Thermodynamics conditions for Guerbet ethanol reaction

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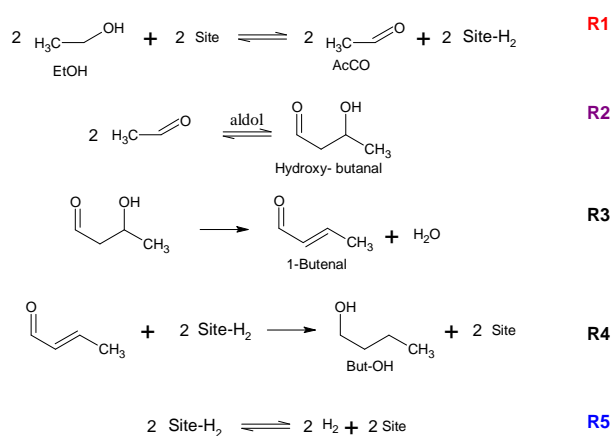[1]Laboratoire Réactions et Génie des Procédés (LRGP), Université de Lorraine, Nancy 54000, France
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1 Introduction

Ethanol (EtOH) is now produced from fermentation of carbohydrates [1]. Guerbet reaction is a possible way to couple C-C bonds of aliphatic alcohols towards higher carbon skeleton molecules that are suitable for diesel, gasoline, aviation fuel and chemicals [2–4]. When vaporized EtOH is contacted to solids at temperatures near 673.15 K, a lot of different products are obtained containing olefins, paraffins, longer alcohols, diolefins, ketones, aldehydes, ethers, etc. Some H_2 is produced and carbonaceous deposits are formed [5, 6].

On acidic catalyst, gas phase conversion of EtOH to aromatics hydrocarbons can be performed (zeolites) at 673-723K. This reaction involves the dehydration of EtOH to ethylene, and then ethylene is converted to unsaturated hydrocarbons and hydrogen [7]. The drawbacks of this strategy is that the mixture should be vaporized (heat-consuming) and that some hydrogen atoms abandon the carbon skeleton (loosing energy yield in drop-in fuels), however it could be used to obtain bio-based aromatics hydrocarbons from EtOH platform.

Very acid catalyst accelerates excessive dehydration, producing short hydrocarbons without OH functionality capable of undergo C-C coupling. For that reason basic or multifunctional catalysts are employed for EtOH conversion to higher hydrocarbons [6, 8, 9]. The most accepted mechanism for Guerbet reaction using basic catalyst is the aldol mechanism (Scheme 1) [3, 9]. In the first step (Scheme 1, R1), EtOH is dehydrogenated by a solid catalyst to produce acetaldehyde (AcCO). Then AcCO can undertake acid-base catalyzed aldol addition (Scheme 1, R2). H_2O is then released from the molecule. Basic catalysts have the capacity to store hydrogen by heterolytic dissociation. In a desired Guerbet reaction, adsorbed hydrogen is re-inserted into carbon skeleton (1-butenal to 1-butanol in Scheme 1, R4) to generate a higher alcohol that can re-start the catalytic cycle.

Scheme 1. Guerbet reaction of Ethanol (global reaction and most accepted catalytic mechanism).

In this work, the EtOH to butanol (But-OH) probe reaction was studied. Most of catalytic data available on C-C coupling of EtOH are on the gas phase at 1 bar, for that reason this condition was studied. However, in fermentation process, EtOH is produced in a solution of water (at ~6 wt.% EtOH) [1], this aqueous solution was also studied. It is expected that higher alcohols (like octanol) separate spontaneously from water by decantation, avoiding energy-intensive distillation (consider that fuel EtOH should be anhydrous).

The formation of AcCO is not favored at low temperatures. For that reason, this study concentrates in this step of reaction (Scheme 1, R1). The determination of EtOH/AcCO equilibrium will guide experimental catalyst researchers to favorable conditions and materials. R2 has low $\Delta_{R2}G$ in the whole range of temperature (K_{eq-R2} is between 2-0.02). This step can limit reaction rate but it is never impeded (K<0.01) in the whole range of temperature. R3 and R4 are quite favorable reactions ($\Delta_r G \ll 0$). The global EtOH to BuOH reaction is quite favorable both in gas phase (298.15-773.15K) and liquid phase (298.15 – 523.15 K, 1-50 bar). The equilibrium of adsorption of H_2 (Scheme 1, R5) is of great importance. If R5 is too favored ($\Delta_{R5}G<0$), this means that H atoms can abandon solid in the molecular form (H_2) without going to the carbon skeleton. On the other way, if this

reaction is too disfavored, this means that it will be more difficult to transfer H atoms to the carbon skeleton (R4).

