

Electronic Supplementary Information

Catalytic oxidation of aqueous bioethanol: an efficient upgrade from batch to flow

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1 Diffusion and mass transfer limitations

The grain size and mass in the batch reactor were studied. Figure 1a shows that grain size did not impose diffusion limitations. The larger grain size was finally preferred because it exhibited higher catalyst recovery yields (about 60%). Figure 1b indicates a linear relation of the conversion as a function of catalyst mass. The zero point corresponds to a blank test. The 0.1 g was chosen so that enough catalyst could be recovered for further characterization.

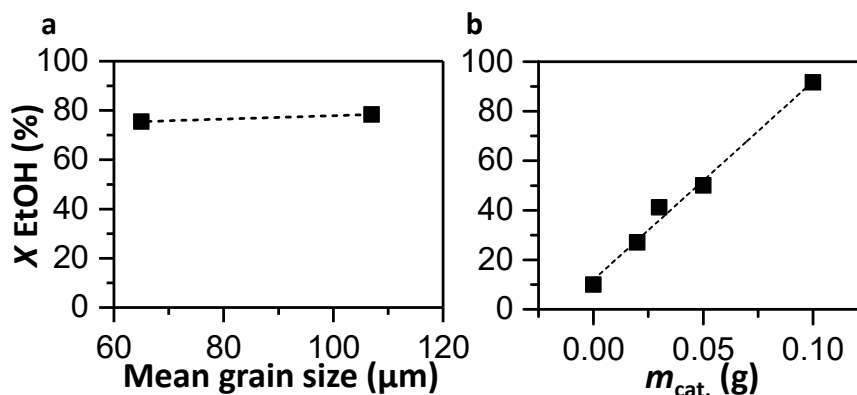


Fig. 1 The effect of the catalyst's grain (a) and catalyst's mass(b) on the ethanol conversion

2 Adsorption of carbon species on the catalyst

During the catalytic testing, the reaction conditions may induce the formation of carbon species, such as coke, that adsorb on the catalyst surface. The presence of such species was identified by Thermogravimetric analysis (TGA). TGA was conducted in a TGA/SDTA 851e by Mettler Toledo. The sample (about 9 mg on an alumina crucible) was heated to 1023 K with 5 K/min under synthetic air (PanGas, 20 ± 5%) or nitrogen (PanGas, 99.999%). As gold and titania are stable up to 1023 K, maximum temperature during TGA, any weight loss is attributed to carbon species. Figure 2a shows the TGA analysis of the samples in a flow of synthetic air. The fresh sample (black) exhibited minor weight loss, about 0.2%, below 373 K, which corresponds to adsorbed water. A small increase of the mass at 435 K could be attributed to oxidation of partially reduce titania, since gold species cannot be oxidized at that temperature. This increase corresponds to a 0.75 mol%, indicating a TiO_{1.999} support phase. The catalyst after batch reaction exhibits similar trend as the fresh powder; a weight loss below 373 K corresponding to water and an increase at about 435 K. The difference with the fresh

was observed at 530 K, where a significant weight loss was observed. This weight loss was attributed to carbon species, probably not coke at such low temperature. The carbon species were not identified, however, assuming that it originates from carbon to calculate the selectivity of the reaction to those species. The loss was about 0.8%, which corresponds to a selectivity to the adsorbed species less than 1%. Similar selectivity to the adsorbed species was calculated for the catalyst tested in flow. However, the catalyst tested in flow exhibited different behaviour in the TGA below 500 K; there was no water evaporation adsorbed below 373 K and the weight increase at 435 K was 1.5 mol% increase, double that in batch. The corresponding titania phase was estimated as $\text{TiO}_{1.970}$, denoted that titania was more reduced in flow. This can correlate with the higher activity in flow, as the oxygen needed for the reaction is expected to originate from the titania lattice, which forms oxygen vacancies. Figure 2b shows the TGA analysis in a stream of nitrogen. Water desorption was observed in the fresh catalyst. The used catalyst, both in batch and flow, showed constant weight increase above 350 K, which was not identified. Desorption of the carbon species was also observed around 600 K, same temperature as the main weight loss in air TGA. The weight loss was 0.17%, 4 times less than in the presence of air, indicating the adsorbed carbon species are unstable even at reducible conditions.

