Catalysts preparation and investigation: laboratory exercise for students

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1. INTRODUCTION

Catalysts preparation, investigation its basic properties, activity and selectivity measurements in carbon dioxide methanation reaction was proposed as laboratory course for international students doing a period of study at Maria Curie-Sklodowska University within the frame of the Erasmus mobility programme.

2. ORGANIZATION OF CLASSES

Among various courses in the Faculty of Chemistry given in English students can choose Adsorbents and catalysts. The course consists of lectures and laboratories devoted to adsorbents (part I) and catalysts (part II). The catalysts laboratories consists of four exercises: i. Synthesis of nickel based catalyst, ii. Precursor decomposition studies, iii. Temperature programmed-reduction studies, iv. Activity and selectivity measurements in carbon dioxide methanation reaction. All of mentioned topics are given as individual laboratories, that is 5-hours units every week. The students work in 3 groups. Each group counts 3-4 students. The classes were adjusted to 5 x 45 min.

3.   EXERCISE 1, CATALYSTS SYNTHESIS

This topic is covered by each group of students simultaneously. The students are given exercise manual and follows one of the procedure described. The example procedure is given below:

Nickel based catalyst with given Ni content should be prepared by impregnation method with citric acid addition. Commercially available gamma aluminum oxide (Alfa Aesar) should be used as support material. Before catalyst preparation the support must be crushed and sieved to a defined grain size of 0.3-0.6 mm and subsequently dried at 120°C for an hour. The proper amounts of citric acid and nickel nitrate $Ni(NO_3)_2 \cdot 6H_2O$ (1 mol of Ni to 1 mol of citric acid) should be placed in crystallizer and dissolved in 300 cm^3 of distilled water. The crystallizer should be placed on a hot plate (105°C) for evaporation. The sample should be finally dried at 110°C overnight.

There are multiple parameters that teacher can manipulate during this experiment: the amount of nickel loading, the type of support material (commercially available: α-Al_2O_3, γ-Al_2O_3, CeO_2, ZrO, ZnO), the presence of supporting chemicals (citric acid, ethylene glycol, glycerol). It is important to assign an individual task to each group with different parameters influencing final properties of the catalysts.

The next three topics are covered simultaneously by each group of students during three following classes. Each group of students investigates its own catalyst prepared during first exercise.

4.   EXERCISE 2, PRECURSOR DECOMPOSITION

The goal of this class is to introduce students in basics of thermogravimetric analysis. The students perform TG experiment according to following procedure:

Precursor decomposition studies should be performed in a homemade TG system consisting of analytical balance (Ohaus), tube furnace (placed vertically under the balance) and temperature controller (Shimaden). One gram of the sample should be located in a quartz container hanged under the balance in the heating zone of the furnace. The heating rate should be kept constant at 5 deg/min up to 450°C. Sample weight and temperature is recorded along with

elapsed time automatically with LabVIEW software (Kalcynacja). The students should calculate percentage of weight loss and derivative.

5. EXERCISE 3, CATALYSTS ACTIVATION IN HYDROGEN

The goal of this class is to introduce students in temperature-programmed techniques for catalysts investigation. The students perform TPR-H_2 experiment according to following procedure:

Reducibility of the catalyst should be determined by the application of temperature-programmed reduction in hydrogen (Autochem II 2920, Micromeritics Instrument Corporation). The system is equipped with TCD detector and cold trap (–89°C) to remove traces of water evolved during oxides reduction. The reducibility is measured in flow of 5% H_2/Ar at constant rate of 10 deg/min up to 800°C.

6. EXERCISE 4, CATALYSTS ACTIVITY AND SELECTIVITY IN CO_2 METHANATION REACTION

The goal of this class is to introduce students to basic catalytic tests and measure catalyst activity and selectivity in carbon dioxide methanation reaction.

Methanation reaction

Carbon dioxide methanation reaction despite of its high industrial importance is relatively easy to be conducted in laboratory scale. This is why this process can be easily be applied as an exercise for students. Methanation reaction (Eq. 1) performed over nickel based catalysts yields only few products, such as: CH_4, CO and water. The reaction is highly exothermic and typically operated between 200-450°C.

$$CO_2 + 4H_2 \rightleftarrows CH_4 + 2H_2O \quad \Delta H^o_{298K} = 164 \text{ kJ mol}^{-1} \quad (1)$$

There is no general consensus in the literature regarding reaction mechanism mostly due to uncertainty in determining intermediate species involved in rate determining step.

