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The effect of synthesis parameters on ordered mesoporous nickel alumina catalyst for CO₂ methanation

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Graphical Abstract



Highlights

- Compared to hydrochloric and citric acid, using nitric acid during the synthesis led to ordered mesoporous catalysts with higher surface area and superior catalytic activity.
- Evaporation induced self-assembly (also known as "one pot") synthesis technique produced catalysts with highly dispersed nickel clusters with very small diameter of around 2.8 nm.
- Ordered mesoporous nickel alumina catalyst calcined at 700°C exhibited the best results towards CO₂ methanation.
- At lower reaction temperatures (<400°C) the CO₂ methanation proceeds most likely via the direct dissociation of CO₂.

Abstract

A series of ordered mesoporous nickel alumina catalysts were synthesized via the evaporation induced self-assembly technique (EISA). Varying synthesis parameters such as the type of acid, nickel loading, calcination temperature as well as synthesis method influenced the catalyst morphology and its activity towards CO_2 methanation. Catalyst prepared without acid formed macroporous structures with a very low surface area (47 m² g⁻¹), whereas using a mixture of hydrochloric and citric acid resulted in incomplete formation of mesoporous micelles with surface area of 173 m² g⁻¹. On the other hand, using nitric acid lead to complete formation of long cylindrical micelles with a combined surface areas up to 260 m² g⁻¹ and highly dispersed nickel clusters with a size of 3-5 nm. An optimum calcination temperature of 700°C was determined yielding the highest CO_2 conversion and CH_4 selectivity. This catalyst displayed a stable performance and did not exhibit any sign of deactivation during a 150 h test. Catalysts calcined at lower and higher temperatures had smaller surface areas as well as lower catalytic activity.

Keywords: CO₂ methanation • Ordered mesoporous nickel alumina catalyst • Catalyst synthesis and

characterization

1 Introduction

Energy storage is a pressing topic in the development of renewable energies such as wind and solar, mainly due to the intermittencies of electricity production. Growing interest has been observed towards the Power-to-Gas process (P2G) in which excess electrical energy is used to produce hydrogen via water-electrolysis, which is subsequently converted with captured CO₂ to grid compatible gas (methane). The P2G process combines electricity storage and CO₂ utilization leading potentially to a closed carbon cycle (Circular Economy)[1]. Beside water-electrolysis, the methanation is the most important and technically challenging step in the P2G process. Current areas of research focus on (1) evaluating suitable carbon oxides sources (i.e., biogas, power plants, extraction from air), (2) catalyst design, and (3) reactor and process design including heat integration.

The main overall reactions are the CO_2 methanation (eq. 1), the competing reverse water-gas-shift reaction (eq. 2), which leads to undesired CO, and the subsequent CO methanation (eq.3).

$$CO_2 + 4H_2 \to CH_4 + 2H_2O$$
 $\Delta H_R^o = -165 \, kJ \, mol^{-1}$ (1)

$$CO_2 + H_2 \leftrightarrow CO + H_2O \qquad \qquad \Delta H_R^o = 41 \ kJ \ mol^{-1} \tag{2}$$

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O \qquad \Delta H_R^o = -206 \ kJ \ mol^{-1} \tag{3}$$

The reactions involved are catalyzed by supported Ni, Ru, and Rh systems of which the latter two noble metals are more active than Ni-based catalysts [2–4]. Nickel might still be the first-choice due to lower costs and its high catalyst stability shown for syngas/CO methanation (eq.3) [5]. For the CO₂ methanation, however, the stability of Ni-catalysts is not proven on a commercial scale. New catalysts have been developed of which the ordered mesoporous alumina catalysts (OMA) show great promise due to larger surface areas, larger pore volumes and uniform pore size distribution compared to traditional catalyst systems allowing for a better interaction between the metal-oxide and the support resulting a high metal dispersion [6,7]. In addition, the metallic nanoparticles are stabilized

due to the confinement effect of the mesoporous framework that suppresses sintering and agglomeration of the metal atoms (e.g., Ni) even at high reaction temperatures. Therefore, ordered mesoporous alumina materials are considered an ideal catalyst support for reforming [7–9], oxidation [10,11] and hydrogenation [12] reactions.

Ordered mesoporous alumina catalysts can be synthesized by various methods as outlined in [13–15]. The "one-step" facile route with evaporation induced self-assembly (EISA) has become one of the most adopted techniques due to its simple and flexible procedure [14,15]. In EISA, the precursors are mixed together at the desired concentrations until a homogeneous solution is obtained, which is then dried and calcined. A polymeric surfactant/copolymer is often used as soft template and mixed with a polar organic solvent and acid. Using a non-polar solvent like toluene would result in a water-in-oil emulsion and would lead to rod formation rather than a mesoporous structure. Providing an acidic environment is key in inducing the mesoporous structure since the polymerization and cross-linking rate are too fast at a pH of 6-8.5 [14,15]. Nitric acid as well as mixtures of hydrochloric and citric acid have been used in the synthesis of alumina and silica based catalysts. Besides the acidic environment, the calcination temperature influences the catalyst structure and morphology hence its activity as observed for the partial oxidation of methane [11].