2 Methods

Gibbs energy variation of reaction in the ideal gas phase was obtained with THERGAS (Benson's method) [10]. Liquid phase equilibrium was modeled in ASPEN Plus ® using a Gibbs free energy minimization algorithm. UNIFAC-Dortmund prediction method was used for gamma between 1-8 bars. For higher pressures (50 bar) Peng-Robinson EoS coupled to Wong-Sandler mixing rule (PR-WS) was used. At 100 bar, PR-WS did not converged in ASPEN, so Predictive Soave-Redlich-Kwong EoS (PSRK) was used instead.
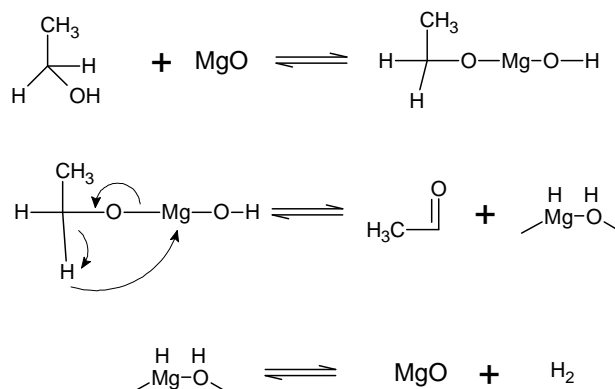
3 Results

3.1 Gas Phase

In a first approach the equilibrium of the non-catalytic AcCO formation was studied in gas phase:

$$EtOH \leftrightarrows H_2 + AcCO \quad R1 \text{ (non cat.)}$$

In the catalytic mechanism, this reaction also occurs with same thermodynamics. H_2 formed is re-adsorbed for completion of the reaction to 1-butanol. Also, formally, one can consider that ethanol rather decomposes into free AcCO (observed as an intermediate [5]) and a surface complex of H_2 as written in R1. This step corresponds to the breaking of a C-H bond by abstraction of hydride specie by the catalyst. It is probably rate limiting, also determination of energy exchanged may be a good simulation of the energy barrier to overcome in the chemical processes involved in the Guerbet reaction.

Scheme 2 shows a probable mechanism for the formation of AcCO by dehydrogenation of EtOH on MgO, a typical basic catalyst.

The thermodynamic properties of the hydride surface complex are not easy to predict. However, experimental data on H_2-storage materials is available. Salam et al. [11] compiled data of the reaction R5_inverse (adsorption of H_2) for some solids. Typical values for H_2 storage materials (Cobalt or Magnesium based metal-organic framework, Na-ZMS-5 zeolites) are $\Delta_{R5}h = +9.4$ to $+18$ KJ/mol and $\Delta_{R5}S = +120$ to $+136$ J/(mol.K), but significant differences can be obtained with materials like Co-Mg-Al nano-crystalline mixed oxides with $\Delta_{R5}h = +25$ KJ/mol and $\Delta_{R5}S = +59$ J/mol.K; these values will be refereed as "Advanced solid").

Scheme 2. A possible chemical form of R1.

The addition of "R1 -no cat-" (i.e. considering molecular H_2 and not an adsorbed specie) and R5 gives R1 as showed in Scheme 1. The equilibrium constant of R1 for an ideal gas was calculated considering $\Delta_{R5}h = +15$ KJ/mol and $\Delta_{R5}S = +130$ J/(mol.K) for "Solid A" (a mean performing H_2 storing material). R4 was always favored ($\Delta R4G \ll 0$) for solids in the whole range of temperature whatever the performances of the solid catalyst.

