

Controlled Formation of Nickel Oxide Nanoparticles on Mesoporous Silica using Molecular Ni₄O₄ Clusters as Precursors: Enhanced Catalytic Performance for Dry Reforming of Methane

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Supported NiO nanoparticles (NPs) were prepared by impregnation of mesoporous silica SBA-15 with a molecular, metalorganic [Ni₄O₄] cubane cluster as precursor. By using this ligandstabilized Ni cluster, deposition of four Ni ions in close proximity on the silica support was achieved; this resulted in the formation of small and highly dispersed NiO NPs after heat treatment. These clusters were shown to have a significant influence on the formation of NiO NPs compared to a conventional Ni(OAc)₂ precursor. After a further reduction step, the materials were used as catalysts for the dry reforming of methane, which showed that preorganization of the Ni atoms on the support surface had a beneficial effect on the methane conversion rate.

Methane is the principal component of most natural gas reserves and thus one of the major sources of energy for homes and industry. However, many of these reserves are found in regions far from industrial complexes; therefore, much of the methane is just flared or vented, a process that wastes hydrocarbon resources and causes severe environmental problems. These concerns and the increasing price of oil have led to global investigation for the conversion of methane into easy transportable products through processes such as dry reforming of methane (DRM, $CH_4 + CO_2 \rightarrow 2H_2 + 2CO$). Syngas, the product of the DRM reaction can be converted into higher hydrocarbons or fuels through Fischer–Tropsch synthesis.^[1] Nickel is known to be an efficient non-noble metal catalyst for the DRM reaction. For example, high and stable conversions can be reached if very small Ni particles are dispersed on a robust,

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	Supporting Information for this article is available on the WMMW und

Supporting Information for this article is available on the WWW under http://dx.doi.org/10.1002/cctc.201402983. ing.^[2,3] Stabilization of small Ni nanoparticles (NPs) is also important to prevent coking of the catalysts, which is a severe side reaction observed on larger Ni particles. Different synthetic approaches such as impregnation of high surface area supports with solutions of Ni salts^[4-9] or the preparation of Nibased solid solutions^[10-12] or Ni-containing perovskites^[13-15] and subsequent reduction to form the Ni⁰ NPs have been reported to prepare such materials. If Ni salts are used as precursors in the first step, NiO nanoparticles are formed on the support during heat treatment under an atmosphere of air or oxygen, and it can be assumed that the size and dispersion of these NiO NPs will have a direct impact on the finally observed particle size and dispersion of the catalytically active Ni⁰ species. The size and dispersion of metal-oxide particles formed from impregnated metal-salt precursors is, however, difficult to predict and control and crucially depends on several factors such as the precursor type and concentration, the heat treatment, and the surface chemistry of the support. An interesting option to gain better control of metal-oxide NP formation could be the use of small molecular metal-oxo clusters instead of mononuclear metal salts, that is, to start from molecular precursors, in which a defined amount of metal atoms is already located in close proximity.^[16-18] These single source precursors (SSP), for which all desired elements of the target material are preorganized in a metal organic compound, are therefore intriguing starting materials for the preparation of supported metal-oxide catalysts. The herein applied "Ni4 cubane" SSP is a tetranuclear complex prepared from Ni(OAc)₂ and di-2-pyridinylmethanone [(C_5H_4N)₂CO, dpk]; dpk is hydrolyzed into the di-2-pyridinylmethanediolato [(C₅H₄N)₂C(OH)₂, dpd] ligand in aqueous solution.^[16–19]. The preparation of small quantities of the cubanoid metal cluster [μ -(acetato- κO)]bis(acetato- κO)tetrakis{ μ_3 -[di(2-pyridinyl- κN)methanediolato- $\kappa O:\kappa O:\kappa O$]}tetra-Nickelperchloratehydrate (Ni4) bearing the triscoordinate di-2pyridinylmethanediolato ligand was described by several groups.^[18,19] For this work, we adapted the synthetic scheme to obtain larger quantities of the material on the basis of our preliminary studies of the respective Co and Zn compounds.^[17] The core of this complex consists of a [Ni₄O₄] cubane, as shown in Figure 1, which can also be described as one of the smallest possible ligand-stabilized NiO nanoparticles. Attaching these cubane structures to the surface of a high-surface area support should, after calcination, yield four Ni atoms in close

high surface area support and, thus, are stable against sinter-

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Figure 1. Schematic illustration of the Ni4/SBA-15 catalyst prepared by using a ligand-stabilized Ni4 cubane precursor.

