Promoting zirconia with carbon: enhanced hybrid ZrO_2/C ketonization catalyst for the valorization of e-acetic acid

Jacopo DE MARON*[,1], Gaetano Maria D'ONOFRIO[1], Eleonora TOSI BRANDI[1], Andrea FASOLINI[1], Gloria GOTTARDI[2], Francesco BASILE[1], Fabrizio CAVANI[1], Tommaso TABANELLI[1].
[1]University of Bologna, "Toso Montanari" Industrial Chemistry Dept., Viale Risorgimento 4, Bologna, Italy.
[2] Bruno Kessler Foundation, Center for Sustainable Energy., Via Sommarive 18, Trento, Italy.
** Jacopo.demaron2@unibo.it*

Significance and Relevance

A novel hybrid catalyst was developed by deposition of ZrO_2 over a high surface area activated carbon. The material was investigated for the gas-phase ketonization of acetic acid (AA, 15wt.% aqueous solution) and thoroughly characterized to uncover structure-activity relationships. The carbon support created a hydrophobic environment at the boundary with ZrO_2 nanoparticles, hindering water adsorption on the active phase and preventing deactivation. The comparison with literature showed that the AC productivity in optimized conditions is among the highest reported so far, paving the way for the application to the valorization of AA derived from CO_2-electroreduction and fermentation.

Preferred and 2nd choice for the topic: Green chemistry and biomass transformation, renewable resources conversion, CO_2 utilization and recycling
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

Power-to-liquid (PtL) technologies aim at achieving a carbon-neutral energy cycle by converting CO_2 emissions into useful products. The electroreduction of CO_2 fuelled by renewable electricity (CO_2ER) can be exploited to produce valuable compounds such as acetic acid (AA) with satisfying faradaic efficiencies (e.g., Cu:Mg:Al-LDH-2:1:1/carbon paper, productivity = 2 $mmol_{AA}/h*g_{cat}$, FA = 84 %, voltage = -0.4 V vs RHE)[1] and even free from electrolytes and in relatively high concentrations with solid-state electrolyte membrane-electrode assemblies[2]. However, the production of longer-chain compounds with electrochemical methods remains extremely difficult. Instead, CO_2-derived AA could be used as a building block to produce multicarbon e-fuels and e-chemicals by means of well-established heterogeneous thermocatalytic processes such as ketonization, aldol condensation, aromatization, and hydrodeoxygenation. As previously mentioned, the AA produced by CO_2ER is diluted in water, which exerts a strong inhibitory effect on the activity of most ketonization and aldol condensation catalysts[3]. This issue is quite general and is encountered also when these processes are applied to other renewable feedstocks such as the water streams co-produced by the hydrothermal liquefaction of biomass or the volatile fatty acids produced by fermentation. Therefore, addressing the problem of mitigating water inhibition in the ketonization of both CO_2-derived and biomass-derived feedstocks is of paramount relevance.

Materials and Methods

Catalytic runs were carried out in a gas-phase plant operating at atmospheric pressure over 0.5 cm^3 of catalyst pellets (30-60 mesh). AA and water were mixed in the desired molar ratio and fed with a volumetric pump into a stainless-steel line to be vaporized before the catalytic bed. The LHSV and the flow of N_2 carrier were adjusted to obtain the desired molar fractions in the gas-phase maintaining a contact time t (at reaction temperature) = 0.5 seconds. The effluent from the reactor was condensed in a methanol-filled cold trap kept at 0 °C and analyzed offline with a Shimadzu GC 2010 PRO instrument quipped with FID detector (internal standard = dodecane, capillary column: HP-5, 30 m × 320 µm × 0.25 µm). The effluent from the cold trap was analyzed online by means of a Agilent 3000A micro GG equipped with a TCD detector (columns: PlotQ, OV1 and molecular sieve 5A).

