Characterization of silica supported Ni and Mg basic carbonate catalyst precursors

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In Mg-doped Ni-silica catalyst precursors, magnesium preferentially precipitates as basic carbonate species by isomorphous substitution of nickel in basic nickel carbonate network. This has been confirmed by thermal and infrared studies. Presence of magnesium decreases the reducibility of neighbouring nickel atoms due to electronic effects and also acts as spacer/barrier thus minimizing sintering via nickel particle migration. As a consequence, the nickel dispersion in Mg/Ni-silica samples is higher than in Ni-silica samples at all SiO_2/Ni ratios.

Keywords: Ni/SiO_2; Mg-doping; thermal studies; infrared studies

1. Introduction

Nickel catalysts are used in industrial reactions like hydrogenation, hydrotreating and steam reforming. Since catalytic reactions occur on the surface of the metal particles, supports like silica, alumina and titania are used to achieve a high degree of dispersion of nickel metal in the support. The properties of dispersed metal particles are considered to change with various metal dopants and also with the type and extent of metal–support interactions. Nitta et al. [1] have used TGA/DTG studies exclusively to demonstrate metal–support interactions in Ni-silica systems. They observed a shift toward high OH^-/CO_3^{2-} ratios in the precipitate and a drop in degree of reduction of metal with increase in metal–support interactions. Metal–support interactions and OH^-/CO_3^{2-} ratios are dependent on severity in precipitation conditions as indicated by infrared studies of Ni-silica precursors [2]. The strong interactions lead to formation of nickel hydrosilicate type species which is difficult to reduce at 450°C as compared to basic nickel carbonate [3–5]. Also, the role of metal dopants which might form similar salts as that of the parent metal is not well discussed in the literature. Therefore, the purpose of the present work was to focus on the basic carbonate network to study the effects of magnesium as a dopant on the reduction properties and surface area of nickel in precipitated Ni-silica systems. Also, the identification of the existence of magnesium in Ni-silica precursor is done by utilising thermal and infrared studies.

2. Experimental

All the chemicals used were of LR grade. The amorphous silica used had a surface area of 40 m^2/g. The Ni-silica precipitated catalyst precursors were prepared by using the procedure of Nitta et al. [1]. This involved simultaneous addition of nickel sulphate solution and sodium carbonate solution to silica slurry under optimum temperature (92 ± 0.5°C) and pH conditions (9 ± 0.2). Magnesium sulphate heptahydrate was added through nickel sulphate solution. Three sets of samples have been prepared for these studies. In the first set, the Ni/SiO_2 ratio was varied. In the second set, the Mg/Ni ratio was kept constant and the Ni/SiO_2 ratio was varied. In the third set, the Ni/SiO_2 ratio was kept constant and the Mg/Ni ratio was varied. Reaction volumes were maintained constant (±10 ml) in all the experiments.

Thermal studies of catalyst precursors were carried out using Dupont-990 thermal analyser (temperature range: 25–600°C; heating rate: 10°C/min; N_2 flow rate: 100 ml/min). Infrared spectra were recorded on a Nicolet FTIR spectrophotometer 20 SXB. Metal area measurements were carried out by the hydrogen chemisorption method.

3. Results and discussion

The DTG curves recorded for Ni-silica precursors prepared at varying SiO_2/Ni ratios (0.2–2.0) are shown in fig. 1a. For the low silica samples ($SiO_2/Ni = 0.2$, 0.3 and 0.5), three weight loss steps were observed at (i) 70°C due to moisture loss, (ii) 150°C due to water of hydration loss, and (iii) 310°C due to decomposition of basic nickel carbonate to nickel oxide with CO_2 and H_2O as gaseous decomposition products. A fair agreement can be observed between our TGA/DTG profiles and those of Nitta et al. [1]. However, at high silica content, i.e. $SiO_2/Ni = 1.0$ and 2.0, the DTG peaks at 150 and 310°C were less intense and broad. This observation indicates that most of the nickel is present as non-decomposible species, i.e. nickel hydrosilicate type species which could in turn act as the "support" to the easily decomposible basic nickel carbonate species. The formation of nickel hydrosilicate species has been studied in detail by many workers [3–5]. In thermal studies [6], the nickel hydrosilicate does not show any weight loss steps between 25 and 400°C.

