

γ -Alumina-Supported Ni-Mo Carbides as Promising Catalysts for CO₂ Methanation

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Abstract

CO₂ methanation with Hydrogen to form CH₄ offers a solution for off-peak renewable energy storage. γ -alumina-supported Mo and Ni-Mo catalysts were used in CO₂ methanation, either in their reduced or in their carburized form. The presence of Ni improved the carburization extent of Mo-species, resulting in increased catalytic activity and selectivity for the catalytic CO₂ methanation reaction. Carburization generally enhances the basicity of the materials and thus CO₂ absorption on their surface. At 300°C, the conversions of CO₂ for the reduced Ni-Mo/Al₂O₃ catalyst and Ni-Mo₂C/Al₂O₃ catalysts were 5.3% and 13.8% respectively with a corresponding selectivity in CH₄ of 10.0% and 98.1%, respectively.

Keywords

CO₂ Methanation, Carbide Catalysts, Nickel, Molybdenum

1. Introduction

In view of the potential impact of CO₂ on climate change, its atmospheric concentration needs to be controlled and stabilized. Carbon capture and utilization (CCU) technologies, including the catalytic valorization of CO₂, can highly contribute to achieving this goal [1]. Among the different processes, CO₂ methanation, *i.e.* its hydrogenation to form CH₄, stands as a very promising technology, which also offers a solution for off-peak renewable energy storage [2]. Though thermodynamically feasible even at ambient temperature, CO₂ methanation is considerably hindered by its extremely slow reaction kinetics. The use of active catalysts is imposed, moreover, undesirable byproducts such as CO start to be

produced at temperatures higher than 350 °C. Unfortunately, most of the commercially existing catalytic systems start to be active at this temperature.

Noble metal-based catalysts (Ru, Rh, and Pd) are well known to be active in CO₂ methanation [3] [4]. Ni-based catalysts display somehow lower but still acceptable activity being substantially cheaper than noble-metal based ones [5] [6]. Moreover, Ni-containing catalysts suffer from deactivation by: 1) sulfur poisoning; 2) carbon deposition; and 3) Ni-phase sintering [7]. Besides, it was reported that the stability of the nickel on the Al₂O₃ carrier is much higher than on the other carriers [8], and the Al₂O₃ has a strong interaction with NiO, which may promote the formation of NiAl₂O₄ spinel phase [9].

Since Levy *et al.* reported that tungsten carbides displayed similar activity as Pt in neo-pentane isomerization [10]. These materials have been subject of growing interest, since they can be employed in many other catalytic reactions [11]. Indeed, the activity of molybdenum and tungsten carbides (Mo₂C and WC) in dry reforming of methane, partial oxidation and steam reforming of methane to synthesis gas was found to be higher than Pt and Pd-based catalysts, though still lower than the activity measured for Ru and Rh catalysts [12]. Shi *et al.* reported high catalytic activity and stability for a Ni-Mo₂C catalyst in dry reforming of methane [13]. The activity of Mo₂C and WC was linked to their facility to activate the extremely stable CO₂ molecule. They can be also used as hydrogenation catalysts and, in fact, Huo and co-workers recently reported interesting activity, selectivity and stability in CO methanation for Co-supported on Mo carbide [14]. Mo₂C- and/or WC-based catalysts can be therefore promising materials, able to boost the CO₂ methanation reaction. However, to the best of our knowledge, there are no studies considering the use of Mo₂C-supported catalysts for this particular application.

In our previous work, we found carbide Ni-Mo/Al₂O₃ catalyst (Ni-Mo₂C/Al₂O₃) was a better catalyst for dry reforming of methane than that of reduced Ni-Mo/Al₂O₃ catalyst [15]. It was investigated the influence of preparation condition (the ratio of H₂/CH₄) for the carburization process in detail in the previous work [15].

The present work considers the preparation and characterization of Ni-Mo₂C/Al₂O₃ catalysts for CO₂ methanation. These catalysts aim to combine the well-known high catalytic activity of Ni, together with the promoting features of Mo₂C. The activity of the carbide-containing catalysts was compared to that of bimetallic Ni-Mo catalysts, proving an important promotion effect of the presence of Mo₂C.

