

CHARACTERIZATION OF STEAM-REFORMING CATALYSTS

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Abstract - The effect of the addition of Mg and Ca to Ni/ α -Al₂O₃ catalysts was studied, aiming to address their role as promoters in the steam reforming reaction. Temperature-programmed reduction and H₂ and CO temperature-programmed desorption experiments indicated that Mg interacts with the metallic phase. Mg-promoted catalysts showed a greater difficulty for Ni precursor reduction besides different probe molecule (H₂ and CO) adsorbed states. In the conversion of cyclohexane, Mg inhibited the formation of hydrogenolysis products. Nonetheless, the presence of Ca did not influence the metallic phase.

Keywords: steam reforming, Ni, promoters.

INTRODUCTION

The process of steam reforming of hydrocarbons, developed in 1924 (Rostrup-Nielsen, 1984), is the main industrial method for production of hydrogen. Hydrogen is a fundamental feedstock for refining processes such as hydrotreating and hydrocracking and for petrochemical processes such as the synthesis of methanol, methanol to gasoline, and the synthesis of ammonia (The British Sulphur Corp. LTD. 1992; Twigg, 1997) and hydrocarbon synthesis via Fischer-Tropsch processes (Dry, 1984; Anderson, 1984).

The demand for hydrogen has been increasing during the past years due to the need to reduce the sulfur content in fuels. Thus, the production of hydrogen has become relevant in both economic and social terms, as it is related to quality of life (Peña et al., 1996; Rostrup-Nielsen, 1984; Lercher et al., 1999).

As steam reforming of methane is a highly endothermic process ($\Delta H = +49.6$ kcal/mol), it has to

be carried out at high temperatures. Under these reaction conditions, deactivation of the catalyst due to carbon deposition on its surface occurs (Rostrup-Nielsen, 1984).

Commercial catalysts consist essentially of Ni supported on α -alumina. Earth alkaline metals (Mg and Ca) are normally used in the catalyst formulations to improve stability (Peña et al., 1996). The effect of these promoters has usually been ascribed to the acceleration of the steam-carbon reaction and to the neutralization of the acidity in the support, retarding cracking and polymerization reactions (Twigg, 1987). However, Rostrup-Nielsen and Alstrup (1999) showed that carbon formation and the activity in the steam reforming reaction are influenced by the size of the nickel surface ensembles. In the present work, the role of promoters was investigated by means of physicochemical characterization techniques (temperature-programmed reduction and temperature-programmed desorption) and through the dehydrogenation of cyclohexane, a

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model reaction which allows probing of the metallic surface of the catalyst.

EXPERIMENTAL

Preparation of Catalysts

The support used was α -Al₂O₃ (ALCOA 1.5 m²/g). Ni catalysts with 5 wt%, 10 wt% and 20 wt% were prepared by incipient wetness, using Ni(NO₃)₂·6H₂O as precursor. After impregnation, the samples were dried at 120°C and calcined at 650°C for 6 hours. A 20 wt% Ni/ α -Al₂O₃ sample was also prepared by wet impregnation. The drying and calcination procedures were the same as those used for the samples prepared by incipient wetness.

Mg- and Ca-containing catalysts were prepared by impregnating α -Al₂O₃ (incipient wetness) with Mg(NO₃)₂·6H₂O or Ca(NO₃)₂·4H₂O precursors, followed by drying at 120°C and calcination at 650°C (Cheng et al., 1996). The samples were then impregnated with the Ni(NO₃)₂·6H₂O aqueous solution, followed by the drying and calcination procedures already cited. By this procedure, 5% MgO-10% Ni/ α -Al₂O₃, 5% CaO-10% Ni/ α -Al₂O₃ and 5% MgO-5% CaO-10% Ni/ α -Al₂O₃ catalysts were obtained.