The DTG profiles of Mg/Ni-silica precursors were recorded to see the influence of magnesium additive on decomposition characteristics of basic nickel carbonate; their profiles are shown in fig. 1b. The number of weight loss steps and the peak positions of the Mg/Ni silica appeared at identical temperatures as observed with Ni-silica precursors. This behaviour can be expected only when the coprecipitated basic magnesium carbonate also decomposes at the same temperatures as that of basic nickel carbonate.

Therefore, in anticipation of the existence of basic magnesium carbonate and basic nickel carbonate as separate species in Mg/Ni-silica precursor and to arrive at unambiguous conclusions, a Mg-silica sample prepared under identical conditions (in the absence of nickel) was also analysed by thermal studies. The DTG profile showed (fig. 2) three weight loss steps with peak maxima at (i) 70°C due to moisture loss, (ii) 260°C due to water of hydration loss, and (iii) 420°C (extending up to 500°C) possibly due to decomposition of basic magnesium carbonate to MgO, CO_2 and H_2O. The results are consistent with the information available in the literature indicating that the decomposition of basic magnesium carbonate is complete only at high temperature, i.e. 700°C [7]. The peaks at 260 and 420°C are not observed in the presence of Ni, suggesting the possibility of a homogeneous basic nickel magnesium carbonate, where Ni has been isomorphously substituted by Mg.

Pursuing this point further, a physical mixture of Ni-silica and Mg-silica precursors was prepared maintaining a Mg/Ni ratio of 0.18 to scan the decom-

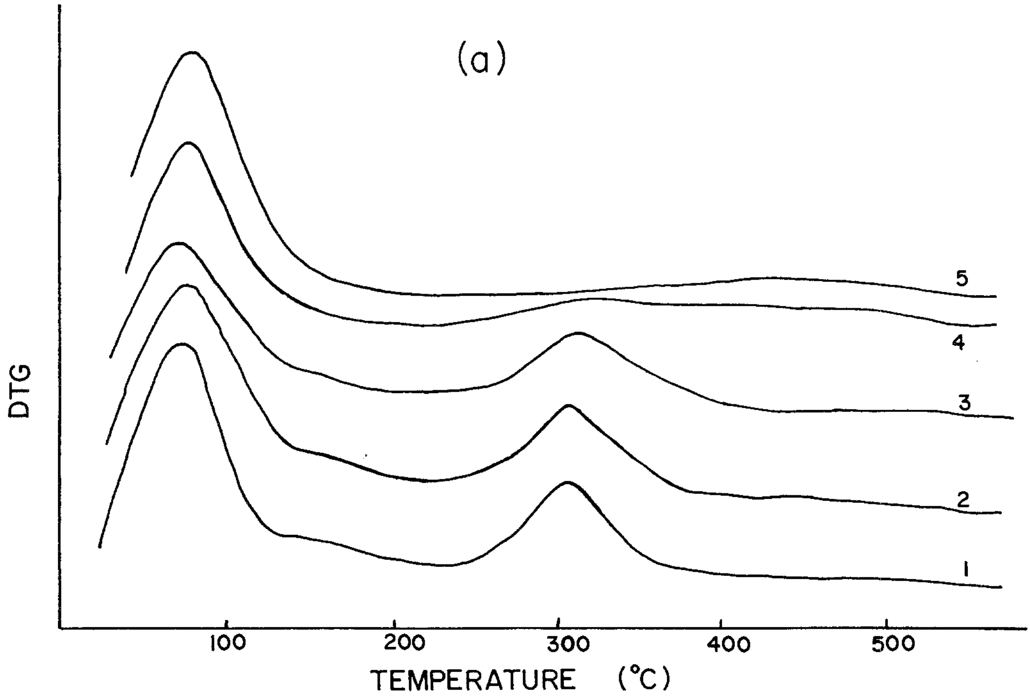


Fig. 1. DTG profiles of (a) Ni-silica and (b) Mg/Ni-silica precursors prepared at varying SiO_2/Ni ratios, i.e. (1) 0.20, (2) 0.33, (3) 0.50, (4) 1.00 and (5) 2.00.