Recently, Ni-OMA catalysts were tested for CO₂ methanation and showed higher CO₂ conversion and CH₄ selectivity compared to non-mesoporous nickel alumina catalysts [12]. Considering the promising results, this work deals with the development of alumina based ordered mesoporous catalysts using EISA synthesis method with various synthesis parameters. The objective was to study the effect of different Ni loadings, calcination temperatures, and the acid used on the catalyst morphology and activity towards the CO₂ methanation at different reaction temperatures and gas hourly space velocities.

2 **Experimental**

2.1 Catalyst Preparation

EISA technique was chosen as it was reported to be a robust mesoporous catalyst synthesis pathway. Approximately 1 g of triblock copolymer (Pluronic[®] P-123, Sigma Aldrich) was dissolved in 20 ml of anhydrous ethanol until a homogeneous solution was obtained. Subsequently 2-4 g of aluminumisopropoxide (\geq 98%, Sigma Aldrich) and up to 1.5 g of nickel (II) nitrate hexahydrate (\geq 98.5%, Sigma Aldrich) were added to achieve the desired catalyst mass and nickel target loadings (Table 1). Nitric acid (68 wt%, Fisher Scientific) or a mixture of hydrochloric (37 wt%, Fisher Scientific) and citric acid (Sigma Aldrich) was then added to provide the acidic environment to enhance mesopore formation. The solution was stirred for 5 h at 600 rpm at room temperature. The homogenized solution obtained, was dried at 60°C for 48 h and subsequently calcined in a muffle furnace with heating rate of 1°C min⁻¹ for 5 h at the targeted calcination temperature (i.e., 400, 500, 700 or 900°C). Samples with three different nickel loadings (5 wt%, 15 wt% and 30 wt%) and four different calcination temperatures (400-900°C) were prepared. The catalysts were named OMA-15Ni-500, where OMA refers to ordered mesoporous alumina, 15Ni refers to the nickel loading in wt% and 500 to the calcination temperature in degree Celsius (°C). OMA-500 denotes to the support only, calcined at 500°C; whereas catalysts prepared without no acid or with hydrochloric + citric acid, were labeled OMA-500-No Acid or OMA-500-HCl and OMA-15Ni-500-HCl, respectively (Table 1). In addition, a 15 wt% Ni/OMA catalyst was synthesized via wet impregnation for comparison. First, the OMA support was prepared via the aforementioned technique and calcined at 500°C. Secondly, the OMA support was added slowly to the nickel (II) nitrate hexahydrate solution and stirred vigorously (~600 rpm) for 6 h. The mixture was dried for 24 h at 100°C and then calcined at 500°C with heating rate of 1°C min⁻¹ for 5 h. The catalyst was named 15Ni/OMA-500.

All of the produced catalyst samples were sieved into three different particle size categories (45-90 μm, 90-125 μm, and 125-150 μm) using a DUAL D-4326 motorized sieve.

2.2 Catalyst Characterization

Various characterization techniques were used to study catalyst morphology, crystallinity and composition. Sieved particles with 45-90 μ m were used in all characterization techniques, whereas particles of 125-150 μ m were used in H₂ temperature programmed reduction and activity measurements.

Inductively Coupled Plasma - Optical Emission Spectroscopy (ICP-OES, iCAP 6500 dual view Thermo Scientific) was used to assess the actual nickel concentration in each sample. Prior to the analysis, 100 mg of the catalyst sample was digested in a mixture of 2 ml of nitric acid (67 wt%, Fisher Scientific) and 3 ml of hydrochloric acid (37 wt%, Fisher Scientific) at 95°C for 3 h. N₂ adsorption/desorption measurements (-196°C) were conducted using Micromeritics Tristar 3000 BET analyzer to determine total surface area, pore size distribution and pore volume. Before the

analysis, the samples were degassed under vacuum for 12 h at 200°C.

X-Ray Diffraction (XRD) was used to identify the crystallinity of the catalyst. Analyses were conducted on a Bruker D8 Discovery X-Ray Diffractometer with two-dimensional VANTEC-500 detector and CuK_{α} (λ = 1.54056 Å) radiation source. The measurements were done with a scan rate of 5° min⁻¹ at a tube voltage of 40 kV and a tube current of 20 mA.

Temperature program reduction (H₂-TPR) experiments were carried out in fixed bed reactor setup coupled with a calibrated mass spectrometer (Pfeiffer Omnistar GSD 301). Approximately, 100 mg of fresh calcined catalyst was heated under Ar atmosphere (40 ml_N min⁻¹, 99.999%, Megs) with a rate of 10° C min⁻¹ to 310° C for 3 h to remove moisture. After cooling the sample to room temperature, H₂ (99.999%, Megs) was introduced and the sample was heated at a rate of 8.5° C min⁻¹ to 950° C while the

corresponding mass to charge ratio for H₂O (m/z = 18) was recorded. Flow rates of H₂ and Ar were respectively set to 10 and 40 ml_N min⁻¹ (subscript *N* denotes normal condition with T = 0°C and 1 bar). Temperature programmed oxidation was carried out for both fresh and spent OMA-15Ni-700 (used at 400 °C for 150 h) catalysts using a thermogravimetric analyzer (TGA, Q500 TA instrument). Note, the fresh catalyst was calcinated, while the spent catalyst was passivated after the long-term experiment. Approximately, 9 mg of sample was placed in the TGA and heated in presence of N₂ to 130°C at the rate of 5°C min⁻¹, while the weight change was recorded. After a holding time of 30 minutes to remove moisture, the sample was then heated in Air to 900°C at 5°C min⁻¹ to combust possible carbon deposition.