Figure 1 shows results of calculations in ideal gas phase at 1 bar and pure EtOH, R1-no cat- is not favored at room temperature, but $K_{eq-R1-nocat-}$ approach 1 at about 600K. The equilibrium constant of R1 in Solid A is very low in the whole temperature range. However, if we consider an advanced material, these values get enhanced significantly. Ndou et al. [5] studied EtOH conversion on MgO as catalyst at different temperatures, the reaction did not take place until T> 673.15 K, then a sharp increase in activity is observed and a peak in selectivity appears near 723.15 K, then selectivity falls down at 773.15K, probably because of the departure of molecular H_2. However, Tsuchida et al. [6,9] observed activity at temperatures as low as 545.15 K for advanced Ca/P catalysts.
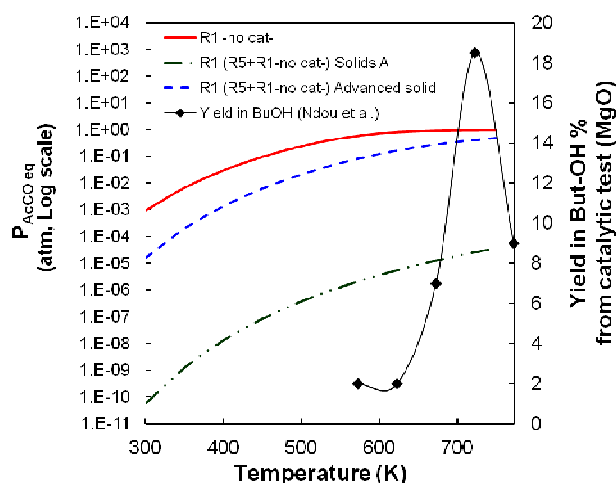

Figure 1. Plot of Keq (log scale) for different reactions as a function of temperature (1 bar, ideal gases, pure EtOH) and data of catalytic conversion of EtOH into But-OH using MgO as catalyst.

Desorption of hydrogen (R5) should be avoided in our reaction system to prevent the departure of energy-rich

H_2 from carbon skeleton. In the "Advanced material" the H_2 desorption becomes possible at $T>433.15K$ but temperatures about 523.15 K are needed to reach a significant value of conversion of R1 (P_{AcCOeq}=0.01 bar). So, even with the advanced material, we cannot simultaneously favor AcCO formation (R1) and impede H_2 departure (R5).

3.2 Liquid Phase

Evaporation of water and EtOH requires energy. Liquid phase is preferred to avoid this step [8]. In order to avoid vaporization in equilibrium calculations, conditions were always P>Pbubble point of the mixture. In the range of 298.15 to 433.15 K, a pressure of 8 bar satisfy the P>P_{bubble} point conditions. In this range UNIFAC-Dortmund method was used to model equilibrium into a RGIBBS Aspen tool (Gibbs energy minimization). A solution of 6 wt.% EtOH, 94 wt.% H_2O was inserted into the reactor where R1-nocat- was the only possible reaction (Figure 2). A reasonable accordance is observed with UNIFAC-DMD model and PRWS model from 298.15 to ~350 K. At temperatures about 408.15 K and 8 bars, H_2 forms a gaseous phase and equilibrium is displaced towards products. In both cases, a positive effect of temperature is observed.
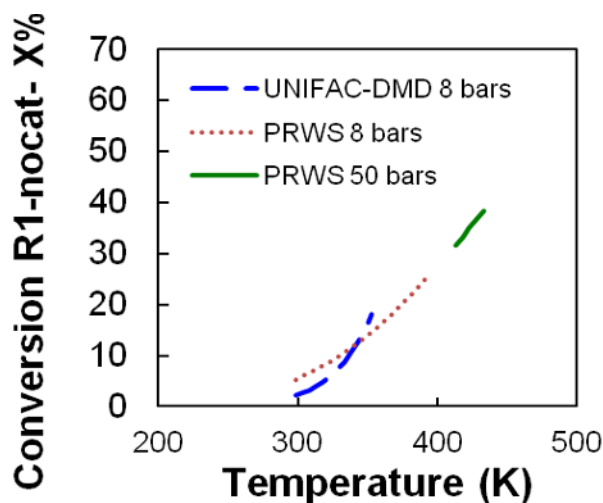

Figure 2. Equilibrium conversion of R1-no cat- at 8 bars as a function of temperature and prediction models.

At 50-100 bars only a EoS can be considered, at 50 bars the study of equilibrium conversion can be extended to 433.15 K (then a H_2 rich gas phase is formed).