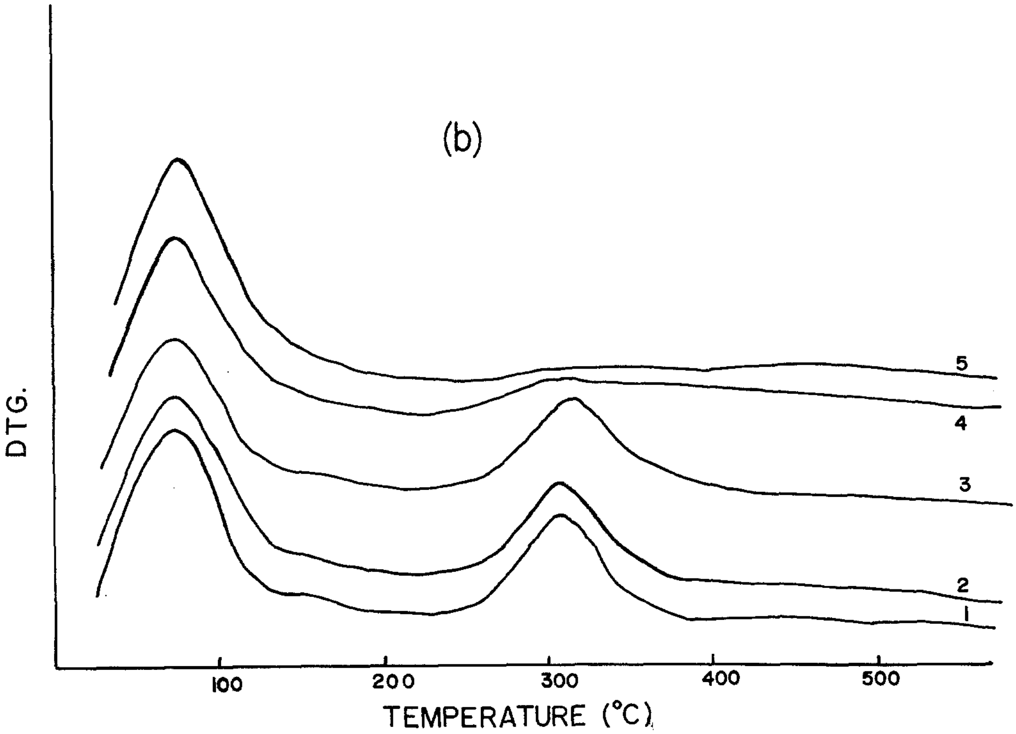


Fig. 1. (continued).

position behaviour when the species exists separately. From fig. 2, it is observed that there are five DTG peaks positions at (i) 70°C, (ii) 150°C, (iii) 260°C, (iv) 310°C, and (v) 420°C. Among these, the DTG peaks (i), (ii) and (iv) are from the Ni-silica precursor and peaks (i), (iii) and (v) are from the Mg-silica precursor. The physically adsorbed free moisture is less influenced by the type of metal species in the precursor. Therefore, the DTG peak (i) at 70°C was unaffected and found to be common for both the samples.

The above TGA/DTG results, therefore, confirm the absence of separate basic magnesium carbonate species in Mg/Ni-silica precursor. It is known [8,9] that the nickel precipitates in the form of a complex network (scheme 1) at high pH (≈ 9) and high temperatures (90–98°C). The length of the network is a function of alkalinity and temperature during the precipitation step. Further, Ni–OH of the basic carbonate network can react with Si–OH of silica to form $-\mathrm{Ni{-}O{-}\overset{|}{\underset{|}{Si}}}-$ linkages (hydrosilicate type species). Evidence for such $-\mathrm{Ni{-}O{-}\overset{|}{\underset{|}{Si}}}-$ linkages in Ni/SiO_2 systems (prepared by homogeneous precipitation with urea [10] or alkoxide route [11]) has been shown by EXAFS studies. The ionic radii of nickel and magnesium being very close (i.e. 0.69 and 0.66 Å respectively), it is possible that magnesium also could find a position similar to nickel in the basic nickel carbonate network (scheme 2). As a result decomposition patterns of