Volumetric hydrogen uptake (chemisorption) was conducted in an Autosorb iQ (Quantachrome) gas sorption instrument. Approximately 100 mg of fresh calcined sample was placed in a U-shaped quartz tube, preheated in He at 120°C with a heating rate of 20°C min⁻¹ for 0.5 h, then reduced with H₂ (5 vol% H₂ in He or 100 vol% H₂) at its main peak reduction temperature obtained from H₂-TPR (Fig. 3) for another 3 h, then evacuated for 1 h and subsequently cooled to 40°C, where all adsorption measurements were taken at pressures ranging from 0.05 bar to 0.8 bar. Specific surface area (m² g⁻¹), metal dispersion (*D* in %) and average crystallite size (*d* in nm) were calculated based on the amount of H₂ adsorbed assuming an atomic stoichiometric ratio of H/Ni = 1 and a hemispherical cluster with a nickel density of 8.9 g cm⁻³.

Transmission electron microscopy (TEM) of fresh and calcined catalyst was carried out on FEI Tecnai G2 F20 with 200 kV. Prior to the analysis, a thin (100 nm) section of the catalyst was prepared using a dual-beam focused ion beam (FEI Helios 600 NanoLab, Hillsboro) equipped with a gallium ion source.

The ICP-OES, H₂-TPR, N₂-physisorption and H₂-chemisorption analyses were repeated at least twice for each batch to assure that catalysts prepared with the same recipes at different days had the same properties.

2.3 Activity Measurements

The catalyst performance was tested in a fixed bed reactor (FBR) system at atmospheric pressure. The setup included mass flow controllers, gas mixing station, tube furnace, condenser and gas analyzer (mass spectrometer). The reactant gases, Ar (99.999%, Megs), H₂ (99.999%, Megs) and CO₂ (99.99%, Praxair), were mass flow controlled using calibrated Vögtlin red-y smart controller GSC (Switzerland). The reactor was stainless steel (SS316) with a double tube counter-current flow configuration. The inner tube (ID = 4.57 mm) was closed with a 5 μ m thick stainless steel frit on which the catalyst was placed. The exit gas line was electrically heated between 150-180°C to avoid condensation of water. A split stream of the exit gas was analyzed using a calibrated mass spectrometer (Pfeiffer Omnistar GSD 301), while the rest of the exit gas was exhausted after condensation. The experiments were performed in the 300 to 500°C temperature range with gas hourly space velocities (GHSV) ranging from 45-115 $L_N g_{cat}^{-1} h^{-1}$. The reaction temperature was controlled by a K-type thermocouple inserted into the catalyst bed. Prior to the experiments, the catalysts were reduced with 20 vol% H₂ in Ar for 3 h at their respective main peak reduction temperature determined via H₂-TPR (Fig 3). The reactions were performed at 1 bar with H₂/CO₂ ratio of 5:1. Argon gas was used as an internal standard. The catalyst was subjected to each experimental condition for at least 3 h. The OMA-15Ni-700 catalyst was used in a 150 h long-term run to study the catalyst stability. The test was performed at 400°C with a GHSV of 91 $L_N g_{cat}^{-1} h^{-1}$. After the reaction, all catalysts were passivated and then removed, stored and analyzed. Conversion of carbon dioxide (X_{CO2}), and product selectivity (S_i) were defined per eqs. 4 and 5.

$$X_{CO_2} = \frac{\dot{n}_{CO_{2,in}} - \dot{n}_{CO_{2,out}}}{\dot{n}_{CO_{2,in}}}$$
(4)

$$S_i = \frac{\dot{n}_i}{\dot{n}_{CO_{2,in}} - \dot{n}_{CO_{2,out}}} \tag{5}$$

Where \dot{n}_i is the molar flow rate of species *i* (i.e., CH₄, CO). Only CH₄ and CO, but no C₂+ hydrocarbons were detected during all activity experiments.

To ensure the reproducibility of the results, three different batches of the catalysts (e.g., OMA-15Ni-500) were synthesized using the exact procedures and tested in the reactor under the same conditions and reduced at the same temperature. The results (CO₂ conversion and CH₄ selectivity) varied within \pm 3 % and were very small compared to the change in conversion and selectivity obtained for different catalysts.

3 Results and Discussion

3.1 Characterization of fresh catalyst

3.1.1 N₂ Adsorption/desorption analysis

 N_2 adsorption/desorption isotherms and the pore size distributions of the synthesized supports and nickel catalysts are depicted in Fig. 1. All the samples prepared with nitric acid showed a type-IV isotherm with H1 hysteresis loop, indicating the formation of uniform cylindrical mesoporous structure [11]. Acidic media were important in creating mesoporous structure; samples prepared without acid did not exhibit a type-IV isotherm (Figure 1A and B labeled OMA-500-No Acid) and had a very small total surface of 47 m² g⁻¹, of which 43 m² g⁻¹ was macroporous (Table 1). Lack of acidity in the synthesis media resulted in low tendency towards mesopore formation as the copolymer became less hydrophilic [16].

