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Unraveling the mechanism of catalytic reactions through combined kinetic and thermodynamic analyses: Application to the condensation of ethanol

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The combination of kinetic and thermodynamic analyses can provide an in-depth knowledge of the crucial steps of catalyzed reactions. Earlier examples are recalled to stress how a reaction mechanism can be supported or rejected based on trivial reactant and product concentration analyses. The method is then applied to the important reaction of alcohol condensation, the so-called Guerbet reaction, which enables converting ethanol, a renewable feedstock, into higher alcohols. Important conclusions regarding the design of ethanol condensation processes can be drawn, as the main reaction mechanism occurring at high temperatures (ca. 350–420 °C) appears to be different from that proposed at low temperatures (< 250 °C). In the former case, the pathway involving acetaldehyde is negligible, and therefore a multi-step process based on ethanol dehydrogenation followed by acetaldehyde self-aldolization would be irrelevant.

1. Introduction

Process design benefits from understanding the various steps involved in the chemical conversion of a given feedstock into the desired products so that each step can be:

- promoted by a suitable catalyst and/or;
- carried out under appropriate operating conditions as to push away the limiting conversion associated with the thermodynamics of the system.

Thermodynamics is thus routinely used as a tool to determine favorable reaction conditions so that high yields into the products of interest can be achieved. It is yet far less common to relate the proportions of reactants and products present in a reactor to thermodynamic equilibrium constants pertaining to the system to unravel the details of the reaction mechanism. Three examples are described thereafter emphasizing the power of this approach, which is then applied to the condensation of ethanol to butanol.

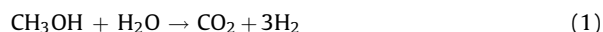## 2. Unraveling reaction mechanisms through thermodynamics

The hydroisomerisation of *n*-butane to isobutane over reduced molybdena provided an example in which

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thermodynamics enabled one to positively determine both the reaction mechanism and the rate-determining step (RDS) [1]. The concentration of butenes, potential reaction intermediates in a bifunctional mechanism, could be accurately measured, despite being present at levels more than three orders of magnitude lower than that of butane. The proportions of butenes corresponded to those at the hydrogenation/dehydrogenation thermodynamic equilibrium with the corresponding saturated compound. On the contrary, the skeletal isomerisation between butenes and isobutene had not reached equilibrium and was proposed as being the RDS. The cases of *n*-pentane and *n*-hexane were also addressed and it was shown that the same bifunctional mechanism operated, with the main difference that the dehydrogenation/hydrogenation steps were rate-determining for these longer alkanes [2].

The steam reforming of methanol (Eq. (1)) over a Cu–Zn–Zr–Al–O catalyst provided an example of a system in which a combination of kinetics and thermodynamics enabled discarding a reaction mechanism [3]. A critical question was whether or not CO was a primary reaction product, which would be formed prior to CO_2 (Eq. (2)) and would then be converted into CO_2 via the water-gas shift reaction (forward Eq. (3)).

$$CH_3OH + H_2O \rightarrow CO_2 + 3H_2 \qquad (1)$$

$$CH_3OH \rightarrow CO + 2H_2 \qquad (2)$$

$$CO + H_2O \rightleftharpoons H_2 + CO_2 \qquad (3)$$

CO only appeared after the other reaction products H_2 and CO_2 as the contact time was increased. Moreover, the proportions of H_2 and CO_2 first matched the thermodynamic composition associated with a CO-free system, being in excess with respect to the proportion associated with a system containing CO. Therefore, these data unambiguously and surprisingly proved that CO was not the precursor of CO_2, but that CO was rather formed from CO_2 as a result of a reverse water-gas shift reaction (backward (3)).

Finally, the selective catalytic reduction of NO with propene over alumina provided another example in which the long-thought-crucial reaction step described by Eq. 4 was actually found to be irrelevant [4]:

$$NO + 0.5O_2 \rightarrow NO_2 \qquad (4)$$

This was demonstrated by noting that the NO_2/NO ratio obtained during the reaction was far greater than that associated with the thermodynamics of the reaction described by Eq. 4. Several other catalysts based on Ag- or Co-alumina led to similar observations [5,6]. These observations were rationalized by realizing that NO_2 was formed through a more complex pathway, probably involving the formation and combustion of organo-nitrogen species. It was concluded that one of the major roles of Ag was to oxidize NO to adsorbed NO_x species (but not to gas-phase NO_2), which then reacted with hydrocarbon-derived species to form the organo-nitrogen species eventually leading to N_2 [5]. Having a dedicated catalyst and/or additional reactor to oxidize NO to $NO_2(g)$

was therefore shown not to be a requirement to improve the process.

The examples above underline the potential of thermodynamics in understanding the mechanistic details of a reaction and suggest better catalyst and/or process design. In the present contribution, a similar approach was used to unravel the mechanism of the (metal-free) high-temperature condensation of ethanol to butanol over one of the best catalysts reported for this reaction, a hydroxyapatite (noted "HAP") [7,8]. In particular, the role of acetaldehyde was investigated, since this compound was often proposed as being a crucial reaction intermediate, through its self-aldolization [7,9–11].

3. Experimental

The hydroxyapatite (noted "HAP") was supplied by Acros Organics ($Ca_3(PO_4)_2Ca(OH)_2$, batch A0312711) and exhibited a surface area of 82 $m^2 \cdot g^{-1}$. The limits of concentration of the main impurities given by the supplier were as follows: sulfate $\leq$ 5000 ppm, $Cl \leq$ 1500 ppm, $Fe \leq$ 400 ppm, $F \leq$ 50 ppm, $Cu \leq$ 20 ppm, $Zn \leq$ 20 ppm, $As \leq$ 2 ppm, $Hg \leq$ 1 ppm.

Powder X-ray diffraction patterns were recorded using a PANalytical X'Pert Pro diffractometer equipped with a copper radiation source (λ = 1.5406 Å). The diffraction pattern of HAP (Fig. 1) perfectly matched that associated with the hydroxylapatite reference pattern 00-024-0033 and that reported by Costentin and co-workers (see Ca-HAP-1 in Fig. 1 of this reference) [8].

Ethanol (from Prolabo 99.5%, the main impurity being water) was fed using a saturator kept at 45 °C into a heat-traced stainless steel flow setup. The sample was activated under Ar at 480 °C for one hour before introducing the ethanol/Ar feed at the reaction temperature. The catalyst was placed in a quartz tube reactor and held between quartz wool plugs. The reactor was located in a tubular furnace. Ar was used as the carrier gas. A combination of mass spectrometry, gas chromatography, and gas-phase FT-IR spectroscopy was used to determine the concentration of ethanol and the main products of interest (including H_2O and H_2).

The gas chromatograph (Bruker 450-GC) was fitted with Zebron ZB-Bioethanol column (30 m, 0.25 mm, film thickness: 1.00 μm). A flame ionization detector (FID) was used and a precise quantification of all the detectable products was realized through the use of an internal standard (i.e. toluene) added to the analyzed stream before injection in the column. The concentration of most reaction products, including H_2, could also be monitored by online mass spectrometry (Pfeiffer Omnistar 320). The contribution of large molecules to the fragment $m/z = 2$ was taken into account to determine H_2 concentration, also using calibration curves. The concentration of some reaction products, in particular acetaldehyde and water, was also monitored by online FT-IR gas analysis using a 27-cm-long single path gas cell fitted in a Nicolet 560 spectrometer. Calibration curves were drawn to relate IR band signal intensity to concentrations.

The thermodynamic calculations were done with the HSC Chemistry® software (version 6.2, by Outotec). For the