2. Experimental

2.1. Catalysts Preparation

2.1.1. Mo/Al₂O₃ and Ni-Mo/Al₂O₃ Catalysts

Mo/Al₂O₃ and Ni-Mo/Al₂O₃ catalysts were prepared through excess solvent impregnation. Mo and Ni precursors were used, (NH₄)₆Mo₇O₂₄·4H₂O (Sigma-Aldrich)

and Ni(NO₃)₂·6H₂O (Sigma-Aldrich), corresponding to nominal loadings of 10 wt.% of each metal. The support, γ-Al₂O₃, was obtained through air calcination of a commercially available boehmite (Disperal, Sasol), at 500 °C for 4 h. After 2 h impregnation, the excess solvent (deionized water) was removed in a rotary evaporator at 60 °C. Then the catalyst was dried in an oven at 110 °C overnight, and finally calcined in synthetic air at 550 °C for 4 h.

2.1.2. Mo₂C/Al₂O₃ and Ni-Mo₂C/Al₂O₃ Catalysts

A temperature-programmed method in CH₄/H₂ atmosphere ($F_{\text{CH}_4} = 10$ mL/min and $F_{\text{H}_2} = 40$ mL/min) was followed, in order to obtain the Mo₂C/Al₂O₃ and Ni-Mo₂C/Al₂O₃ catalysts [16] [17]. Both Mo₂C/Al₂O₃ and Ni-Mo₂C/Al₂O₃ catalysts were obtained by the carburization of the Mo/Al₂O₃ and Ni-Mo/Al₂O₃ catalysts, respectively. Temperature was raised from room temperature to 300 °C at a rate of 5 °C/min, then from 300 °C to 700 °C at a rate of 1 °C/min, and subsequently kept at 700 °C for 2 h. The gas flow was then switched from CH₄/H₂ to Ar for cooling down (overnight).

2.2. Catalytic Activity Experiments

The CO₂ methanation activity tests were carried out in a tubular quartz reactor at atmospheric pressure using a H₂/CO₂/Ar = 12/3/5 reactant mixture (total flow 100 ml/min). The gas hourly space velocity (GHSV) was 20,000 h⁻¹. Both Mo/Al₂O₃ and Ni-Mo/Al₂O₃ catalysts were either carburized or reduced prior to activity runs.

For the reduced catalyst, prior the activity tests, the Mo/Al₂O₃ and Ni-Mo/Al₂O₃ catalysts were reduced *in-situ* at 900 °C in 5% H₂ in Ar for 1 h, and then cooled down to 250 °C. The catalytic activity experiments were carried out from 250 °C to 500 °C. Steady-state conversions were reached at each temperature (30 min isothermal step). For the carbide catalyst, the methanation experiments were carried out after the *in-situ* carburization of the sample and its cooling in Ar to 250 °C. The reactants and products were analyzed by a micro gas chromatograph (Varian CPi 4900), equipped with a TCD detector.

The conversions of CO₂ and the selectivity of CH₄ during the methanation reaction were calculated using the following equations, respectively:

$$X_{\text{CO}_2} = \frac{n_{\text{CO}_2,\text{in}} - n_{\text{CO}_2,\text{out}}}{n_{\text{CO}_2,\text{in}}} \times 100\%$$

$$S_{\text{CH}_4} = \frac{2n_{\text{CH}_4}}{n_{\text{H}_2,\text{in}} - n_{\text{H}_2,\text{out}}} \times 100\%$$

in which X_{CO_2} is the conversion of CO₂ (%), S_{CH_4} is the selectivity for CH₄ (%).

2.3. Physico-Chemical Characterization

CO₂ temperature programmed desorption (CO₂-TPD) was performed in a

BELCAT-M apparatus (BEL Japan). The reduced and carburized catalysts after CO₂ methanation were first degassed at 500 °C for 2 h, then cooled to 80 °C. 10% CO₂-He was fed for 1 h in order to saturate the catalyst's surface. After flushing He for 15 min, the materials were heated up from 80 °C to 800 °C under He, at the rate of 10 °C/min, while the evolution of CO₂ followed with the aid of a TCD detector. H₂ temperature programmed reduction (H₂-TPR) carried out in the same device as the CO₂-TPD, for both the calcined and the carburized catalysts. The materials were first pretreated at 100 °C for 2 h, then reduced from 100 °C to 900 °C at a rate of 7.5 °C/min in 5% H₂ in Ar flow. X-ray photoelectron spectroscopy (XPS) experiment was performed on an AXIS Ultra DLD (KRATOS) spectrometer.

