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Short Communication

The effect of impregnation strategy on structural characters and CO₂ methanation properties over MgO modified Ni/SiO₂ catalysts

Meng Guo^{a,b}, Gongxuan Lu^{a,*}

^a State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, PR China ^b University of Chinese Academy of Sciences, Beijing 100049, PR China

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ABSTRACT

Mg-modified Ni/SiO₂ catalysts with different MgO contents were prepared by two impregnation methods. The catalysts prepared by co-impregnation method could show better activity and stability than those prepared by sequential impregnation method. The modification of MgO acted as a key factor in enhancing the capacity of CO₂ adsorption and accelerating the activation of CO₂. Moreover, modified MgO could also increase Ni species dispersion and suppress the metallic Ni sintering and oxidation.

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1. Introduction

Methane as one of the renewable energy carriers can be produced from the Sabatier reaction. If hydrogen in this reaction is provided by renewable energy, the sustainable cycle of carbon can be achieved. For the above purposes, extensive studies have been carried out on group VIII metal catalysts [1–5]. However, the industrialization of CO₂ methanation remains a great challenge due to the lack of the efficient and stable catalysts [2].

For this process, the adsorption and activation of CO_2 are especially critical. Park et al. [6] have revealed that MgO can initiate the reaction by binding a CO_2 molecule *via* forming a magnesium carbonate species on the surface. And then, a supply of atomic H is essential for further hydrogenation of magnesium carbonate to methane. Obviously, the addition of MgO can improve the catalytic performance due to its strong basicity, which can enhance the capacity of CO_2 adsorption, alter the acid–base property of catalysts and improve the dispersion of active phase [7,8]. In addition, different impregnation methods can affect significantly catalyst surface characteristics and catalytic behavior [7,9,10].

Therefore, a series of Mg-modified Ni/SiO₂ materials were prepared by co-impregnation and sequential impregnation methods. The obtained samples with good thermal stability were investigated as the catalysts of CO₂ methanation. The influence of MgO loadings and impregnation sequences on the performance of Mg-modified Ni/SiO₂ catalysts was studied in order to find the catalysts with better activity and stability.

2. Experimental

2.1. Catalyst preparation

Using Ni(NO₃)₂·6 H₂O as a metal precursor, 10 wt.% Ni/SiO₂ and 10 wt.% Ni/MgO (denoted as Ni/Si and Ni/Mg) catalysts were prepared by the wet impregnation method followed by spontaneous dispersion upon calcination. Prior to the impregnation, SiO₂ and MgO supports were calcined 773 K for 6 h. After the stabilization, their specific areas were 438 and 8.1 m²/g, respectively. After the impregnation, the catalysts were dried at room temperature for 24 h, dried further at 383 K for another 24 h, and finally calcined at 773 K for 6 h.

10 wt.% Ni-*x*MgO/SiO₂ (x = 1, 2 and 4 wt.%) catalysts were denoted as co-Ni/*x*Mg/Si catalysts and prepared by co-impregnation method using the mixed solution containing both Ni(NO₃)₂ and Mg(NO₃)₂. The drying and calcination procedures were the same as for Ni/Si catalyst.

10 wt.% Ni/xMgO/SiO₂ (x = 1, 2 and 4 wt.%) catalysts were denoted as se-Ni/xMg/Si catalysts and prepared by sequential impregnation method, in which impregnation of magnesium nitrate aqueous solution was followed by heat treatment and then by impregnation of nickel nitrate aqueous solution. The two drying and calcination procedures were the same as for Ni/Si catalyst.

2.2. Catalyst characterization

Hydrogen-temperature programmed reduction (H_2 -TPR) measurements were carried out by heating a sample (50 mg) at 10 K min⁻¹ in





^{*} Corresponding author. Tel.: + 86 931 4968178; fax: + 86 931 4968178. *E-mail address:* gxlu@lzb.ac.cn (G. Lu).



Fig. 1. H₂-TPR profiles of fresh co-impregnation (a) and sequential impregnation (b) catalysts: A, Ni/Si; B, co-Ni–1Mg/Si; C, co-Ni–2Mg/Si; D, co-Ni–4Mg/Si; E, se-Ni/1Mg/Si; F, se-Ni/2Mg/Si; G, se-Ni/4Mg/Si. The data of Ni/Si were plotted for comparison.

a flow 5 vol.% H₂/Ar gas mixture (40 ml min⁻¹). The amount of consumed H₂ was measured by a TCD.

X-ray diffraction (XRD) was performed on selected samples using Cu K α radiation (Philips X'pert MPD instrument) at a scattering rate of 4°/min at 40 mA and 50 kV.

