acrolein (Figure SI4). The liquid product was further divided into a major aqueous phase and a small quantity of oil phase. In addition to the condensed acetaldehyde, propionaldehyde, and acrolein, aqueous byproducts mainly consisted of acetol, methanol, allyl alcohol (2-propen-1-ol), acetic acid, phenol, a 1,3-dioxolane derivative, and 1,4-dioxane derivatives (Figures SI5 and SI6). Due to the very small amount of oil phase in the liquid product, only qualitative analysis by GC-MS was conducted, revealing the presence of 3-methyl-2-cyclohexen-1-one, (2-ethyl-1,3-dioxolan-4-yl)methanol, and derivatives of benzaldehyde, acetophenone, and phenol (Figure SI7), which are obviously washed-out coke precursors. The dioxane and dioxolane derivatives in the aqueous phase and the ring-structured chemicals in the oil phase have rarely been reported for glycerol dehydration in gas-phase or sub- and supercritical water, indicating the special role of SC-CO_2 in removing these coke precursors from the catalyst bed.

The spent HZSM-5 was extracted by using methanol and the GC-MS analysis of the extract indicated the presence of significant amounts of acetol and glycerol (indicating the two were not well removed by SC-CO_2), along with phenol and derivatives of benzofuran, benzopyran, acetophenone, and naphthalene (Figure SI8). Direct analysis of the fresh and spent catalysts by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) (Figure 2 b and details in the Supporting Information) revealed depositions on the spent HZSM-5, showing IR bands characteristic of glycerol and acetol, along with those of coke or coke precursors.

Although the complex coking mechanisms in gas-phase glycerol dehydration have previously been extensively discussed,[1b, 2b] we can infer from the above analyses that catalytic cyclization of acetol, glycerol, and possibly 3-hydroxypropional-
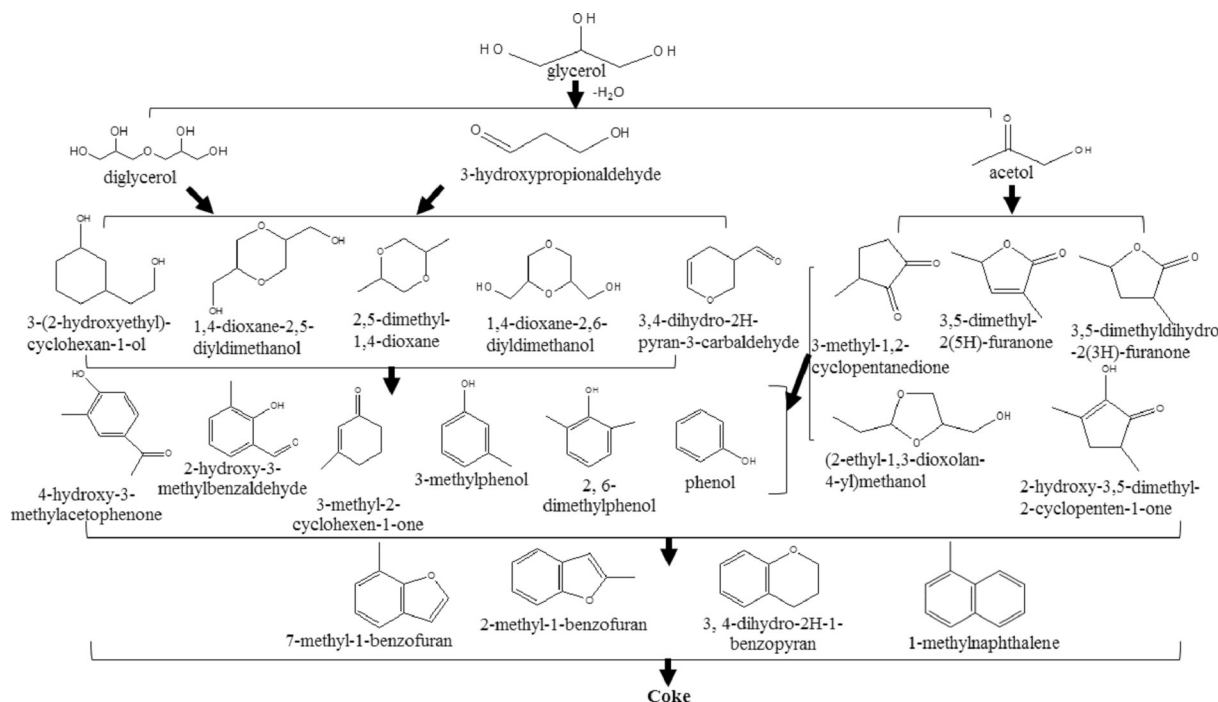
Scheme 1. Major coking pathway for glycerol dehydration in SC-CO_2.