The type of acid used during the synthesis played an important role in the formation of organized mesoporous structures. The catalyst prepared with hydrochloric and citric acid had a smaller

mesoporous surface area (134 m²g⁻¹ for OMA-500-HCl) compared to the one prepared with nitric acid (258 m² g⁻¹ for OMA-500), see Table 1. This might be related to the role of anion (e.g., NO³⁻, Cl⁻) and their binding strengths when adsorbed on the positively charged surfactant during the synthesis [17]. The binding strength of NO³⁻ ions was sufficient to promote long micelles, hence, a more ordered and organized structure.

Table 1 Sample overview: Synthesis parameter (target Ni loading, calcination temperature T_{cal} , acid used) and N₂ adsorption/desorption results (total and mesoporous surface area, average pore size, pore volume).

Sample	Ni [wt%]	T _{cal} [°C]	Acid used	S_{BET}^{a} [m ² g ⁻¹]	S_{Meso}^{b} [m ² g ⁻¹]	D _{Pore} c [nm]	V _{Pore} ^d [cm ³ g ⁻¹]
OMA-500-No Acid	0	500	none	47	43*	11.6	0.14
OMA-500-HCl	0	500	HCl+CA	173	134	7.2	0.31
OMA-400	0	400	HNO ₃	175	153	14.0	0.60
OMA-500	0	500	HNO ₃	262	258	8.0	0.52
OMA-700	0	700	HNO ₃	202	190	8.3	0.42
OMA-15Ni-400	15	400	HNO ₃	140	124	11.7	0.41
OMA-15Ni-500	15	500	HNO ₃	242	234	10.0	0.60
OMA-15Ni-700	15	700	HNO ₃	206	198	8.2	0.42
OMA-15Ni-900	15	900	HNO ₃	123	115	8.9	0.28
OMA-05Ni-500	5	500	HNO ₃	217	206	9.4	0.52
OMA-30Ni-500	30	500	HNO ₃	174	168	12.7	0.58
15Ni/OMA-500	15	500	HNO ₃	135	122	8.5	0.29
OMA-15Ni-500-HCl	15	500	HCl+CA	83	72	12.7	0.25

^a S_{BET} = BET total specific surface area obtained from adsorption data in the p/p^{0} range from 0.05-0.2; all reported data are within ± 4 m² g⁻¹ based on repeated analysis. ^b S_{Meso} = mesoporous surface area determined via subtracting the microporous surface area. ^c D_{Pore} = average pore diameters calculated using Barrett-Joyner-Halenda (BJH) method; ^d V_{Pore} = pore volume was obtained at p/p^{0} = 0.97; * macropores.

Surface area and pore volume were influenced by the calcination temperature and catalyst loading as depicted in Figure 1C to H. The maximum mesoporous surface area for support (258 m² g⁻¹ for OMA-500) and nickel catalyst (234 m² g⁻¹ for OMA-15Ni-500) was found for a calcination temperature of 500°C (Table 1). Calcination temperatures of 400 or 900°C yielded a much smaller surface area of 153

to 115 m² g⁻¹ for samples with and without nickel (Table 1). Interestingly, the surface area for the samples calcined at 400°C exhibited a bimodal pore size distribution (Figure 1D and F), probably due to the incomplete combustion of the soft template (P123 copolymer). The reduction in surface area and pore volume for the samples calcined at 900°C might be associated with the reconstruction of the surface and/or thermal collapsing of the mesoporous structure.

A temperature of 500°C for the calcination has been used as basis to investigate the influence of the nickel loading. Adding nickel reduced the mesoporous surface area slightly (e.g., 258 m² g⁻¹ and 234 m² g⁻¹ for OMA-500 and OMA-15Ni-500, respectively). However, calcined at 700°C the sample with and without nickel had about the same mesoporous surface area of $194 \pm 4 \text{ m}^2 \text{ g}^{-1}$. In contrast, adding nickel to the solution containing hydrochloric and citric acid during the synthesis reduced the total surface area significantly from 173 to 83 m² g⁻¹ (OMA-500-HCl and OMA-15Ni-500-HCl), implying that nitric acid is a better reagent. Similar results have been reported for mesoporous silica materials [17]. Using hydrochloric and citric acid might require a much longer induction time.

Increase in nickel loading to 30 wt% led to a decrease in the mesoporous surface area, larger pores and less uniform pore size distribution (Table1 and Figure 1H).

The catalyst prepared via impregnation (15Ni/OMA-500) had a mesoporous surface area of 122 m² g⁻¹, which is significantly smaller than 234 m² g⁻¹ for OMA-15Ni-500. A considerable number of pores might be blocked by adding nickel clusters to mesoporous framework. Thus, following the EISA technique yielded in highly organized samples with larger surface areas compared to the sample prepared via impregnation.