3. Results and Discussion

The relative sensitivity factor (RSF)-corrected Mo/C area ratios calculated from XPS peak integration for both calcined and carburized catalysts are presented in **Table 1(a)**, & **Table 1(b)**.

The XPS spectra corresponding to Ni-Mo₂C/Al₂O₃ carbide catalysts are presented in **Figure 1**.

Though the presence of carbon-containing compounds, and thus the C 1s peak area, may be dependent on sample/device contamination, the Mo/C ratios are somehow smaller for the two carburized catalyst, in comparison to the calcined ones. This points already to a higher carbon content in the former, as a consequence of effective carburization. The results of the deconvolution of the C 1s, Mo 3d and Ni 2p orbitals can be also found in **Table 1**. The experimental peaks were decomposed into mixed Gaussian-Lorentzian contributions. The deconvolution of the C 1s orbital was performed as described elsewhere [18] [19], considering different species: carbides (238.1) polymeric C-species (284.5 eV), oxidized carbon (286.8 eV), graphite (285.5 eV) and carbonyls/quinones (288.8 eV). The deconvolution points to higher amount of carbide species in the case of the catalysts submitted to the carburization treatment. The Mo 3d orbital

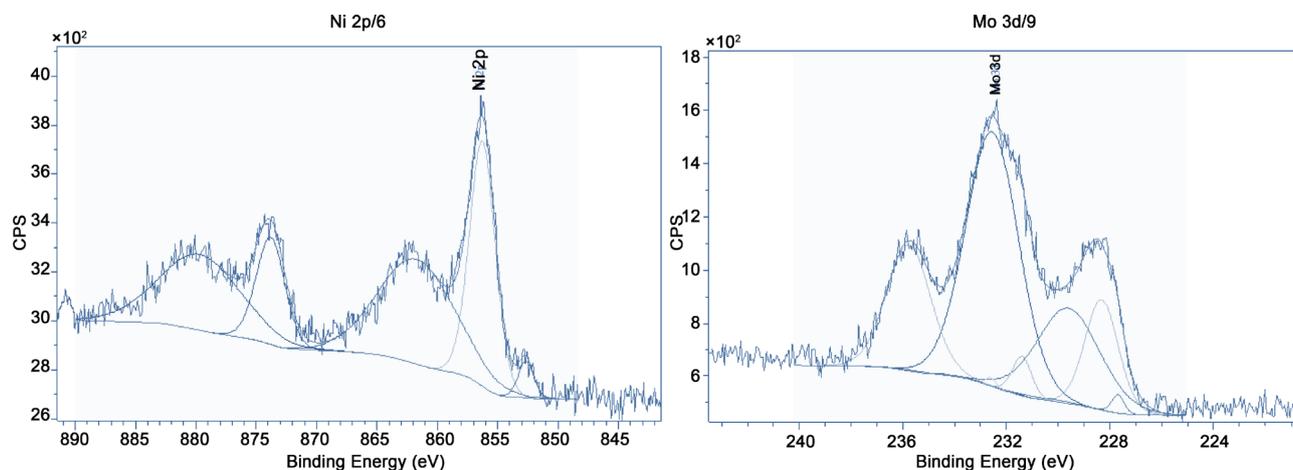


Figure 1. XPS spectrum of Ni 2p, Mo 3d binding Energies for Ni-Mo₂C/Al₂O₃ carburized catalysts.

Table 1. (a) Deconvolution of the C 1s, orbital for the different catalysts before and after carburization (BE in eV in italics); (b) Deconvolution of the Mo 3d and Ni 2p orbitals for the different catalysts before and after carburization (BE in eV in italics).

(a)					
Catalyst	C 1s				
	Carb.	Poly.	Oxy.	Graph.	C=O
Mo/Al ₂ O ₃	1.4%	2.8%	18.6%	58.0%	19.2%
	283.1	284.5	286.8	285.2	288.8
Ni-Mo/Al ₂ O ₃	1.9%	4.3%	18.9%	57.8%	17.1%
	283.3	284.5	286.7	285.3	288.9
Mo ₂ C/Al ₂ O ₃	7.8%	2.7%	22.6%	46.9%	20.0%
	283.1	284.5	286.8	285.3	288.8
Ni-Mo ₂ C/Al ₂ O ₃	9.2%	2.8%	12.7%	58.0%	17.3%
	283.1	284.4	286.8	258.3	288.8

