# Steam Reforming of Naphthalene on Ni–Cr/$Al_2O_3$ Catalysts Doped with MgO, $TiO_2$, and $La_2O_3$

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*Magnesium, lanthanum, and titanium oxide-doped nickel–chromium/alumina catalysts were prepared and their performances assessed in the steam reforming of naphthalene (T: 1,023 K; water-to-naphthalene molar ratio: 16, atmospheric pressure, residence time of 0.55 s; and* $GHSV = 10{,}080\ h^{-1}$*). Impregnation of nickel and chromium in MgO- and* $La_2O_3$*-doped alumina gave the most active, stable catalysts. Nickel was active in aromatic ring opening, while chromium inhibited the encapsulation of the nickel crystallites by inactive carbon filaments. The use of MgO had a significant effect on the robustness of catalyst due to the formation of* $MgAl_2O_4$ *spinel phase.* $La_2O_3$ *was necessary to drive the reaction toward total gasification. The addition of* $TiO_2$ *gave poor activity and a soft catalyst. Some of the catalyst preparations were characterized before and after reaction by XRD, SEM, DTA, and surface measurements. The physical and catalytic properties are discussed in light of these characterizations. The catalyst optimized during this study showed high crystallite dispersion, excellent crushing strength, and good thermal stability. When comparing the data obtained using* $Ni/Al_2O_3$ *with* $Ni-Cr/Al_2O_3 \cdot MgO \cdot La_2O_3$*, it is clear that the improved catalyst reached higher conversion and gas yield performances.*

## Introduction

In the past decade, steam-reforming feedstocks have been limited to sulfur-free gas containing predominantly methane and desulfurized naphtha with boiling points up to about 473 K (Leftin et al., 1985). In recent years, the desirability of reforming sulfur-containing feeds and complex feedstocks rich in aromatics, as well as the degradation of polycyclic aromatic compounds from waste pyrolysis and gasification, led us to consider an appropriate process for the treatment of these feedstocks for which naphthalene was chosen as a surrogate molecule.

When properly understood and applied, steam reforming of naphthalene could lead to other applications. For example, the valorization (by hydrogenation and hydrocracking) of heavy aromatic fractions derived from catalytic cracking requires heavy consumption of hydrogen; hence there is a need for a conversion process that utilizes water in place of hydrogen (Bonneau et al., 1991; Grenoble, 1978; Duprez et al., 1980). Another possible application is related to environmental concerns. Of particular interest is the cleaning of gases from thermal (pyrolysis and gasification) treatment of biomass and solid wastes: the catalytic steam reforming of tar present in flu gas offers a number of advantages over traditional methods of tar removal, such as scrubbing or thermal cracking (Bangala et al., 1997). The temperature of the steam-reforming treatment is essentially the same as in the thermal converter, and depending upon conditions, the product gas is known as hydrogen-rich producer or synthesis gas (Abatzouglou et al., 1997).

Supported metal catalysts, and in particular, supported nickel catalysts are the common catalysts used in a variety of steam-reforming processes (Van den Berg et al., 1985). These catalysts, which have been essentially designed for paraffinic hydrocarbons reforming, are not necessarily well-suited for the molecular structures present in tar compounds and heavy feedstocks (Bangala et al., 1997). The reasons for their rapid deactivation have been reported by several investigators as described below.

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Bartholomew et al. (1980) have shown the loss of activity as a result of encapsulation of nickel crystallites by inactive carbon filaments or layers. Their data provided evidence that the metal concentration has a significant effect on the deactivation of the $Ni/Al_2O_3$ by carbon deposition, suggesting that a low metal concentration may be more resistant to deactivation by carbon due to its stronger interaction with the support and a high metal dispersion. For example, during catalytic methanation of coal-derived gases, they observed that 30% $Ni/Al_2O_3$ lost 60% of its initial activity within 10–15 h of treatment, while 3% $Ni/Al_2O_3$ lost only 20%. Bartholomew and Sorensen (1983) also reported that under high-temperature reaction conditions, conventional nickel catalysts lose their surface area quite rapidly.

Deactivation by coking mechanisms is complex because coke precursors can arise from reactant molecules, products, intermediates, and combinations thereof. However, in agreement with Bartholomew's findings (1980, 1983), other studies (Rostrüp-Nielsen and Trimm, 1977; Baher and Harris, 1979) had proposed two explanations for the carbon-induced reduction of the activity of nickel catalysts: (1) encapsulation of nickel crystallites by layers of inactive carbonaceous material, and (2) the formation of inactive, bulk nickel carbide phases.

Besides carbon deposition and sintering, Corella and Monzon (1988) reported that the deactivation can also be caused by poisoning due to sulfur, metals, basic compounds of nitrogen, and the loss of active agent by volatilization. Sulfur or chlorine poisoning of catalysts can be interpreted in terms of electronic effects and surface morphology changes. Strong electronic effects have been suggested for sulfur poisoning of Ni by Goodman and Kiskinova (1981a): one sulfur atom deactivates about ten Ni atoms sites. The same authors, Goodman and Kiskinova (1981b), explored the effects of three electronegative poisons (P, S, Cl) on the Ni catalyst. The presence of these electronegative atoms on the surface reduced the adsorption rate. The extent of poisoning correlates well with the increased electronegativity of the sequence P, S, Cl. Somorjai and Hashimoto (1984) reported that the [111] face of Ni develops a [100] orientation in the presence of sulfur, and proposed that the presence of electron acceptors may alter the surface free energies of the crystal planes, which will then rearrange to new planes with lower free energies. Thus the electron acceptors cause a recrystallization of the surfaces. In other words, the presence of electron acceptors destabilizes the metal clusters (Ruckenstein and Halachev, 1981).

Beltrame and Torrazza (1979) reported the adsorption of polycyclic aromatic by-products on acidic sites of the carrier, followed by the formation of carbon deposits on the catalyst. The deposits foul the surface and plug catalyst pores, causing the loss of catalytic activity, physical destruction of catalyst pellets and increases in pressure drop through the reactor. The sensitivity of the $\gamma$-$Al_2O_3$ structure toward water vapor was also reported to be another reason for the decline in catalyst activity.

Taking into account the difficulties encountered with Ni catalysts, there has been interest in developing catalysts for steam reforming with the aim of reducing the coke formation as well as increasing robustness and resistance to chlorinated and sulfur-containing feedstocks at high temperature and high steam environments.

Very limited information is available on catalytic steam reforming of polycyclic aromatic hydrocarbons. We thought that it would be highly interesting to develop catalysts having greater robustness and resistance to formation of and deactivation by deposits of carbon at high temperatures and at high $H_2O$/naphthalene molar ratios.