In order to model equilibrium between liquid phase EtOH, AcCO and surface complex values of γ were calculated in a mixture of 6 wt.% EtOH, 94 wt.% H2O and 0.006 wt.% AcCO (modeling the beginning of the reaction (Figure 3). UNIFAC-DMD (8 bars), PR-WS (50 bars) and P-SRK (100 bars) were used to calculate $γ_i$.$K_γ$=$γ_{AcCO}$/$γ_{EtOH}$ is always about 0.7-1.3 in the range 298.15-573.15 K, and EtOH/H_2O mass ratio from 6/94 to 50/50. Very low effect of pressure was observed (1-100 bar).

The value of C_{AcCO}/C_{EtOH} (K_{eq} in ideal gas, K_{eq}/$K_γ$ in liquids) is slightly lower for liquid phase.

If we consider that a reaction becomes possible when C_{AcCO}/C_{EtOH}>0.01, the advanced solid of Salam et al. [11] satisfy this condition at 493.15 K in the liquid phase (at this temperature liquid mixture bubble point is 25 bars). Since R4 is a very favored reaction, R2 Gibbs energy could be as low as -120 KJ/mol (i.e. H_2 can be very stable in the adsorbed form, avoiding formation of H_2).
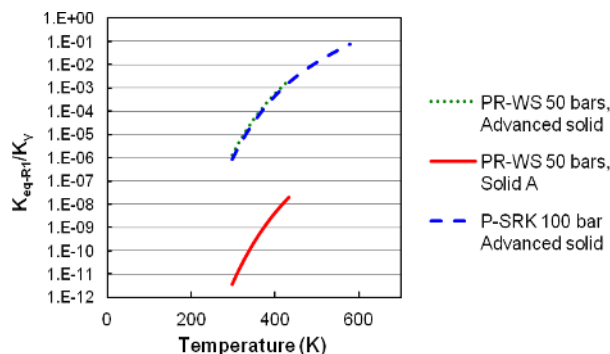

Figure 3. $K_{equilibirum-R1}$ / $K_γ$ ($γ_{ACCO}$/$γ_{EtOH}$) for different conditions, models, and catalytic solids.

High temperature will require great energy supply and costly high pressure equipment to avoid evaporation. Only a global cost analysis can determine the best operative conditions. Catalyst for this reaction should present desirable H_2 sorption thermodynamics characteristics, but also has to respect other criterion: activity, selectivity, resistance to aqueous medium, etc. Moreover, it has to catalyze aldol condensation from AcCO. Probably, AcCO forms also a complex with catalytic sites that should be considered in more fine thermodynamic/kinetic predictions.

4 Conclusions

The transformation of aqueous EtOH into base hydrocarbons for drop-in fuels require advanced materials with good H_2 sorption thermodynamic characteristics. 573.15 K and 50 bars are limit conditions to test a catalytic material; theoretically an advanced material can catalyze the EtOH Guerbet reaction at 493.15 K, 25 bars; however the concept should be still proved experimentally. Great effort of theoretic and experimental research is required to conceive a catalytic process capable to compete with other alternatives like current direct use of EtOH as fuel.

References

1. Ó.J. Sánchez, C.A. Cardona, Bioresour. Technol. **104** 305 (2012)
2. E.L. Kunkes, D.A. Simonetti, R.M. West, J.C. Serrano-Ruiz, C.A. Gärtner, J.A. Dumesic, Science **322** 417 (2008)
3. J.I. Di Cosimo, G. Torres, C.R. Apesteguía, J. Catal. **208** 114 (2002)

4. E. Hemo, R. Virduk, M.V. Landau, M. Herskowitz, Chemical Engineering Transactions **21** (2010)
5. A. Ndou, Appl. Catal. A **251** 337 (2003)
6. T. Tsuchida, T. Yoshioka, S. Sakuma, T. Takeguchi, W. Ueda, Ind. Eng. Chem. Res. **47** 1443 (2008)
7. M. Inaba, K. Murata, M. Saito, I. Takahara, Reaction Kinetics and Catalysis Letters **88** 135 (2006)
8. T. Riittonen, J. Mikkola, in: *1st International Congres of Catalysis for Biorefineries*, Malaga, Spain, 2011, p. 813‒818
9. T. Tsuchida, J. Kubo, T. Yoshioka, S. Sakuma, T. Takeguchi, W. Ueda, J. Catal. **259** 183 (2008)
10. C. Muller, V. Michel, G. Scacchi, G.M. Côme, J. Chim. Phys. **92** 1154 (1995)
11. M. Salam, S. Sufian, T. Murugesan, Nanomaterials 1 (2013)