It is commonly accepted that carbon monoxide is formed due to reverse water–gas shift reaction (Eq. 2) at relatively high temperatures.

$$CO_2 + H_2 \rightleftarrows CO + 2H_2O \quad \Delta H^o_{298K} = 41 \text{ kJ mol}^{-1} \quad (2)$$

Nowadays scientists has broaden the aspect of carbon dioxide methanation into environmentally important CO_2 reduction problem.

Students perform catalytic test with the application of Microactivity Effi system (PID Eng & Tech) equipped with fixed-bed reactor according to following conditions: feed composition – F_{H_2} = 61.6 cm³/min, F_{CO_2} = 15.4 cm³/min, F_{Ar} = 23 cm³/min, total flow rate – F_{tot} = 100 cm³/min, reactor pressure – p = 1.9 bar, sample weight – m_{cat} = 200 mg. The catalyst sample must be diluted with 800 mg of quartz grains to maintain temperature balance and prevent reactor overheating. Prior to the activity test the catalyst should be activated in the flow of hydrogen (F_{H_2} = 80 cm³/min). The temperature of catalyst activation must be estimated on the basis of TPR experiment.
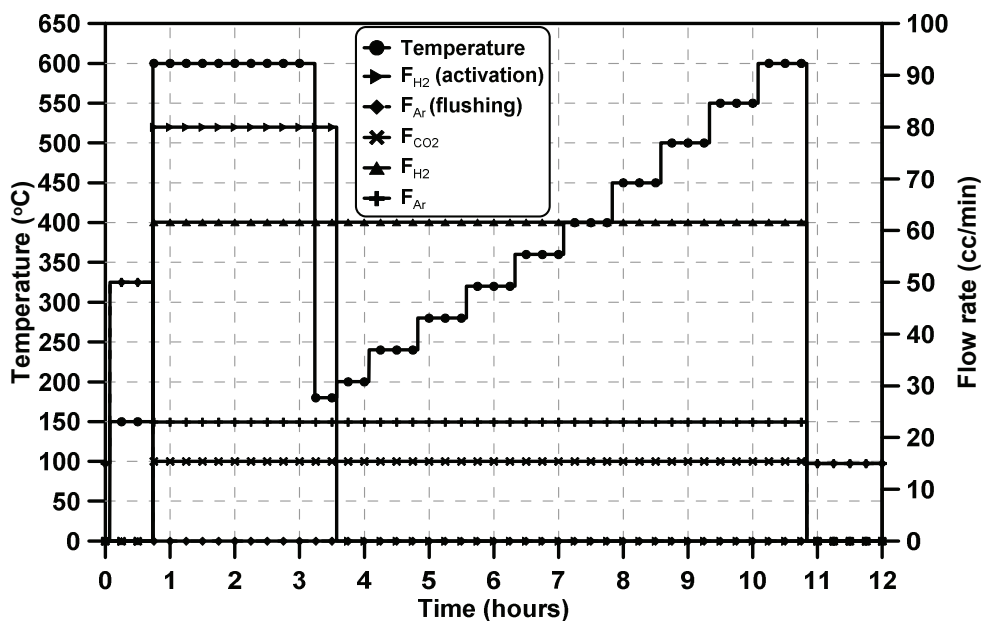

Fig. 1. The methodology of catalysts activity and selectivity test in CO_2 methanation reaction.

Microactivity Effi system is operated by Process@ software that allows to control set points and monitor present values of all

measurement parameters. Process@ software is designed to be operated according to a session table, which is a bunch of MA-Effi parameters changed with time. The students are responsible to modify a session table by themselves during the classes. The example methodology of catalysts activity and selectivity test was shown in Fig. 1. In this example the catalyst was reduced at 600°C for two hours. The activity of the catalysts was tested step wise at isothermal conditions form 200 to 600°C.