3.1.2 ICP analysis

ICP-OES was used to confirm the presence of nickel in the catalysts. Results showed that the actual nickel loadings were close to the targeted theoretical values indicating an effective synthesis of the ordered mesoporous nickel alumina catalyst (Table 2).

Catalyst Code	Target [wt%]	Actual [wt%]	
OMA-05Ni-500	5.0	4.7 ± 0.1	
OMA-15Ni-500	15.0	13.5 ± 1.3	
OMA-30Ni-500	30.0	28.6 ± 3.2	

Table 1 Target and actual nickel loadings for ordered mesoporous catalysts determined by ICP-OES.

3.1.3 TEM analysis

The fresh and calcined OMA-15Ni-500 catalyst was analyzed with TEM. During the preparation, the catalyst was cut with a focused ion beam along the axis of the pores and not perpendicular. Thus, the typical hexagonally shape of the pores with p6mm symmetry could not be confirmed. However, aligned cylindrical pores were clearly visible (Fig. 2 A and B). The average pore diameter determined with nitrogen physisorption measurements was 9-11 nm and smaller than observed via TEM. Here, the cylindrical micelles had a diameter between 50-100 nm containing multiple holes in the wall along the axis with approximately 10-20 nm in diameter. Highly dispersed nickel clusters with a crystallite sizes between 2 to 5 nm were observed as well (Fig. 2C), which were much smaller compared to values reported in the literature [18], but similar to the values determined via hydrogen chemisorption (see section 3.1.5). Analysis with an image processing software (ImageJ) showed that the average nickel crystallite size was around 2.8 nm.

3.1.4 H₂-TPR analysis

Temperature programmed reduction (H₂-TPR) was used to investigate the interactions between nickel and the alumina support. The H₂O signal (m/z = 18) was monitored and recorded by mass spectrometry.

The synthesis method affects the TPR results as illustrated in Fig. 3 A. The catalysts prepared via the one-pot ESIA technique OMA-15Ni-500 (with nitric acid) and OMA-15Ni-500-HCl (with citric and hydrochloric acids) have similar catalyst TPR characteristics. From 300° C to 400° C the first H₂O peaks were observed corresponding to weak NiO interactions, whereas the reduction peaks for strong the NiO interactions were detected between 575°C and 590°C for OMA-15Ni-500 and OMA-15Ni-500-HCl, respectively. The impregnated sample (15Ni/OMA-500) exhibited a different TPR behavior with a much broader H₂O peak consisting of three peaks; the first at around 400°C, the second at around 600°C and the third at 710°C. The impregnated sample, even though calcined at the same temperature of 500°C produced NiO clusters with a much stronger interaction than other two sample. This might indicate a higher degree of crystallinity of the NiO clusters from the 15Ni/OMA-500 catalyst (Fig 4A). With increasing nickel loading the reduction peak did only vary slightly from 575°C to 620°C (Fig. 3B). The influence of calcination temperature was studied for the OMA-15Ni catalyst. A broader H₂O peak at around 550°C was observed for the OMA-15Ni-400 compared to the OMA-15Ni-500 (Fig. 3C). At calcination temperatures of 700°C and 900°C, the TPR peaks shifted to higher temperatures of 780°C and 870°C, respectively, indicating a stronger interaction of the nickel with the alumina support, which might be related to the formation of nickel aluminates. Small peaks appeared between 400-500°C for both catalysts calcined above 700°C. This small reduction peak might correspond to weak NiO interaction with the OMA support. TPR measurements were also conducted on the support (OMA-500), but did not result in any H₂O formation (Fig. 3B), which verifies that the observed peaks are related to the reduction of NiO only.

*3.1.5 H*₂*-uptake*

The mesoporous surface area of the OMA support impregnated with nickel (15Ni/OMA-500) was about half of that for the sample prepared with the one-pot EISA method (OMA-15Ni-500, Table 1), but had a 25% higher H₂-uptake and specific surface area (Table 3, 179 vs. 142 μ mol g⁻¹, 14 vs. 11 m² g⁻¹) for the same nickel loading. This might suggest that some nickel atoms were encapsulated by the alumina framework during the one-pot synthesis and not accessible. The sample synthesized with hydrochloric and citric acid had a much smaller H₂-uptake and specific surface area (Table 3, 30 μ mol g⁻¹ and 2.3 m² g⁻¹), demonstrating that the type of acid used is important for both the formation of the mesoporous structure and distribution of the active metal.

The effect of the calcination temperature on the H₂-uptake shows that with higher temperature the H₂uptake decreased from 166 to 96 μ mol g⁻¹, while the average crystallite size increased from 3.5 to 6.1 nm for OMA-15Ni-400 to OMA-15Ni-900 (Table 3). The crystallite size determined with TEM were in the same range and matched nicely with the H₂-chemisoption measurements.

Catalyst Code	H2-uptake [µmol g ⁻¹]ª	Specific surface area [m ² g ⁻¹] ^a	Crystallite size, <i>d</i> [nm] ^b	Metal dispersion, D [%] ^b
OMA-15Ni-500	142	11.1	4.1	11.1
15Ni/OMA-500	179	14.0	3.2	14.3
OMA-15Ni-500-HCl	30	2.3	19.4	2.6
OMA-15Ni-400	166	13.0	3.5	13.3
OMA-15Ni-700	144	11.3	4.0	11.5
OMA-15Ni-900	96	7.5	6.1	7.7
OMA-05Ni-500	32	2.6	6.2	8.2
OMA-30Ni-500	295	23.1	4.2	12.1
OMA-15Ni-500*	152	11.9	3.8	12.2

Table 3 H₂-uptake [μ mol g⁻¹], specific surface area [m² g⁻¹], average nickel crystallite size [nm] and metal dispersion [%].

