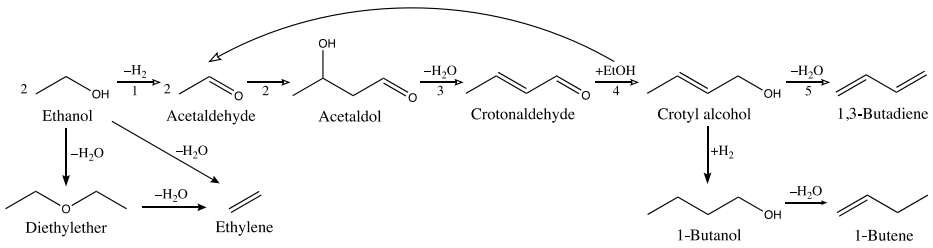
Innovative sol-gel routes to metal doped mesoporous Ta-SiO_2 catalysts for the upgrading of bioethanol to butadiene

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The production of bioethanol has been promoted by strong incentives to exploit it in blended fuels. Yet, nowadays, many companies face a surplus of ethanol and are keen to find other ways to valorise it as a chemical. In parallel, the market for C4 hydrocarbons is under tension. Butadiene is produced via the steam cracking of crude petroleum and represents a huge and growing market (12 000 kT in 2015). Yet, the petrochemical industry is currently witnessing a shift towards shale gas, from which only a small proportion of C4 can be produced. Thus, there is a strong incentive to find efficient ways to upgrade bioethanol towards butadiene.

The direct catalytic conversion of ethanol to butadiene is long known,[1] but remains a challenge in terms of catalyst developments. The reaction mechanism consists of a complex network of dehydration and dehydrogenation reactions catalysed respectively by acid and redox active sites. These two types of active sites must operate in a controlled and balanced fashion to maximize the butadiene yield (at the expense of by-products such as ethylene, diethyl ether, etc.).

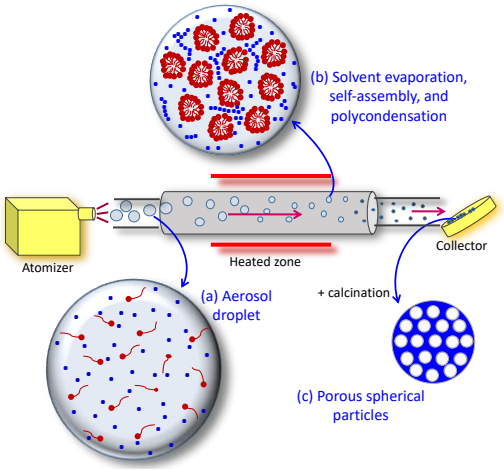


Scheme 1: Reaction mechanism for the direct conversion of ethanol to butadiene[2]

Here, we exploit (i) aerosol-assisted sol-gel (AASG)[3] and (ii) non-hydrolytic sol-gel (NHSG)[4] as original preparation routes to prepare bifunctional heterogeneous catalysts. We show how these allowed us to tailor the key properties of the catalysts (composition, acidity, metal dispersion, homogeneity, texture), to improve their catalytic behaviour (activity, selectivity, stability).

NHSG allows synthesizing highly homogeneous and mesoporous metallosilicate catalysts in a one-pot fashion.[5] Here, it was used to prepare Ta-SiO_2 materials that exhibited high dehydration activity.[2] Via the use of a templating agent, we achieved high specific surface area and large mesopores that ensure rapid mass transfer (SSA≈700 m^2 g^{-1}; Vp≈0.7 mL g^{-1}; D_p≈4.0 nm). Using FTIR spectroscopy, XPS, DRUVS and NH_3-TPD, we show that the introduction of tantalum through NHSG promotes the formation of a homogeneous metallosilicate with abundant Si–O–Ta–O–Si bonds. As compared to a catalyst of similar composition prepared by classical impregnation of Ta onto SiO_2 (in which the formation of polymeric Ta oxide species is unavoidable), the NHSG catalyst is more acidic and therefore more active in ethanol dehydration. Yet, to guide the reaction towards butadiene, a dehydrogenating metal must be added. The addition of silver by dry impregnation allowed us to obtain a bifunctional catalyst that efficiently catalyses the formation of butadiene. Upon optimization, a formulation containing 2 wt.% Ta and 5 wt.% of Ag was selected as the most active towards butadiene. At

355 °C (WHSV = 1.10 h^{-1}), an ethanol conversion of 85 % and a butadiene yield of 17 % was reached. Interestingly, we showed that it is also possible to incorporate Ag directly in the NHSG process. The catalyst prepared by such one-pot sol-gel route, however exhibited lower butadiene yield. Replacing silver by copper, much higher performance was achieved mainly owing to a boost in selectivity (conversion 75 %, selectivity 30%, yield 24 %).[2]



The AASG method consists in atomizing a solution containing reactive molecular precursors in the form of air born droplets which are then rapidly dried. During drying, precursors undergo inorganic polycondensation reactions. Taking advantage of the evaporation-induced self-assembly of a surfactant, it is possible to control the texture of the material.[3] Thus, nanomaterials can be produced with controlled properties (texture, surface chemistry, homogeneity), which showed great promises for the development of high performance heterogeneous catalysts.[3,6,7]

Scheme 2: Schematic view of the aerosol assisted sol-gel process[3]

Here, we present the first example of the preparation of bifunctional Cu- and Ta-based mesoporous catalysts by AASG. An aqueous solution containing Cu nitrate, Ta ethoxide and pre-hydrolyzed TEOS (supplemented with a pluronic surfactant) is sprayed and dried to yield spherical particles with calibrated porosity. After calcination, the catalysts display advantageous texture (SSA≈450 m^2 g^{-1}; Vp≈0.5 mL g^{-1}; D_p≈4.5 nm). As evidenced by in situ XRD and by XPS, the Cu species that are initially dispersed in the bulk of the metallosilicate undergo a migration towards the surface during calcination, to form small CuO nanoparticles. Tests in the ethanol to butadiene reaction allowed us to select the optimal calcination temperature (500°C), to maximize the dehydrogenation activity of Cu nanoparticles. All in all, the best catalyst (2 wt%Ta and 5 wt%Cu) reached a 27 % yield at 355 °C.

In conclusion, these two bottom-up sol-gel techniques are powerful tools to tune the properties of the bifunctional catalysts so that the dehydration and dehydrogenation functions of the catalyst are well balanced, allowing to push the reaction process towards the selective production of butadiene.

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