dehyde (an unstable precursor to acrolein), catalyzed by the acid sites, were the major paths of coking in our SC-CO_2 system (Scheme 1), due to the low solubility of these species in SC-CO_2. Nonetheless, our system still achieved a longer TOS and lower rate of coking than in previously reported studies. Although coking is not totally avoidable, there appeared to be a subtle equilibrium between coking and decoking by SC-CO_2 that could be achieved by tuning the catalyst properties and process conditions for a better acrolein yield and longer catalyst life. As proposed by Gu et al.,[10a] catalyst crystal morphology, specific surface area, pore volume and structure, channel complexity, and distribution of acid strengths may all have interacting effects on the catalytic performance and coking/decoking processes. Future design of better catalysts should consider not only the acidic property to increase acrolein yield, but also the structure to facilitate the coke removal by SC-CO_2.

Analysis of the fresh and spent HZSM-5 by TEM (Figure SI9) confirmed that the crystalline structure remained after long reaction times. Further analysis of the liquid product by inductively coupled plasma optical emission spectroscopy (ICP-OES) detected no obvious leaching from the zeolite.

In conclusion, the present work provides a new strategy for the development of a sustainable catalytic process to produce acrolein from glycerol, overcoming a major hurdle encountered in the catalytic conversion of glycerol into high-value chemicals. Carbon dioxide emissions are reduced as the longer operation period allows a less frequent need for coke burning and provides an alternative use for CO_2, especially when the process can reuse CO_2 produced by power plants, leading to an indirect decrease in CO_2 emissions. It should be noted that only a commercial catalyst was tested in our SC-CO_2 reaction system, showing unprecedented catalyst stability. Better-designed solid acids together with deeper investigation into the reaction kinetics in the SC-CO_2 medium would potentially further increase the acrolein yield and extend catalyst life towards industrial applicability.

Experimental Section

All glycerol dehydration experiments catalyzed by HZSM-5 in SC-CO_2 were conducted at 8 MPa and 320 °C (see Figure SI1 for details). A measured amount of catalyst (5 mL, 3.08 g) was diluted with the same volume of quartz sand and packed into a down-flow stainless steel reactor (9.4 mm I.D., 12.7 mm O.D., and 457 mm long). Quartz sand and quartz wool were put on top of the catalyst bed to serve as a preheating zone. The reactor was then placed in an electric tube furnace. The temperature of the catalyst bed was monitored by a K-type thermocouple and controlled by a PID controller. Before reaction, liquid CO_2 (Industrial grade, 99.97% purity, Airgas, Knoxville, TN) was metered into the system by a liquid CO_2 pump (1 mL min^{-1} at -4 °C) and preheated to 300 °C. After stabilization of temperature and pressure for roughly 1 h, a 20 wt% aqueous solution of glycerol (99.5%, Sigma Aldrich) was injected into the reactor by a high pressure pump at a flow rate of 0.1 mL min^{-1} to obtain a molar ratio of glycerol/H_2O/CO_2 = 0.008:0.170:0.822. After depressurization through a back pressure regulator, the reaction effluent flew through a condenser with circulating coolant at 0 °C and the condensed liquid product was collected. The non-condensable gaseous product was sampled by using a gas syringe through the sampling port. The gas and liquid samples were taken every three hours for analysis. The gas-phase glycerol dehydration was conducted on the same reaction system with modification so that CO_2 gas at atmospheric pressure was metered in at 120 mL min^{-1} through a rotameter; all other conditions, including temperatures of preheating and reaction, catalyst loading and packing, and flow rate of 20 wt% aqueous solution of glycerol, were all kept the same.

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