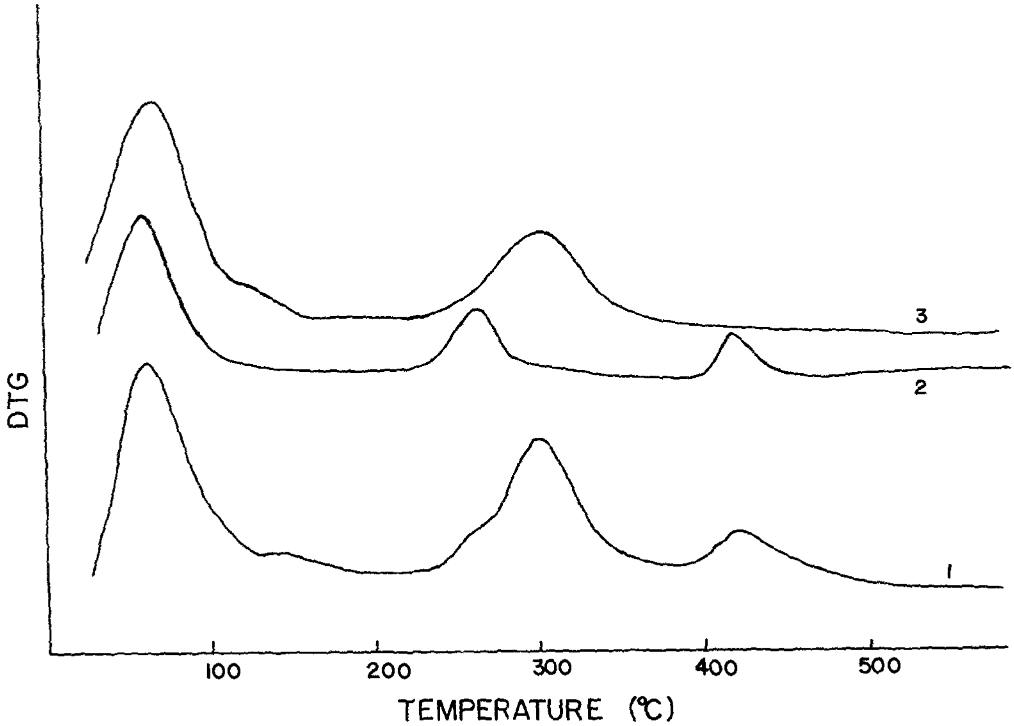
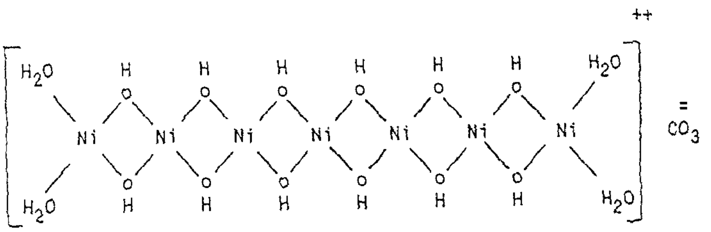
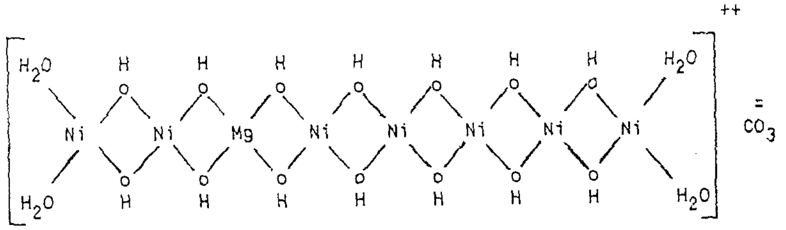


Fig. 2. DTG profiles of (1) physical mixture of Ni-silica and Mg-silica, (2) Mg-silica and (3) Mg/Ni-silica precursors.



Scheme 1.



Scheme 2.

Table 1
Properties of Ni-SiO_2 and Mg/Ni-SiO_2 precursors

Sample No.	SiO_2/Ni	Mg/Ni (mole ratio)		% Mg yield	% DR (at 450°C)	Metal area (m^2/g Ni) at 450°C	Crystallite size [a] (Å)
		added	found				
Ni-SiO_2							
1	0.20	NIL	NIL	–	89.0	54.1	70.9
2	0.33	NIL	NIL	–	82.6	64.5	55.2
3	0.50	NIL	NIL	–	74.3	78.9	40.5
4	1.00	NIL	NIL	–	62.9	72.6	37.3
5	2.00	NIL	NIL	–	53.2	65.1	35.2
Mg/Ni-SiO_2							
6	0.20	0.20	0.181	90.5	73.6	100.0	35.7
7	0.33	0.20	0.144	72.0	68.5	98.0	30.1
8	0.50	0.20	0.132	66.0	56.7	101.3	24.1
9	1.00	0.20	0.110	55.0	54.8	104.0	22.7
10	2.00	0.20	0.070	35.0	49.7	94.6	22.6
Mg/Ni-SiO_2							
11	0.33	NIL	NIL	–	82.6	64.5	55.2
12	0.33	0.13	0.097	74.6	72.1	95.0	32.7
13	0.33	0.27	0.191	70.7	66.3	104.1	27.4
14	0.33	0.45	0.328	72.8	54.3	114.3	20.4

[a] Crystallite size = 4310 − (metal area/% DR) × 100.