Chemical states of the atoms on the catalyst surface were investigated by X-ray photoelectron spectroscopy (XPS) on a VG ESCALAB 210 Electron Spectrometer (Mg K α radiation; $h\nu = 1253.6$ eV). XPS data were calibrated using the binding energy of the Si 2p (103.4 eV) as the standard.

2.3. Catalytic performance

Catalytic performance tests were carried out in a fixed bed continuous flow quartz reactor (i.d. 8 mm) at atmospheric pressure and temperatures ranging from 473 to 773 K using a mixture of H_2 (40 ml min⁻¹) and CO_2 (10 ml min⁻¹) at the molar ratio of 4 balanced with N_2 (30 ml min⁻¹). Typically, 0.2 g of catalyst was used in each turn. Previous to the reaction tests, the calcined catalysts were reduced *in situ* at 723 K for 3 h and then cooled down to room temperature under a 50 vol.% H_2/N_2 mixture

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(60 ml min⁻¹). The products were collected after half an hour of steady-state operation and analyzed on two on-line chromatographs equipped with thermal-conductivity detectors (TCD). Nitrogen was used as a carrier gas and internal standard for gas analysis. CO₂ conversion (X_{CO₂}), CH₄ selectivity (S_{CH₄}) and CO selectivity (S_{CO}) were described as follows:

$$X_{CO_2}(\%) = 100 \times (F_{CO_{2in}} - F_{CO_{2in}}) / F_{CO_{2in}}$$
 (1)

$$S_{CH_4}(\%) = 100 \times F_{CH_{4out}} / (F_{CH_{4out}} + F_{CO_{out}})$$
⁽²⁾

$$S_{CO}(\%) = 100 \times F_{CO_{out}} / (F_{CH_{4out}} + F_{CO_{out}}).$$

$$(3)$$

3. Results and discussion

3.1. Characterization of catalysts

3.1.1. H₂-TPR analysis

Profiles of H_2 -TPR for the bare and modified Ni/SiO₂ samples were presented in Fig. 1 and the quantitative data of Ni species were given in Table 1. TPR profile of Ni/Si catalyst was composed of a sharp peak and a shoulder peak. This sharp peak was constituted by two maxima at 668 and 697 K, respectively. The two peaks were attributed to the reduction of some inhomogeneous NiO phases that interacted weakly with the silica [11]. The shoulder peak at 757 K could be attributed to the stronger interactions between the bulk NiO phase and the support [12].

The reduction peaks of Mg-modified Ni/SiO₂ materials gradually migrated toward higher temperatures with the increase of the MgO contents. However, the impregnation strategies had less influence on the reduction behavior of the same loading catalysts due to their similar properties in shapes and peak positions (Fig. 1 and Table 1). For co-Ni–1Mg/Si sample, the δ , ε and ζ peaks were attributed to the surface, subsurface and bulk phase reduction of Ni²⁺ ions in the outer-like layers of MgO [13–15]. The η peak was attributed to the reduction of Ni²⁺ ions located in the subsurface layers of MgO lattice [14]. With the increase of the MgO loadings, the reduction peaks of co-Ni-2Mg/Si and co-Ni-4Mg/Si samples were shifted significantly to higher temperatures. The reduction behavior of the Ni oxides over Mg-modified Ni/SiO₂ catalysts prepared by sequential impregnation and co-impregnation methods was similar. For se-Ni/4Mg/Si sample, the H₂-uptake fraction of total area of the ζ peak at 907 K was up to 97%, which indicated that MgO could be dispersed highly to the SiO₂ support. The lower H₂-uptakes indicated that less metallic Ni species could be reduced. In summary, compared with co-Ni-xMg/Si catalysts, se-Ni/xMg/Si catalysts exhibited high temperature H₂-uptakes, which indicated the stronger surface interaction. In addition, the addition of higher amount of MgO (2 or 4 wt.%) could result in more uniform NiO species formed over Mg-modified Ni/SiO₂ catalysts.