The aim of our study was to investigate the effect of loading of the active metal, the role of chromium as promoter, and the effect of certain oxides, such as MgO, $La_2O_3$, and $TiO_2$, on mechanical, thermal stability, and coke-formation resistance during steam reforming of naphthalene.

## Behavior of Promoters During the Reforming Reaction

The enhancement of Ni catalytic properties produced by a promoter is the subject of few theories. Laine et al. (1985) grouped these theories as follows (1) the promoter increases the number of active sites; and (2) the promoter has a significant effect on the surface metal dispersion and pore dimensions.

Bartholomew et al. (1980) performed a detailed study on the activity of Mo-, Co-, and Pt-promoted $Ni/Al_2O_3$ catalyst. Their data provided evidence that Ni–Pt and Ni–Co are significantly more, and Ni–Mo significantly less resistant to deactivation by carbon compared to Ni only. They proposed that the behavior of a given catalyst toward deactivation by carbon may relate to its ability to hydrogenate atomic carbon as it is formed by dissociation of oxygenated species. If the rate of hydrogenation of atomic carbon is substantially lower than the rate of formation, then accumulation and transformation to filamentous carbon will occur. Thus, they postulate that Pt and Co act as promoters for hydrogenation of active carbon, thereby lowering the overall extent of inactive carbon formation and deactivation. On the other hand, the molybdenum oxide sites in the $Ni$-$Mo/Al_2O_3$ may serve to dissociate carbon, but do not readily activate hydrogen (Fowler and Barthol-omew, 1979). This means that $Ni$-$Mo/Al_2O_3$ is a relatively poor hydrogenation catalyst and is rapidly deactivated by accumulated carbon.

The role of tungsten-promoted $Ni/Al_2O_3$ catalyst was discussed by Bonneau et al. (1991) during steam reforming of 1-methylnaphthalene. They reported that tungsten promoted the selective opening of the naphthalene ring into benzene and toluene. Chromium was reported as a promoter having hydrogenation–dehydrogenation and dehydrocyclization activity (Hensley et al., 1975).

The addition of small amounts of alkali metal has been known to modify the activity and the selectivity of heterogeneous catalysts, as well as to improve their lifetime (Rostrüp-Nielsen, 1984; Trimm, 1985). Chen and Shiue (1988) found that nickel catalysts promoted by Li, Na, K, or Ca could be kept away from sulfur poisoning. Alkali species are generally interpreted in terms of electronic effects (Proliaud et al., 1986; Chen and Chen, 1990). For example, potassium as a promoter is known to act as an electron donor to metal (McClory and Gonzalez, 1984). On the other hand, alkali species may serve to dilute the metal surface and subsequently suppress adsorption of coke precursors on the metal surfaces and in the acidic sites of catalysts (Blackmond et al., 1986). Morita et al. (1983) also reported that alkali additives may promote the steam gasification of carbonaceous residues.

## Experimental Section

### *Catalyst preparation*

Our strategy for catalyst development has been described in our previous work (Bangala et al., 1997). The improved Ni-based [UdeS] catalyst was prepared by thoroughly mixing the required amounts of $\gamma$-$Al_2O_3$ (Johnson Matthey Company, 99.99%, 82 $m^2 \cdot g^{-1}$, 0.01 micron powder, pore volume: 0.54 $cm^3 \cdot g^{-1}$), $La_2O_3$ or $TiO_2$, and MgO, followed by subsequent calcination at 1,073 K for 6 h. This mixture was used as support. To prepare 30 g of catalyst, 24 g of the mixture was used. The active element and promoter were introduced by impregnation using aqueous solutions of metal precursors: nickel nitrate [22.3 g of $Ni(NO_3)_2 \cdot 6H_2O$] and chromium nitrate [11.5 g of $Cr(NO_3)_3 \cdot 9H_2O$]. The chromium nitrate was first impregnated and the mixture was dried at 383 K for 20 h. The nickel nitrate was subsequently impregnated and the mixture was dried at 383 K for 20 h. After drying, the mixture was thoroughly mixed with 20–25 mL of 1 N solution of nitric acid, which was used as binder. The mixture was molded into cylindrical pellets of 3-mm diameter and aged in an oven at 383 K for 24 h. After aging, the pellets were placed in a furnace and were calcined at 1,023 K for 6 h. The catalysts were then cooled to room temperature and stored in a sealed glass bottle until they were used in the catalytic steam reforming tests with naphthalene.

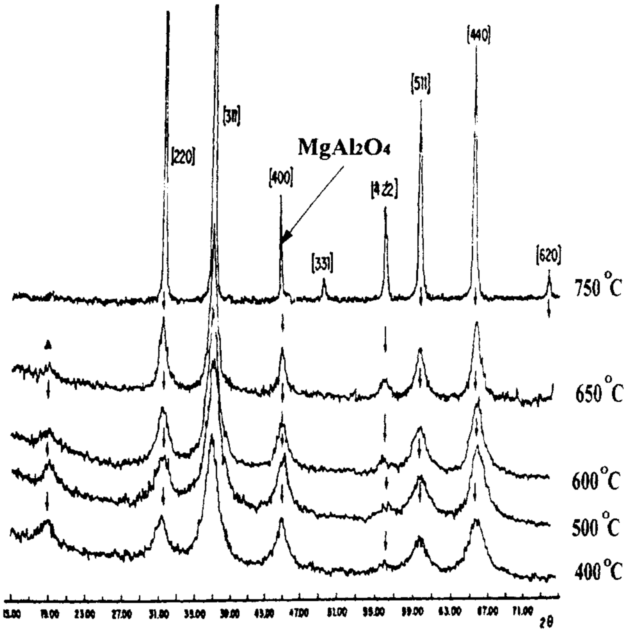


**Figure 1. XRD diffraction patterns of ($Al_2O_3$ + MgO) structure as a function of calcination temperature.**

### *Catalyst characterization*

The prepared catalysts were characterized by X-ray diffraction (XRD), DTA, SEM, and surface-area measurements. XRD measurements were carried out in a Rigaku diffractometer model using monochromated Cu K-$\alpha$ radiation. The calculated interplanar distances were compared with standard values. The diffraction pattern of the MgO-doped $Al_2O_3$ support confirmed that a $MgAl_2O_4$ crystalline phase was present (Figure 1). The catalyst optimized during this study showed good crystallinity, as measured by XRD, and had a high crushing strength (Bangala, 1996). DTA studies were performed with an American Instrument TG equipment model with a transducer coil as sensor, and the results showed that the improved catalyst has good thermal stability when compared to commercial dolomite and zeolite catalysts (Bangala, 1996). In order to characterize the morphology of carbon and the presence of chlorine or sulfur in the catalyst, SEM studies were performed in a VG microscope equipped with an X-ray energy-dispersion analyzer. The results showed filamentous forms. This is in good agreement with observations reported by Bernado and Lacava (1982). The total surface area of the $Al_2O_3$ and the mixed $Al_2O_3$–MgO, both heated at 1,073 K, were measured using the dynamic pulsing technique on a Micromeritics Pulse Chemisorb 2,700 unit. Nitrogen was used as the adsorbent. The total surface area of the calcined $Al_2O_3$ was 58 $m^2 \cdot g^{-1}$, while the total surface areas of fresh $Al_2O_3$ and $Al_2O_3$–MgO were, respectively 82 $m^2 \cdot g^{-1}$ and 72.8 $m^2 \cdot g^{-1}$. This in itself is an advantage of support stabilization.

