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Optimization of the synthesis of Ni catalysts via chemical vapor deposition by response surface methodology

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ABSTRACT

The effects of synthesis parameters during the preparation of Ni catalysts for the CO_2 methanation reaction via chemical vapor deposition (CVD) were investigated. For this purpose, a central composite design from the design of experiment approach was conducted to identify and investigate the most significant parameters. A surface response methodology was applied to identify promising synthesis parameter combinations that led to highly dispersed Ni catalysts and to understand the interaction of the synthesis parameters. Finally, the methanation activity of a CVD-prepared catalyst was compared with two different Ni catalysts with the same metal loading but prepared with different methods. The CVD preparation herein presented proved to be a promising method to obtain low-loaded Ni catalysts in CO_2 methanation.

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1. Introduction

The naturally occurring CO_2 in the atmosphere acts as an important climate regulator. The CO_2 ensures the liquid state of H_2O and also stabilizes the mean temperature of the Earth. Due to the increasing emission of CO_2 by modern industry, this natural climate regulation is no longer in equilibrium. The consequence of this alteration is the so-called climate change, which has led to an increased interest in renewable energy sources like wind, sun, and biomass. However, these renewable energy sources come with several drawbacks. One of the most important drawback is the mismatch of energy demand and energy production. In order to buffer the fluctuation in energy production, several ideas have recently come forward, such as the direct use of the produced electricity by intensification of thermal (Salpakari et al., 2016) or electrochemical processes (Haug et al., 2017). Another promising concept is the electrolysis of water to generate pure H_2, which is used in several industrial processes involved in chemical plants, green refineries, or fossil fuel refineries. A third way involves the storage of the excess electricity in chemical compounds. In this regard, the power-to-gas (PtG) concept is very promising (Sterner, 2009). In this case, the produced H_2 is used to generate methane by the reduction of CO_2 in the so-called Sabatier reaction, which has come to the fore of scientific investigation in recent years (El Sibai et al., 2015; Frontera et al., 2017; Hoekman et al., 2010; Liu and Tian, 2017; Xu et al., 2017). Since methane is a main constituent of natural gas, synthetic natural gas (SNG) can be fed, store, and transport into the existing energy grid.

The CO_2 methanation reaction is given in the following equation:

$$CO_2 + 4H_2 \rightleftarrows CH_4 + 2H_2O \quad \Delta H_R^0 = -165 \frac{kJ}{mol}, \tag{1.1}$$

Since its discovery in 1902, the Sabatier process has been intensively investigated (P. Sabatier, 1902), and a wide range of metals have been found to be active for this reaction (Frontera et al., 2017). In par-

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ticular, noble metals like Ru (Brooks et al., 2007; Garbarino et al., 2016; Rynkowski et al., 2000; Xu et al., 2016), Rh (Kusama et al., 2000; Novák et al., 2002), and Pd (Mihet and Lazar, 2016; Park and McFarland, 2009) show very high activity. However, due to the very high cost of these metals, the use of Ni has prevailed at the industrial scale (Rönsch et al., 2016). Compared to Fe (Fournier et al., 1985) and Co (Kok et al., 2011), Ni (Koschany et al., 2016) exhibits a very high selectivity for methane. Because the support of the catalyst also plays a very important role in this process, a variety of metal oxides have also been investigated, e.g., Al_2O_3, MgO, TiO_2, SiO_2, and CeO_2 (Abelló et al., 2013; Fukuhara et al., 2017; Garbarino et al., 2014; Tada et al., 2012; Zhou et al., 2016).

Chemical vapor deposition (CVD) is a popular method for coating synthesis (Luo et al., 2017) and the preparation of very thin films of pure metals (Pawbake et al., 2016). Furthermore, CVD is used for the preparation of carbon nanotubes (Schlüter et al., 2004) and catalysts like Pd/C or Pd/SiO_2 (Binder et al., 2009; Mu et al., 2003; Park and McFarland, 2009; Xia et al., 2007). In this work, Ni catalysts for the CO_2 methanation reaction were prepared via CVD. For a better understanding of the different process parameters and their influence on the synthesis process, a central composite design (CCD) was applied. The design of an experiment approach has allowed the study the main factors' effect and the associated interactions on the specific metal surface area ($a_{surface}$) of the prepared catalysts. A quadratic model was proposed for a specific metal surface area as a function of temperature, pressure, and time during the deposition. These catalysts were subsequently investigated by XRD, BET, and H_2 chemisorption. Finally, the activity of the most promising CVD-prepared catalyst was compared in the catalytic CO_2 methanation reaction with an impregnated Ni/SiO_2 and a co-precipitated $NiAlO_x$.