Mg/Ni-silica and Ni-silica were identical. Also, a few interesting observations were made from the analysis of magnesium and nickel contents of the solutions used for precipitation and the product precursors. Firstly, the Mg/Ni-silica samples prepared at constant SiO_2/Ni (0.33) ratio and $pH = 9.0 \pm 0.2$ showed precipitation of only 72–75% of the added magnesium and the rest remained in the solution and was lost during the filtration step (table 1). However, the precipitation of nickel was found to be > 99%. Earlier, systematic studies by Mallya et al. [8,9] have also shown that nickel precipitation was complete (> 99% yield) at ≈ 92°C and $pH = 8.9$. Only at low alkalinity and at 25°C, the nickel yields dropped to 80%. The precipitation of magnesium was reported [12] to be complete at $pH \approx 11$. Therefore, the experiments conducted between $pH = 8.8$ and 9.2 resulted in 72–75% magnesium yields. Secondly, the analysis of precursors prepared by using the solutions containing a constant Mg/Ni ratio of 0.20 and increase in SiO_2/Ni ratios (0.2–2.0) have shown a gradual drop in the magnesium yields from 90% (Mg/Ni = 0.18) to 35% (Mg/Ni = 0.07) (table 1). In high silica samples (SiO_2/Ni = 1.0 and 2.0), distribution of nickel is more toward nickel hydrosilicate and less toward nickel basic carbonate species [6]. From TGA studies, it is assumed that nickel and magnesium precipitate homogeneously as basic carbonate. Therefore, the lower the concentration of basic nickel carbonate the lower is the chance for magnesium to form a precipitate. This accounts for the drop in magnesium yield in the precursor.

This interpretation of the distribution of nickel as basic carbonate and hydrosilicate species is further supported by infrared studies. For both Ni-silica and Mg/Ni-silica precursors, the vibrations characteristic of basic (hydroxy) carbonate appeared at 1380 and 1450 cm^{-1} and at 1000 and 1050 cm^{-1} for hydrosilicate vibrations. The decrease in intensity of bands due to basic carbonate and a corresponding increase in intensity of bands due to silicate vibrations with increase in SiO_2/Ni ratios of the precursor confirms the observations made by TGA studies.

Also, appearance of infrared bands at identical wave numbers for Ni-silica and Mg/Ni-silica precursors supports our earlier assumption made from TGA results that magnesium is incorporated homogeneously and assumes the characteristics of basic nickel carbonate (Mg/Ni mole ratio between < 0.01 and 0.18). For Mg-silica precursor (in the absence of nickel), the infrared bands appeared at higher wave numbers when compared with Ni-silica precursors. That is, basic carbonate vibrations appear at 1423 and 1484 cm^{-1} instead of 1382 and 1450