proximity on the support surface (see Figure 1), which are then able to form very small Ni clusters upon reduction, possibly to yield an efficient catalyst for the dry reforming of methane. To investigate a possible beneficial influence of the preorganization of Ni atoms, two series of materials were prepared in this work. For the first series, a mesoporous silica support (SBA-15) was impregnated with an aqueous solution of the Ni4 cubane precursor ("A-Ni4/SBA-15"). For comparison, in a second series a conventional nickel acetate precursor was used in the same way ("A-Ni/SBA-15", A = initial wt% of Ni). The concentration of the precursors in the aqueous solution was varied to investigate the effect of nickel loading on the structure and activity of the catalysts. All obtained materials were treated likewise; thus, first dried at room temperature, then calcined at 550°C for 4 h, and finally subjected to an in situ reducing atmosphere (pure H_2) at 500 °C for 1 h before catalytic tests. The actual metal contents of the samples were determined after the calcination step by inductively coupled plasma (ICP) and are presented in Table 1. In almost all cases, the actual Ni content is lower than the nominal one, probably as a result of a washing

Table 1. Characterization and test results of the Ni4/SBA-15 and Ni/SBA-15 catalysts.						
Sample	Ni ^[a] Activity ^[] [wt%] 500 °C		ivity ^[b] [mol _{CH4} mol _{Ni} ⁻ 550 °C	⁻¹ min ⁻¹] 600 °C		
1-Ni4/SBA-15	0.52	3.2	6.0	13.9		
2-Ni4/SBA-15	0.81	3.5	5.5	9.7		
5-Ni4/SBA-15	1.67	3.1	3.8	5.3		
1-Ni/SBA-15	0.51	3.9	3.9	-		
2-Ni/SBA-15	0.97	3.0	5.0	8.3		
5-Ni/SBA-15	2.53	1.4	2.6	3.4		
[a] Metal content from ICP measurements [b] Reaction rate based on mole CH, con-						

[a] Metal content from ICP measurements. [b] Reaction rate based on mole CH_4 corverted per mole Ni per time on stream.

step after impregnation. Notably, variations in the actual Ni content do not allow for straightforward comparison of the Ni4 and Ni catalysts prepared from the same initial amount of Ni. Therefore, in a first step the Ni4/SBA-15 and Ni/SBA-15 series are discussed separately by regarding their catalytic performance in the DRM, whereas a comparison between the two series is made only on the basis of the actual Ni amount evaluated by ICP. Materials in both series were studied by X-ray diffraction (XRD) measurements. The powder XRD pattern at low angle provides information about the support structure after

impregnation and calcination (Figures S1 and S2, Supporting Information). The patterns show the characteristic (100), (110), and (200) peaks, which can be assigned to the hexagonal pore structure of SBA-15;^[20] this shows that the ordered mesoporous structure has been maintained during formation of the metal-oxide phase. The wide-angle XRD patterns of the Ni4/ SBA-15 and Ni/SBA-15 samples after calcination but before reduction are presented in Figures S3 and S4. The characteristic reflexes for NiO at $2\theta = 37.2$, 43.1, and 62.8°, corresponding to the (111), (200), and (22 0) planes of cubic NiO, respectively,^[4,21] are observed only for the 5-Ni4/SBA sample even though the actual Ni content is smaller (1.67 wt%) than that, for example, in the 5-Ni/SBA sample (2.53 wt%). Still, the observed reflexes are very weak and broad, which points to the formation of very small NiO NPs. For samples with lower loadings, hardly any crystal phase line can be recognized, which might be a sign of the formation of small, highly dispersed Ni species. Nitrogen physisorption measurements were performed for the calcined materials (Figure S5). Corresponding isotherms show the characteristic type IV isotherm with H1-type hysteresis loop for mesoporous materials, which again shows that the mesoporous structure of SBA-15 was maintained after impregnation and calcination. Figures 2 and S6 show the TEM images of the catalysts prepared from Ni4 cubane and nickel acetate precursors, respectively. Formation of few isolated metal-oxide particles can be observed for the lowest concentration in the Ni4/SBA-15 series, whereas for Ni/SBA-15, metal-oxide NPs can be spotted only for the highest concentration (5-Ni/SBA-15). However, only for 5-Ni4/SBA-15 is a larger amount of NiO nanoparticles seen, and these NPs are highly dispersed on the silica support, which also supports the results obtained from the XRD measurements.