### *Apparatus and procedure*

The experimental setup used in this work has been described elsewhere (Bangala et al., 1997). It is a continuous-flow reactor with a fixed-bed catalytic system operated at 1,023 K and barometric pressure. The fixed bed was typically loaded with 45 g of catalyst. The reactor was electrically heated. Nitrogen was used to carry the naphthalene vapors into the reactor. The flow rate of nitrogen was calibrated in order to obtain the required flow rate of naphthalene. The flow of nitrogen was 3 $L \cdot min^{-1}$ carrying 0.5 $g \cdot min^{-1}$ of naphthalene. The water was pumped at a flow rate of 1.1 $g \cdot min^{-1}$ in order to achieve a GHSV of 10,080 $h^{-1}$. The gas leaving the reactor was fed through two condensers, connected in series. Most of the unconverted feed, liquid products, and steam were recovered in the first condenser. The noncondensible gases, which included $C_1$–$C_4$ hydrocarbons, carbon monoxide, carbon dioxide, and hydrogen were analyzed by gas chromatography using molecular sieve (5A) and a Porapak Q column. Determination of $C_1$–$C_4$ was done by the Porapak Q column. Hydrogen in the product gases was determined by the molecular sieve column. All the catalysts were tested under the same experimental conditions: GHSV: 10,080 $h^{-1}$; residence time: 0.55 s; water-to-naphthalene molar ratio: 16; and atmospheric pressure. Their activity and performance are given in terms of conversion, gas yield, and the amount of coke deposited on the catalysts.

## Results and Discussion

### *Effect of metal loading*

Significant articles have been published concerning the effect of metal loading and the metal-particle dimensions on the reforming of some typical compounds (Corolleur et al., 1972; Brunelle et al., 1976; Santacesaria et al., 1978). However, there are a few studies (Bonneau et al., 1991; Duprez et al., 1982) concerning the influence of both parameters with polyaromatics as feed. Four series of $Ni/Al_2O_3$ catalysts with

5, 10, 15, and 20 wt. % Ni were impregnated in a high-purity $Al_2O_3$ powder as mentioned earlier. After impregnation, the samples were dried at 383 K for 20 h and then heated in air stream to 1,073 K for 6 h. All tests were carried out at 1,023 K, GHSV: 10,080 $h^{-1}$, and a residence time of 0.55 s at atmospheric pressure.

Figure 2 shows the effect of metal loading on naphthalene conversion and yield of dry gas (Figure 2a); product gas distribution (Figure 2b); coke yield (Figure 2c); and catalyst weight loss (Figure 2d). As can be seen in Figure 2a the conversion and gas yield increase with the loading percentage of nickel until 15% and decrease above this percentage. In agreement with the trends reported by Bartholomew and Farrauto (1976), we attributed this decrease to the low dispersion of nickel at higher metal loadings. The maxima in the selectivities of hydrogen and carbon monoxide occurs at metal loadings of 15%. Hydrocarbons, $C_2$–$C_4$ (ethylene, propane, and butane) were not detected in the produced gas, in disagreement with Apesteguia et al. (1978), who reported that the C–C bond scission on acidic sites occurs mainly with formation of propane and butane, whereas methane is formed through hydrogenolysis on the metal. Our results could be explained in light of the nature of sites in catalyst. Since the presence of hydroxyl sites plays a major role in the reforming of hydrocarbons (Dydykina and Robinovich, 1972), we suggest that the $C_2$–$C_4$ hydrocarbons are the intermediate products that undergo (over hydroxyl sites) steam reforming into CO, $CO_2$, and hydrogen. It also can be seen in Figure 2c that coke yield continuously increased when metal loading was increased, indicating that deactivation produced by cok-

