

SPATIALLY RESOLVED OPERANDO-RAMAN ANNULAR REACTOR: AN APPLICATION TO THE METHANE DRY REFORMING ON RHODIUM

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Abstract

In this work, we present the development of a novel reactor for the operando-Raman analysis of gas-solid catalytic processes. The tool combines Raman spectroscopy and kinetic studies in annular reactor in chemical regime. Engineering solutions to minimize the mutual invasiveness of the spectroscopy and annular reactor techniques are presented and discussed. The final configuration allows for the quantitative understanding of catalytic reaction mechanism based on the simultaneous investigation of kinetics and of the state of the catalyst surface in terms of phases, morphology and adsorbed intermediates. As an example, we apply the operando-Raman annular reactor for the analysis of the kinetic consequences of C-formation during the dry reforming of methane on Rh. We show that the C-formation at the catalyst is not uniform along the catalyst and it is strongly related to the activation routes for CO₂ activation. These pieces of information are used for the development of a microkinetic model able to account for the routes at the catalyst surface.

Keywords

Operando-Raman spectroscopy, annular reactor, dry reforming, microkinetic modeling

Introduction

The detailed analysis of the relation between structure and activity is of primary importance to reach a fundamental understanding of the catalytic phenomenon. In this respect, spectroscopic studies substantially contribute in providing fundamental insights into the mechanism of heterogeneous catalytic reactions. Among the number of characterization techniques that provide a detailed understanding of a relationship between the structure and the activity of a catalyst, Raman spectroscopy stands out as a very informative and rather advantageous. It allows the identification of organic and sulfur compounds and can provide pieces of evidence about the structure of both the C-aggregates and of the S-compounds, as well as about their interactions with the catalyst during a deactivation process. However, the spectroscopic information needs to be integrated with the constraint of a kinetically-relevant experimental investigation. Here, we present the integration

of Raman spectroscopy and kinetic analysis in annular reactor. First, we show the engineering solutions adopted in order to minimize the mutual invasiveness among the techniques. Then, we apply the operando-Raman reactor to the analysis of the kinetic consequences of C-formation in Methane Dry Reforming (MDR) on Rh. The operando-Raman experiments are then employed for the development of a microkinetic model that accounts also for C-formation routes.

Design and development of the Raman-annular reactor

Several configurations are available for spectroscopic reactors (e.g., Meunier, 2010). However, these studies usually imply that the reaction is performed under conditions that are far from those relevant to a simultaneous kinetic analysis. Typically, these cells are optimized for

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collecting spectroscopic information, but the fluid dynamic patterns are poorly defined or lead to strong interactions between transport and kinetic effects. Several different constraints (optical, kinetic and material) must be taken into account to obtain reliable kinetic information and Raman spectra. Considering all the specifications the reactor has to comply with, the use of an annular reactor provides an ideal solution both to overcome kinetic limitations of both traditional packed bed and capillary reactors and to allow for the full integration of spectroscopic and kinetic tests. The annular reactor configuration must be adequately adapted to meet the Raman requirements. The quartz reactor is coaxially inserted in a stainless-steel which is wrapped by a temperature-controlled heating tape. A hole is drilled on the steel tube and a sapphire window is tightened to limit the heating dissipation and to protect the Raman objective from overheating. Upstream of the steel tube, a tubular oven is used as a preheater. A cylindrical shell of a ceramic microporous insulator is clamped around the steel tube to minimize the thermal dissipation. In order to have an optimal focus on the catalyst surface, the Raman probe can move in the whole set of directions (Maghsoumi et al., 2017). Moreover, thanks to a motorized stage, we are able to move the reactor along the axial direction, making it possible to perform Spatially Resolved Raman Analysis.

Application of the operando-Raman annular reactor MDR on Rh

We performed a long term MDR test by keeping constant the T at 600°C and the CH₄ inlet concentration at 8%. The CH₄ conversion was monitored for more than 2 hours, showing a decreasing trend (Figure 1a). At the same time, we performed spatially resolved Raman analyses in order to monitor the catalyst surface (Figure 1b). Two peaks, related to graphitic (G peak at 1580 cm⁻¹) and disordered (D peak at 1350 cm⁻¹) carbonaceous species, appeared in the Raman spectra. Thanks to the spatially resolved analysis, it was also evident that carbon is not uniformly present along the axis of the catalyst, but more deposits accumulated at the end of the 2 cm catalyst bed compared to the inlet, which maintained almost clean. This result suggests that formation of the stable carbonaceous species is stratified along the reactor length and they tend to accumulate towards the outlet of the reactor.

The Reaction Path Analysis performed with the microkinetic model shows that CH₄ is responsible for the formation of C intermediates while CO₂ provides OH species that oxidize the C intermediate (Maestri et al., 2014). However, CO₂ is only weakly adsorbed at the surface and as CO₂ decreases with the time on stream CH₄ dehydrogenation prevails over the OH formation, which is no longer equilibrated. As a consequence, the C-species are not oxidized by OH and tend to organize in complex C-aggregates at the surface. This leads to the formation and accumulation of stable C-deposits at the surface. Such C-aggregates cover the active sites and thus reduce the conversion of CH₄ (Figure 1a). These evidences are then

used to introduce additional routes in the microkinetic model to account for the formation of stable C-species at the surfaces. The resulting microkinetic model was found to successfully reproduce the kinetic consequences of C-formation during the MDR.

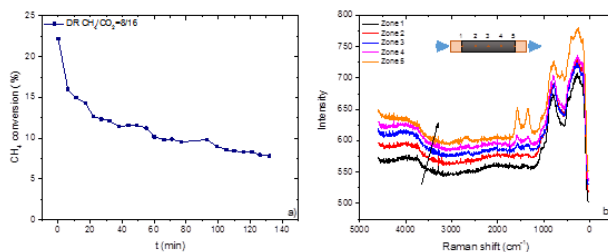


Figure 1. CH₄ conversion (a) and Raman spectra (b) recorded during MDR run with CH₄/CO₂ = 8/16 performed at 600°C.

Conclusions

An operando-Raman annular reactor was developed to obtain information on the status of the catalyst surface, while collecting data under kinetically relevant conditions. Specific procedures were developed in order to correctly focus the laser in the catalyst surface and to obtain relevant and accurate kinetic information. Operando Spatially-Resolved Raman Spectroscopy was applied to the study of catalyst deactivation in MDR reaction. In particular, this tool helped revealing that the observed deactivation of the catalyst is mainly due to the accumulation of C-deposits at the catalyst surface. By means of Spatially-Resolved Raman analyses, it was possible to observe that these C-deposits are not uniformly present along catalyst, but their formation and accumulation are favored towards the outlet. On the basis of these pieces of information, we extended the microkinetic model in order to directly account for the routes leading to stable C-species at the surface.

Acknowledgments

Financial support from the European Research Council (Grant 677423) is gratefully acknowledged.

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