Product gas composition at the system outlet was measured automatically by customized Bruker Rapid Gas Analyser based on GC-450 operated by Galaxy Software. GC analysis run according to session table performing at least three analysis at isothermal conditions. Carbon dioxide conversion (X_{CO_2}) was calculated on the basis of reactor feed (CO_2 inlet – $C_{CO_2}^{in}$) and outlet $C_{CO_2}^{out}$ concentrations:

$$X_{CO_2} = \frac{C_{CO_2}^{in} - C_{CO_2}^{out}}{C_{CO_2}^{in}} \times 100\% \qquad (3)$$

Carbon monoxide (S_{CO}) and methane selectivity (S_{CH_4}) were calculated according to Eq. 4 and 5.

$$S_{CO} = \frac{C_{CO}}{C_{CH_4} + C_{CO}} \times 100\% \qquad (4)$$

$$S_{CH_4} = \frac{C_{CH_4}}{C_{CO} + C_{CH_4}} \times 100\% \qquad (5)$$

7. RESULTS AND DISCUSSION

Two nickel based catalysts supported on γ-Al₂O₃ with 20 and 40 wt.% of nickel loading were examined. The catalysts were prepared by "wet" impregnation method with the presence of citric acid. The catalysts were calcined at 400°C for two hours. Calcination temperature was estimated on the basis of TG experiments shown in Fig. 2 and 3.
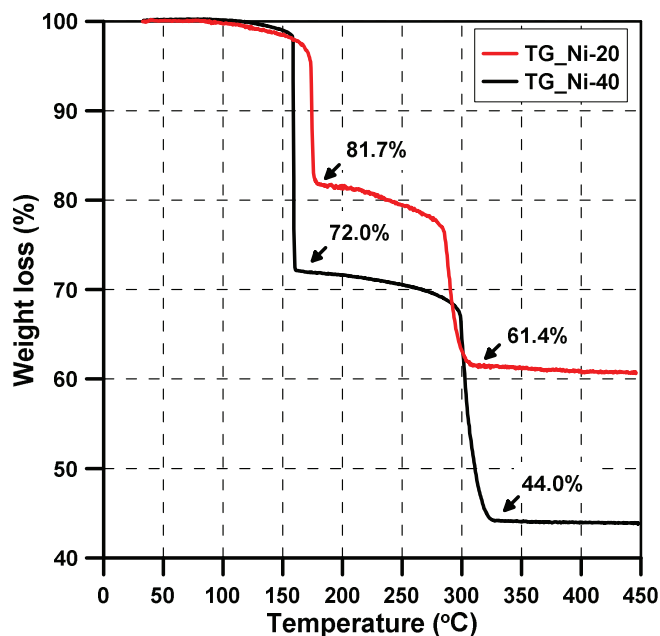
Fig. 2. TG curve of precursor decomposition of nickel based catalysts.
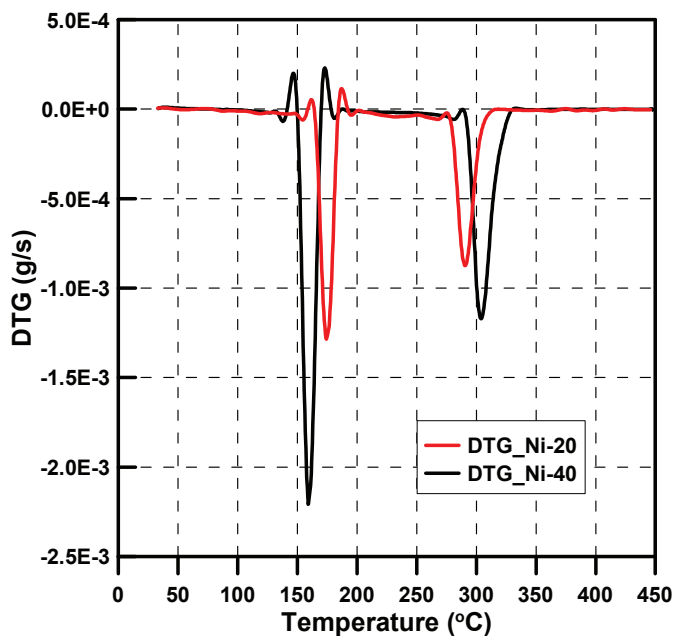

Fig.3. DTG curve of precursor decomposition of nickel based catalysts.

According to the literature, decomposition of supported nickel nitrate hydrate proceeds through several stages [1]. First, dehydration process takes place. It starts at around room temperature and completes below 200°C. Similarly, decomposition of hydrated citric acid precedes releasing of hydration water at the

temperatures below 100°C. It is important to mention that drying the catalysts precursors at 110°C may partially remove hydration water. Anhydrous citric acid is thermally stable up to around 148°C [2]. At the beginning it decomposes slowly. With the use of DSC one can observe melting point of citric acid at 153°C. The decomposition rate increases after melting and has a maximum at 159°C and 175°C for the Ni-40 and Ni-20 accordingly. Literature data reveal the possibility of decomposition of anhydrous nitrate with NO_2 evolution below 200°C, although the formation of nitrogen dioxide takes place at 250°C [1]. For a given samples anhydrous nitrate decomposition attains the maximum at 291 and 304°C.