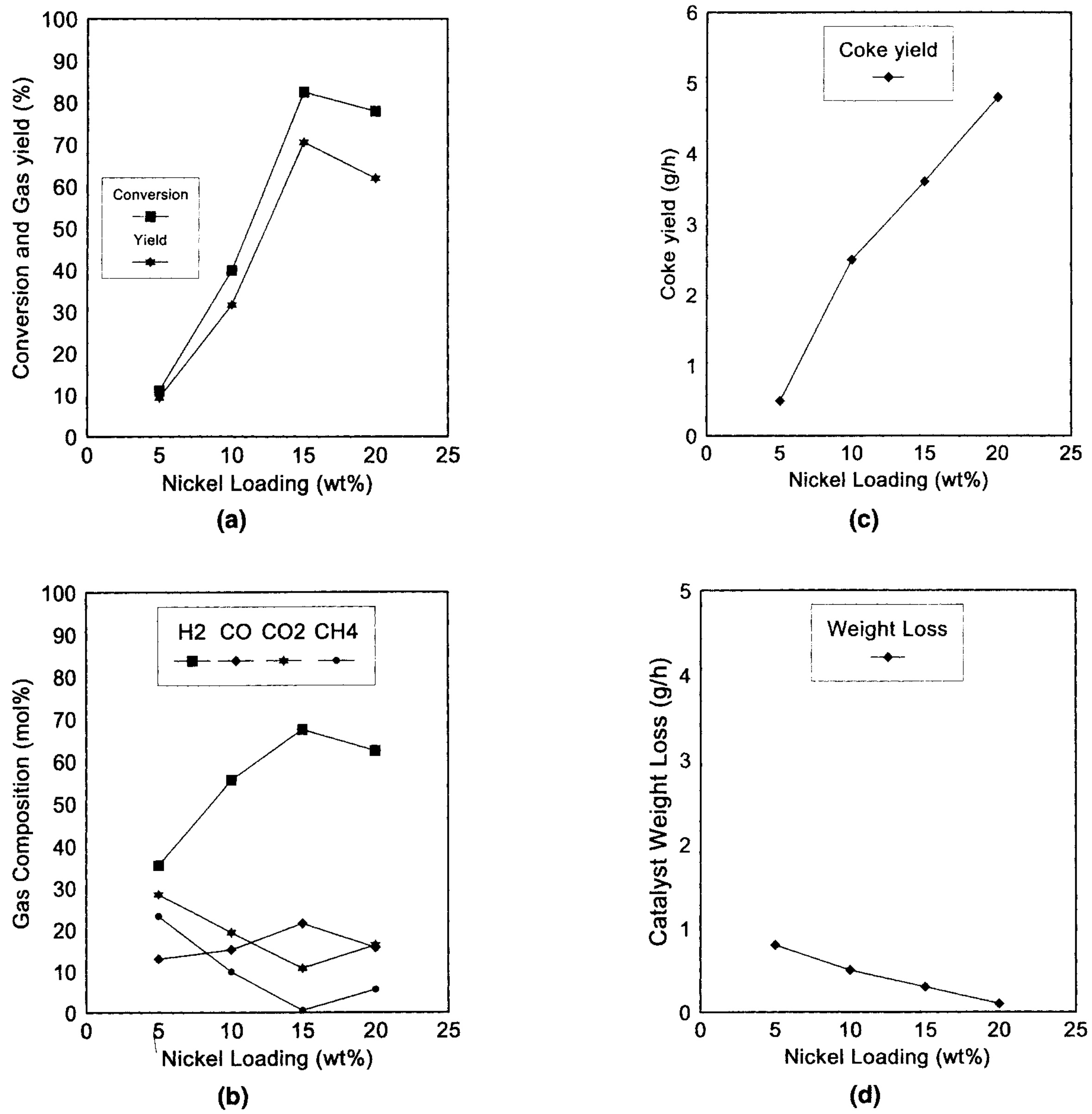


**Figure 2. Conversion and gas yield (a); gas composition (b); coke yield (c); and catalysts weight loss (d) as a function of nickel loading.**

*T*: 1,023 K; steam/naphthalene molar ratio: 16; GHSV: 10,080 $h^{-1}$; residence time: 0.55 s.

ing is related to metal loading, in agreement with Richardson and Crump (1973), who reported that higher metal loading would cause more dehydrogenation of hydrocarbons. This may lead to more hydrogen-deficient hydrocarbons, which tend to be precursors of coke formation on the catalyst. From our results, it clearly appears that 15% of metal loading would be an appropriate choice. The conversion obtained was 85% and the gas yield was 71%. We then decided to investigate the role of calcination temperature in order to increase the catalyst activity.

### *Effect of temperature calcination on $Ni/Al_2O_3$ catalyst activity*

Analytically pure $Ni(NO_3)_2 \cdot 6H_2O$ was used in the preparation of a catalyst containing 15% of nickel. Solutions of this salt were impregnated onto $\gamma$-alumina; after impregnation the samples were dried in air at 383 K followed by calcination at different temperatures (773 K, 873 K, 923 K, 1,023 K, and 1,073 K) for 6 h. Five catalysts were thus prepared and tested under the same conditions: GHSV: 10,080 $h^{-1}$; residence time: 0.55 s; water/naphthalene molar ratio: 16; temperature: 1,023 K.

Figures 3a–3d show the effects of calcination on the activity of catalyst. The following points can be made: (1) the conversion and gas yield decrease with increasing calcination temperature; (2) the catalysts calcined at 773 K–873 K show high performance in terms of conversion (100%) and gas yield (95%). Nevertheless, they have poor stability (after 2 h on stream, the catalysts lost 23% of their initial weight); (3) the coke deposits increase while the catalyst weight loss decreases with calcination temperature; (4) the selectivities for

