XAFS study of Ni/Al,O, catalysts: effect of the support acidity

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Introduction

Supported Ni catalysts are an appropriated choice for the CO_2 methane reforming although, in general, they suffer a high coking rate [1]. It has been shown that the surface chemical properties of the support can affect the catalyst performance by influencing in the Ni structure and the interaction with reactants [2].

In this study we analyze the effect of the support surface acidity in the state of Ni in Ni/Al_2O_3 catalyst after reduction with hydrogen and after 6h reaction time.

Experimental

Three nickel catalysts were obtained by excess solution impregnation of three alumina with different surface acidity. The total nickel content was 10 wt.%. The surface pH has been measured using ASTM-D-3838-05 and the results are presented in Table 1.

Table 1. Catalysts prepared with Al_2O_3 supports with different surface acidity

Support	pН	Catalyst
Al ₂ O ₃	2,9	Ni/Al-2,9
Al_2O_3	8,2	Ni/Al-8,2
Al_2O_3	9,1	Ni/Al-9,1

XAFS measurements were done in samples after the reduction step (H_2 , 773K, 2 h.) and after reaction (0.18 g catalyst, mixture CH_4 :CO₂: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.

These results indicate that the surface acidity of the alumina support has a clear effect on the reduction of nickel: The reduction degree increases with the surface acidity of the alumina. This is observed by the increase in the intensity of the peak placed at about 2\AA that corresponds to Ni-Ni bonds in metallic nickel. This behavior can be explained by a different interaction between the aluminum oxide and the nickel phase related with the surface acidity. It is known that NiO can react with Al₂O₃ to form a highly stable NiAl₂O₄ which has a

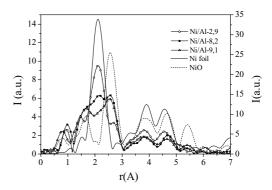


Figure 1. FT-EXAFS of the reduced catalysts.

lower reducibility than NiO [3]. According to the present results, it seems that the formation of $NiAl_2O_4$ is hindered by the acidic properties of the alumina support.

XANES data confirm, as well, these results as the intensity of the white line is lower for the catalyst supported on the acidic alumina.

Figure 2 shows the FT-EXAFS obtained for the used samples. After having been used under reaction conditions, the three catalysts show a very similar Ni structure, that is very close to that of Ni foil, although probably with a lower coordination number. It means that the reaction conditions used are extreme enough to produce the complete reduction of Ni, even if it is forming the NiAl₂O₄ species.

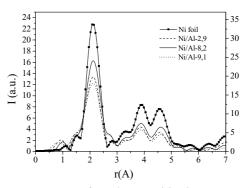


Figure 2. FT-EXAFS of catalyst used in the CO₂ methane reforming (973K, 6h).

References

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