9A, 7C, 1B/2003G067

Effect of calcination and reduction of Ni/Al$_2$O$_3$ catalysts analyzed by XAFS

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Introduction

Ni/Al$_2$O$_3$ 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. Preparation of the mentioned catalysts is usually done by impregnation, followed by calcination and reduction steps. Current investigations show a minor effect of the activation treatments in the catalytic activity of the samples. In this study we analyze the effect of calcination and reduction treatments of a Ni/Al$_2$O$_3$ catalyst in the state of Ni in order to find a relation between catalytic properties and structure.

Experimental

A Ni/Al$_2$O$_3$ catalyst was prepared by excess solution impregnation using a pelletized γ-Al$_2$O$_3$ support and an aqueous solution of Ni(NO$_3$)$_2$.6H$_2$O of the appropriate concentration to obtain about 10 wt% Ni. Activation treatments were: i) Calcination: in air at 773K, 12 h, and ii) Reduction: in H$_2$ flow at 773K for 2h.

XAFS measurements were done in the following samples:

CR: calcined and reduced, both fresh and used in reaction

R: only reduced, both fresh and used in reaction

NT: with no treatment, only used in reaction

Reaction conditions: 0.18 g catalyst, mixture CH$_4$:CO$_2$ (50:50), 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 Ni/Al$_2$O$_3$ catalysts CR and R. The signals corresponding to NiO and Ni foil have been also included.

These results show that calcination previous to the reduction treatment has an important effect in the extent of the reduced state, being clearly higher for the CR sample. This was also verified by the XANES data.

As already reported [1,2], the catalysts become further reduced under reaction conditions. It was even suggested that probably there is no need for a reduction treatment [2]. In fact, catalysts CR, R and NT give a similar activity for CO$_2$ methane reforming in the conditions indicated above. However, they differ in selectivity as the amount of coke deposited is not the same (180, 140 and 280 mg/g,

respectively for catalysts CR, R and NT after 6h reaction time).
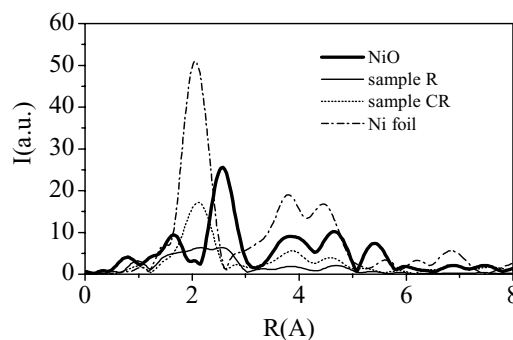

Figure 1. FT-EXAFS of fresh catalysts.

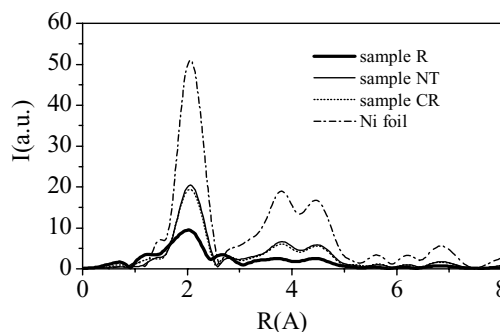The FT-EXAFS spectra obtained for the used catalysts are shown in Figure 2.

Figure 2. FT-EXAFS of catalyst used in the CO$_2$ methane reforming (973K, 6h).

According to these data, the modification of the catalysts under reaction conditions is strongly influenced by the pretreatments. Used catalysts CR and R have Ni particles with a very different structure, being for the first one more similar to that of metallic nickel. On the other hand, it is striking that the used catalyst NT shows, like sample CR, Ni particles with a defined structure. These results reveal the important effect of the conditions of the heat treatment and the nature of the reducing atmosphere. These data also confirm the well known structure sensitivity of the coke deposition reaction.

References

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