ZrO_2 (62 m^2/g) and TiO_2 (149 m^2/g) benchmark materials were prepared by means of precipitation[4] and inverse microemulsion[5] respectively according to literature methods. 30 wt. % ZrO_2/C (488 m^2/g) was prepared by incipient wetness impregnation of a commercial Norit SX2 activated carbon with a Zr(IV)butoxide solution in butanol. The activated carbon was dried under vacuum at 100 °C before impregnation and the resulting wet solid was left 48 hours to hydrolyze with atmospheric moisture before thermal treatment under N_2 up to 550 °C for 3 hours. Catalytic materials were characterized by means of N_2-porosimetry, XRD, XPS, TEM, SEM-EDS, Raman, and TGA.

Results and Discussion

The superior water-resistance of 30 wt. % ZrO_2/C was demonstrated by comparing its activity with that of ZrO_2 and TiO_2 in catalytic runs carried out at 350 °C, t = 0.5 s and feeding 50 wt. % AA aqueous solutions. Bulk ZrO_2 displayed commendable activity and selectivity in dry conditions but suffered from a severe lack of resistance in the presence of steam, resulting in the complete suppression of ketonization activity. On the other hand, TiO_2 exhibited a much higher water tolerance, retaining high activity with the steam-containing feed, but fell short in terms of selectivity due to coke formation (confirmed by low carbon balance, Raman and TGA), which occurred more extensively with the dry feed. Finally, the promotion of ZrO_2 with carbon enabled a much more selective ketonization of AA to AC both in dry condition and in the presence of steam, thus outperforming both bulk oxide benchmarks. Moving from these results, the concentration of AA in the feed was progressively reduced to 15 wt. %, and a complete conversion of AA with > 90 % selectivity to acetone was achieved at 400 °C. Reaction conditions were then further optimized achieving an acetone space-time yield among the highest reported so far in the literature for ketonization processes in the presence of steam (Figure 1A).

This work is significant because it demonstrates that the diluted AA in the aqueous stream at the outlet of state-of-the-art electrochemical CO_2ER flow-cells with solid-state electrolytes can be quantitatively converted into acetone with selectivities exceeding 90 % and STY > 3.5 h^{-1}. The same catalytic system could, in theory, have a wider application (e.g., ketonization of volatile fatty acid solution from fermentation, ketonization of the oxygenated molecules in aqueous streams co-produced by hydrothermal liquefaction etc.).

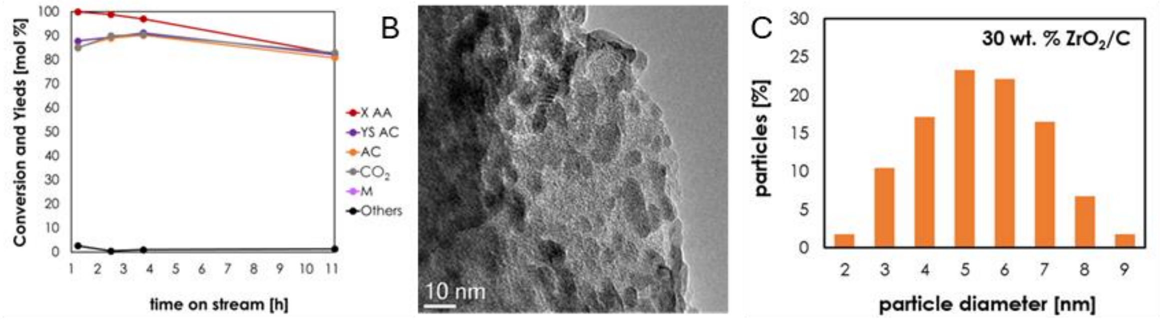

Figure 1 A: ketonization of 15 wt. % AA solution (0.25 cm^3 of 30 wt. % ZrO_2/C, T = 425 °C, τ = 0.125 s, 3 mol % of AA in gas-phase); B: TEM image of 30 wt. % ZrO_2/C; C: ZrO_2 particle size distribution.

References

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