Samples	T _m (K)							Fraction of total area (%)						
	α	β	γ	δ	3	ζ	η	α	β	γ	δ	3	ζ	η
Ni/Si	668	697	757	-	-	-	-	27	43	30	-	-	-	-
co-Ni-1Mg/Si	-	-	750	810	870	917	1007	-	-	9	42	31	15	2
co-Ni-2Mg/Si	-	-	771	821	862	905	1014	-	-	11	22	13	50	4
co-Ni-4Mg/Si	-	-	-	790	842	904	1023	-	-	-	13	12	74	1
se-Ni/1Mg/Si	-	-	740	797	863	906	1009	-	-	25	30	26	16	2
se-Ni/2Mg/Si	-	-	751	811	863	905	1004	-	-	10	25	10	53	3
se-Ni/4Mg/Si	-	-	729	-	-	907	1012	-	-	1	-	-	97	2

3.1.2. XPS analysis

The patterns related with binding energies of Ni $2p_{3/2}$ and the derived atomic composition in the different samples were analyzed and summarized in Fig. 2 and Table 2, respectively. The binding energies of the surface Ni $2p_{3/2}$ species were not affected by different preparation methods and MgO loadings. But the relative contents of nickel species changed significantly. For all the catalysts, the peaks of binding energies of Ni $2p_{3/2}$ were mainly distributed around 853.8, 854.8 and 856.8 eV, which were assigned to different sorts of NiO species [16]. But these NiO species were not fully in agreement with those NiO species studied in TPR experiment. The two higher binding energies of Ni $2p_{3/2}$ (around 859.5 and 863.0 eV) could be assigned to the shake-up satellite peaks of NiO species. The XPS results of samples in Table 2 demonstrated that Ni species increased on the modified catalyst surface with the increase of MgO loadings, as observed by the higher surface Ni/Si.

3.1.3. XRD analysis

XRD patterns of bare and modified Ni/SiO₂ catalysts reduced at 723 K for 3 h were presented in Fig. 3. The typical broad diffraction peaks of SiO₂ support could be observed. For Ni/Si catalyst, the diffraction peaks located at $2\theta = 44.5$, 51.8 and 76.4° (JCPDC Card No. 87-0712), indicated the existence of the characteristics of Ni metal phase [7,17]. The NiO peaks were located at $2\theta = 37.2$, 43.3 and 62.8° (JCPDC Card No. 89-5881), which suggested that some NiO species existed in the bulk phase of catalysts [3,18].

By comparison of Mg-modified Ni/SiO₂ catalysts, it was found that the XRD peaks could be attributed to Ni phase (near 44.5 and 51.8°), NiO (near 37.2, 43.3 and 62.8°), and NiO–MgO mixed phases (near 37.2, 43.3 and 62.8°, JCPDC Card No. 24-0712) [8]. With the increase of MgO loadings, both metallic Ni particle sizes and peak intensities decreased. The metallic Ni particle sizes of Ni–1Mg/Si, Ni–2Mg/Si and Ni–4Mg/Si catalysts were 36.2, 31.7 and 21.1 nm, respectively, as



Fig. 2. XPS spectra of Ni 2p_{3/2} over fresh co-impregnation (a) and sequential impregnation (b) catalysts: A, Ni/Si; B, co-Ni–1Mg/Si; C, co-Ni–2Mg/Si; D, co-Ni–4Mg/Si; E, se-Ni/1Mg/Si; F, se-Ni/2Mg/Si; G, se-Ni/4Mg/Si. The data of Ni/Si were plotted for comparison.

shown in Table 3. In addition, the metallic Ni peak intensity ratios of Ni/Si, co-Ni–1Mg/Si, co-Ni–2Mg/Si and co-Ni–4Mg/Si catalysts were 1:0.29:0.12:0.04. For se-Ni/xMg/Si catalysts, the changes of peak intensities were similar. It also demonstrated that Ni species over Mg-modified Ni/SiO₂ catalyst were more difficult to be reduced than those over Ni/Si catalyst under the same condition. However, the formation of small crystallites improved the metal dispersion of Ni species and then affected the catalyst performances, which was discussed further in the following content. In brief, both impregnation sequence and MgO loadings could influence the catalyst structure. The catalysts prepared by sequential impregnation method exhibited higher NiO dispersion. In addition, the catalysts with high MgO loadings possessed high NiO dispersion.

3.2. Influence of SiO₂ and MgO supports

In order to show the influence of SiO₂ and MgO supports on CO₂ methanation performances over monometallic Ni-based catalysts [19], Ni/Si, Ni/Mg and a physical mixture of two monometallic catalysts (a weight ratio of 1:1) were investigated and the results were compared in Table 4. The nature and texture of supports could affect significantly the distribution of active sites for CO₂ hydrogenation. CO₂ methanation occurred mainly over Ni/Si catalyst but the reverse water gas shift reaction occurred largely over Ni/Mg catalyst. Previous studies [20] had shown that the central carbon atom of adsorbed CO₂ (bent) could coordinate with Ni metal and make system energy reduce. At this circumstance, adsorbed CO₂ reacted with activated H₂ by progressive hydrogenation and dehydration. The catalytic performances of a physical mixture of two monometallic catalysts were very similar to the ones of Ni/Si catalyst, which demonstrated that CO generated from Ni/Mg catalyst could be adsorbed once again and then be hydrogenated to CH₄.