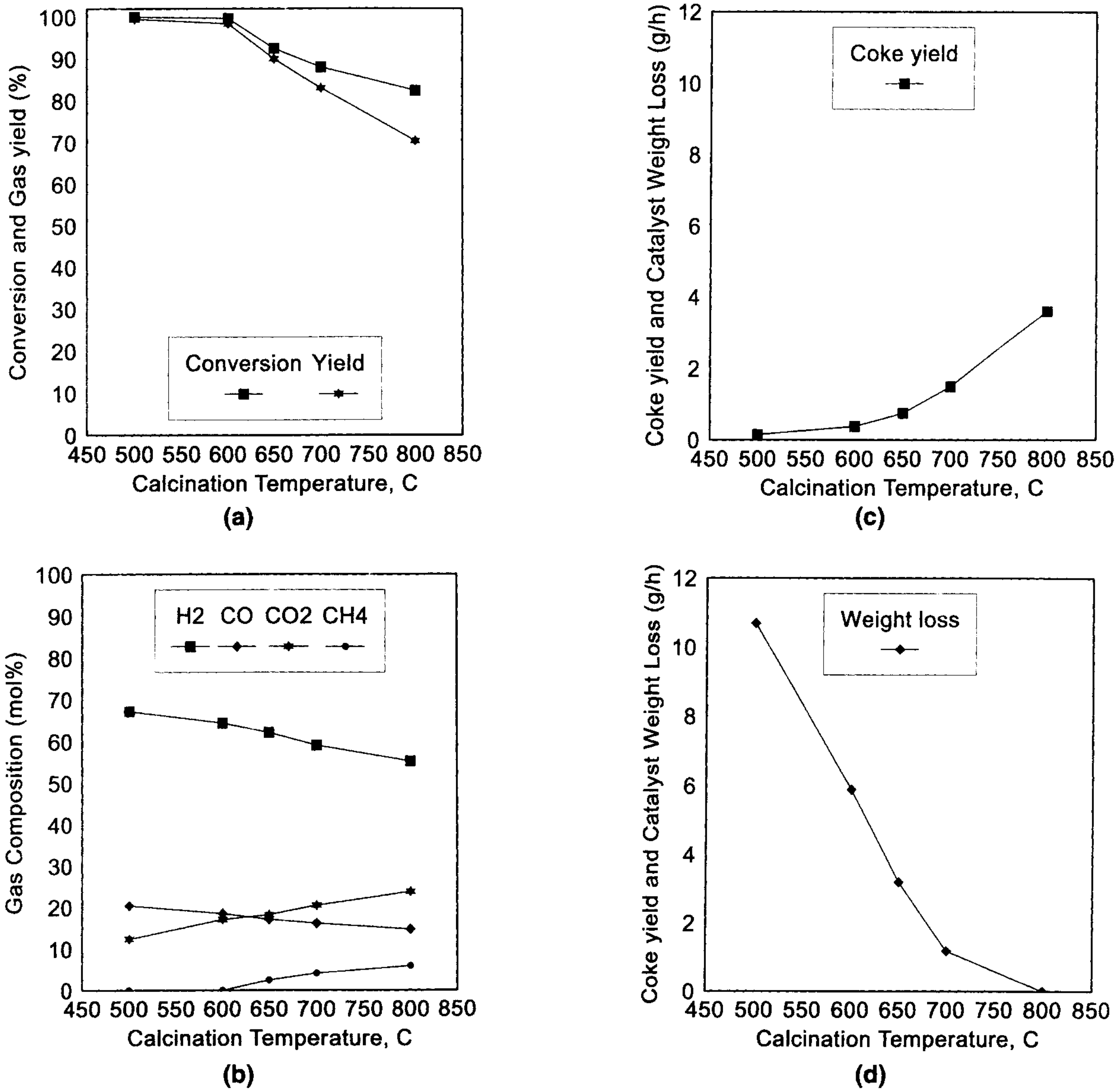


**Figure 3. Conversion and gas yield (a); gas composition (b); coke yield (c); and catalysts weight loss (d) as a function of calcination temperature.**

*T*: 1,023 K; steam/naphthalene molar ratio: 16; GHSV: 10,080 $h^{-1}$; residence time: 0.55 s.

hydrogen and carbon monoxide decrease. The carbon dioxide changes only slightly. The observation of lower activity but robustness for catalysts calcined above 1,023 K has at least two possible explanations: (1) increasing the temperature of calcined leads, by sintering, to relatively large particles of nickel oxide; subsequently, the dispersion of metal crystallites decreases (Bartholomew and Boudart, 1972) and the activity declines; (2) at high calcination temperature NiO interacts with $Al_2O_3$ to form a very stable $NiAl_2O_4$ spinel that cannot be reduced even under very severe, high-temperature conditions. The presence of spinel increases the robustness of catalyst, but reduces the number of sites responsible for steam reforming. The high-temperature solid-state reaction of NiO with $Al_2O_3$ to form a $NiAl_2O_4$ spinel is well documented in the literature (Swift and Lutinski, 1965; Andrew, 1976; Bartholomew and Farrauto, 1976). The decrease of active sites was not apparent from experimental evidence. The X-ray diffraction scans of nickel–alumina catalysts in this study showed considerable overlap of Ni, NiO, and alumina, making it practically impossible to differentiate various phases and to estimate crystallite sizes (Bangala, 1996).

### *Effect of MgO doping $Al_2O_3$ support*

The search for a more stable catalyst was undertaken by mixing $Al_2O_3$ support with MgO oxide as the first step. Their concentrations were selected in order to obtain 5 wt. % MgO and 60 wt. % $Al_2O_3$ in the final formulation with the other additives. The mixture was calcined at different temperatures (923 K, 1,023 K, 1,073 K, and 1,123 K). These four samples

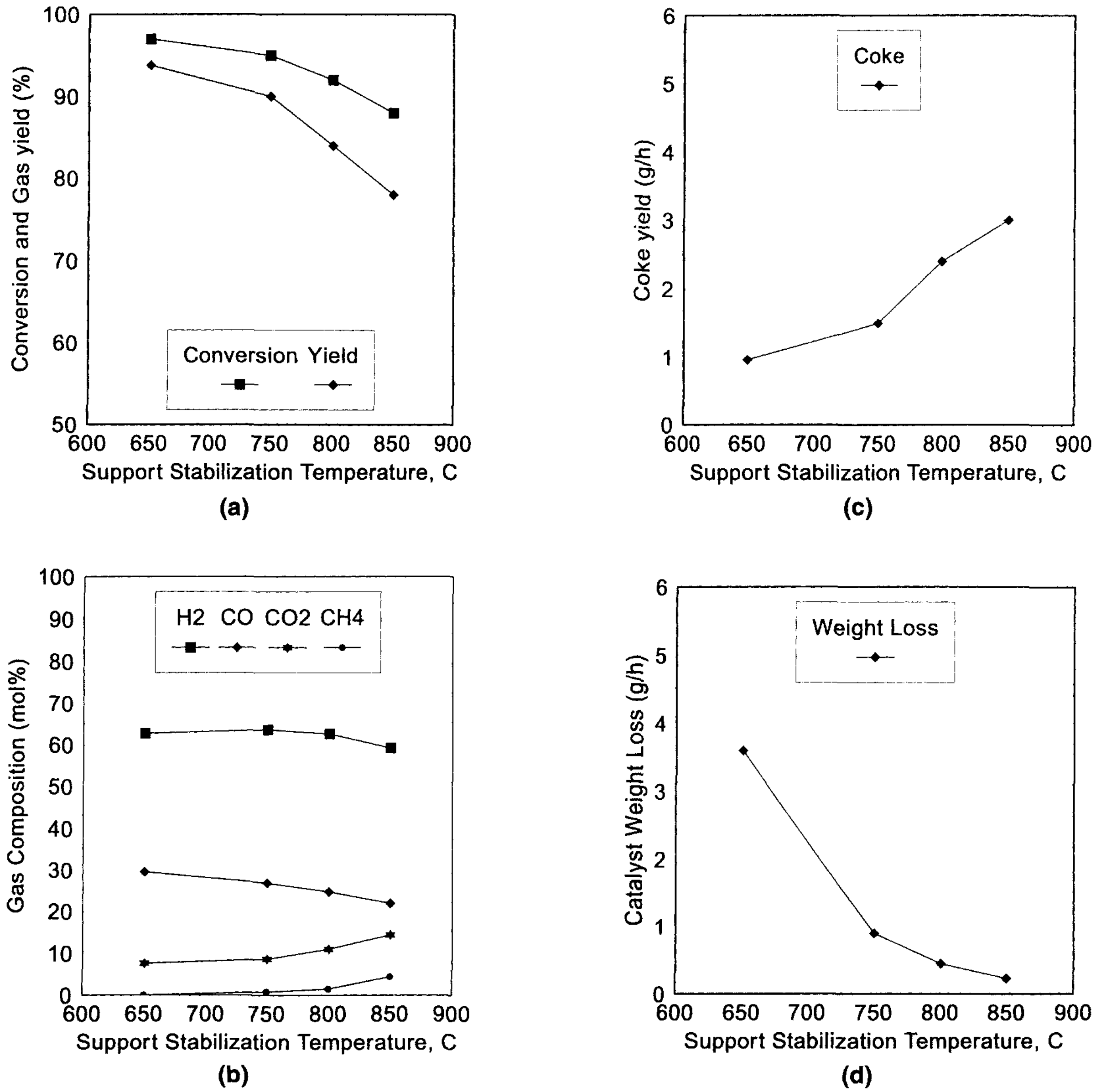


**Figure 4. Conversion and gas yield (a); gas composition (b); coke yield (c); and catalysts weight loss (d) as a function of support stabilization temperature.**

*T*: 1,023 K; steam/naphthalene molar ratio: 16; GHSV: 10,080 $h^{-1}$; residence time: 0.55 s.

were used as support. Each support was impregnated with a solution of $Ni(NO_3)_2 \cdot 6H_2O$. After impregnation, the samples were dried at 383 K for 4 h, followed by calcination at 873 K for 6 h. The catalysts, containing 15 wt. % nickel were tested at the conditions mentioned earlier.

