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Role of chromium in the stability of Ni/Al_2O_3 catalysts for natural gas reforming

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Abstract

Ni/Al_2O_3 and Ni–Cr/Al_2O_3 catalysts prepared with melt salts of Ni and Al ($Al/Ni = 0.5$) were studied by magnetic measurements, electron microscopy and catalytic properties. An increase in the catalytic activity and stability during partial oxidation of methane and CO_2 reforming reactions at 973 K was produced by the chromium addition. The Ni–Cr alloy was formed by reduction at high temperature (1073 K), producing a dilution effect of Ni crystal and modifying the basicity of the support. Both effects would inhibit the catalyst deactivation increasing the useful life and stability of the nickel.

Keywords: Magnetic studies; Ni/Al_2O_3 catalyst; Chromium promoted catalyst; Synthesis gas reactions

1. Introduction

Reaction conditions used in methane reforming are the main cause for the deactivation of nickel supported catalysts. These catalysts are frequently used in industry, and the deactivation produced by carbon deposition and metallic phase sintering affects their catalytic properties. Therefore, different metals that modify the active phase were added to increase the useful life and the stability of the nickel supported catalysts.

A previous work [1] showed that the addition of chromium and molybdenum reduced carbon deposition and the sulfur poisoning.

The aim of this work was to study the structure and reactivity of Ni/Al_2O_3 catalyst promoted by chromium. Magnetic techniques were used to correlate structural and catalytic properties due to the ferromagnetic character of nickel. The activity, selectivity and stability of the resulting systems were analyzed in the partial oxidation of methane (OX), and CO_2 reforming (R) reactions (1) and (2).

$$CH_4 + 1/2\,O_2 \leftrightarrow CO + 2H_2 \qquad (1)$$

$$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2 \qquad (2)$$

2. Experimental

Two catalysts were used: Ni/Al_2O_3 and Ni–Cr/Al_2O_3, which were obtained by impregnation of α-Al_2O_3 (T-708 Girdler) with melt salts of Ni and

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Al $\{(NO_3)_2\ Ni \cdot 6H_2O$ and $(NO_3)_3Al \cdot 9H_2O\}$ with an atomic ratio $(Al/Ni) = 0.5$. The metal content is 5 wt.% of nickel. Chromium was incorporated, in an atomic ratio $(Cr/Ni) = 0.1$, by impregnation of the precursor with a solution of $Cr(NO_3)_3$. After the impregnation, the solids were dried during 1 h at 383 K and calcined in air at 673 K for 3 h.

The catalysts were characterized by magnetic measurements, scanning transmission electron microscopy (STEM/EDX) and catalytic activity tests.

Magnetic measurements were performed by the Weiss extraction method over the samples reduced during 2 h in a flow of dry hydrogen (4 l/h) at temperature between 773 and 1073 K and a heating rate of 5 K/min. The magnetization (M) was measured in an electromagnet that provides a field (H) up to 21 kOe at 294 K.

From experimental data $(M$ vs. $H)$, the saturation magnetization (M_s) can be determined by extrapolation $M(1/H)$ to $1/H \rightarrow 0$, according to Langevin's equation for high fields [2].

The amount of Ni^0 was obtained by dividing M_s by the specific magnetization of the Ni (s) at the experimental temperature $(s = 54.4$ emu cgs at 300 K). It was possible to deduce the dispersion $(d\%)$ from the relative increase of saturation magnetization $(\Delta M_s/M_s)$ observed when samples were outgassed.

The size and composition of metallic particles were determined by the use of scanning transmission electron microscopy associated with energy dispersive X-ray emission (STEM/EDX) using a JEOL 2010 instrument.

The experimental catalytic measurements in the partial oxidation of methane (OX) and CO_2 reforming (R) reactions were carried out in a conventional flow tubular quartz reactor. The operating conditions were atmospheric pressure, 973 K, a flow rate of 65 $cm^3\ min^{-1}$, with a feed composition for OX: $N_2/CH_4/O_2 = 11/2/1$, and for R: $N_2/CH_4/CO_2 = 6/1/1$. The catalyst weight was 0.020 g, and the catalyst particle size between 0.12 and 0.15 mm. These conditions were defined so as to eliminate the intraphase and interphase transport resistances.

Stability tests were determined at constant temperature (973 K) for 24 h. The stability was evaluated in terms of an activity coefficient a_{CH_4}, which is the ratio between the rate of consumption of CH_4 after 24 h on stream and the initial rate value. The feed flow composition and the reaction products were analyzed by gas chromatography. The carbon content was determined on post-reaction samples using temperature programmed oxidation with thermogravimetric analysis (TPO/TGA) in a Shimadzu TGA-50H equipment.

