

Critical aspects in the kinetics study of exothermic reactions

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Highlights

- Temperature-transient measurements of CO oxidation on commercial TWC Pd/Rh catalyst
- Thermal hysteresis: role of heating rate, fuel content and reactor temperature control
- Dynamic pseudo 1-D reactor model predicts hysteresis with simple power-law reaction rate

1. Introduction

Experiments and model calculations are performed to investigate a model exhotermic reaction (CO oxidation on a commercial TWC monolith) in a flow tubular reactor. Particularly, the hysteresis in the conversion vs. temperature curves during ignition and extinction phases has been observed, as frequently reported in literature. It is often motivated by either modifications in the catalyst or thermal effects, due to the local overheating of the catalyst [1], [2]. However, Literature is not always clear about the details of temperature used to report the data [3], leading to uncertain coupling of the actual catalyst temperature and its activity. Here, we investigated the interpretation of the experimental data in temperature-transient conditions.

2. Methods

The experiments of CO oxidation are performed on 400-CPSI cordierite monoliths, Pd/Rh washcoated, in a tubular reactor, electrically heated. The temperature varies within the range RT-300°C with different policies. We investigated the CO feed concentration (0.07 to 1.4% v/v), the GHSV (45000, 75000 and 105000 h⁻¹), the heating rate (0.5, 2.0 and 5.0° C/min) and the reactor temperature control position (entrance of the catalyst or inside the monolith central channel). A transient heterogeneous pseudo 1-D model has been implemented to describe a single monolith channel. The bulk of the gas phase is described as plug-flow; in the boundary layer the transport phenomena are quantified by means of heat and mass transfer coefficients. The energy balances for both the gas and the solid are accounted for. Reaction rate is formulated either as power law or as Langmuir-Hinshelwood type.

3. Results and discussion

The effect of fuel concentration in the feed is evident when the conversions during heating and cooling are compared (Figure 1, left), leading to a large deviation (i.e. hysteresis) from the expected reversible behavior (diagonal); at 4% CO the difference between heating and cooling is extreme. The temperatures (Figure 1, right) at different positions during the reaction are significantly affected by the action of thermal control loop; also, the temperature selected to report the catalytic activity may introduce severe artifacts. At the same time, an inappropriate positioning (e.g. upstream of the catalyst, quite common) of the thermpocouple controlling the oven is responsible for instabilites at ignition. The results obtained with the model (Figure 2) prove that account for thermal evolution of solids and gas allows to reproduce the hystersesis with a single rate law, predicting the temperature increase of catalyst surface at ignition, but it overestimates the actual temperature because of the inaccurate account of thermal dissipations. So, while the estimation of the activation energy is consistent among tests at different inlet concentrations, the pre-exponential factor accommodates the uncertainties on the heat dissipations, varying by 4 orders magnitude: 4.49×10^{17} and 1.27×10^{13} mol/m³/s with 0.7 and 2% of fed CO respectively.



Figure 1. CO conversion is compared between heating and cooling phases at corresponding inlet temperature (left), feeding 0.7% or 4% equimolar CO and O₂ in He; heating/cooling rate = 0.5°C/min from RT to 300°C RT. GHSV = 45000 h⁻¹.
Evolution of CO conversion, and monolith, gas at catalyst inlet and set point temperatures (right); heating/cooling rate = 2°C/min from RT to 300°C; 2% equimolar CO and O₂ in He, GHSV = 45000 h⁻¹.



Figure 2. Gas at catalyst inlet and monolith temperature evolution: experimental data (symbols) and computed values (lines), with a single power law kinetic. Feed: 0.7% of CO and O₂, on the left, and 2% of CO and O₂, on the right, in He. GHSV = 45000 h⁻¹.

4. Conclusions

In this work we proved that irreproducible results in catalyst testing under temperature program may arise in case of significant heat of reaction (also determined by the feed concentration), leading to the so-called hysteresis effect. We proved that with CO oxidation over a commercial (Johnson Matthey) monolith for TWC applications. Especially at increasing fuel content (e.g. from 0.7% to 4%), the local overheating of the catalyst confuses the results, because large temperature gradients misalign reading at different positions. Also, an inappropriate temperature control loop, in terms of the position of the set temperature with respect to the catalyst, leads to reactor instabilities and misleading results. A dynamic pseudo 1-D model accounting for the catalyst temperature can describe, with a single rate law, both branches of hysteresis. Kinetics can be more detailed, but the major limitation remains in the thermal behavior, where the dissipation must be estimated.

References

- [1] A.N. Subbotin, I.R. Subbotina, E.Z. Golosman. Mendeleev Commun. 25 (2015) 216-218.
- [2] A.N. Subbotin. React. Kinet. Lett. 66 (1998) 97-104.
- [3] S. Salomons, R.E. Hayes, M. Votsmeier, A. Drochner, H. Vogel, S. Malmberg et al. App. Cat. B: Environ. 70 (2007) 305-313.

Keywords

Exothermic oxidation; catalyst testing on non-isothermal reactor; hysteresis; pseudo 1-D reactor model; kinetic modeling.