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Structure-dependent multiscale modelling of catalytic processes: an application to the catalytic partial oxidation of methane on rhodium

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Highlights

- Multiscale reactor modelling is applied in the context of the CH_4 CPO on Rh/Al_2O_3.
- *Ab initio* thermodynamics and Wulff-Kaishew construction are employed to simulate morphological changes of catalyst nanoparticles inside the chemical reactor.
- Drastic change in the process selectivity is found to be accompanied by a change in the structure of the catalyst.

1. Introduction

Several experimental studies clearly demonstrated the existence of strong mutual interactions between the structure and the activity in heterogeneous catalysis [1]. Moreover, the catalyst structure is strongly dependent on the reaction environment. As a result, catalyst materials in heterogeneous catalytic reactors are intrinsically dynamic systems: they change their morphology in response to the conditions of the reaction environment, which in turn affects the reactivity [2]. Microkinetic modelling is a key tool for the investigation of the behavior of complex chemical reactions, making it suitable for the fundamental understanding of the structure-activity relations of catalytic processes. However, state-of-the-art microkinetic models in heterogeneous catalysis lack in the description of the catalyst structure. In fact, they typically rely on an abstract and "structureless" concept of catalyst active site. This assumption enables the study of the macroscopic kinetic behavior of reacting systems [3], but it does not allow to reach an atomistic detailed understanding of the structure-activity relations. As a consequence, the incorporation of the catalyst structure in microkinetic modelling becomes of paramount importance for the fundamental understanding of the structure-activity relations, which is widely recognized as one of the main progress area in modelling of catalysis towards the design and the optimization of catalysts based on functional understanding rather empirical testing. Such atomistic level understanding of the catalyst functionality can only be achieved by explicitly including the effect of the structure in microkinetic model simulations. In this contribution we couple microkinetic modelling and *ab initio* thermodynamics for the characterization of catalyst nanoparticles in terms of surfaces morphology and three-dimensional shape as a function of the reaction environment in the context of the methane catalytic partial oxidation on Rh/Al_2O_3.

2. Methods

Multiscale reactor modelling is employed for evaluating the gaseous composition profiles inside a chemical reactor and for identifying the most abundant reaction intermediates (MARIs) that populate the catalyst surfaces. Density functional theory calculations and *ab initio* thermodynamics are then exploited to calculate the most stable bulk and surface structures of the catalyst at different conditions of the reaction environment. With this approach we consider the presence of the MARIs in thermodynamic equilibrium with their reservoirs in the gas phase surrounding the catalyst. Atomistic Wulff-Kaishew construction is eventually applied to estimate the shape of the catalyst nanoparticles and to calculate the relative amount of the catalyst active sites as function of the chemical environment inside the reactor.

3. Results and discussion

Previous mechanistic analysis of CPO systems on Rh have shown a sharp change in the reaction environment with residence time and temperature [3]. In particular, when oxygen is present at the catalyst surface interface, no syngas production is observed (zone 1 in Fig. 1a). Once oxygen has been totally depleted from the surface, CO and H_2 start producing (zone 2 in Fig. 1a). We have investigated the most stable structure of the catalyst in these two different zones of the reactors. First, the most stable

Figure 1. (a): Major species partial pressures axial profiles at the catalyst interface. Temperature: 500°C; pressure: 1 atm. Inlet mole fractions: CH_4 0.01, O_2 0.01, Balance N_2. Gas hourly space velocity: 2E6 Nl/kgcat/h. Annular reactor: I.D. 4 mm, O.D. 5 mm, Length 22 mm [2]. (b) Bulk phase diagram of Rh (blue) and Rh_2O_3 (red).

bulk phase of the catalyst has been calculated, considering the thermodynamic equilibrium with the gas phase. Then, the morphology of different crystal facets of the nanoparticles has been analyzed: for each facet, the thermodynamically most stable surface structure in equilibrium with the surrounding gas has been calculated. The results are reported in terms of bulk phase diagram in Figure 1b as a function of temperature and partial pressure of O_2. We found that the change from zone 1 to zone 2 is accompanied by a change in the bulk structure and the morphology of the catalyst. In particular, in the oxidizing zone of the reactor (zone 1), we calculated the rhodium (III) oxide to be the thermodynamically stable bulk phase, and the nanoparticle exposes mainly the (0001), (1-102) and (11-23) crystal facets (Fig. 1b). In zone 2 of the reactor, instead, where O_2 drops to very low values at the catalyst interface, metallic rhodium turns out to be the most stable bulk phase structure. CO and H are the MARIs, and Rh(110) and the Rh(111) are the facets most exposed by the nanoparticle. However, high Miller index facets become more stable with the increase of coverage of the MARIs, observed during reaction, yielding a change in shape of the catalyst. The change of the oxidation state of Rh as a response of the change in O_2 concentration in the gas phase is in agreement with operando spectroscopy studies [2]. Particle shape and size are found to be in agreement with TEM observations and chemisorption of CO and H_2.
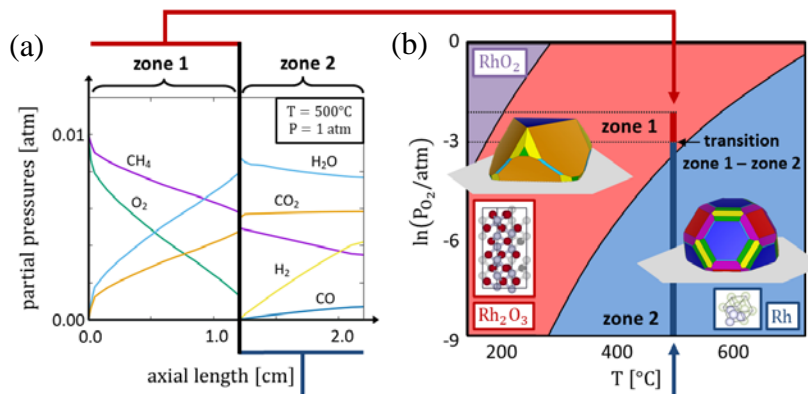
4. Conclusions

Multiscale reactor modelling and *ab initio* thermodynamics have been coupled for predicting surface morphology and three-dimensional shape of crystalline catalyst nanoparticles under reacting conditions, in the context of the CH_4 CPO on Rh. Our results – in agreement with spectroscopic studies – show that Rh can undergo strong variation of bulk phase composition and morphology in response to different reaction environment in the reactor.

Acknowledgments

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Keywords

Multiscale modelling; Microkinetic modelling; Supported catalyst nanoparticles; *Ab initio* thermodynamics.