(b)							
Catalyst	Mo 3d _{5/2}				Ni 2p _{3/2}		Mo/C
	Mo ⁰	Mo ²⁺	Mo ⁴⁺	Mo ⁶⁺	Ni ⁰	Ni ^{δ+}	
Mo/Al ₂ O ₃	1.2%	-	-	98.8%	-	-	0.18
	227.6	228.2	229.6	232.8	-	-	
Ni-Mo/Al ₂ O ₃	-	0.7%	0.3%	99.0%	-	100%	0.24
	227.7	228.4	229.5	232.7	852.6	856.2	
Mo ₂ C/Al ₂ O ₃	0.9%	8.7%	27.6%	62.8%	-	-	0.16
	227.5	228.4	229.7	232.8	-	-	
Ni-Mo ₂ C/Al ₂ O ₃	1.0%	15.7%	25.8%	57.5%	8.2	100%	0.14
	227.7	228.3	229.6	232.8	852.6	856.3	

was deconvoluted into two linked doublets Mo 3d_{5/2} and Mo 3d_{3/2}, using an intensity ratio of 2/3 and a splitting of 3.2 eV. Five different contributions to the 3d_{5/2} orbital were considered, respectively corresponding to Mo⁰, Mo²⁺, Mo⁴⁺, Mo⁵⁺ and Mo⁶⁺ species. Concretely, the presence of Mo²⁺ species, also denoted as Mo^{δ+}, has been clearly linked to Mo involved in a Mo-C bond, whereas relatively high content of Mo⁴⁺ and Mo⁵⁺ was assigned to the formation of oxycarbides [19] [20]. In agreement to the deconvolution of the C 1s orbital, the presence of Mo-carburized species increases after the carburization treatment.

However, higher amount of oxycarbides seems to be as well produced as a consequence of this treatment. This can be due either to the partial oxidation of molybdenum species during passivation upon or to their incomplete carburization [13] [21]. In any case, carburization seems to be more effective when Ni is present in the formulation of the catalyst [13] [22]. The Ni 2p orbital was deconvoluted into two doublets Ni 2p_{3/2} and Ni 2p_{1/2}. The Ni 2p_{3/2} core-level photoemission spectra presents two states: Ni⁰ and Ni^{δ+}, respectively appearing at 852.6 and 856.5 eV, together with a shake-up satellite at 861.7 eV. A main peak at 873.8 eV and its shake-up satellite at 880.1 eV conform Ni 2p_{3/2} contribution.

The spin-orbit splitting value between Ni 2p_{3/2} and Ni 2p_{1/2} was found to be around 17.5 eV, pointing to the presence of NiAl₂O₄ [23]. A certain amount of reduced Ni⁰ species are formed upon the carburization treatment. Let us note here that the X-ray diffraction patterns acquired for this series of catalysts (not shown) did not evidence the presence of Mo₂C species, presumably due to its relative low concentration and high dispersion [24] [25].

Table 2 shows the results of the integration of the CO₂-TPD profiles for this series of catalysts, upon either reduction or carburization, whereas the CO₂-TPD profiles acquired for the carburized catalysts Mo₂C/Al₂O₃ and Ni-Mo₂C/Al₂O₃ are detailed in **Figure 1**. Total basicity extremely increases for the catalysts submitted to the carburization treatment. While both the reduced Mo and the Ni-Mo containing catalysts show very small ability to absorb CO₂, the carburized are able to absorb more than 40 times more CO₂ than the reduced ones.

Figure 2 showed that both CO₂-TPD profiles (acquired for Mo₂C/Al₂O₃ and Ni-Mo₂C) covered almost all the temperature window, which pointing to the presence of basic sites with different strength. The most important part for the CO₂-TPD was the desorption occurred at low and moderate temperatures, which reflects a major presence of weak and medium-strength basic sites in these carburized catalysts. Note here moreover that the presence of Ni in the bimetallic

Table 2. Total basicity, *i.e.* integration of the CO₂-TPD profiles, for the different catalysts before and after carburization.