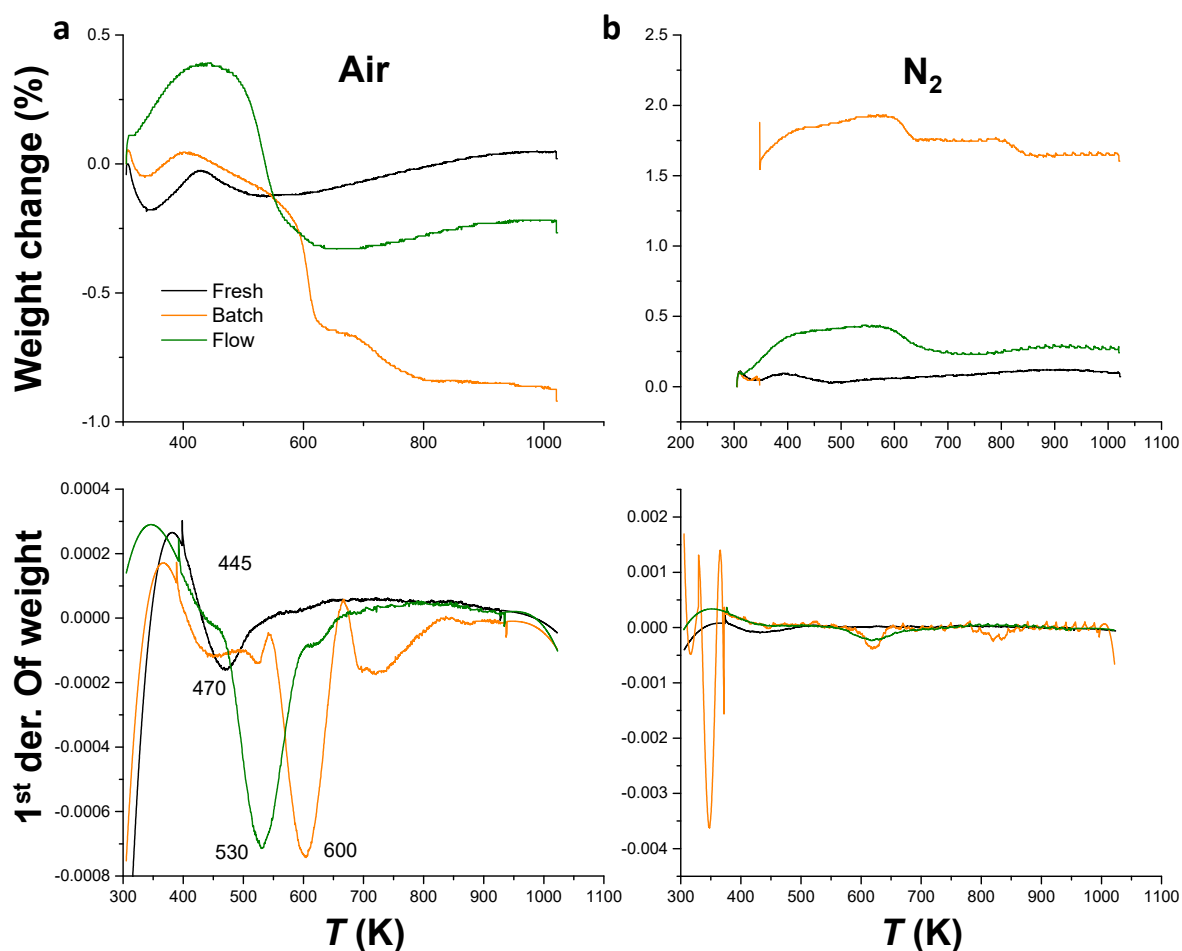


Fig. 2 TGA analysis on air (a) and nitrogen (b) environments of the fresh catalyst (black) and tested in batch (orange) and flow (green).

3 Characterization

X-ray Diffraction

The X-ray diffraction (XRD) patterns of the catalyst before and after reaction were acquired on a PANalytical X'Pert PRO-MPD diffractometer. Data were recorded in the $10\text{-}70^\circ$ 2θ range with an angular step size of 0.050° and a counting time of 2 s per step. Figure 3 shows the XRD patterns of the fresh and tested catalyst. The observed peaks are of titania; Anatase (01-086-1157) and Rutile (01-077-0445); the Rutile percentage is presented on the right side of each peak. The peak at

22°, after reaction in flow, corresponds to Cristobalite silica (01-076-1390) used to dilute the catalyst. Peaks indicating metallic gold (01-071-4616) were not observed due to the low amount of gold present. The crystal size of titania was not influenced by reaction. (b) Difference in intensity of the XRD patterns between the tested catalyst and pure titania (P25, 99.5%, Acros, 28% rutile). A positive difference is observed, at the main gold peaks (reference pattern 01-071-4616) at 38° 2θ corresponds to alteration in the titania structure, since remaining peaks of gold, at 44, and 64° 2θ, are not observed. The absence of gold peaks in XRD is due to the low gold loading (1 wt%)