The diffraction pattern (Figure 1) of the mixed oxides ($Al_2O_3 + MgO$) confirmed that $MgAl_2O_4$ spinel phase is present in the samples calcined at 1,023 K. The intensity of this phase increases with calcination temperature; this is in agreement with the trends reported by Chen et al. (1988). The mixed oxides treated at different temperatures had significant influence on the activity and robustness of the Ni–alumina catalysts. As it can be seen in Figure 4a, the conversion and gas yield decrease for the catalyst, whose supports were treated above 1,023 K. The coke formation increases while the catalyst weight loss decreases with stabilization temperature. The solid-state formation of $MgAl_2O_4$ spinel by reaction of MgO with $Al_2O_3$ at high temperature has significant influence on the fraction of the total hydroxyl sites on $Al_2O_3$. In view of a previous study (Dydykina and Robinovich, 1972), which shows that hydroxyl sites present in the carrier are mainly responsible for the steam reforming of hydrocarbons, we attributed the decline of conversion and gas yield to the reduction of hydroxyl sites with increasing stabilization temperature.

In order to obtain a more detailed understanding of the MgO loading effects, we prepared four catalysts containing 5, 10, 20, and 25 wt. % MgO. Figure 5 shows the effects of

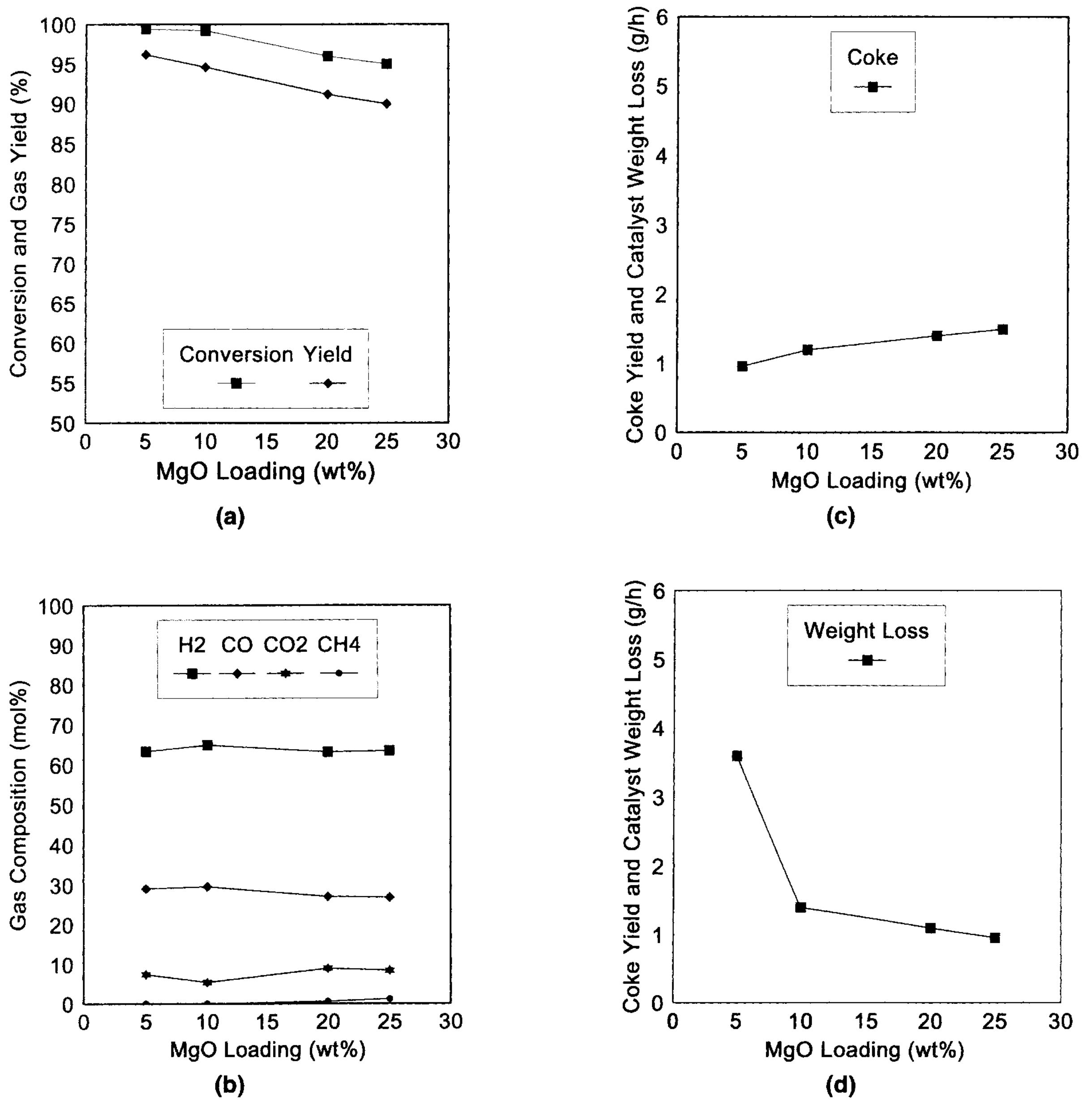


**Figure 5. Conversion and gas yield (a); gas composition (b); coke yield (c); and catalysts weight loss (d) as a function of MgO loading.**

$T$: 1,023 K; steam/naphthalene molar ratio: 16; GHSV: 10,080 $h^{-1}$; residence time: 0.55 s.

