

Liquid chromatographic analyses can be carried out on a Waters LC system incorporating a Waters 515 pump, Waters 2410 Refractive Index Detector (RID), and a Waters 717plus Autosampler for sample introduction. Analyses can be performed utilizing Empower Pro Software. Separations of 10 μL injections can be effected on an Aminex HPX-87H Organic Acid Analysis column operated at 35° C. and employing a 0.005M H_2SO_4 as the eluent with a flow rate of 0.55 mL/min. Total run times of 45 minutes were sufficient to elute all compounds of interest. Calibration curves can be prepared as described for GC calibrations and using the same set of standard solutions used for GC calibration.

Referring to product reservoir 26 of system 20, upon exiting reactor 22, product can be acquired by time collection of reactor 22 effluent in a known quantity of a chilled scrub solution containing 1 wt % n-BuOH with mass balances for a given reactor run determined by a ratio of collected effluent mass to expected mass based on feed rate and run time. For example, two small aliquots can be removed and diluted to concentrations appropriate for GC and LC analyses. The diluted samples can then be analyzed as described previously and wt % compositions determined from calibrated detector responses used to determine absolute compositions of the collected effluent. The use of known quantities of n-BuOH in the scrub solutions can permit a primary check of analytical sampling technique, but was not used as an internal standard by which response factors for effluent components were measured. Reported values for conversion, yield, selectivity, and carbon balance present averages of those values determined by both GC and LC analyses. Glycerol conversion can be calculated by the differences between calculated quantity of glycerol feed (based on feed rate and run time) and the quantity of glycerol collected in the reactor effluent and may be uncertain when mass balances are not satisfactory. Values exclude any experimental runs that did not provide mass balances in excess of 90%. Product yields can be calculated by the ratio of quantity of product formed to the quantity of glycerol. Field product selectivities can be calculated from the quantity of product formed divided by the quantity of glycerol converted. Carbon balances can be calculated from the sum of the molar quantities of glycerol, acrolein, and acetol components divided by the molar quantity of glycerol fed. Liquid Chromatographic techniques can permit the quantification of formic acid and acetic acid by-products. However, since their combined quantity rarely exceeded 3%, their presence was not included in carbon balance determination.

As the examples illustrate, when the dehydration reaction is conducted with fresh catalyst without palladium doping, acrolein contact time yields of approximately 50 lbs $\text{ft}^3 \text{h}^{-1}$ can be realized initially, dropping to half that value within 5 hours of continuous operation and experiencing a further reduction after an additional 5 hours of running. Acetol contact time yields demonstrated quantitatively the same behavior exhibiting half lives of approximately 5 hours. The catalyst containing 0.5% (wt./wt.) Pd can exhibit identical behavior with respect to both acrolein and acetol contact time yields. The catalysts can be removed and regenerated at 500° C. in the presence of supplied air. The catalyst lacking Pd supplement can regain less than half of its original activity, losing half of its activity after 4 hours of operation. In contrast, the Pd-supplemented catalyst can be returned to its original productivities for both acetol and acrolein and can behave similarly to fresh catalysts in 4 hours of operation.

Utilization of a promoter can allow for catalytic glycerol dehydration technology that would otherwise be nonviable due to short catalyst lifetimes by facilitating catalyst regeneration in air, a practice particularly amenable to moving or fluidized bed reactor operations. The published literature

describing catalytic glycerol dehydration does not mention coking as reason for catalyst deactivation. Consequently, published literature is devoid of any solution to the problem of deactivation by coke. As such, a method to prepare catalysts with long duty times is useful and constitutes platforms for strong catalysts.

In compliance with the statute, this disclosure has been provided in language more or less specific as to structural and methodical features. It is to be understood, however, that the disclosure is not limited to the specific features shown and described, since the means herein disclosed comprise preferred forms of putting the invention into effect. The invention is, therefore, claimed in any of its forms or modifications within the proper scope of the appended claims appropriately interpreted in accordance with the doctrine of equivalents.

What is claimed is:

1. A chemical production process comprising:
 - providing a supplemented dehydration catalyst to within a reactor, the supplemented dehydration catalyst comprising at least one element of group 10 of the periodic table of elements;
 - exposing a multihydric alcohol compound to the dehydration catalyst, the exposing producing a dehydration product of the multihydric alcohol compound, and forming coke within the reactor; and
 - providing oxygen to the reactor to remove at least a portion of the coke.
2. The chemical production process of claim 1 wherein the supplemented catalyst comprises both an element from group 10 of the periodic table and an element from group 5 or 6 of the periodic table.
3. The chemical production process of claim 1 wherein a portion of the interior volume of the reactor is heated to at least about 500° C.
4. A chemical production system comprising a reactant reservoir coupled to a reactor, the reactor containing a catalyst comprising both one or more elements from group 10 of the periodic table of elements, and a phosphate composition, the phosphate composition comprising one or more of Cr, Mn, Fe, Co, Ni, Zn, La, Ca, Sr, Ba, Mo, and Ru, wherein the reactant reservoir contains a multihydric alcohol compound.
5. The system of claim 4 wherein the catalyst composition comprises Pd.
6. The system of claim 4 wherein the catalyst composition comprises at least 5% (wt./wt.) of the one or more elements.
7. The system of claim 4 wherein the catalyst composition comprises a solid substrate comprising one or more of SiO_2 , $\text{SiO}_2\text{—Al}_2\text{O}_3$, and TiO_2 .
8. The system of claim 4 wherein the catalyst composition comprises a solid support composition, the solid support composition comprising one or more of $\text{F—Al}_2\text{O}_3$, $\text{ZrO}_2\text{—CO}_2$, $\text{SiO}_2\text{—Al}_2\text{O}_3\text{—CO}_2$, $\text{SiO}_2\text{—Al}_2\text{O}_3$, and Alundum.
9. The system of claim 4 wherein the catalyst composition further comprises one or more of Nb, Mo, and W.
10. The system of claim 4 wherein the catalyst composition further comprises one or more of niobia, hydrated niobia, tungstic acid, phosphotungstic acid, and phosphomolybdic acid.
11. The catalyst of claim 1 wherein the multihydric alcohol compound is glycerol and the dehydration product of the multihydric alcohol compound is one or both of acetol and acrolein.
12. The system of claim 4 wherein the multihydric alcohol compound is glycerol.