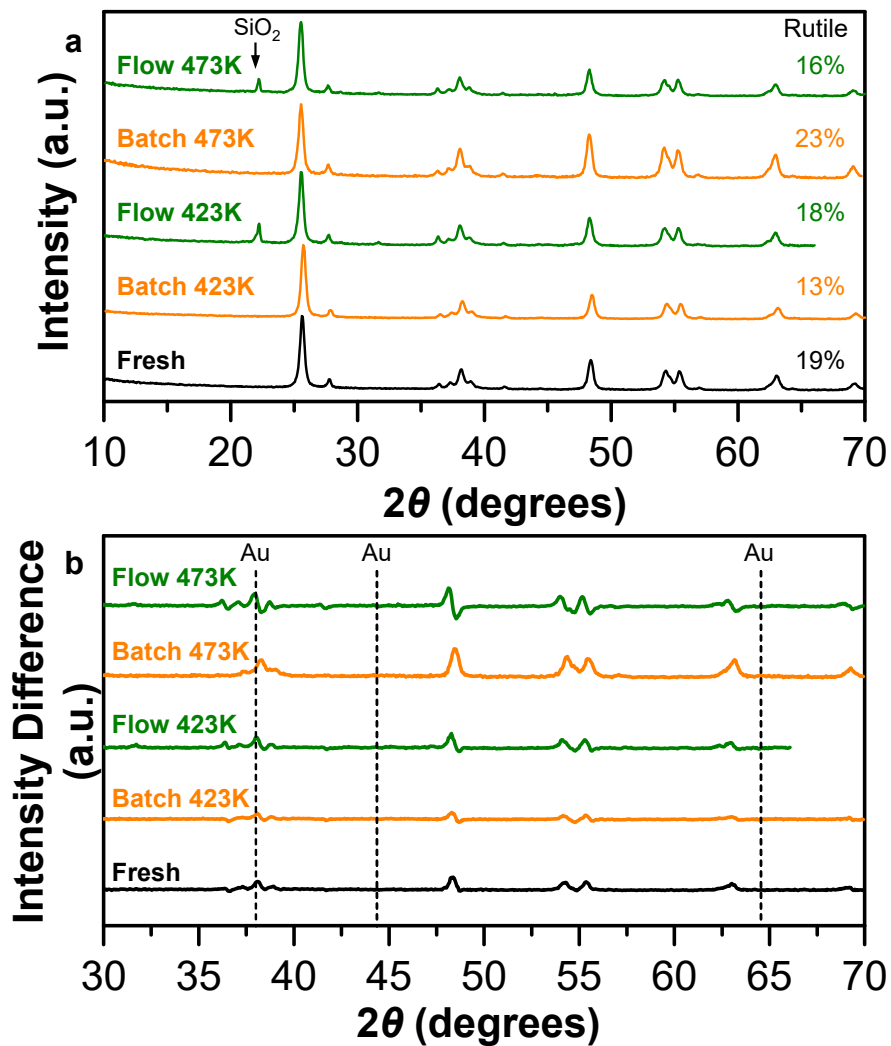


Fig. 3 (a) XRD patterns of the catalyst before (Fresh) and after reaction in batch and flow at 30 bars.

Energy-dispersive X-ray spectroscopy

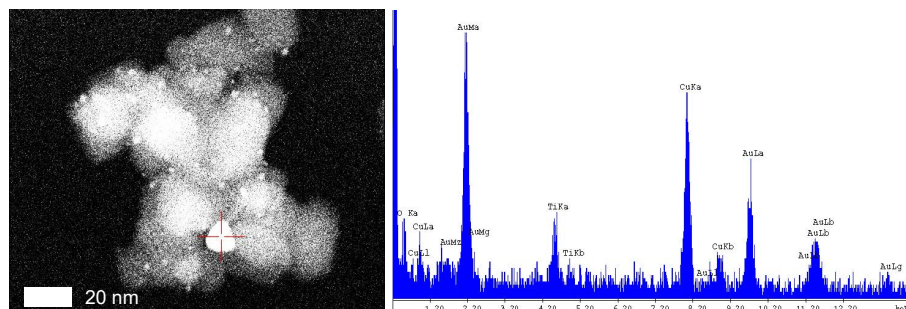


Fig. 4 EDX mapping (right) of the bright spots (red cross) in the STEM image (left). The main peak corresponds to gold at 2.2 keV.

4 Stability in flow

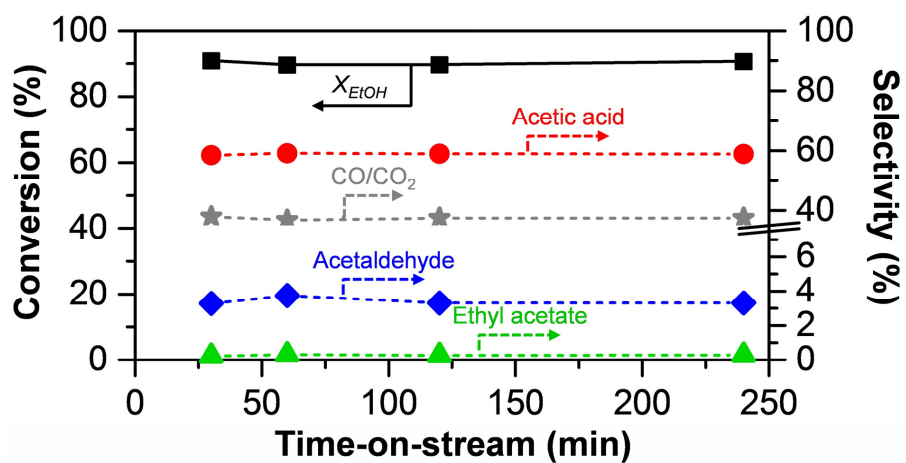


Fig. 5 Catalyst's stability in the flow reactor at 473 K and 30 bars.