Temperature-Programmed Reduction (TPR)

TPR experiments were performed in a multipurpose unit coupled to a Balzers Omnistar quadrupole mass spectrometer. The samples (150 mg) had been previously dried at 150°C for 30 min under He flow (30 mL/min). For the TPR a 5% H₂/Ar gas mixture, a heating rate of 10°C/min and a final temperature of 1000°C were used.

Temperature-Programmed Desorption (TPD)

H₂ and CO TPD experiments were conducted in the same unit as that used for the TPR experiments. The pretreatment of the samples consisted in drying at 150°C for 30 min under He flow (30 mL/min), followed by reduction in H₂ at 800°C for 1h. The surfaces of the catalysts were purged by flowing He at 800°C for 1h. The samples were cooled to room temperature and exposed to pulses of 5% H₂/Ar until saturation. The temperature was then increased to 800°C at a heating rate of 20°C/min while the desorption of H₂ was monitored. A similar procedure was followed for the CO TPD experiments.

Cyclohexane Conversion

This reaction was performed at 10⁵ Pa in a flow microreactor. The samples (100mg) had been previously dried at 150°C for 30 min under N₂ flow (30 mL/min) and reduced at 500°C under H₂ flow (30 mL/min). The reactant mixture was obtained by bubbling hydrogen through a saturator containing cyclohexane at 12°C (H₂/C₆H₁₂ = 13.6). The temperature was kept at 320°C and the conversion was kept below 10%. The effluent gas phase was analyzed by an on-line gas chromatograph (HP 5890) equipped with a flame ionization detector and an HP-Innowax capillary column. Under these conditions, there was no significant deactivation of the catalysts.

RESULTS AND DISCUSSION

Temperature-Programmed Reduction (TPR)

The temperature-programmed reduction profiles of the catalysts with Ni contents of 5, 10 and 20 wt% supported on α -Al₂O₃ are presented in Figure 1. The 5% Ni/Al₂O₃ catalyst showed reduction peaks at 450°C and 516°C. The lower temperature peak may be attributed to the reduction of NiO with less interaction with the support, while the peak with the higher temperature corresponds to the reduction of NiO by incorporation of Al⁺³ ions originating in the dissolution of α -Al₂O₃ during the impregnation step (Richardson and Twigg, 1998, Agnelli et al., 1987). For the samples with higher Ni contents there was a shift in the reduction peak to higher temperatures.

The reduction profile of the catalysts with promoters are presented in Figure 2. The reduction peaks occurred at higher temperatures, because Ca and Mg hydrophilic promoters increase the incorporation of water on the catalyst surface, inhibiting the reduction. As observed in Figure 1, the peak at the lower temperature corresponds to NiO reduction while the peak at the higher temperature is related to NiO with Al⁺³. A greater difference in the temperature of the peaks was observed for Mg promoted catalysts. With Ca the effect is reduced as observed by Dias and Assaf (2001). These results point out to an greater influence of Mg on the Ni precursor, which probably affects the final state the catalyst after activation. The following temperature-programmed desorption results confirmed this hypothesis.

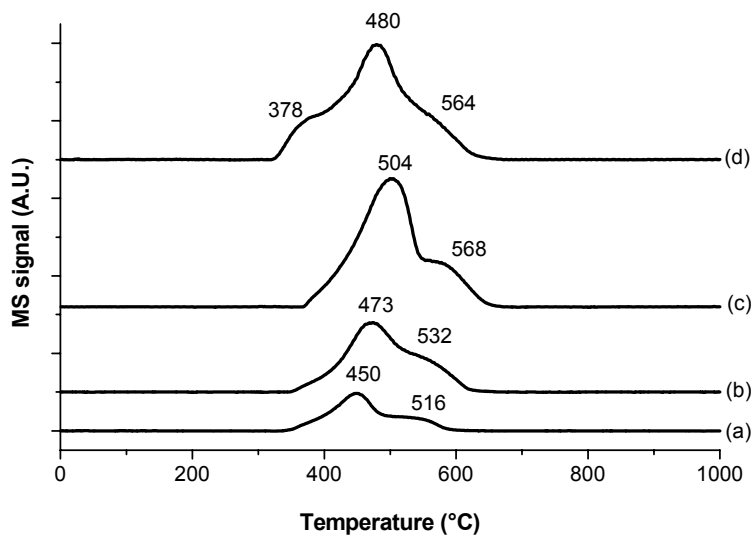


Figure 1: TPR profiles for Ni catalysts: (a) 5% Ni/ α -Al₂O₃, (b) 10% Ni/ α -Al₂O₃, (c) 20% Ni/ α -Al₂O₃, (d) 20% Ni/ α -Al₂O₃ (wet impregnation).

