Kinetic Modeling of the Direct Amination reaction of *n*-Octanol with ammonia over a Ag-Co/Al_2O_3 catalyst

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Abstract:

Direct amination of *n*-octanol with NH_3 was investigated over a 5wt.% Ag_3-Co_{97}/Al_2O_3 catalyst in the temperature range 160-180 ºC as a function of the of the *n*-octanol, NH_3 and H_2 partial pressures. Unexpectedly, the H_2 pressure enhanced the *n*-octanol conversion and promoted the formation of the secondary amine. A kinetic model was developed, proposing a plausible coking-regeneration mechanism accounting for the *a priori* non-intuitive effect of the H_2 pressure. The intermediate octylimine was identified as the most likely coke source *via* statistical model discrimination. An excellent fitting of the experimental results was obtained, covering a wide range of experimental conditions at low and high *n*-octanol conversions.

Keywords: Kinetic Modeling, Amination, Reversible Deactivation

1. Introduction

Despite the strong scientific interest dedicated to the discovery of catalytic formulations for amination reactions, only very few comprehensive kinetic studies can be found in the open literature[1–3]. More specifically, the effect of the H_2 partial pressure has been generally omitted, being only integrated in a recent kinetic model developed by Ruiz *et al.*[4] To fill the existing gap in the current understanding of amination catalysts, herein we conducted a rigorous and comprehensive kinetic study surveying the effect of the different operation variables on a homemade Ag_3-Co_{97}/Al_2O_3 catalyst for the gas-phase direct amination of *n*-octanol with NH_3. The study covered the effect of the *n*-octanol, NH_3 and H_2 pressures, as well as the temperature and contact time. Different trends of the catalytic activity and selectivity could be drawn for the formation of *n*-octylamine, dioctylamine and octanenitrile matching the reaction network depicted in Figure 1. An ensemble of plausible models was developed, which were further discriminated through rigorous statistical analysis. A kinetic model could be formulated, describing properly the experimental trends as a function of the operation variables and most especially the H_2 pressure.

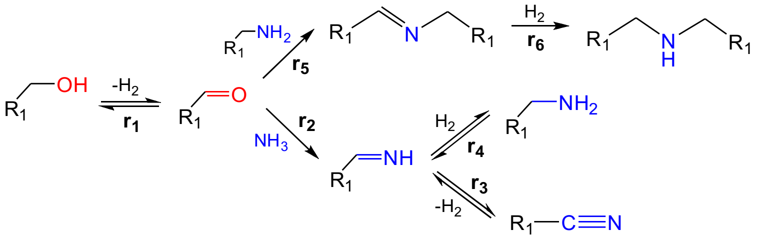

Figure 1 Reaction network for the direct amination of *n*-octanol with NH_3, leading to the formation of *n*-octylamine, dioctylamine and octanenitrile.

2. Experimental

The 5wt.%Ag_3-Co_{97}/Al_2O_3 catalyst was prepared by sequential incipient wetness impregnation of aqueous solutions of $AgNO_3$ and $Co(NO_3)_2{\cdot}6H_2O$ over γ-Al_2O_3. The $AgNO_3$ solution was first impregnated at room temperature for 2 h, dried at 120 ºC during 12 h and calcined at 400 ºC for 4 h. The $Co(NO_3)_2{\cdot}6H_2O$ solution was further impregnated over the as-obtained calcined material using a similar protocol.

A full factorial design of experiments (DoE) was implemented. The total pressure was set at 200 kPa, while three levels were considered for the temperature (160, 170, 180 ºC), the catalyst loading (10, 20, 30 mg) and the H_2 pressure (12.5, 37.5, 62.5 kPa). Besides, two levels and a central point were considered for the NH_3 pressure (37.5, 56.3, 75 kPa) and the *n*-octanol pressure (12.5, 18.8, 25.4 kPa). Overall, 126 gas-phase catalytic tests were carried out in a high-throughput Flowrence unit (Avantium®, REALCAT platform), consisting of 16 parallel fixed bed reactors. Prior to the tests, the catalysts were *in situ* reduced at 500 ºC under a 20% v/v H_2-N_2 mixture. After reduction, the reaction conditions were set and left to stabilize for 1 h. Samples were recovered every 1.5 h after stabilization and analyzed offline by gas chromatography.