3. Results and discussion

Table 1 shows results obtained by magnetic measurements for the Ni/Al_2O_3 and $Ni–Cr/Al_2O_3$ catalysts reduced at 773, 923 and 1073 K. A remanent magnetization (M_r) for all samples at room temperature was observed. This indicates that a fraction of Ni particles, due to their large size, is not in thermodynamic equilibrium with the magnetic field applied. For this conditions, the Langevin equation [2] is not applied and it is not possible to calculate the average diameter of nickel particles from the $M(H)$ curve. The 2 M_r/M_s ratio provides the fraction of particles with size larger than the critical diameter $(D_c = 15$ nm), which may be calculated with the aid of crystallographic anisotropy constants [3].

The reduction degree $(R\%)$ expressed as the ratio of Ni^0 to initial Ni^{2+}, was calculated from the saturation magnetization (M_s). The Ni/Al_2O_3 catalyst presents a $R\%$ that is nearly constant at the different reduction temperatures. The incomplete reduction $(R\%$ between 80% and 84%) may be attributed to the existence of interaction between the nickel and the support produced during the preparation steps. The Ni–Cr sample presents a $R\%$ of about 85% at 923 K and decreases approximately up to 60% at 1073 K. This indicates the formation of

Table 1
Magnetic data of catalysts

Catalysts	Temp. reduction (K)	2 M_r/M_s	$M_s/54.4$	R (%)
Ni/Al_2O_3	773	52	0.82	83
	923	51	0.87	84
	1073	46	0.86	80
$Ni–Cr/Al_2O_3$	773	52	0.81	83
	923	42	0.80	85
	1073	27	0.57	60

Table 2
Changes in saturation magnetization (Ms)
n.d.: not determined.

Catalysts	Temp. reduction (K)	M_s^a (emu cgs)	M_s^b (emu cgs)	d (%)
Ni/Al_2O_3	773	45.7	44.9	n.d.
	923	45.7	47.3	n.d.
	1073	49.9	47.0	n.d.
$Ni–Cr/Al_2O_3$	773	42.1	45.8	6.6
	923	42.8	46.6	8.2
	1073	28.6	32.4	11.8

[a] In H_2 atmosphere.
[b] In vacuo.

nonferromagnetic phases at the expense of metallic nickel. It is expected that with the increase of the reduction temperature, the M_s value will also increase, but this behavior is not observed for the Ni–Cr catalyst (Table 1). In this case, the steep drop of the M_s value at 1073 K may be attributed to the formation of Ni–Cr intermetallic compounds, which do not provide any contribution to the magnetization values [4].

Samples were studied by STEM/EDX in order to check the formation of these Ni–Cr intermetallic compounds. The Ni–Cr sample reduced at 1073 K showed two kinds of bimetallic particles: (a) particles with a diameter between 5 and 6 nm, enriched in Cr; (b) particles with a diameter of about 50 nm, enriched in Ni, in good agreement with magnetic results.

During experiments of hydrogen adsorption and desorption (Table 2), both catalysts showed a different magnetic behavior. With the H_2 desorption, the magnetization (M_s^+) would increase as a consequence of a larger amount of Ni^0 superficial atoms. However, in the Ni/Al_2O_3 catalyst the magnetization did not increase after H_2 desorption. This behavior can be explained, according to Dalmon et al. [5], by the presence of two kinds of H_2 species involved in the interaction with the surface. These H_2 species cause opposite effects on the M_s magnetization. The molecular hydrogen (H_2) bonded to the Ni^0 produces a M_s decrease whereas the atomic hydrogen (H) that reacts with unreduced species (Ni^+) leads to a M_s increase according to Eq. (3):

$$H_2 \underset{Ni^0}{\leftrightarrow} 2H \quad \text{and} \quad 2H + 2Ni^+ \leftrightarrow 2Ni^0 + 2H^+ \tag{3}$$

The proton formed migrates toward the basic sites of alumina by a spillover redox phenomenon from the metallic phase to the support.

An increase of magnetization M_s^+ is observed on the Ni–Cr catalyst after hydrogen desorption. This result suggests a change in the support basicity and/or a total reduction of nickel. For the bimetallic catalyst, it was possible to deduce the dispersion (d%) from this relative increase of the saturation magnetization ($\Delta M_s/M_s$) when the samples were outgassed (Table 2). The Ni–Cr catalyst reduced at 1073 K presents a better dispersion of the metallic phase and a larger alloying effect.