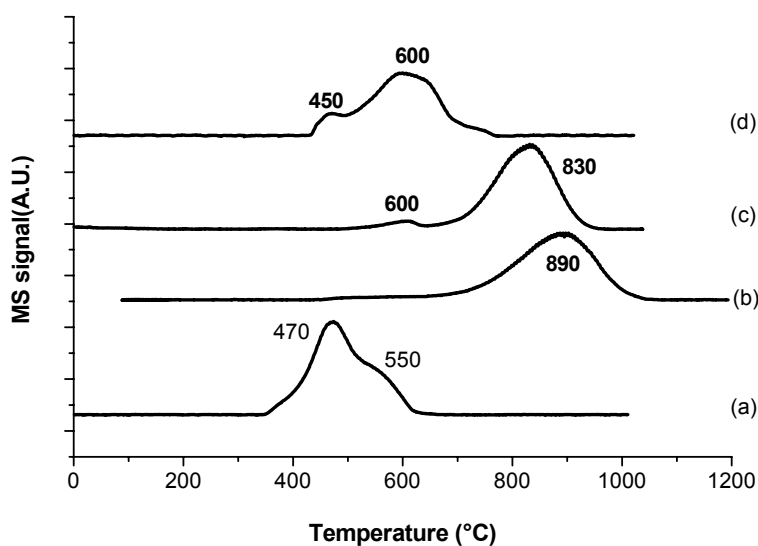


Figure 2: TPR profiles for Ni catalysts: (a) 10% Ni/ α -Al₂O₃, (b) 5% MgO-10% Ni/ α -Al₂O₃, (c) 5% MgO-5% CaO-10% Ni/ α -Al₂O₃, (d) 5% CaO-10% Ni/ α -Al₂O₃.

Temperature-Programmed Desorption (TPD)

The H₂ TPD results are presented in Figures 3 and 4. The H₂ desorption profiles for Ni/ α -Al₂O₃ catalysts had desorption peaks between 170°C and 400°C. The first peak is usually attributed to H₂ desorbed from the metal particles and indicates the exposed fraction of Ni atoms. The peaks at the higher temperatures are attributed to hydrogen located in the subsurface layers or to H₂ due to spillover on the support. In the case of 5% Ni/ α -Al₂O₃, only one peak was observed, while in the case

of the 10% Ni/ α -Al₂O₃ catalyst a larger amount of desorbed hydrogen from the metal surface was observed.

For Mg-promoted catalysts (Figure 4), the peaks are broader, pointing to a continuous distribution of adsorption strength on the catalyst support. The Ca-containing catalysts had only two desorption peaks.

The CO TPD profiles are presented in Figures 5 and 6. For Ni/ α -Al₂O₃ catalysts a desorption peak at 180°C and a desorption peak at 400°C was observed. The lower temperature peak is related to CO molecularly adsorbed on flat Ni particles, while the

peak at the higher temperature is attributed to CO dissociatively adsorbed on the steps (Hu and Ruckenstein, 1996).