^a based on replicated analyses all values for H₂-uptake and specific surface area are within $\pm 8 \ \mu mol \ g^{-1}$ and $\pm 0.6 \ m^2 \ g^{-1}$, respectively. ^b based on ICP measurements (total nickel content) the values reported for the

average nickel crystallite size and metal dispersion are within $d \pm 0.4$ nm and $D \pm 1.1$ % (absolute), respectively. * reduced with 100% H₂;

The H₂-uptake increased as expected with the nickel loading from 32 to 295 μ mol g⁻¹ for OMA-05Ni-500 to OMA-30Ni-500. However, the average crystallite size decreased slightly from 6.2 to 4.2 nm. In most cases, an increase in the metal loading results in an increase of the crystallite size, but for the ordered mesoporous catalyst prepared via EISA technique the opposite was observed. Again, this suggest that some nickel atoms were encapsulated by the alumina framework during the one-pot synthesis, especially for the OMA-05Ni-500 sample with a high alumina/nickel ratio. A minimum amount of nickel might be needed to achieve a good distribution and dispersion.

Prior to the chemisorption, the samples were reduced with 5 vol% H₂ in He at its TPR-peak temperature (see section 3.1.4 and Fig. 3) for 3 h. For comparison, the OMA-15Ni-500* sample was reduced with 100 vol% H₂ prior to the chemisorption measurement to assure a complete removal of the oxygen and formation of the active zero-valent nickel (NiO + H₂ \rightarrow Ni + H₂O). Both catalysts reduced with 5 vol% and 100 vol% H₂ had a comparable H₂-uptake and average crystallite size (i.e., 142 vs. 152 µmol g⁻¹ and 4.1 vs. 3.8 nm), indicating a similar degree of catalyst reduction.

3.1.6 XRD analysis

Fig. 4 shows the XRD patterns of the catalysts synthesized using different methods, calcination temperatures and nickel loadings. Reference patterns for NiAl₂O₄, NiO and γ -Al₂O₃ are also shown for comparison and taken from the International Centre for Diffraction Data (ICDD) with the powder diffraction file (PDF) #010-0339, #044-1159 and #050-074, respectively. Samples prepared via wet impregnation (15Ni/OMA-500) and with hydrochloric acid (OMA-15Ni-500-HCl) exhibited distinct and sharp NiO diffraction peaks (Fig. 4A), representing a higher degree of crystallinity compared to the OMA-15Ni-500 sample. For the latter, the absence of specific NiAl₂O₄, NiO and γ -Al₂O₃ peaks indicate that alumina and nickel were homogenously mixed and amorphous in nature. The same was

observed for the sample calcined at 400°C (Fig. 4B). When the calcination temperature was increased to 700°C, crystallinity of the support started to increase and small diffraction peaks were observed on the (3 1 1), (4 0 0) and (4 4 0) lattice planes of γ -alumina. The sample calcined at 900°C had a highly crystalline γ -alumina structure. However, the sample was not thermally stable as the surface area and pore volume dropped by 50% compared to sample calcined at 500°C (Table 1).

Diffraction peaks associated with NiO (i.e., $2\theta = 37.2^{\circ}$, 43.2° and 62.8° ; Fig. 4B) were very broad for the nickel containing catalysts, indicating amorphous structure. The diffraction peaks became more pronounced with higher nickel loadings and crystalline structure. Again, no peaks associated with NiAl₂O₄ were detected, even for the OMA-30Ni-500 sample.

To study the structural change during the synthesis, OMA-30Ni-500 was analyzed by XRD before and after calcination as well as in its reduced form. Prior to the calcination the dried catalyst showed only a small diffraction peaks for NiO (i.e., $2\theta = 43.2^{\circ}$) and a broader peak at around 20-26° corresponding to carbon of the soft template (Fig. 5). The transition to wider and broader peaks at $2\theta = 43.2^{\circ}$ upon analysis of the calcined catalyst revealed the formation NiO, which was mostly reduced to Ni after 3 h under reduction conditions (T = 580°C). Only a small peak for NiO was observed at 37.2° as the catalyst was passivated. The peak at $2\theta = 66^{\circ}$ is associated with the crystal structure of Al₂O₃ that started to appear at temperatures higher than 500°C.