Table 1. Effects of $La_2O_3$ and $TiO_2$ Doping Support ($Al_2O_3$ + MgO)

| Catalyst | Conv. (%) | Coke Yield (%) | Gas Yield (%) | Cat. Initial Wt. Loss (%) | Surface Area ($m^2/g$) |
|---|---|---|---|---|---|
| Ni-$Al_2O_3$·MgO | 99.2 | 15.6 | 84.2 | 3 | 73 |
| Ni-$Al_2O_3$·MgO·$TiO_2$ | 88.1 | 18.3 | 75.4 | 10 | 54 |
| Ni-$Al_2O_3$·MgO·$La_2O_3$ | 99.4 | 2 | 97.6 | 4 | 69 |

MgO loading on the conversion (Figure 5a), gas composition (Figure 5b), coke yield (Figure 5c), and catalyst weight loss (Figure 5d). For samples containing more than 15% MgO, the conversion and gas yield decrease. However, the catalyst weight loss decreases with increasing MgO loading. Taking this previous result into account, we selected 10% MgO as the best choice. We also selected 1,023 K as the optimum temperature for support stabilization. The catalysts prepared under these conditions demonstrated good activity; the conversion reached 99%, the catalyst weight loss was less than 5%. Nevertheless the disadvantage of these catalysts is the coke yield, which is still higher than 15%.

### *Effects of $La_2O_3$ and $TiO_2$ doping support ($Al_2O_3$ + MgO)*

The support ($Al_2O_3$ + MgO) was mixed, respectively, with 5% of $TiO_2$ and $La_2O_3$. Two samples, $Al_2O_3$ + MgO + $TiO_2$ and $Al_2O_3$ + MgO + $La_2O_3$ were obtained and were calcined at 1,023 K for 6 h. Fifteen wt. % nickel was impregnated in each support, and after impregnation the samples were dried at 383 K for 4 h, followed by calcination at 873 K for 6 h. All tests were carried out at 1,023 K; GHSV: 10,080 $h^{-1}$; and residence time of 0.55 s at atmospheric pressure.

Table 1 compares the behavior of Ni/$Al_2O_3$, Ni/$Al_2O_3$·

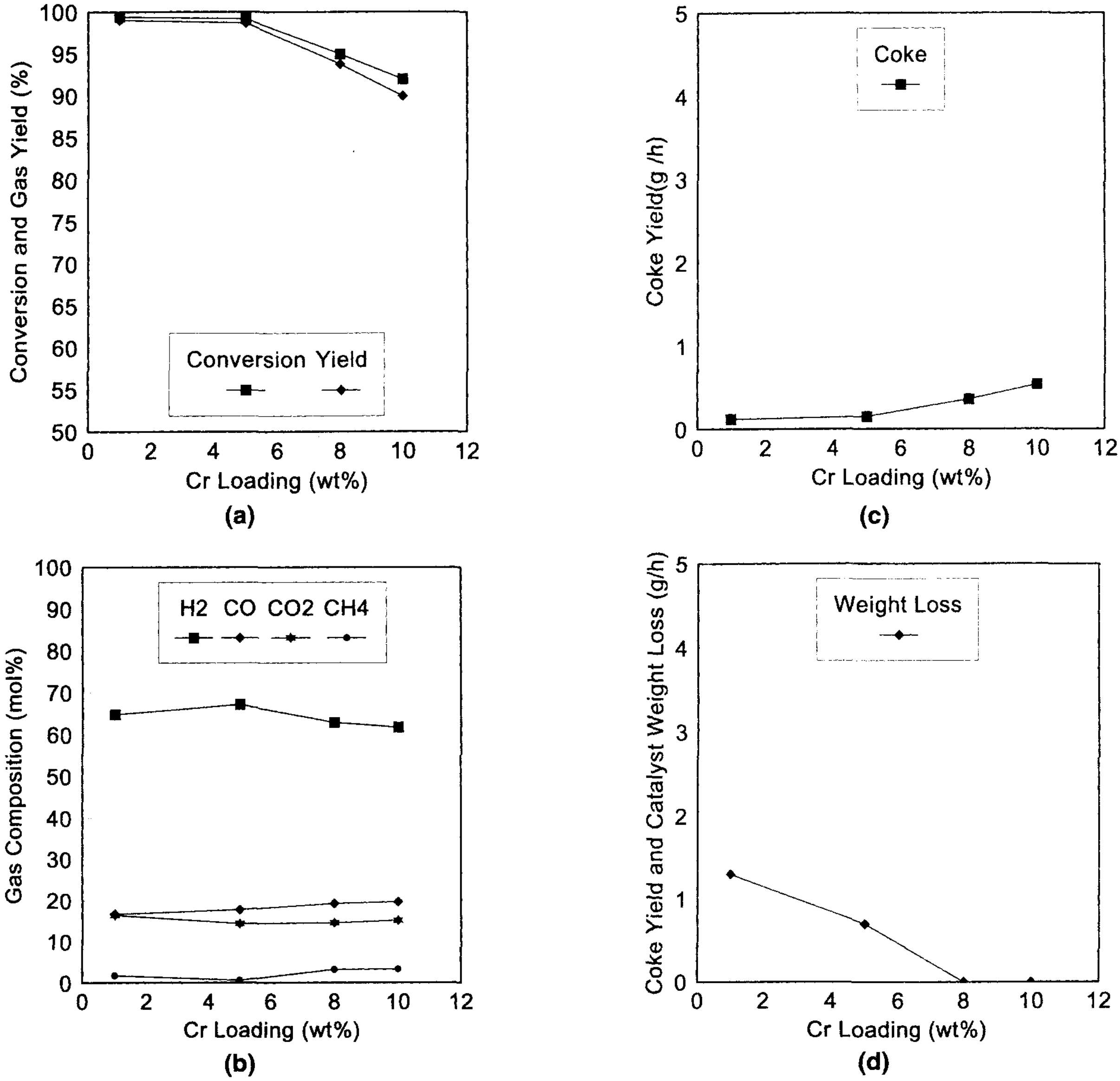
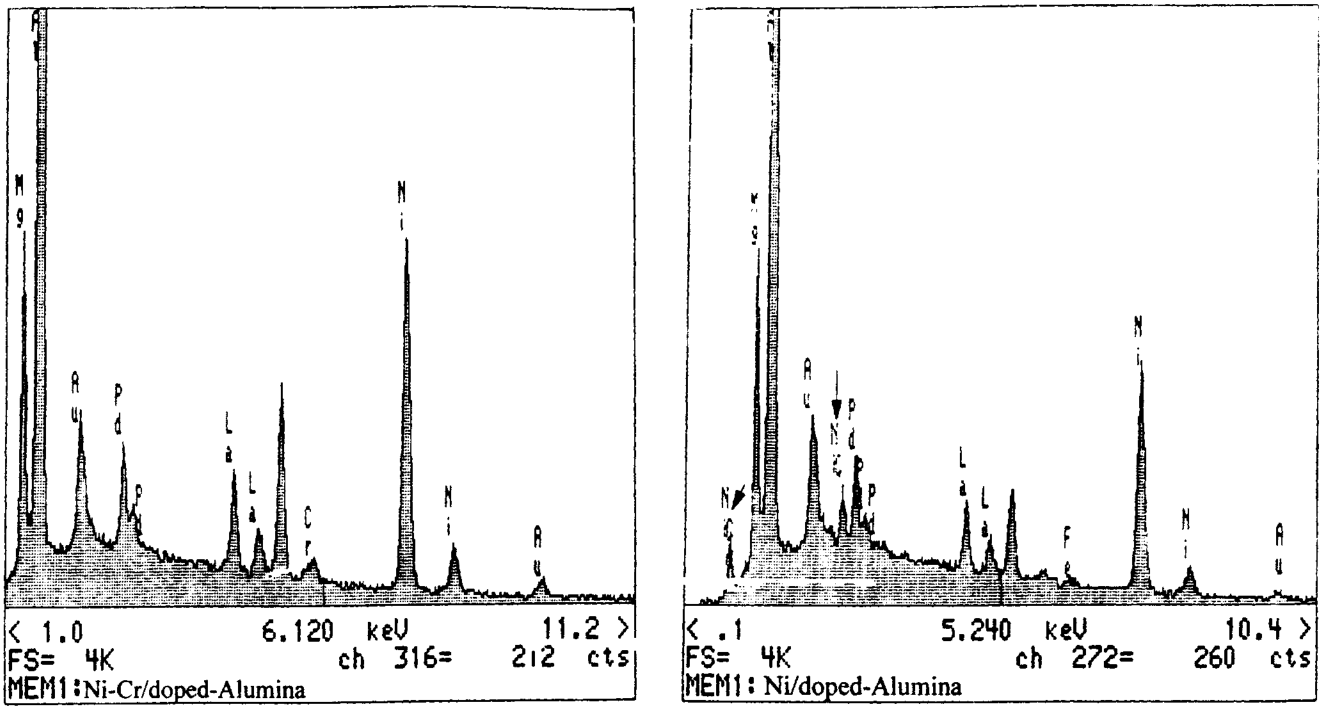