The 5% MgO-10%Ni/ α -Al₂O₃ catalyst showed a decrease on the desorption peak at higher temperature, indicating the influence of Mg on the Ni surface. With Ca, a different effect was observed, with the higher temperature peaks being more important. Furthermore, CO₂ desorption was also observed during the high temperature CO desorption peak. This CO₂ formation results probably from the Boudouard reaction ($2\text{CO} \rightarrow \text{C} + \text{CO}_2$). The CO₂ release was more intense for the Ca-containing

catalysts than for the Mg-containing catalysts. This result is consistent with the temperature-programmed reduction results that showed Mg modifies the Ni phase. NiO and MgO may form solid solutions (Hu and Ruckenstein, 1996), which may explain the dilution of Ni atoms by Mg after reduction of the catalyst. This dilution inhibits the Boudouard reaction (Ruckenstein and Hu, 1995). This effect impacts the performance in the steam reforming of hydrocarbons, for which Ni is the active phase. The modification of Ni active phase by Mg was further demonstrated by the following conversion of cyclohexane catalytic runs.

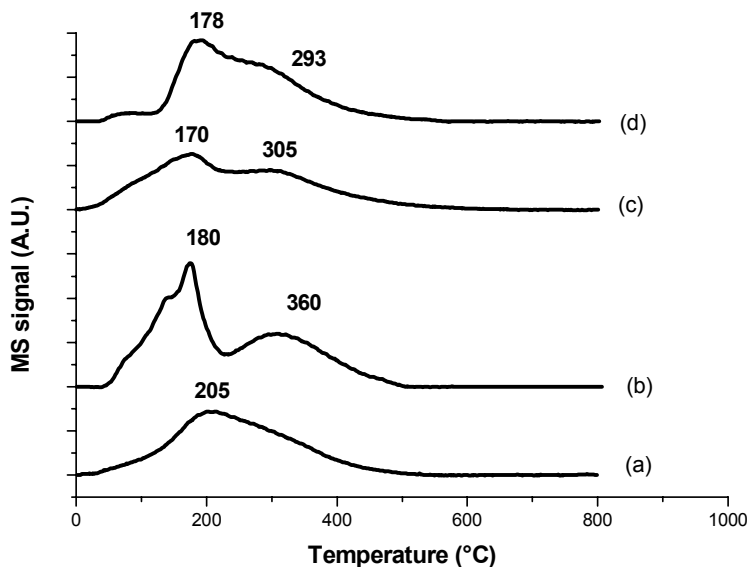


Figure 3: H₂ TPD profiles for Ni catalysts: (a) 5% Ni/ α -Al₂O₃, (b) 10% Ni/ α -Al₂O₃, (c) 20% Ni/ α -Al₂O₃, (d) 20% Ni/ α -Al₂O₃ (wet impregnation).

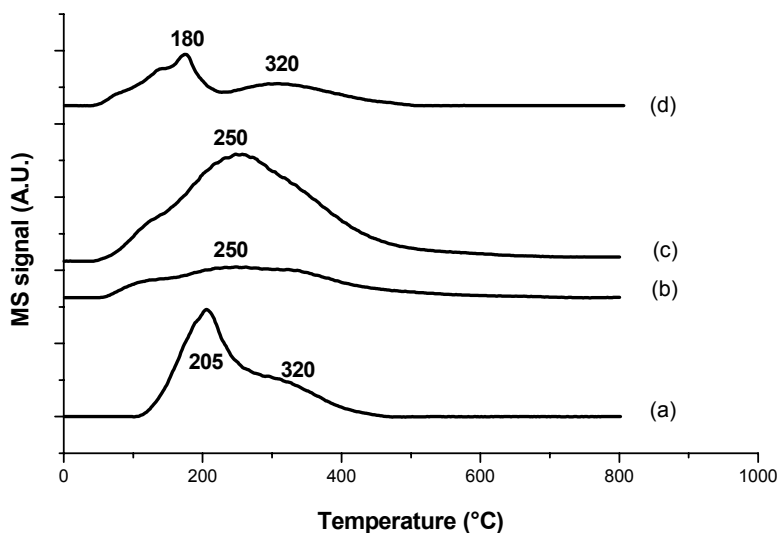


Figure 4: H₂ TPD profiles for Ni catalysts: (a) 10% Ni/ α -Al₂O₃, (b) 5% MgO-10% Ni/ α -Al₂O₃, (c) 5% MgO-5% CaO-10% Ni/ α -Al₂O₃, (d) 5%CaO-10% Ni/ α -Al₂O₃.