3.2 Activity measurements

3.2.1 Effect of synthesis parameter

As discussed in section 3.1, the synthesis method significantly influenced the catalyst properties and thus the catalytic activity. The catalyst prepared with nitric acid (OMA-15Ni-500) exhibited a higher catalytic activity towards CO_2 methanation over the temperature range of 300-500°C compared to the catalysts prepared via impregnation and with hydrochloric + citric acid, 15Ni/OMA-500 and OMA-

15Ni-500-HCl, respectively (Fig. 6). Larger mesoporous surface area (234 vs. 122 vs 72 m² g⁻¹) and larger pore volume (0.6 vs. 0.29 vs. 0.25 cm³ g⁻¹) of the OMA-15Ni-500 sample made the highly dispersed active nickel clusters easily accessible, which resulted in higher CO₂ conversions and CH₄ selectivities at every reaction temperatures (300-500°C) tested (Fig. 6A and B; Table 1). Even though the H₂-uptake of the impregnated catalyst (15Ni/OMA-500) was 25% higher than for the OMA-15Ni-500 sample (Table 3), the mesoporous surface area was 50% smaller leading to a lower CO₂ conversion. This indicates that both active and mesoporous surface area are important catalyst parameters.

The CO₂ conversion for the OMA-15Ni-500 increased until it reached a maximum close to the theoretical equilibrium conversion at a temperature of 450°C. Thereafter, the CO₂ conversion as well as the CH₄ selectivity declined following the equilibrium. At 450°C the OMA-15Ni-500 achieved its maximum CH₄ selectivity of 0.982 \pm 0.01, whereas only a value 0.778 and 0.959 was attained at 300°C and 500°C, respectively. In all the experiments, no C₂+ and higher hydrocarbons were detected as illustrated with the MS signal at mass-charge ratio m/z = 0 to 45 in Fig. 7. Thermodynamically, temperatures lower than 400°C are favorable for a high CO₂ conversion, but due to kinetic limitations temperatures; however, in the current study CO was produced at lower temperatures only. For example, at 300°C selectivity values of *S*_{CO} = 0.21, *S*_{CO} = 0.35 and *S*_{CO} = 0.56 were determined for OMA-15Ni-500, 15Ni/OMA-500 and OMA-15Ni-500-HCl, respectively. Again, this shows clearly that the EISA synthesis with the use of nitric acid is the best method for this application.

The reaction mechanisms for the CO_2 and CO methanation differ slightly and depend not only on the catalyst (e.g., active metal, promoter, support) but also the operating conditions. No unified mechanism exists, rather, multiple reaction pathways have been proposed assuming different elementary steps and

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adsorbed surface intermediates [19]. For example, it has been hypothesized that the C-O bond cleavage occurs on the catalyst surface via direct dissociation (i.e., from $CO_{2,ads} \rightarrow CO_{ads} + O \rightarrow C_{ads} + O$) or via hydrogen-assisted dissociation (e.g., COH_{ads} , $HCOO_{ads}$ surface intermediate) [20–22]. For the latter, it is assumed that hydrogen lowers the energy of the C-O bond activation leading eventually to a C_{ads} or $CH_{x,ads}$ carbon surface intermediate, which is then stepwise hydrogenated to methane. The results of the current study might indicate, that at lower temperatures the CO_2 methanation proceeds via direct dissociation to form a CO_{ads} intermediate. CO_{ads} formation and desorption to CO seems to be faster than the stepwise hydrogenation to CH_4 . However, without detailed analysis of the surface intermediates using for example diffuse reflectance FTIR (DRTIFS) experiments, no concrete conclusions about the reaction mechanism can be drawn.

3.2.2 Effect of calcination temperature

Catalytic activity also depends on the calcination temperature. With increasing calcination temperature from 400 to 700°C, the conversion of CO₂ as well as the selectivity of CH₄ for all reaction temperatures increased (Fig. 8). A further increase of the calcination temperature to 900°C, however, showed a huge decline of the catalytic activity. For example, at a reaction temperature of 350°C, the conversion of CO₂ increased from 0.374 to 0.618 for calcination temperatures of 400 to 700°C and then decreased to 0.140 for a calcination temperature of 900°C. The results are in good agreement with the surface area analysis in which the samples calcined at 400 and 900°C (OMA-15Ni-400 and OMA-15Ni-900) had the smallest mesoporous surface areas and pore volumes. Furthermore, the mesoporous structure of the OMA-15Ni-900 catalyst became more crystalline as illustrated in Fig. 4B and the specific surface area was 30% smaller than for the OMA-15Ni-500 and OMA-15Ni-700 sample (Table 3).

3.2.3 Effect of nickel loading

As the nickel loading increased from 5 wt% to 30 wt% the CO₂ conversion as well as the CH₄ selectivity increased. For example, at 350°C CO₂ conversion values of 0.23, 0.45 and 0.69, and CH₄

selectivity values of 0.783, 0.911 and 0.966 were determined for OMA-05Ni-500, OMA-15Ni-500 and OMA-30Ni-500, respectively (Fig. 9). It is very likely, that the 30 wt% nickel catalyst provided more active sites (confirmed with H₂-chemisorption measurements) for the competitive adsorption of hydrogen and thus stepwise hydrogenation of the assumed CO_{ads} surface intermediate compared to the catalyst with a lower nickel loadings. The current results do not allow the determination of the relative surface coverage of each catalyst. For that steady-state isotopic transient kinetic analysis combined with diffuse reflectance FTIR and mass spectrometry (SSITKA-DRIFTS-MS) experiments need to be conducted.