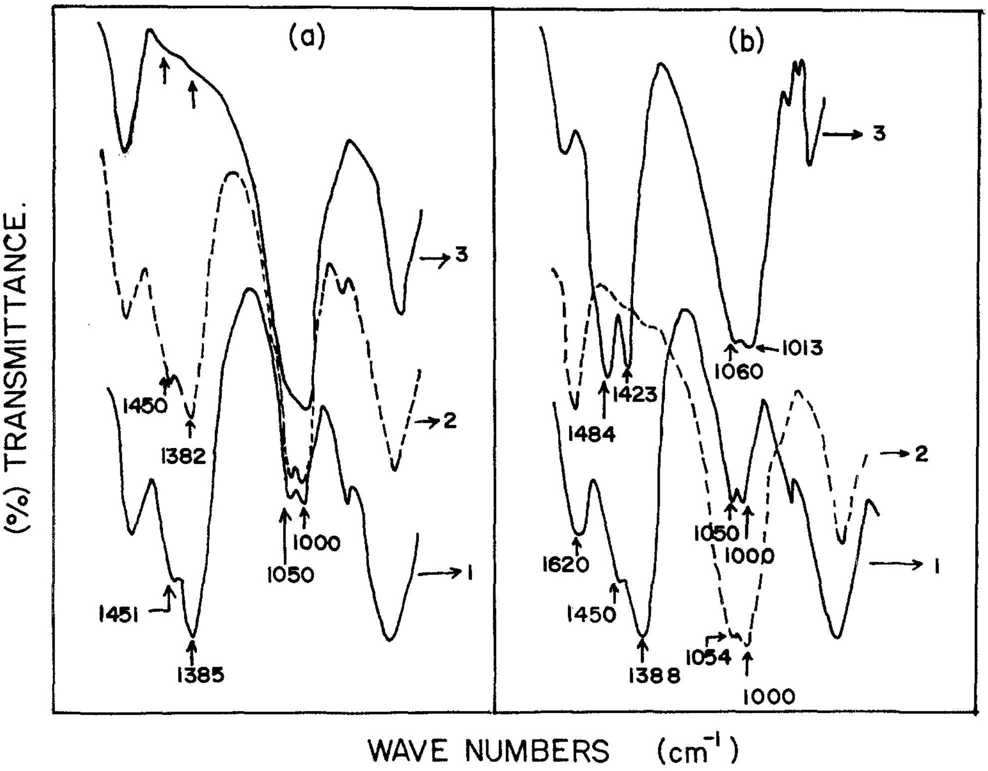


Fig. 3. Infrared spectra of (a) Ni-silica precursors with varying SiO_2/Ni ratios, i.e. (1) 0.2, (2) 0.5 and (3) 2.0; (b) Mg/Ni-silica precursors with SiO_2/Ni ratios of (1) 0.2 and (2) 2.0; and (3) Mg-silica precursor.

cm^{-1} and hydroxy silicate vibrations at 1013 and 1060 cm^{-1} instead of 1000 and 1050 cm^{-1} (fig. 3). Two factors can explain the observed shifts towards high wave numbers for Mg/silica precursor. First, the bond lengths in the case of magnesium species are shorter than in the case of nickel. Second, the bond strengths are stronger for magnesium species due to the higher charge/radius ratio for magnesium (3.030) compared to that of nickel (2.898).

The results in table 1 clearly indicate a drop in the degree of reduction in Mg/Ni-silica samples and an improvement in metal area compared to Ni-silica samples. In the Mg/Ni-silica precursors electron density effects may be responsible for the observed drop in DR values. A shift in electron density away from the nickel in a –Ni–O–Mg– linkage in the basic nickel carbonate network could lead to rendering the Ni centres less reducible. The effect of Si on the DR ($-\underset{|}{\overset{|}{\mathrm{Si}}}-\mathrm{O}-\mathrm{Ni}-$, in hydrosilicate type species) further corroborates this explanation. Since Si^{4+} has a larger charge-to-radius ratio (9.523) as compared to Mg^{2+} (3.03) its effect on Ni centres should be more pronounced if the above argument is valid. This is, in fact, what is observed in experiments conducted at varying SiO_2/Ni ratios shown in table 1, i.e. a significant drop in DR is seen with increasing SiO_2 content.

During high temperature reduction of Ni-silica systems, it has been shown that sintering of nickel occurs by a particle-migration mechanism [13,14]. In the Mg/Ni-silica system, however, this migration is minimised due to the presence of Mg as a barrier/spacer to sintering of nickel particles. This explains the observed increase in metal area in the presence of Mg.

4. Conclusions

It is evident that the magnesium additive (in the range of Mg/Ni < 0.01–0.20) precipitates preferentially as basic carbonate species and forms a homogeneous precipitate by isomorphous substitution of nickel in basic nickel carbonate network. The thermal and infrared studies also confirm that the structural characteristics of magnesium is similar to that of nickel in Mg/Ni-silica systems. Magnesium has strong influence in decreasing the reducibility and increasing the metal area of nickel metal. Electronic effects may be playing a crucial role in altering the reducibility of nickel species in the presence of Mg. Magnesium also seems to act as a spacer/barrier in reducing the particle migration of Ni that causes sintering, thereby improving the total metal area.

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