Reducibility of the catalysts were studied according to the procedure described in exercise 3. On the basis of TRP-H_2 experiment the final activation temperature was determined. It is important to mention that high reduction temperature facilitates sintering of nickel oxide phases and may cause unfavourable structural changes in the support. Temperature-programmed reduction curves were shown in Fig. 4.
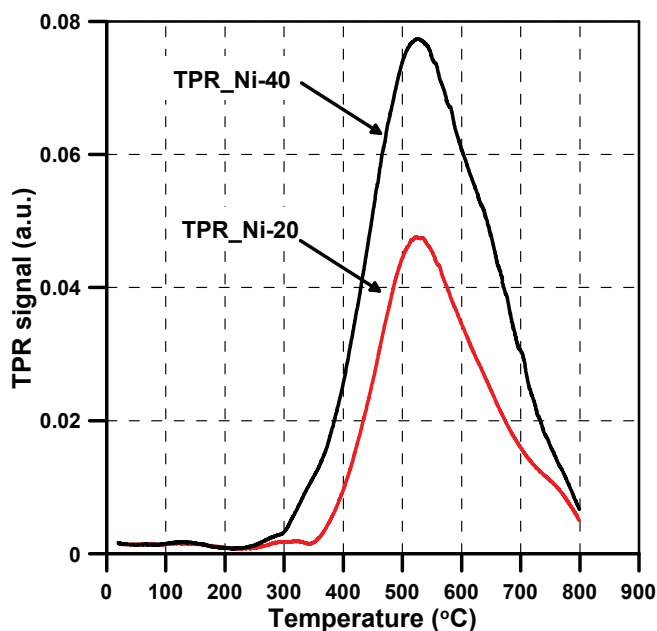

Fig. 4. Temperature-programmed reduction curve of nickel based catalyst.

The reduction starts slowly below 300°C and reveal the maximum of hydrogen consumption at 550°C. The results suggests that optimal activation temperature of the catalyst should exceed

550°C. In order to achieve the complete reduction of nickel oxides one should extend the activation procedure with a proper isothermal step.

The activity and selectivity test in carbon dioxide methanation reaction were performed according to the methodology shown in Fig. 1. The results were shown in Fig. 5, 6 and 7. The catalysts were reduced prior activity tests at 600°C for two hours. For both of the catalysts carbon dioxide conversion rapidly increases together with reaction temperature (Fig. 5). This trend is observed up to 360°C. One can observe much higher activity of the catalyst containing greater nickel content. Above 360°C for both of the catalysts CO_2 conversion drops to approximately 67% witch is governed by thermodynamic limits.
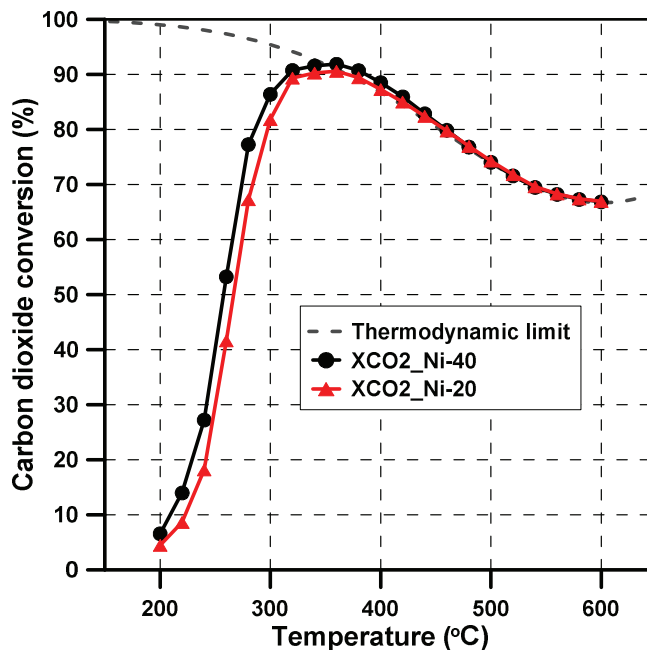

Fig. 5. Carbon dioxide conversion in methanation reaction of Ni/Al_2O_3 catalysts with 20 and 40 wt.% of nickel.