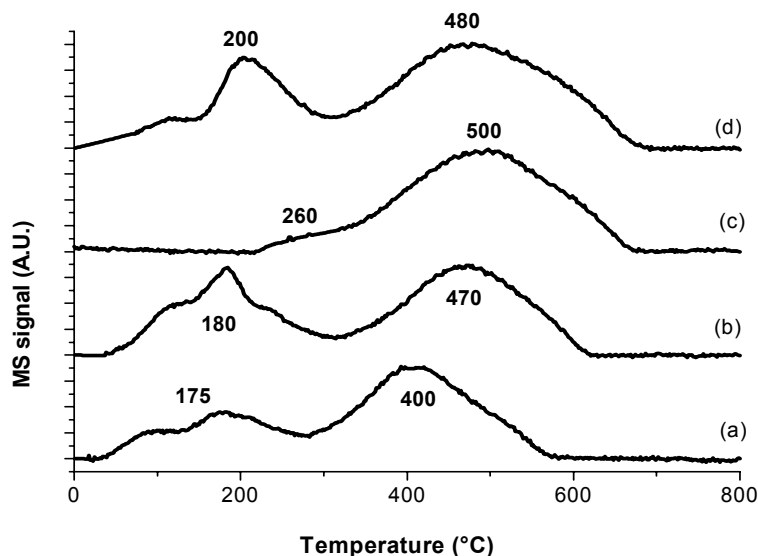


Figure 5: CO TPD profiles for Ni catalysts: (a) 5% Ni/ α -Al₂O₃, (b) 10% Ni/ α -Al₂O₃, (c) 20% Ni/ α -Al₂O₃ (d) 20% Ni/ α -Al₂O₃ (wet impregnation).

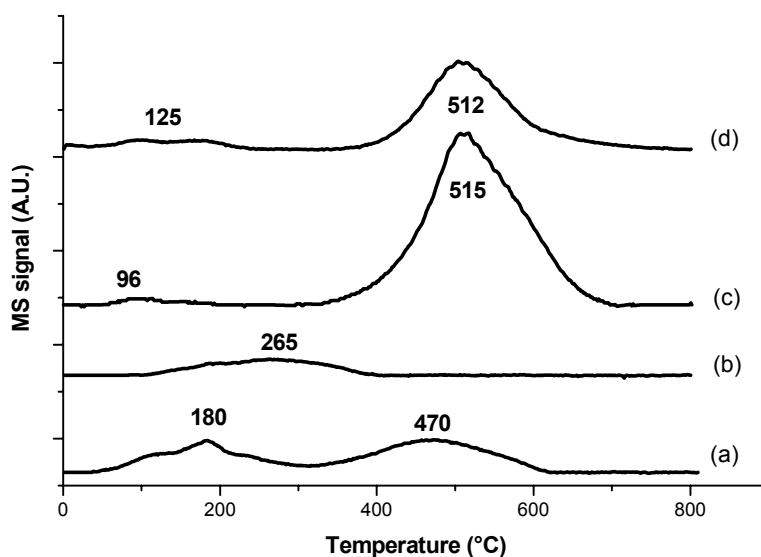


Figure 6: CO TPD profiles for Ni catalysts: (a) 10% Ni/ α -Al₂O₃, (b) 5% MgO-10% Ni/ α -Al₂O₃, (c) 5% MgO-5%CaO-10% Ni/ α -Al₂O₃, (d) 5%CaO-10% Ni/ α -Al₂O₃.

Conversion of Cyclohexane

For Ni catalysts, the conversion of cyclohexane caused not only the formation of benzene, through the dehydrogenation reaction, but also the formation of n-hexane through the hydrogenolysis reaction.

