

Dry reforming of methane on Rh/La₂O₃ and Rh/La₂O₃-SiO₂: The role of lanthanum in the reaction mechanism

Eduardo A. Lombardo^{1*}, John F. Múnera¹, Laura M. Cornaglia¹, Deborah Vargas César², Martín Schmal²

¹INCAPE (FIQ, UNL-CONICET), Santiago del Estero 2829, Santa Fe 3000 (Argentina)

²NUCAT/PEQ/COPPE, UFRJ, Rio de Janeiro CP 68052,21945-0 (Brazil)

*nfisico@fiqus.unl.edu.ar

Introduction

Several metals (e.g. Ni, Rh, Pt) have been supported on La₂O₃ and used in the CO₂ + CH₄ reaction. Very few kinetic and mechanistic studies have been published. The work of Verykios and co-workers [1] for Ni/La₂O₃ and our own on Rh/La₂O₃ [2] coincide in the role of the lanthanum oxycarbonates during this reaction. In the latter case, the Rh dispersion is very low, a difficulty that was overcome when La₂O₃.SiO₂ was the support [3]. In this work through the comparison of the characterization and kinetic data obtained with both systems, we hope to improve the understanding of lanthanum-based dry reforming catalysts.

Materials and Methods

The La₂O₃(27%)-SiO₂ was prepared by incipient wetness impregnation of silica with lanthanum nitrate and calcined at 873 K for 5 h. Rh(0.6%)/La₂O₃ and Rh(0.6%)/La₂O₃-SiO₂ were both prepared by incipient wetness impregnation with RhCl₃.3H₂O followed by calcination at 873 K. The catalysts were characterized by XRD, TPD, DRIFTS and XPS. The kinetic studies under differential conditions were conducted in a conventional flow system.

Results and Discussion

The Rh dispersion of the fresh catalysts after H₂ reduction at 823 K for 2 h was determined by both H₂ and CO chemisorption at room temperature. The La₂O₃ supported formulation had 14% dispersion while the value for Rh/La₂O₃-SiO₂ was 79%. The XPS Rh/La atomic ratio only slightly decreased for the used sample, suggesting that no significant change in the rhodium dispersion had occurred.

XRD data showed the presence of oxycarbonates in the La₂O₃ supported catalysts but this pattern was not observed in the case of the binary support. Instead, in the latter case broad reflections centered at 2θ = 28° and 45° are symptomatic of the presence of lanthanum disilicate that may impair the formation of oxycarbonates. The reactant mixture was fed to the DRIFT cell containing either catalyst. When Rh/La₂O₃ was used several IR bands assigned to different oxycarbonates were observed. In the case of Rh/La₂O₃-SiO₂ only the strongest band at 1505 cm⁻¹ appeared in the spectrum. At the surface level, the Rh/La₂O₃ system develops a well-resolved C1s signal at ca. 289 eV together with a O1s band at 530.1 eV. They clearly demonstrate the presence of carbonates on the surface of this catalyst. Surface and bulk techniques prove the presence of oxycarbonates in Rh/La₂O₃. In the case of the binary support, no definite proof of their presence was obtained. This might be due to the formation of small amounts of carbonates, consistent with the low intensity peak observed at 1073 K in the CO₂ TPD profile.

On the other hand, the kinetic data for both catalysts show similar reaction orders:

$$\text{Rh/La}_2\text{O}_3 \quad r_{\text{r}(\text{CH}_4)} = k_L(\text{P}_{\text{CH}_4})^{0.61} (\text{P}_{\text{CO}_2})^{0.37}$$

$$\text{Rh/La}_2\text{O}_3\text{-SiO}_2 \quad r_{\text{r}(\text{CH}_4)} = k_B(\text{P}_{\text{CH}_4})^{0.56} (\text{P}_{\text{CO}_2})^{0.38}$$

This is symptomatic of the same reaction mechanism similar to the one proposed by Verykios et al. [1] for Ni/La₂O₃, where the oxycarbonates play a central role.



The following rate equation that fits the data obtained with both catalysts at temperatures between 823 and 903 K (Fig.1) was derived:

$$r_{\text{CH}_4} = \frac{K_1 k_2 K_3 k_4 [\text{CH}_4][\text{CO}_2]}{K_1 K_3 k_4 [\text{CH}_4][\text{CO}_2] + K_1 k_2 [\text{CH}_4] + K_3 k_4 [\text{CO}_2]} \quad (5)$$

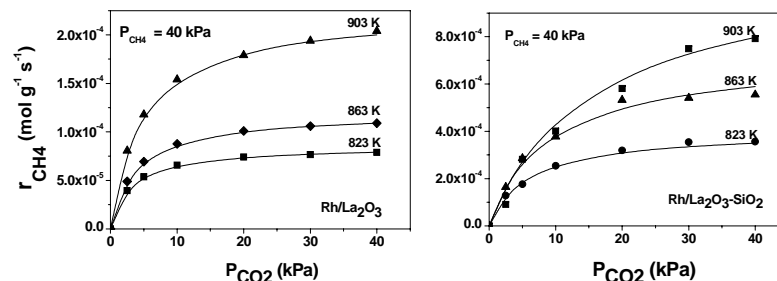


Fig. 1. Fit of the proposed kinetic model for CO₂ reforming of methane.

Significance

The combination of XRD, LRS, XPS and DRIFT techniques supports a reaction mechanism in which the slow steps are the methane decomposition and the surface reaction of the lanthanum oxycarbonate with the carbon residues. This reaction provides a rationale for the stability of the lanthanum-based catalysts.

References

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