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Supplementary Information

Catalytic upgrading of biomass-derived lactic acid to fuels and chemicals by dehydration/hydrogenation and C-C coupling reactions

Juan Carlos Serrano-Ruiz and James A. Dumesic*

University of Wisconsin, Madison, 1415 Engineering Drive, Madison, Wisconsin, 53706, USA
Fax:1 608 262 5434; Tel: 1 608 262 1095; E-mail: dumesic@engr.wisc.edu

Catalyst Preparation

Pt(0.1%)/Vulcan was prepared from a commercial Pt(5%)/Vulcan XC-72 catalyst (BASF, with H_2PtCl_6 as a platinum precursor), diluting it with Vulcan XC-72 (Cabot Corporation, BET surface area equal to 232 $m^{2}\cdot g^{-1}$) to obtain the desired loading of metal. Pt(0.1%)/Nb_2O_5 was prepared by incipient wetness impregnation of a commercial niobium oxide (HY-340 from CBMM-Brazil, BET surface area equal to 118 $m^{2}\cdot g^{-1}$) with an aqueous solution of $[Pt(NH_3)_4(NO_3)_2]$ (Aldrich) as a platinum precursor salt. The catalyst was dried at 380 K overnight, followed by calcination at 773 K in flowing air (250 cm^3(STP) min^{-1}, 1 K min^{-1} ramp) for 2 hours. The ceria-zirconia catalyst with Ce:Zr molar ratio of 1:1 was prepared according to Serrano-Ruiz, et al. [1]. Commercial Ru(5%)/C catalyst was prchased from Sigma-Aldrich and it was activated at 673 K for 3 hours (2 K min^{-1} ramp) under flowing hydrogen (100 cm^3(STP) min^{-1}) before reaction.

Reaction Kinetics Studies

The catalysts were loaded into a 1/4” tubular stainless steel reactor. The catalysts (2.5 g for Pt(0.1%)/Nb_2O_5 and 1.0 g in case of Pt(0.1%)/Vulcan) were mixed with fused SiO_2 granules (4-16 mesh size, Aldrich) to avoid a large pressure drop across the reactor using large amounts of catalyst. The bed of SiO_2 granules and catalyst was contained in the tubular reactor between two end-plugs of quartz wool (Grace). For the double-bed experiments, a 1/4” tubular stainless steel reactor was loaded first with Pt(0.1%)/Nb_2O_5 (2.5 g) followed by ceria-zirconia (3.3 g). Both beds were separated by a quartz wool plug. The reactor was mounted in an upflow configuration and surrounded by aluminum blocks heated externally by a well-insulated furnace (Applied Test Systems Inc.). A K-type thermocouple (Omega) was attached to the outside of the reactor to measure temperature, which was controlled with a 1600 series type temperature controller (Dwyer Instruments). Prior to reaction kinetics studies, fresh catalyst was reduced in flowing H_2 (80 cm^3(STP) min^{-1}). The catalyst was heated, using a linear temperature ramp (1 K min^{-1}) to the final reduction temperature of 523 K and held at this temperature for 4 h, and then heated to the reaction temperature (623 K) under flowing H_2. The flow-rate of H_2 was fixed with a Brooks Model 5850 mass-flow controller. The system pressure (57 bar) was controlled by a backpressure regulator (GO Regulator, Model BP-60). A liquid solution containing 60 wt% lactic acid (Aldrich) in deionized water was introduced into the upflow reactor using an HPLC pump (Lab Alliance Series 1) along with a co-feed H_2 flow of 80 cm^3(STP)/min. The effluent liquids (organic and aqueous) were collected at room temperature in a gas-liquid separator and drained for gas chromatography (GC) analysis (Shimadzu GC-2010 with a FID detector and Rtx-5 column) and identification (Shimadzu GC-2010 with a mass spectrometer and DB-5ms column). The effluent gas stream passed through a back-pressure regulator and was then analyzed by gas chromatography: CO and CO_2 with a Shimadzu GC-8A (equipped with TCD detector and an Alltech packed column model HayeSep DB 100/120) and gaseous alkanes with a Varian GC (Saturn 3) using a FID detector and a GS-Q capillary column (J&W Scientific). The overall carbon balance gave recoveries ranging from 85-110 %.

Reproducibility and stability studies

Reaction kinetics data at variable WHSV (Table 1 in the manuscript) were obtained by changing the flow rate of lactic acid feed in the HPLC pump and using the same catalyst bed in the reactor. After several hours of reaction (depending on the flow rate used) at one specific condition, the reaction was stopped to analyze the gas phase and collect the liquid for GC analysis. Subsequently, a new flow rate was established and the process was repeated at different flow rates. When all of these experiments were finished, to check the reproducibility of the results and to be sure that significant deactivation of the catalyst had not taken place during the collection of the experimental data, a new experiment at a specific WHSV previously checked was performed (second run) and the results compared with those obtained in the first run (see Tables 1 and 2 below). Importantly, no significant deactivation and excellent reproducibility of the experimental data were observed for both Pt/Nb_2O_5 and Pt/Vulcan catalysts.

Table 1. Reproducibility and deactivation studies for lactic acid conversion over Pt/Nb_2O_5 at 623 K and 57 bar.

Carbon selectivities (%)	623 K/57 bar/5.0 h^{-1} 1st run	623 K/57 bar/5.0 h^{-1} 2nd run
CO_x	37	41
C_4-C_7 Condensation products	19	16
Propanoic acid + Esters	18	18
Acetaldehyde	9	10
Ethanol	4	3
C_1-C_7 Alkanes	4	4
Propanol/Acetone	2	2
Lactic acid (unreacted)	0	0
Others	7	6

Table 2. Reproducibility and deactivation studies for lactic acid conversion over Pt/Vulcan at 623 K and 57 bar. (these data are not included in Table 1 of the manuscript).

Carbon selectivities (%)	623 K/57 bar/3.3 h^{-1} 1st run	623 K/57 bar/3.3 h^{-1} 2nd run
CO_x	42	41
C_4-C_7 Condensation products	0	0
Propanoic acid + Esters	6	5
Acetaldehyde	10	10
Ethanol	14	12
C_1-C_7 Alkanes	7	6
Propanol/Acetone	0	0
Lactic acid (unreacted)	17	22
Others	4	4

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References

[1]. J. C. Serrano-Ruiz, J. Luettich, A. Sepulveda-Escribano, F. J. Rodriguez-Reinoso, *J. Catal*. **241** 45 (2006).