Table 1 shows the dehydrogenation reaction rates. The different catalysts had dehydrogenation reaction rates of the same order of magnitude. The addition of the promoters altered the reaction rates

with a more important effect in the case of the addition of Mg.

Table 1 also contains the hydrogenolysis reaction products. The addition of Mg suppressed the formation of hydrogenolysis products, indicating a modification of Ni by this promoter. The presence of Ca, however, did not cause this effect.

The turnover frequency (TOF) results are presented in Table 2. The number of Ni-exposed atoms was obtained from irreversible CO

chemisorption at room temperature ($\text{CO}/\text{Ni}_s = 1$). Essentially, the turnover frequency for the dehydrogenation reaction was not modified by the promoter. This is consistent with the structure insensitivity of this reaction. However, the hydrogenolysis reaction is structure sensitive. Thus, suppression of the hydrogenolysis reaction indicates a modification of Ni particles by Mg. This may explain the promoter role in the steam-reforming catalysts. Mg hinders the structure-sensitive reactions that result in coke formation. This is a mechanism similar to that observed for bimetallic catalysts: the promoter suppresses the structure-

sensitive reactions, which require large ensembles of atoms in order to occur, while structure-insensitive reactions require smaller ensembles of atoms and are practically not influenced at all (Sinfelt, 1983). The geometric model of dilution of active phase atoms by the promoters atoms seems to be suitable in our case, with the Mg ion particles diluting Ni particles. These results are in agreement with the findings of Rostrup-Nielsen and Alstrup (1999) who showed that the dilution of Ni atoms by Cu atoms affects the catalysts behavior in the steam reforming reaction. Additional experiments are necessary to evaluate possible electronic effects.

Table 1: Cyclohexane conversion at 320°C on Ni Catalysts.

Catalyst	Dehydrogenation Rate ($\times 10^{-3} \text{ mol/h/g}_{\text{cat}}$)	Hydrogenolysis Rate ($\times 10^{-3} \text{ mol/h/g}_{\text{cat}}$)
5% Ni/ α -Al ₂ O ₃	16.0	3.2
10% Ni/ α -Al ₂ O ₃	15.0	7.6
20% Ni/ α -Al ₂ O ₃	14.0	9.3
20% Ni/ α -Al ₂ O ₃ wet imp.	11.0	8.8
5%MgO-10% Ni/ α -Al ₂ O ₃	7.0	0
5%CaO-10% Ni/ α -Al ₂ O ₃	9.1	8.1
5%MgO-5%CaO-10% Ni/ α -Al ₂ O ₃	3.3	0

Table 2: TOF for Cyclohexane Conversion

Catalyst	CO irreversible chemisorption ($\mu\text{mol/g}_{\text{cat}}$)	TOF for dehydrogenation (s^{-1})	TOF for hydrogenolysis (s^{-1})
5% Ni/ α -Al ₂ O ₃	8.4	0.53	0.11
10% Ni/ α -Al ₂ O ₃	11.6	0.36	0.18
20% Ni/ α -Al ₂ O ₃	22.8	0.17	0.11
20% Ni/ α -Al ₂ O ₃ wet imp.	19.1	0.16	0.13
5% MgO-10% Ni/ α -Al ₂ O ₃	4.6	0.43	0
5% CaO-10% Ni/ α -Al ₂ O ₃	14.7	0.17	0.15
5% MgO-5% CaO-10% Ni/ α -Al ₂ O ₃	6.4	0.14	0

CONCLUSIONS

The effect of the addition of Mg and Ca to Ni/ α -Al₂O₃ catalysts was studied in this work. From the experimental results the following conclusions were drawn:

- 1) Addition of Mg causes the Ni precursor reduction to occur at a higher temperature.
- 2) The spillover and metal-adsorbed hydrogen states are modified by Mg. Similar experiments were observed for adsorbed carbon monoxide.

3) Mg inhibits the hydrogenolysis reaction, indicating a dilution of Ni atoms by Mg.

4) Ca does not strongly modify the metallic phase. The role of Ca is probably related only to decrease the acidity of the support.

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