Catalyst	Amount of CO ₂ desorbed (μmol/g)
Mo/Al ₂ O ₃	2.6
Ni-Mo/Al ₂ O ₃	114.8
Mo ₂ C/Al ₂ O ₃	3.3
Ni-Mo ₂ C/Al ₂ O ₃	121.7

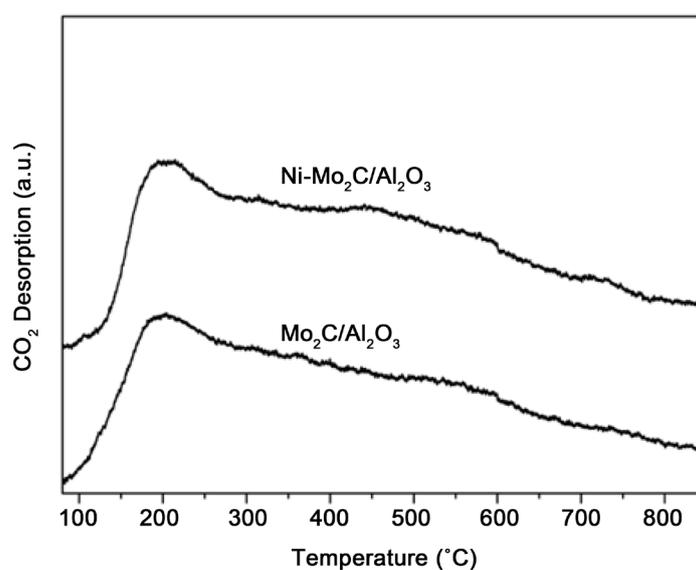


Figure 2. CO₂-TPD profiles for the Mo₂C/Al₂O₃ and Ni-Mo₂C/Al₂O₃ carburized catalysts.

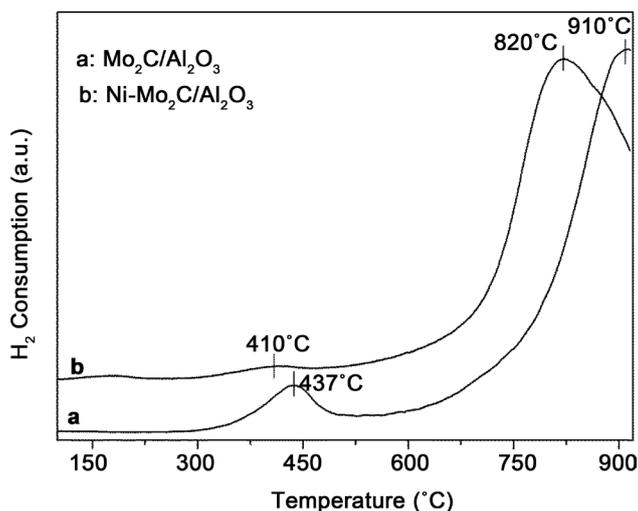


Figure 3. H₂-TPR profiles for the Mo₂C/Al₂O₃ and Ni-Mo₂C/Al₂O₃ carburized catalysts.

catalysts resulted in enhanced CO₂ absorption in comparison to both the reduced and carburized Mo-catalysts.

Figure 3 presents H₂-TPR profiles for the carburized catalysts. The Mo₂C/Al₂O₃ catalyst exhibited two main H₂ consumption peaks respectively centered at about 437°C and 910°C.

The low temperature reduction peak (437°C) can be assigned either to the reduction of MoO₃ to MoO₂ or to the reduction of some high valent Mo species (MoO_{*x*}). The reduction peak occurring observed around 910°C results from the reduction of MoO₂ to metallic Mo, but can also be ascribed to the reduction of Mo₂C species [26]. If this high temperature peak could be ascribed to the further reduction of MoO₂ to metallic Mo, the first low temperature peak corresponding to the reduction of MoO₃ to MoO₂ should have very similar intensity, *i.e.* similar H₂ consumption, than the high temperature one, which, indeed, is not the case. Therefore, the high temperature peak can be directly linked to the presence of molybdenum carbide and oxycarbide species. In the case of the Ni-Mo₂C/Al₂O₃ catalyst, the peak corresponding to the reduction of high valence Mo-species at low temperature appears shifted to lower temperatures, *i.e.* around 410°C, and becomes much weaker. The high temperature peak, corresponding to the reduction of molybdenum carbide and oxycarbide species, also shifts to lower temperature, *i.e.* around 820°C. This latter result points out that the presence of Ni affects the carburization process and the type of carburized species formed. In the presence of Ni, the carburization treatment leads most probably to favored carburization of molybdenum and to a lower extent of formation of oxycarbides, which confirming the results obtained through XPS analysis. The H₂-TPR profiles acquired for the calcined Mo/Al₂O₃ and Ni-Mo/Al₂O₃ catalysts can be found elsewhere [27], but they only evidenced the H₂-consumption peaks typical of Mo and Ni oxide and mixed oxides species.