A series of kinetic models were developed based on Langmuir-Hinshelwood type expressions. The kinetic parameters of the models were fitted to the experimental data using a Levenberg-Marquardt algorithm based on non-linear least-square minimization. Isothermal plug flow reactor hydrodynamics were assumed on the basis of well-established heuristic criteria. External and internal diffusion resistances were found negligible.

3. Results and discussion

Aiming to develop a chemically sound and robust kinetic model, we first conducted a detailed analysis of the experimental results. The use of a full factorial experimental design allowed the analysis of the individual kinetic trends, as well as interactions between the different operation variables. The effect of each variable on the selectivity was assessed at iso-conversion.

This analysis led to the following observations:

- **Temperature:** increases conversions and favors the *n*-octylamine and nitrile selectivities.
- **NH_3 pressure:** no relevant effect on the conversion, but favors *n*-octylamine selectivity.
- ***n*-Octanol pressure:** no relevant effect on the conversion, but promotes slightly the *n*-octylamine selectivity
- **H_2 pressure:** remarkable positive impact on the conversion and negative effect on the *n*-octylamine selectivity.

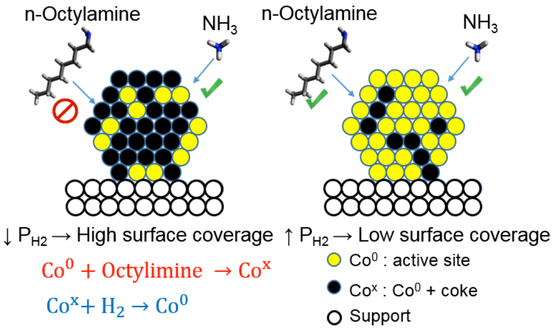

Figure 2 Proposed coking-regeneration mechanism.

The experimental trends for temperature and the NH_3 pressure agree well with the literature.[1,3,4]. In contrast, the experimental trends of the *n*-octanol and H_2 pressures are somehow unexpected. Both effects could be properly explained using a coking-regeneration mechanism (Figure 2) in line with the model proposed by Ruiz *et al.*[4] In this model, H_2 favors the regeneration of the surface metal from coke, explaining its positive reaction order on the *n*-octanol conversion. Regarding the negative effect of the H_2 pressure on the *n*-octylamine selectivity, this can be well accounted by assuming non-competitive adsorption between bulky (*e.g.*, *n*-octanol, *n*-octylamine, dioctylamine, octylimine) and smaller molecules (H_2, NH_3, H_2O). At low H_2 pressure, the metal surface is expected to be highly covered by coke. The adsorption of the bulkier *n*-octylamine, requiring multiple sites, is then hindered, while the smaller NH_3 can still adsorb on isolated vacant metal sites. Increasing H_2 pressure reverses this process, enhancing the surface concentration of *n*-octylamine (Figure 2). The adsorbed *n*-octylamine might then compete with NH_3 (r_5 *vs* r_2, Figure 1) favoring the formation of dioctylamine, which is in line with the experimental results. Finally, the *a priori* counterintuitive positive effect of the *n*-octanol pressure on the *n*-octylamine selectivity suggests a correlation between the concentration of this reactant and coke formation.

With this in mind, several kinetic models were built by considering different plausible coke sources and stoichiometries. Statistical discrimination of the different models and further simplification led to a successful model relying on the *n*-octylimine as coke source. The model afforded an excellent description of the different experimental trends, with a coefficient of determination of $R^2 = 96.8\%$, negligible correlation between the fitted parameters, and an optimal description of the experimental results at higher conversions.

4. Conclusions

A kinetic model was developed accounting for the gas-phase amination of *n*-octanol with NH_3 over a 5wt.% Ag_3-Co_{97}/Al_2O_3 catalyst. A coking-regeneration mechanism was proposed describing properly the experimental trends on a broad range of experimental conditions and including the complete reaction network for the *n*-octanol amination. Most especially, the model provides a plausible explanation of the unexpected effect of the H_2 pressure on the catalytic properties.

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