2. Experimental

2.1. Design of experiments

A large number of factors may potentially influence the chemical vapor deposition process, ranging from the deposition time, pressure, and temperature to the different volume flow ratios in the set-up or the weight of the Ni precursor. In total, six factors have to be investigated. We decided to use the design of experiments (DoE) approach to identify the main influence factors on the deposition process (Box et al., 1978; Kleppmann, 2009). A 16-run Plackett–Burman design was performed to identify the most important factors and thus to reduce the experimental effort (Plackett and Burman, 1946). With this design, the significance of the original six factors was determined, which allowed us to reduce these factors to three (pressure, temperature, and deposition time). The weight of the precursor is excluded due to analytical reason. Judging from the PB design runs, interactions between the factors could probably have a significant influence on the results of the deposition. Therefore, factor interactions are not negligible. As a first step, we chose to perform a full factorial design, which provided the estimation of the main effects and the two-factor interaction effects. For all factors only two levels of variations (−1 and +1) were used. The corresponding values are shown in Table 1. All higher interactions were neglected. Because the model may be subjected to quadratic effects when interaction terms are added, the addition of a central point allows to check the model for quadratic effects. In addition, an estimation of the experimental uncertainty can be obtained by re-running the central point. Finally, to estimate the impact of the quadratic effects, six additional points were added to the design in a star-like pattern where α is the distance of the axial points from the center. The resulting design was a so-called central composite design (CCD), which was developed by Box and Wilson (Box and Wilson, 1951). Fig. 1 shows a sketch of this experimental design.

Table 1 – Matrix of runs for the central composite design according to Box and Wilson (1951).

Experiment number	x_1	x_2	x_3	Explanation
1	−1	−1	−1	Full factorial design
2	1	−1	−1	
3	−1	1	−1	
4	1	1	−1	
5	−1	−1	1	
6	1	−1	1	
7	−1	1	1	
8	1	1	1	
9	−α	0	0	Star points
10	α	0	0	
11	0	−α	0	
12	0	α	0	
13	0	0	−α	
14	0	0	α	
15	0	0	0	Central points
16	0	0	0	
17	0	0	0	
18	0	0	0	
19	0	0	0	
20	0	0	0	

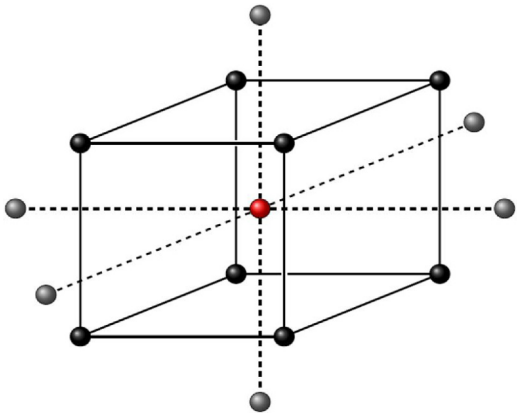

Fig. 1 – The three factor composite design (Kleppmann, 2009).

A quadratic model with the generalized form described in Eq. (2.1), was used to empirically describe the dependence of the response from the factors.

$$y_i = a_0 + \sum_{1}^{N} a_i x_i + \sum_{1,i\neq j}^{N} a_{ij} x_i x_j + \sum_{1}^{N} a_{ii} x_i^2 + e_i \quad (2.1)$$

where y_i is the response, a_0 represents the constant effect, a_i is the main effect, a_{ij} is the first order interaction effect, a_{ii} is the first order quadratic effect, and e_i is the residual. For each desired response, a least square algorithm was employed to estimate the coefficients of the model. Range and levels of the investigated variables are listed in Table 2. Factors were pressure (x_1), temperature (x_2), and deposition time (x_3). The specific metal surface area of the reduced catalyst was chosen as the response y_1.

2.2. Catalyst preparation

The Ni/SiO_2 samples were prepared by means of the CVD of nickelocene ($NiCp_2$) on SiO_2 in a fluidized-bed reactor with a diameter of 20 mm and a height of 300 mm. SiO_2 was purchased from Merck as Silica gel 60 and was sieved to obtain

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