3.3. Catalytic activity over Mg-modified Ni/SiO₂ catalysts

The catalytic performances of Mg-modified Ni/SiO2 catalysts were investigated at different temperatures and the results were shown in Fig. 4. As shown in Fig. 4a, CO₂ conversions depended largely on reaction temperatures [2–6]. Their highest catalytic activities at 673 K were observed in the temperature range studied. Compared with Ni/Si catalyst, the catalytic activity of co-Ni-1Mg/Si catalyst increased. However, with the further increase of MgO loadings, the catalytic activities of co-Ni-2Mg/Si and co-Ni-4Mg/Si catalysts decreased. Moreover, coimpregnation of Ni and Mg and the suitable content of MgO were more beneficial to improve the activity for this reaction. In addition, as shown in Fig. 4c, CO selectivities were also related closely to the reaction temperatures, especially in the high temperature region ranging from 673 to 773 K. Sharma et al. [21] indicated that the reverse water gas shift reaction competed with CO₂ methanation main reaction over Ni-based catalysts. The high reaction temperature favored the reverse water gas shift reaction according to the thermodynamics [22]. Therefore, the produced CO from the reverse shift reaction increased with the increase of the temperature [23]. At the same time, high temperature was not beneficial to CO₂ methanation reaction due to the constraint of thermodynamics [24]. These two factors might account for the reasons of the high selectivities to CO in high temperature ranges.

3.4. Stability tests

The several catalyst performances during 50 h were monitored by means of CO₂ conversions and CH₄ selectivities. Ni/Si, co-Ni–1Mg/Si and se-Ni/1Mg/Si catalysts were selected as the representative catalysts. The results of catalyst stability and deactivation were listed in Fig. 5. As shown in Fig. 5, Ni/Si, co-Ni–1Mg/Si and se-Ni/1Mg/Si catalysts exhibited similar initial CO₂ conversions and CH₄ selectivities. However, compared with Ni/Si and se-Ni/1Mg/Si catalysts, co-Ni–1Mg/Si catalyst exhibited higher CO₂ conversions, higher CH₄ selectivities and more stable catalytic behavior in the whole 50 h time on stream [3,6]. As

Table 2
XPS results of fresh catalysts.

Samples	B.E. (Ni 2p _{3/2}) (eV)					Fraction of total area (%)					Ni/Si ^a	Mg/Si ^a
	α	β	γ	δ	3	α	β	γ	δ	3		
Ni/Si				859.5	863.0	7.1	2.8	49.3	9.4	31.3	0.015	0
co-Ni-1Mg/Si				859.5	862.8	3.9	23.1	31.6	17.4	24.0	0.017	0.066
co-Ni-2Mg/Si				858.5	862.8	2.9	10	33.1	25.5	28.5	0.019	0.071
co-Ni-4Mg/Si	853.8	854.8	856.8	858.3	862.5	1.7	6.1	37.2	22.8	32.2	0.022	0.111
se-Ni/1Mg/Si				860.9	862.7	11.5	24.6	28.3	17.6	18.0	0.022	0.065
se-Ni/2Mg/Si				860.3	863.1	11.4	16.4	31.7	23.8	16.7	0.026	0.085
se-Ni/4Mg/Si				859.5	862.9	6.7	2.9	49.6	8.2	30.5	0.034	0.120

^a Calculated by Ni (or Mg) atom%/Si atom% from XPS spectra.



Fig. 3. XRD patterns of reduced (a, co-impregnation; b, sequential impregnation) and used (c) catalysts: A, Ni/Si; B, co-Ni–1Mg/Si; C, co-Ni–2Mg/Si; D, co-Ni–4Mg/Si; E, se-Ni/1Mg/Si; F, se-Ni/2Mg/Si; G, se-Ni/4Mg/Si. The data of Ni/Si were plotted for comparison.

mentioned above, the excellent catalytic activities of Mg-modified catalysts were attributed to the merits of CO₂ activation, which made the chemical adsorption much easier than Ni/Si catalyst [6]. During stability tests, a fatal drawback of CO₂ methanation catalysts was their deactivation caused mainly by the sintering and oxidation of the metallic phase, which could lead to a decrease of the active metal sites on the catalyst surface and ultimately influence the catalytic stability.