3.2.4 Effect of space velocity

The influence of the gas hourly space velocity (GHSV) was investigated for the OMA-15Ni-700 catalyst since it exhibited the best overall performance towards CO_2 methanation. The experiments were performed at GHSV values from 45 to 115 $L_N g_{cat}^{-1} h^{-1}$. At temperatures, lower than 400°C the CO_2 conversion as well as the CH₄ selectivity declined with increasing GHSV. Whereas at 450 and 500°C the opposite trend was observed. The highest CO_2 conversion and CH_4 selectivity was achieved for GHSV of 45 $L_N g_{cat}^{-1} h^{-1}$ at 400°C. The GHSV values used in this study were considerably higher than those in other reports such as 15 $L_N g_{cat}^{-1} h^{-1}$ in [12,23], but achieving similar high CH₄ selectivity values.

3.2.5 Long-term experiment

The OMA-15Ni-700 catalyst was subjected to a long-term run at 400°C with $H_2/CO_2 = 5$ at a GHSV of 91 L_N g_{cat}⁻¹ h⁻¹. After continues operation of more than 150 h on stream, the catalyst did not exhibit any sign of deactivation, the CO₂ conversion and CH₄ selectivity were stable with ~83% and 97%, respectively (Fig. 12 A).

3.3 Characterization of used catalyst

3.3.1 N₂ Adsorption/desorption analysis

BET surface area analysis was carried out for the spent catalysts with different nickel loadings. Surface area and pore volume of the spent catalysts were reduced by 40-50 m² g⁻¹ and 0.02-0.06 cm³ g⁻¹ (Table 4), respectively. This might be associated with thermal shrinkage of the mesoporous framework and/or sintering of weakly interacted nickel clusters due to the high reduction temperatures of 575 to 620°C, which were considerably higher than the calcination temperature of 500°C and the reaction temperatures.

Sample	S_{BET} (m ² g ⁻¹)		$V_{pore} (\mathrm{cm}^3\mathrm{g}^{-1})$		
	fresh	spent	fresh	spent	
OMA-05Ni-500	217	177	0.52	0.50	
OMA-15Ni-500	242	191	0.60	0.54	
OMA-30Ni-500	174	136	0.58	0.52	
OMA-15Ni-700*	206	176	0.42	0.38	

Table 4 BET surface area analysis for fresh and spent catalysts.

* used in 150 h long term experiment

However, this shrinkage did not lead to a collapse of the mesoporous structure as they showed type IV isotherms with H1-hysteresis and narrow pore size distributions (not shown), demonstrating good thermal stability of the mesoporous catalyst. The catalyst used for the 150 h test (OMA-15Ni-700), exhibited a similar reduction of surface area (by $30 \text{ m}^2 \text{ g}^{-1}$), confirming the excellent stability.

3.3.2 XRD of used catalysts

XRD patterns of the spent catalysts of various nickel loadings are displayed in Fig.11. All the catalysts were subjected to reduction and reaction conditions as each catalyst was used for at least 3 consecutive days. The transformation of NiO to Ni can be observed clearly via XRD where the diffraction peaks of Ni became obvious at higher Ni loadings (15-30 wt%) at $2\theta = 44.4^{\circ}$, 51.8° and 76.3°. The diffraction

peak at 66° for OMA-30Ni-500 corresponds to γ -Alumina which was most likely formed during the reduction.

3.3.3 Temperature programmed oxidation

To further investigate the catalyst stability, temperature programmed oxidation (TPO) of the fresh and used catalyst (150 h) were conducted. The fresh catalyst exhibited a weight reduction by 4 wt% on dry basis upon heating in Air to 500°C, which can be associated with the devolatilization of adsorbed species. A further increase in the temperature resulted in small weight increase for yet unknown reasons. The spent catalyst showed a completely different behavior; no weight decrease was measured. Instead, the weight of the used catalyst increased by approximately 3 wt% on dry basis in the range of 150 to 300°C with a total increase of 8.4 wt% at 900°C. This, result clearly demonstrates the absence of any carbon deposition and the oxidation of the passivated catalyst (i.e., 2 Ni + $O_2 \rightarrow 2$ NiO).

4 Conclusions

A systematic approach was followed to investigate the relationship between the synthesis of nickel containing ordered mesoporous alumina catalysts and its structure and catalytic activity toward CO₂ methanation. Type of acid used, calcination temperature, nickel loading and synthesis method affected the catalyst morphology and activity significantly. Obtaining a complete mesoporous structure was the key for a good catalytic performance. Using nitric acid during the "one-step evaporation induced self-assembly - EISA" synthesis allowed the formation of long and cylindrical micelles with small and highly dispersed nickel clusters. Catalysts prepared via wet impregnation had smaller surface area and lower CO₂ methanation activity. Besides the acid used, the calcination temperature was one of the most important synthesis parameters. 700°C was found to be the optimum calcination temperature in the present study leading to large mesoporous and specific surface areas, and achieving the highest CO₂

conversion and CH_4 selectivity over the whole temperature range studied. In addition, the catalyst proved to be stable under reaction conditions for more than 150 h without any sign of deactivation. Understanding how the synthesis parameters of ordered mesoporous alumina catalysts affect the CO_2 methanation activity is key towards better, more robust and thermally stable catalysts.

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