All of the prepared materials were applied as catalysts for the DRM reaction. Figures 3 and 4 show methane conversion over Ni4/SBA-15 and Ni/SBA-15 after an in situ reduction step at temperatures of 500, 525, 550, and 600 °C. The theoretical thermodynamic equilibrium was also calculated by minimizing the Gibbs free energy of all species in the system (Figure S7). For the Ni4/SBA-15 materials at 500 and 525 °C, the activity is proportional to the amount of nickel in the catalyst. It can be seen that 5-Ni4/SBA is an exceptionally good catalyst for the DRM reaction, as thermodynamic equilibrium is reached at a low temperature (500 °C), and it also shows stable performance at a higher temperature (600 °C) although equilibrium effects should be noted. Moreover, the

other Ni4/SBA-15 catalysts show initially lower performance and stability; however, they seem to be further activated at higher temperatures, especially the 1-Ni4/SBA-15 catalyst. It can, therefore, be concluded that a certain Ni cluster size has to be reached to show sufficient catalytic performance in the DRM and that for the catalysts with highly dispersed Ni particles a certain temperature is needed to form this critical size by particle sintering. As seen from the TEM pictures, a considerable amount of particles is formed in 5-Ni4/SBA-15, which explains its high catalytic activity at low temperatures. For the





Figure 2. TEM images of a, b) 1-Ni4/SBA-15, c, d) 2-Ni4/SBA-15, and e, f) 5-Ni4/SBA-15.



Figure 3. Catalysis results of 1-Ni4/SBA-15, 2-Ni4/SBA-15, and 5-Ni4/SBA-15 based on methane conversion; gas hourly space velocity (GHSV) = 36 Lh⁻¹g⁻¹, CH₄/CO₂/He = 1:1:8. Eq points show the theoretical thermodynamic equilibrium for the DRM reaction at each temperature.

Ni/SBA-15 series, a similar trend is observed. However, only the catalysts with higher amounts of Ni show sufficient activity for the DRM reaction. 2-Ni/SBA-15 and 5-Ni/SBA-15 show stable performance even though the thermodynamic equilibrium is not fully reached (Figure 4).



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Figure 4. Catalysis results of 1-Ni/SBA-15, 2-Ni/SBA-15, and 5-Ni/SBA-15 based on methane conversion; $GHSV = 36 Lh^{-1}g^{-1}$, CH_4 : CO_2 :He = 1:1:8.

From these data, a first assumption can already be made, and that is that the preorganization of Ni in the Ni4/SBA catalysts has a beneficial effect on the catalytic performance, as exemplified by the methane conversions of the 1-Ni4/SBA-15 and 1-Ni/SBA-15 catalysts, which contain similar Ni amounts, as seen from the ICP measurements. Also, it can be noted that 5-Ni4/SBA shows a slightly higher methane conversion than 5-Ni/SBA, even though the Ni content is much lower in this catalyst (1.67 vs. 2.53 wt%, Table 1). With the exclusion of 1% catalysts, Ni4/SBA-15 also produces higher H_2 /CO ratios, and 5% Ni4/SBA-15 is the most selective; furthermore, there is a general trend between activity and H_2 /CO ratio (Table S1). To compare the two catalyst series beyond the qualitative assumptions made above, the reaction rates were calculated as mole methane conversion per mole Ni atom per minute (Figure 5,



CH4 Ni

Figure 5. Catalysis results based on mole methane converted per mole nickel per minute.

Table 1). The rate for each catalyst was calculated by averaging over all the activity values at each ramp, excluding the first point. The catalysts with the highest loadings showed the lowest rate per Ni content in both the Ni4/SBA-15 and the Ni/SBA-15 series. This can be expected, as larger particles are ob-