**Figure 6. Conversion and gas yield (a); gas composition (b); coke yield (c); and catalysts weight loss (d) as a function of Cr loading.**

T: 1,023 K; steam/naphthalene molar ratio: 16; GHSV: 10,080 $h^{-1}$; residence time: 0.55 s.



(a) (b)

**Figure 7a,b. Diffraction pattern of Ni-Cr/doped alumina after naphthalene steam reforming.**

MgO, $Ni/Al_2O_3 \cdot MgO \cdot TiO_2$, and $Ni/Al_2O_3 \cdot MgO \cdot La_2O_3$, during the steam reforming of naphthalene. It clearly appears that the use of $La_2O_3$ results in a definite decrease of coke deposit without affecting the conversion of naphthalene. This observation could be related to the neutralization of strong acidic sites or dispersion of relatively large crystallites of nickel oxides responsible for the coke precursor adsorption (Blackmond et al., 1986).

$TiO_2$ addition decreases both the conversion and gas yield by 10%. The effect of $TiO_2$-doped $Al_2O_3$ is related to poisoning of acidic sites on alumina, as suggested by some authors (Wei et al., 1972; Bacaud and Bussier, 1981). The diffraction pattern of $TiO_2 + Al_2O_3$ showed poor crystallinity, and consequently the catalyst has a low crushing strength. From data in Table 1, it is also seen that the catalyst containing $TiO_2$ exhibits the lowest surface area in the series. This fact may be an indication of the destruction of the alumina matrix because of the $TiO_2$ incorporation (Bangala, 1996).

### *Effect of $Cr_2O_3$ doping nickel/alumina catalyst*

As mentioned early in the literature review, the $Cr_2O_3$ is used as a promoter having hydrogenation–dehydrogenation and dehydrocyclization activity (Hensley, 1975). The extent of $Cr_2O_3$ in the final catalyst is generally higher than 20 wt. % of the total weight of the catalyst. Taking into account that very limited information is available on the effect of Cr as promoter protecting Ni from carbon deactivation or poisoning by sulfur or chlorine, we found it necessary to optimize the Cr loading to have long-lived catalysts without affecting the steam-reforming performance. A series of Ni–Cr/doped alumina catalysts were prepared with Cr loadings ranging from 2% to 10%. Figure 6 shows the effect of Cr loading on naphthalene conversion, gas yield, coke formation, and catalyst weight loss. It clearly appears that an appropriate choice would be 5%. Above this level, the conversion decreases and the coke formation increases. This indicates that the Cr dehydrogenation and dehydrocyclization activity prevails beyond 5% loadings. To elucidate the role played by Cr on protecting Ni from carbon deactivation, two diffraction-pattern micrographs (Figures 7a and 7b) of catalysts with and without Cr were compared after reaction. The presence of NiC carbide phase appears only in the unpromoted samples. In agreement with previous studies (Le Page, 1978), we suggest that Cr forms an alloy with Ni, thereby geometrically rearranging the Ni crystal plane and altering the electronic properties of the Ni atoms in such a way that the encapsulation of nickel by inactive carbon filaments is reduced.

## Conclusions

The following conclusions stem from the results and discussions just presented.

1. The Ni–Cr catalyst supported on $\gamma$-alumina doped with MgO and $La_2O_3$ has the best catalytic properties insofar as the activity and robustness are concerned. This catalyst showed high crystallinity and excellent crushing strength.

2. Nickel–chromium catalysts were found to perform very well during steam reforming of naphthalene. Nickel is essentially active in the selective opening of the naphthalene ring. Conversion increases with increased nickel loading up to 15 wt. %, and decreases at higher loadings.

3. The chromium significantly inhibited the formation of nickel carbide.

4. The solid-state reaction of MgO with $Al_2O_3$ at high temperature leads to the formation of $MgAl_2O_4$ spinel, which

is responsible for the robustness of the catalyst. In order to control the robustness without affecting the activity, the stabilization temperature of the support and the MgO loading were optimized. Optimum values for these variables were found to be 973 K–1,023 K and 10–15 wt. %, respectively.

5. Introduction of $La_2O_3$ leads to a decrease of coke deposits. The role of $La_2O_3$ is related to an increase of the nickel crystallites dispersion as well as the possible neutralization of strong acidic sites.

6. $TiO_2$ addition decreases the conversion and yield of gas. The crystallinity of the catalyst containing $TiO_2$ is rather poor, as is its robustness. The $TiO_2$ destroys the alumina matrix.

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