The results of the methanation experiments are presented in **Table 3**. It is worth to note that the Mo/Al₂O₃ catalyst (reduced) was found to be completely

Table 3. Catalytic activity and selectivity of the different catalysts: CO₂ conversion and CH₄ selectivity at temperatures from 250 °C to 500 °C.

Catal. Perf.	Catalyst	Reaction Temperature (°C)					
		250	300	350	400	450	500
Conversion (%)	Ni-Mo/Al ₂ O ₃	1.2	2.3	5.3	10.7	17.4	22.3
	Mo ₂ C/Al ₂ O ₃	0.3	1.0	4.1	10.6	18.7	26.5
	Ni-Mo ₂ C/Al ₂ O ₃	1.8	7.5	13.8	20.9	25.1	27.3
CH ₄ Selectivity (%)	Ni-Mo/Al ₂ O ₃	0.6	9.4	10.0	12.6	13.2	11.8
	Mo ₂ C/Al ₂ O ₃	5.0	8.4	5.9	3.0	1.5	0.5
	Ni-Mo ₂ C/Al ₂ O ₃	98.2	98.2	98.1	97.3	94.6	86.3

inactive towards CO₂ methanation, and thus we decided to exclude the catalytic results of these experiments from **Table 3**. Both the reduced Ni-Mo/Al₂O₃ and the carburized Mo₂C/Al₂O₃ showed very low catalytic activity and very poor CH₄ selectivity in CO₂ methanation reaction.

As previously observed for this thermodynamically feasible but strongly kinetically hindered reaction, the CO₂ conversion generally increases with increasing reaction temperatures, *i.e.* in the case of the Mo₂C/Al₂O₃ catalyst it increases from 4.1% at 350 °C to 26.5% at 500 °C. Similar CO₂ conversions were obtained over the reduced Ni-Mo/Al₂O₃ catalyst. The activity towards CO₂ methanation substantially was improved in the presence of the carburized Ni-Mo₂C/Al₂O₃ catalyst. CO₂ conversions were increased from 13.8% at 350 °C to 27.3% at 500 °C, whereas CH₄ selectivity was almost 100% at low temperatures, which slightly decreasing with increasing temperature, as predicted by equilibrium thermodynamics. Park *et al.* reported that CO₂ conversion would reach to 40% on Pd/SiO₂ catalyst at 450 °C, but on which the selectivity to CH₄ was only 10% [3]. According to the above results of the physico-chemical characterization, first of all, carburization results in a 40-fold increase the basicity, *i.e.* the CO₂ absorption ability of these catalysts. As a consequence, and even if the amount of oxycarbide species formed was found to be important, the carburized Mo₂C/Al₂O₃ catalyst showed already a better activity vis-à-vis the reduced Mo/Al₂O₃ one. Additionally, the presence of Ni enhanced the carburization of the molybdenum species in the bimetallic Ni-Mo catalysts. The amount of oxycarbides was reduced at the same when Ni and Mo was coexist. All this facts resulted therefore in the further promotion of the activity and selectivity observed on the Ni-Mo₂C/Al₂O₃ catalyst. The formation of a mixed NiAl₂O₄ phase was also observed through the analysis of the XPS results. The presence of Ni in strong interaction with the alumina support may have also affected the carburization process in the case of the Ni-Mo₂C/Al₂O₃ catalyst.

4. Conclusion

γ -alumina-supported Mo and Ni-Mo catalysts were prepared and submitted ei-

ther to reduction or to a carburization treatment, prior to evaluating their catalytic activity in CO₂ methanation. The presence of Ni facilitated the formation of the Mo₂C species, considerably reducing the formation of oxycarbides. The CO₂ absorption substantially increased upon carburization, leading to improved catalytic activity in CO₂ methanation. Moreover, the presence of Ni and thus as a consequence of favored carburization, resulted in further enhanced catalytic activity and selectivity. Nevertheless, the carburized catalysts still contained an important amount of oxycarbide species, pointing to incomplete carburization. Though the results are quite promising and prove that Ni-Mo carbide catalysts can be successfully used for CO₂ methanation, the carburization treatment needs to be consequently optimized.

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