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Scientific Approach Towards Passivation: The Case of Ammonia Synthesis Catalyst

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Highlights

- The kinetics of passivation of iron catalysts with oxygen are shown
- The model agrees with the theory of low-temperature oxidation
- Kinetic parameters are obtained from dynamic experiments in a micro-reactor and are validated with industrial data
- The approach followed can be used for other relevant metal-based heterogeneous catalysts

1. Introduction

Activation of heterogeneous metal catalysts requires their reduction under well-controlled conditions in a process that is usually very time consuming. For this reason, chemicals manufacturers often prefer to acquire catalysts that have been pre-reduced and passivated in dedicated facilities by the catalyst producers. This is the case of ammonia synthesis, methanol synthesis and steam reforming catalysts, among others.

An adequate passivation is necessary not only to handle the catalyst safely but also to ensure an ideal catalytic performance [1]. Despite being such a crucial step in the production of catalysts, passivation kinetics is often disregarded in the open literature. In this contribution, a scientific approach towards the optimization of the passivation step is presented using the ammonia synthesis iron catalysts as case study. A kinetic model, which is in agreement with the theory of oxidation at low temperatures [2], is obtained from dynamic experiments carried out in a micro-reactor. The model is used to simulate an industrial reduction unit and to optimize the passivation procedure.

2. Methods

Temperature-programmed oxidation-reduction cycles were carried out at atmospheric pressure in a quartz tube micro-reactor (ID = 4.6 mm). Approximately 1 g of catalyst sample was loaded as granules in the size range 350 – 850 μm. The reactor was heated up by a concentric electric oven. A thermocouple was attached to the exterior wall of the quartz tube to monitor the temperature. The oxygen slip from the reactor was measured with an online mass spectrometer. After each passivation step, the total O_2 uptake was obtained from the consumption of H_2 during TPR.

The micro-reactor is modelled as a transient non-isothermal, non-adiabatic one-dimensional packed bed with axial dispersion. The set of nonlinear partial differential equations that describe the mass and energy balances in the gas and solid phases were integrated in MATLAB using the method of lines with evenly distributed collocation points in the axial coordinate. The values of the kinetic parameters were optimized using an unconstrained direct-search method. Data from an industrial reduction unit is used to validate the passivation model.

3. Results and discussion

A series of experimental breakthrough curves were fitted to obtain the kinetic parameters of oxygen uptake during passivation. Representative experimental and modeled O_2 slip curves are shown in Figure 1 together with the measured and simulated temperature evolution in the micro-reactor. The low-temperature oxidation of the iron catalyst was modeled by a logarithmic growth law given by

$$r = k_0 e^{\left[\frac{-(E_0 + \gamma X)}{RT}\right]} c_{O_2}^{\alpha}$$

where the activation energy increases proportionally with the oxide thickness, X, until a limiting value is reached.

Parameter optimization results in a value of $\alpha = 0.25$, which coincides with a theoretical model in which the rate is proportional to the concentration of lattice defects in the iron oxide layer. A limiting activation energy of ~ 9 kcal/mol is obtained, in agreement with the value predicted if oxidation is assumed to be controlled by Fe^{3+} movement at the metal-oxide interface [3].
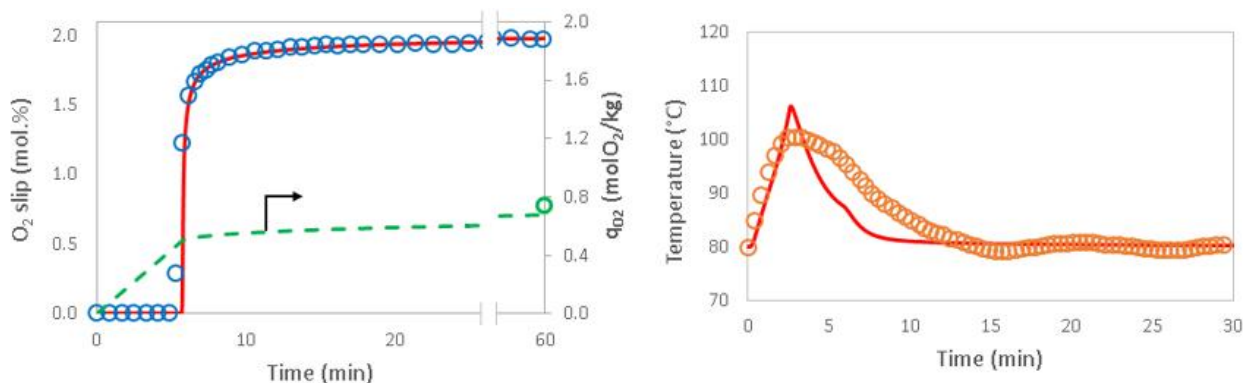
Figure 1. Typical breakthrough data obtained in the micro-reactor. Measured (open circles) and simulated (red lines) O_2 slip and temperature profiles. The temperature is recorded using a thermocouple attached to the exterior of the reactor wall at the middle of the packed bed. Also shown is the calculated average O_2 uptake (green dashed line) and the final uptake measured by re-reduction (open green circle).

The kinetic model for the passivation of iron-base ammonia synthesis catalysts is able to simulate the fast initial and the gradual long-term oxygen uptake. The measured amount of O_2 stored during the passivation steps are evenly distributed with respect to the calculated values. The deviations are acceptable considering the uncertainties associated to the integration of the H_2 consumption signal and the small amount of catalyst loaded. The agreement between the experimental and calculated temperature profiles indicates that the transport parameters used in the model are adequate. The description of the temperature evolution may be further improved if the axial heat conduction through the quartz tube and the thermocouple are included in the model.

The passivation kinetics can simulate adequately the axial temperature profile of an industrial unit during the whole oxidation process. The total oxygen uptake is also predicted.

4. Conclusions

A kinetic model for the passivation of iron catalysts, which is in agreement with the low-temperature oxidation theory, is presented. The expression is obtained from dynamic experiments carried out in micro-reactor and is validated using data from an industrial reduction unit. The approach demonstrated in this contribution can be applied for other metal-based heterogeneous catalysts of industrial relevance.

References

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