The selectivity towards methane and carbon monoxide in CO_2 methanation reaction are shown in Fig. 6 and 7 respectively. Due to the fact that no other compounds than CH_4, CO and H_2O was found in reaction products, CO and CH_4 selectivity add up to 100%. Both catalysts presents high methane selectivity up to 400°C. The selectivity towards methane decreases with reaction temperature reaching 63.5% at 600°C.
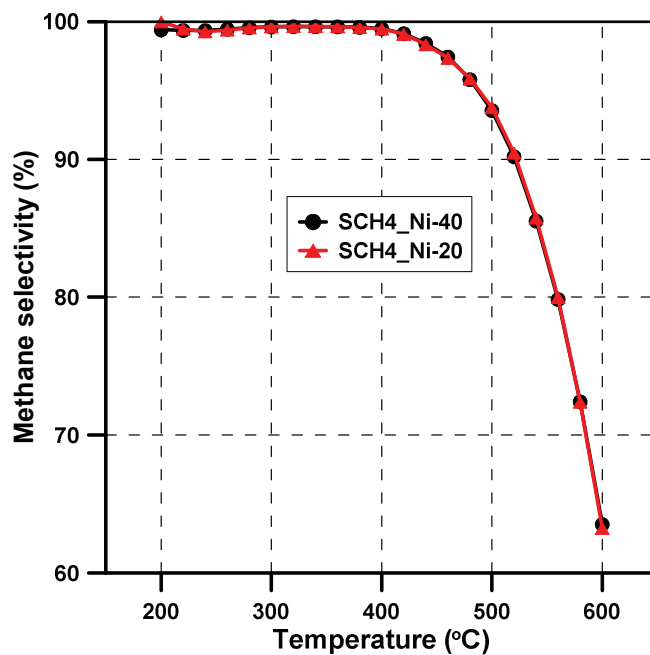
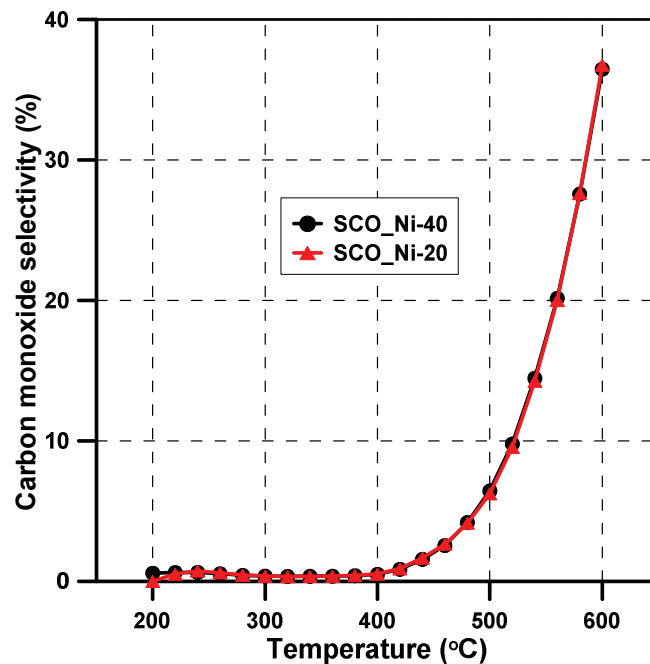Fig. 6. Methane selectivity in methanation reaction of Ni/Al_2O_3 catalysts with 20 and 40 wt.% of nickel.

Fig. 7. Carbon monoxide selectivity in methanation reaction of Ni/Al_2O_3 catalysts with 20 and 40 wt.% of nickel.

CONCLUSIONS

This is widely accepted that experimental work is a fundamental part of any science course. Especially in chemistry, it is taken for granted that the development of experimental skills is very important. Catalysts laboratory course in the given form was successfully introduced for Erasmus students. The experiments are designed to allow the students to understand selected facts regarding the catalysts preparation and investigation and to realize the importance of multiple parameters that influence the final properties of the catalysts. Moreover, the Students develop the skills of apparatus and process operation.

REFERENCES

[1] B. Małecka, A. Łącz, E. Drożdż, A. Małecki, *Journal of thermal analytical calorimetry*, **119**; 1053, (2015)
[2] M. M. Barbooti, D. A. Al-Sammerrai, *Thermochimica Acta*, **98**, 119, (1986)