served in these catalysts, and it can be assumed that only surface Ni atoms take part in the catalytic reaction. Moreover, a considerable deposition of carbon is found for catalysts with higher Ni contents, which can also cause lower accessibility of the Ni atoms and, thus, again lower the reaction rate (Table S2). For the same reasons, the catalysts with lower Ni contents show higher rates per Ni atom, especially the 1-Ni4/ SBA-15 catalyst. The rate of the reaction with the use of the Ni4/SBA-15 series, especially at elevated temperatures, is much higher than the rate for the Ni/SBA-15 series, which proves the significant effect of using a preorganized Ni precursor, as it more quickly forms small but highly dispersed NiO and later Ni clusters. The heteroleptic nature of the Ni4 complex cation allows the labile acetato ligands to be easily replaced by other ligands. This is observed by electrospray ionization mass spectrometry (ESI-MS) experiments (see Figure S8), for which the acetato ligands were replaced by formiato ligands from the buffer solution and a twofold positively charged ion is observed at $m/z = 564 [C_{46}H_{38}N_8O_{12}Ni_4]^{2+}$. The cubanoid cluster core, however, stays intact, as the four di-2-pyridinylmethanediolato ligands are not as easily removed (see thermogravimetry/differential thermal analysis experiment Figure S9). This would allow for the deposition of individual Ni4 cluster cations on SBA-15 by simply replacing the acetato ligands, which would leave the predefined geometry of four Ni atoms intact. It can, thus, be assumed that a certain metal cluster size has to be reached to yield high activity for methane conversion. The Ni4 cubane precursor seems to combine two advantages by first allowing the fast formation of small Ni clusters, which are, however, highly dispersed on the support and, thus, quite stable during the catalytic reaction.

In conclusion, supported nickel oxides were prepared by impregnation of a SBA-15 support by an aqueous solution of two different Ni precursors, Ni(OAc)₂ and a tetranuclear Ni4 cubane precursor. The application of the cubane precursor yielded faster formation of small NiO nanoparticles, which are highly dispersed on the silica support, even at very low precursor concentrations. The preorganization of the metal atoms in this cubane precursor is an obvious explanation for the faster formation of NiO particles upon calcination. The resulting materials are very active and stable catalysts for the dry reforming of methane (DRM) reaction at moderate temperatures (500-600 $^{\circ}$ C), which is an interesting temperature window to conduct the DRM reaction if it is coupled to another exothermic reaction, for example, the oxidative coupling of methane (OCM). The heat produced by such exothermic oxidation reactions could be conveniently used to provide the energy for the endothermic DRM. In this scenario, it is highly desirable to operate the DRM reaction at temperatures 50-100 K below the OCM reaction (typically conducted at \approx 700 °C), considering the energy loss caused by heat transfer between the respective reactors. The catalytic results further show that preorganization has a beneficial effect on the methane conversion rate per Ni content.

Experimental Section

Synthesis of the Ni4 complex

Ni(OAc)₂·4 H₂O (2.488 g, 10 mmol) was dissolved in H₂O (50 mL) in a 100 mL Schlenk flask, and the mixture was stirred at 50 °C under a N₂ atmosphere. Upon complete dissolution of the starting material, di-2-pyridinylmethanone (dpk; 0.911 g, 5 mmol) in acetonitrile (10 mL) was added dropwise to the solution over 15 min. The color of the solution changed from light green to dark green over the course of the reaction. The flask was then removed from the oil bath and cooled to room temperature under a N₂ atmosphere. A solution of NaClO₄ (1.40 g, 10 mmol) in water (2 mL) was added to the mixture and crystallization commenced over 2 days. Green crystals were obtained from the mother liquor by filtration. The product was washed with water and acetonitrile and dried in air.

Preparation of SBA-15

SBA-15 was prepared according to a previously reported method.^[20] Pluronic P123 triblock copolymer (M_{av} = 5800) was dissolved in a mixture of distilled water and 2 \times HCl before the addition of tetraethyl orthosilicate (TEOS). The mixture was stirred for 24 h at 35 °C and subsequently treated hydrothermally at 100 °C for 24 h. Finally, the precipitate product was filtered, dried at 100 °C, and calcined at 500 °C for 4 h.

Synthesis of Ni4/SBA-15 and Ni/SBA-15 catalysts

The incipient wetness impregnation method was used to introduce the Ni4 SSP molecule and Ni nitrate precursors into the SBA-15 pores. A-Ni4/SBA-15 and A-Ni/SBA-15 (A represents the nominal content of Ni) was prepared by impregnation with a Ni4 molecule and Ni nitrate aqueous solutions with different concentrations (Tables S3 and S4). All samples were vacuum dried at room temperature and calcined at 550 °C for 4 h.

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Keywords: dry reforming of methane · heterogeneous catalysis · molecular precursor · nanoparticles · supported catalysts

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Controlled Formation of Nickel Oxide Nanoparticles on Mesoporous Silica using Molecular Ni₄O₄ Clusters as Precursors: Enhanced Catalytic Performance for Dry Reforming of Methane



The knights of Ni: Impregnation of mesoporous silica with an organometallic Ni₄ cubane precursor and subsequent thermal treatment yield highly active and stable catalysts for the dry reforming of methane.