9A, 7C, 1B101/2003G067

# XAFS study of Ni in $NiK/Al_2O_3$ catalysts for $CO_2$ methane reforming

M.Carmen ROMÁN*[1], Jerónimo JUAN[1], M.José ILLÁN[1], Hiromi YAMASHITA[2]
[1]Department of Inorganic Chemistry, University of Alicante, 03080 Alicante, Spain
[2]Department of Material Science and Processing. Graduate School of Engineering. Osaka University 2-1 Yamada-oka, Suita, Osaka, 565-871 Japan

## Introduction

Ni-based catalysts are under investigation in their application for the $CO_2$ methane reforming. Their main drawback is a poor stability caused, mainly, by a high coking rate [1]. Alkaline and alkaline-earth metals are being investigated as promoters to hinder coke deposition, although a decrease in the reforming activity is usually observed.

In this study we analyze the effect of potassium in the state of Ni in order to find a relation between activity and catalyst structure.

## Experimental

A $Ni/Al_2O_3$ catalyst was prepared by excess solution impregnation using a pelletized $\gamma$-$Al_2O_3$ support and an aqueous solution of $Ni(NO_3)_2.6H_2O$ of the appropriate concentration to obtain about 10 wt% Ni. The K-promoted catalysts were obtained by previous impregnation of the alumina support with an aqueous solution of $KNO_3$ and calcination at 773K for 2h. The solutions used allowed to obtain samples with K/Ni ratios of 0.04, 0.08 and 0.22. The reduction treatment consisted of heating in $H_2$ flow at 773K for 2h.

XAFS measurements were done in samples after the reduction step and after reaction (0.18 g catalyst, mixture $CH_4$:$CO_2$:He (10:10:80) 60 ml/min, 973K, 6h).

The Ni K-edge absorption spectra were recorded in the transmission mode at room temperature, in a range of photon energy extending from 8080 to 9375 eV. A FT-transform was performed on the $k^3$-weighted EXAFS-oscillations over the range 3-12 $Å^{-1}$.

## Results and discussion

Figure 1 shows the FT-EXAFS data obtained for the reduced catalysts. The signals corresponding to NiO and Ni foil have been also included.

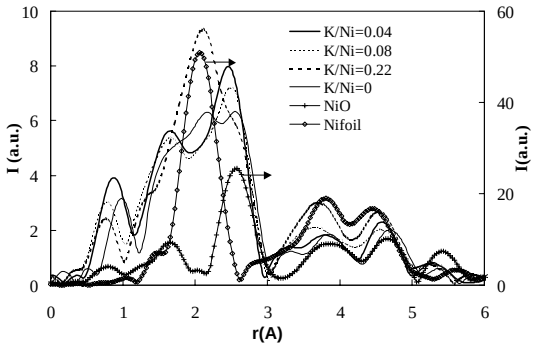


Figure 1. FT-EXAFS of reduced catalysts with different K/Ni ratio.

These results indicate that the addition of K favours the reduction of the Ni phase. It is manifested by the peak at about 2 Å, that clearly appears when the K/Ni ratio is 0.22 and that is coincident with the maximun in the spectrum of Ni foil. For the lower K/Ni ratios this effect is not observed.

The XANES confirm, as well, these results as the intensity of the white line is lower for the sample with the K/Ni ratio of 0.22.

After having been used under reaction conditions for 6h all the catalysts, with and without K, show a very similar Ni structure. And it is very close to that of Ni foil, although probably with a lower coordination number. Figure 2 show the FT-EXAFS obtained for the used samples.

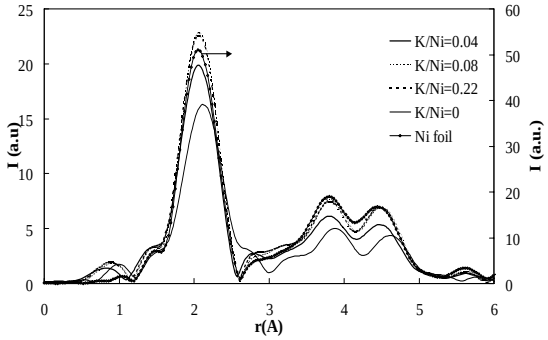


Figure 2. FT-EXAFS of catalyst used in the $CO_2$ methane reforming (973K, 6h).

This means that the samples become activated (reduced) under reaction conditions and that probably there is no need for a previous reduction treatment. The intensity of the white line is only slightly different in the four catalysts, but it is much lower than in NiO although higher than in Ni foil, meaning that Ni atoms interact with some more electronegative element.

It is interesting to point out that according to these results, in the $NiK/Al_2O_3$ catalysts, potassium works as an almost independent catalyst for coke gasification (as a decrease in the amount of coke deposited has been found with K content [2]) without any structural modification of nickel.

## References

[1] M.C.B. Bradford, M.A. Vannice, Catal. Rev. Sci. Eng. 41, 1 (1999).
[2] J. Juan et al., 13th Int. Cong. Catal. Paris, July (2004).

* mcroman@ua.es