The XRD patterns of the used catalysts were plotted comparatively in Fig. 3c. For Ni/Si catalyst, the metallic Ni phase sintered and the metallic Ni species on the catalyst surface could be oxidized with the reaction process, which could lower the catalytic stability. However, for the used co-Ni–1Mg/Si catalyst, there were minor changes of the diffraction peaks of metallic Ni species. The structure of co-Ni–1Mg/Si catalyst was stable, which was also in agreements with the results of the stability test. It demonstrated that in the reaction process, modified MgO by co-impregnation method could inhibit the sintering and oxidation of metallic Ni on the catalyst surface.

In conclusion, the results of characterization and reaction indicated that the introduction of MgO influenced the catalyst structure and activity. Although TPR and XRD results demonstrated that MgO doping enhanced the interaction of NiO with the support, Mg-modified Ni/SiO₂ catalysts still exhibited good activities. In addition, the excessive addition of MgO provided too much basic sites, which could inhibit the catalyst activity further [8,25]. Furthermore, XPS results demonstrated that the surface Ni species on the catalysts prepared by sequential impregnation were easier to enrich than those the catalysts prepared by co-impregnation, which resulted in the significant Ni sintering of se-Ni-1Mg/Si catalyst in stability test. However, the synergistic effect of Ni and Mg species over inhibited significantly the Ni sintering of co-Ni-1Mg/Si catalyst in stability test.

4. Conclusion

In summary, the introduction of 1 wt.% MgO as a promoter to the 10 wt.% Ni/SiO₂ catalyst *via* co-impregnation method led to superior catalytic activity and stability (near 100%) at 623 K for 50 h because of the synergistic effect of Ni and Mg species. In addition, although Ni/Si

Table 3	
XRD results of catalysts reduced at 723 K.	

Samples	Diameter (nm) ^a					
	Ni	NiO or/and NiO-MgO				
Ni/Si	50.9 (61.6) ^b	12.2 (17.7) ^b				
co-Ni–1Mg/Si	36.2 (31.7) ^b	43.4 (34.6) ^b				
co-Ni–2Mg/Si	31.7	28.1				
co-Ni-4Mg/Si	21.1	21.0				
se-Ni/1Mg/Si	36.1 (44.0) ^b	43.4 (45.1) ^b				
se-Ni/2Mg/Si	21.1	34.6				
se-Ni/4Mg/Si	19.6	31.6				

^a Calculated by the Scherrer formula from XRD spectra.

^b Obtained after 50 h.

Table 4

Catalytic performances of monometallic Ni-based catalysts at different temperatures. Reaction conditions: GHSV = 15,000 ml h⁻¹ g⁻¹; H₂/CO₂ molar ratio = 4; 1 atm.

				-					
Samples	573 K			623 K			673 K		
	X _{CO₂}	S_{CH_4}	S _{CO}	X_{CO_2}	S_{CH_4}	S _{CO}	X _{CO₂}	S_{CH_4}	S _{CO}
Ni/Si	30.0	96.5	3.5	64.7	97.5	2.5	73.2	98.7	1.3
Ni/Mg Ni/Si + Ni/Mg	2.7 23.9	8.3 91.7	91.7 8.3	7.8 54.9	12.5 95.2	87.5 4.8	28.9 66.5	9.0 96.8	91.0 3.2



Fig. 4. Catalytic performances of Mg-modified Ni catalysts at various temperatures: A, Ni/Si; B, co-Ni-1Mg/Si; C, co-Ni-2Mg/Si; D, co-Ni-4Mg/Si; E, se-Ni/1Mg/Si; F, se-Ni/2Mg/Si; G, se-Ni/4Mg/Si. Reaction conditions: GHSV = 15,000 ml h⁻¹ g⁻¹; H₂/CO₂ molar ratio = 4; 1 atm.



Fig. 5. Long-term stability tests at 623 K. Reaction conditions: $GHSV = 15,000 \text{ ml } h^{-1} \text{ g}^{-1}$; H_2/CO_2 molar ratio = 4; 1 atm.

and se-Ni/1Mg/Si catalysts exhibited similar initial catalytic activities compared to co-Ni–1Mg/Si catalyst, their stabilities decreased to 91.2 and 89.9% at 623 K for 50 h, respectively. Besides, the addition of higher amount of MgO (2 or 4 wt.%) resulted in a slight decrease in catalytic activities due to the blockage of active sites. Therefore, the improved stability and activity of MgO doped Ni/SiO₂ catalysts for CO₂ methanation could be achieved by applying different impregnation strategies and adding different amounts of MgO.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at http://dx. doi.org/10.1016/j.inoche.2014.05.023. These data include MOL files and InChiKeys of the most important compounds described in this article.

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