In previous studies [6], the IR spectrum of CO adsorbed at 298 K was obtained on Ni/Al_2O_3 sample reduced at 1073 K presenting three bands assigned to: CO adsorbed on Ni^{2+} (at 2150 cm^{-1}), in agreement with the incomplete reduction observed by magnetism; CO adsorbed linearly at Ni^0 (at 2050 cm^{-1}) and CO adsorbed to bridged species (at 1930 cm^{-1}). On the $Ni–Cr/Al_2O_3$ sample, only the band attributed to linear species at 2050 cm^{-1} was observed, whereas the band attributed to species bridged at 1930 cm^{-1} was not present. This fact is consistent with the dilution of ensembles of Ni atoms by chromium atoms and with the formation of Ni–Cr alloy, as already evidenced by magnetic and TEM data. The band of IR spectrum near 2200 cm^{-1} observed in Ni–Cr catalyst corresponds to the presence of chromium ions, which would be responsible for the basicity change of the support.

Table 3 presents the results of the activity test for the catalysts pre-reduced at 1073 K. The methane conversion (X_{CH_4}%) and H_2/CO ratio obtained for the reaction of partial oxidation of methane (Eq. (1)) and CO_2 reforming (Eq. (2)) are shown. It is possible to observe that the addition of Cr improves the CH_4 conversion levels, which is reasonable taking

Table 3
Results of catalytic activity test performed at 973 K (for experimental conditions, see the text)

Catalysts	Reaction	X_{CH4} %	H_2/CO
Ni/Al_2O_3	OX	75	2.2
	R	60	1.0
$Ni–Cr/Al_2O_3$	OX	85	2.3
	R	65	1.0

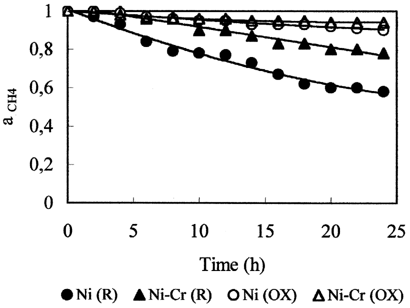

Fig. 1. Results of stability test for OX and R reactions at 973 K.

into account that Ni–Cr samples showed better metallic dispersion.

As previously mentioned in the Introduction, the deactivation, both by sintering and by carbon formation is thermodynamically and kinetically promoted, under the operating conditions corresponding to OX and R reactions, and therefore, the analysis of the stability of the active phase is a very important fact. The catalytic stability, evaluated in terms of the activity coefficient a_{CH_4}, is shown in Fig. 1. The higher stability of both catalytic systems with respect to OX reaction may be attributed to the fact that the oxygen presence in the feed inhibits the carbon deposition. If the catalytic stability is analyzed with respect to the most deactivating reaction, CO_2 reforming (R), the Ni–Cr sample presents notably higher stability.

Post-reaction R samples were analyzed by TPO/TGA to determine the carbon content. These analyses show that the carbon content in the Ni catalyst was about 11 wt.%, whereas in the Ni–Cr catalyst it was 6 wt.%. This indicates that the addition of Cr reduces the amount of carbon formed, although it is not completely eliminated.

The higher stability of the bimetallic catalyst may be attributed to a dilution effect of ensembles of Ni atoms, suggested by results of magnetism and IR techniques. This decrease of Ni atoms necessary to generate intermediary surface species in the formation of carbon deposits would lead to a lower deposition rate of carbon.

4. Conclusions

The Ni–Cr/Al_2O_3 catalyst with an atomic ratio Cr/Ni = 0.1, reduced at 1073 K, showed a different magnetic behavior as a consequence of the formation of nonferromagnetic phases. This sample showed the better catalytic activity levels, which is reasonable taking into account its higher metallic dispersion. With respect to the catalytic stability in the most deactivating reaction (R), the bimetallic sample showed a notably higher stability and the lesser carbon content deposited. The lower deposition rate of carbon observed may be attributed to a dilution effect of ensembles of Ni atoms, evidenced by results of magnetism, TEM and IR techniques. This dilution effect decreases the Ni atoms necessary to generate the intermediary surface species in the formation of carbon deposits.

References

[1] C.E. Quincoces, A. Diaz, N. Firpo, M. Montes, M.G. González, Proc. XIV Simp. Iberoam. Cat. 3 (1994) 225.
[2] M. Primet, J.A. Dalmon, G.A. Martin, J. Catal. 46 (1977) 25.
[3] G.A. Martin, B. Imelik, C. R. Acad. Sci. 270 (1970) 127.
[4] T. Szilagyi, H. Praliaud, M. Primet, G.A. Martin, Appl. Cat. 11 (1984) 235.
[5] J.A. Dalmon, C. Mirodatos, P. Tulier, G.A. Martin, in: G. Pajonk, S. Teichner, J. Germain (Eds.), Spillover of Adsorbed Species, 1983, p. 169.
[6] M.G. González, C.E. Quincoces, N.N. Nichio, B. Moraweck, G. Martin, Proc. XV Simp. Iberoam. Cat. 2 (1996) 829.