Understanding the effect of Sm_2O_3 and CeO_2 promoters on the structure and activity of Rh/Al_2O_3 catalysts for methane steam reforming

Renata Bessa Duarte[a,b], *José M. Corrêa Bueno*[b] *and Jeroen van Bokhoven*[a,c]

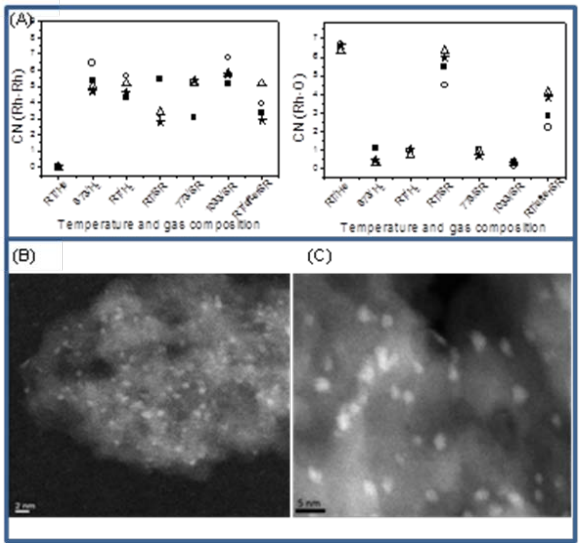
[a] *Institute for Chemical and Bioengineering, Swiss Federal Institute for Technology, Wolfgang-Pauli-Strasse 10, CH-8093, Zürich, Switzerland,* [b] *Universidade Federal de São Carlos, Rod. Washington Luis Km 235, 13565-905 São Carlos-SP, Brazil,* [c] *Paul Scherrer Institute (PSI), 5232 Villigen, Switzerland*

Introduction and Objectives

Conversion of methane into higher value products has been intensively studied because this process is important to reduce our dependence on petroleum. To obtain high methane conversion, an elevated temperature (1033 K or above) is required. The main problems under these conditions are carbon deposition and sintering of active metals, both leading to the catalysts deactivation. This makes development of long-lasting catalysts essential. Recently, it was confirmed that Ru and Rh are the most active metals for methane steam reforming.[1] The most common support for methane reforming catalysts is alumina. Other oxides such as ceria have recently attracted attention mainly due to their oxygen-storage properties and chemical interaction with noble metals. To further enhance the temperature stability of supported ceria it can be promoted with samaria.[2,3] To understand the influence of cerium and samarium oxides on the structure of rhodium nanoparticles and its relation to catalytic performance during methane steam reforming (SR) it is important to study the structure of promoted catalysts under reaction conditions. Giving this, Rh catalysts supported on mixed oxides of Sm_2O_3-CeO_2-Al_2O_3 were investigated by *in situ* by X-ray absorption spectroscopy (XAS) in combination with on-line mass-spectrometry.

Results and Discussion

The values of CH_4 conversion obtained for the catalysts during methane steam reforming were higher for the samples supported in alumina promoted by ceria and samaria. The samples were heated to 773 K and in sequence to 1033 K with dwell times of 1 h. All catalysts showed deactivation with time on stream; however Rh/Al showed the strongest decrease in activity. The Figure (A) shows the coordination numbers for Rh-Rh and Rh-O obtained from the EXAFS analysis of all spectra under the various conditions, where we describe temperature/atmosphere in the x-axis for (■) Rh/Al_2O_3, (○) $Rh/12CeO_2$-Al_2O_3, (Δ) $Rh/12Sm_2O_3$-Al_2O_3, (⋆) $Rh/6Sm_2O_3$-$6CeO_2$-Al_2O_3. Initially at room temperature the samples were fully oxidized. Under reductive atmosphere at high temperature the promoted samples got reduced, however Rh/Al showed lower metallic character. The Rh-Rh



CN for the reduced samples was around 5, indicative of small particles. Differences were also found between the promoted catalysts and Rh/Al during reaction. Under methane SR atmosphere the samples got partially oxidized. With the increase in temperature up t o 773 K, Rh/Al showed a decrease in CN and this could be due re-dispersion of Rh metallic particles owing to CO formation and absorption in the surface, which is an oxidative process. With further increase in temperature up to 1033 K an increase in CN is observed due to the sintering of particles in the unpromoted catalyst. In the samaria-ceria containing samples the Rh-Rh CN remained practically constant with increase in the reaction temperature from 773 K to 1033 K. A possible explanation for the observed behaviour would be the greater metal-support interaction in the presence of promoters. The STEM images for the Rh/Al_2O_3 catalyst after reduction at 873 K (B) and after MSR at 1033 K (C) are depicted in the Figure and they clearly show that sintering of the metallic particles took place during reaction. This process was more pronounced for Rh/Al_2O_3.

Conclusions

The effect of the addition of Sm_2O_3 and CeO_2 on the catalytic behaviour of Rh/Al_2O_3 catalysts was revealed by changes on the structure and eletronic properties of Rh particles. The higher activity observed for the studied Rh catalysts during methane SR was mainly attributed to the high dispersion of the active phase. The improvement in the activity and stability of promoted catalysts is due to the greater Rh-support interaction, which inhibited Rh oxidation and the sintering of the Rh particles, thus maintaining the high dispersion during the drastic reaction conditions. The EXAFS experiments clearly illustrate the alteration of the topology and therefore the lack of stability of rhodium particles when supported in unpromoted alumina.

References

[1] G. Jones, J. G. Jakobsen, S. S. Shim, J. Kleis, M. P. Andersson, J. Rossmeisl, F. Abild-Pedersen, T. Bligaard, S. Helveg, B. Hinnemann, J. R. Rostrup-Nielsen, I. Chorkendorff, J. Sehested, J. K. Nørskov. *Journal of Catalysis* **259** (2008) 147–160

[2] J.B. Wang, W.H. Shih, T.J. Huang, *Appl. Catal. A: Gen.* **203** (2000) 191-199

[3] Y. She, Q. Zheng, L. Li, Y. Zhan, C. Chen, Y. Zheng, X. Lin, *Int. J. Hydrogen energy* **34** (2009) 8929-8936