

# Cu, Ni, Pt Bimetallic Microporous Supported Silica Catalysts for Direct Formaldehyde Synthesis from Carbon Dioxide and Hydrogen

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An increase in world greenhouse gas emissions requires the development of modern technologies for converting them into valuable substances and eliminating their formation during various technological and economic processes. One of the possible ways to solve this problem is the development of sustainable methods for producing widely used products that can be applied in different sectors of the modern economy. Formaldehyde is one of the largest-scale chemicals used in chemical processes. Modern industrial methods rely on the oxidation of methanol using industrial catalysts. This process can be adapted to utilize carbon dioxide for the direct production of formaldehyde. However, some thermodynamic and technical issues prevent the implementation of this process. The current study focuses on the synthesis of bimetallic catalysts based on Cu, Ni and Pt using microporous silica to provide a high concentration of active sites. The catalysts were characterized using nitrogen physisorption, hydrogen and carbon dioxide chemisorption, as well as X-ray fluorescence analysis. The synthesis of formaldehyde was carried out in a high-pressure Parr instrument reactor. Providing catalysts synthesis using micro-mesoporous silica results in the formation of metallic species within the micro- and mesoporous areas of the silica, and in an increase in the formaldehyde yield by 15-20 % compared to the catalysts described in literature.

## 1. Introduction

An increase in carbon dioxide concentrations in the atmosphere (Hepburn et al., 2019) declares the need for new technologies to be developed for its use in sustainable development of modern industry and society (Rauch et al., 2019). Possible methods for utilizing carbon dioxide include the production of fuels (LeClerc et al., 2024) and valuable chemicals (Banerjee et al., 2016). The highest impact of carbon dioxide incorporation in industrial processes can be achieved through a partial or full substitution of typical petrochemical processes such as the production of hydrocarbons, methanol, and formaldehyde (LeClerc et al., 2024). Formaldehyde is one of the most widely used feedstocks for industrial chemicals and polymers production. It is typically produced by the consecutive methane oxidation to syngas, syngas transformation to methanol and methanol catalytical oxidation over a silver or mixed catalyst (Chan et al., 2018). The direct formation of formaldehyde from carbon dioxide can possibly exclude methane application for formaldehyde synthesis, that can play a positive role for carbon dioxide concentration decrease in the atmosphere (Siebert et al., 2019). The other possible way for formaldehyde synthesis is hydrogenation of formic acid produced by carbon dioxide hydrogenation. However, an addition of a second step in carbon dioxide transformation is not technologically and economically favourable (Singh et al., 2021). Therefore, the study of direct carbon dioxide transformation into formaldehyde is of special interest for the sustainable development of modern society toward carbon dioxide zero emission. Formaldehyde direct synthesis from carbon dioxide has several reactions that can take place in the reaction medium, and the possible reaction pathway is shown in Figure 1 (Lee et al., 2001).

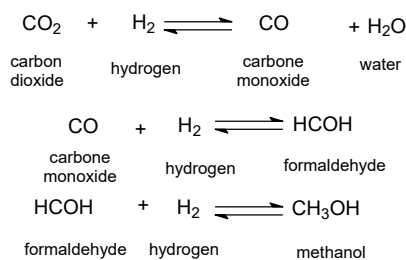


Figure 1: Scheme of the reaction pathway of formaldehyde synthesis from carbon dioxide

The first step in the consecutive reactions can be the conversion of carbon dioxide into carbon monoxide and water. Therefore, a decrease in the water content of the reaction medium can play positive role in the rate of carbon monoxide production. The second stage of this process is the formation of formaldehyde by hydrogenation of carbon monoxide. However, formaldehyde is immediately converted into methanol, so methanol formation must be suppressed in the reaction medium to obtain a high yield of formaldehyde. Here, the catalytic route of formaldehyde formation on bimetallic Cu, Ni, and Pt catalysts is studied and discussed.

## 2. Materials and methods

### 2.1 Materials

For catalyst synthesis, reagent-grade platinum acid, copper nitrate, nickel nitrate, ultra-fine silica, hydrogen, and carbon dioxide (grade A, 99.99 % vol.) were purchased from a local supplier and used as received. Distilled water was purified using an Aqua post water purifier.

### 2.2 Catalyst synthesis

For catalyst synthesis, a sample of silica was suspended in water. A solution of precursor was then added to the suspension, and the suspension was transferred into an evaporation cup, where the water was evaporated. The sample was then reduced in a tube furnace at 500 °C for 3 h in a hydrogen atmosphere. If a second metal was introduced into the sample, the procedure was then repeated twice, with different metals each time.

### 2.3 Formaldehyde synthesis procedure

For formaldehyde synthesis, 100 mg of a catalyst was placed into a reactor vessel (a Parr Instruments 4820 high-pressure reactor apparatus) filled with 30 mL of methanol. The reactor was purged three times with hydrogen, the hydrogen pressure was set to 10 bars, and the reactor vessel was then heated to 250 °C and maintained at that pressure for two hours. After the reactor had cooled to room temperature, it was flushed with a mixture of carbon dioxide and hydrogen with a carbon dioxide-to-hydrogen ratio of 1:10 three times. The gas mixture pressure was set at 70 bars and the reactor was heated up to a temperature of 180 °C. Samples from the reaction medium were collected hourly and analyzed using gas chromatography and mass spectrometry.

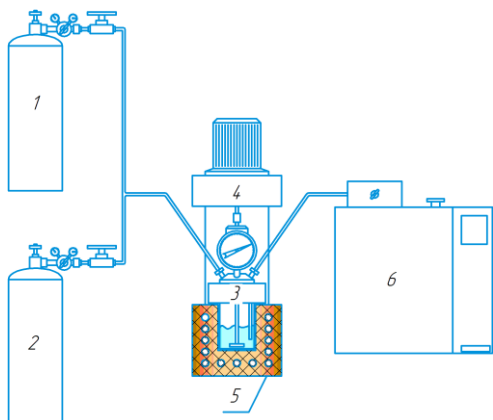


Figure 2: Experimental setup for formaldehyde synthesis (1 – tank with reaction mixture, 2 – tank with hydrogen, 3 – reactor, 4 – mixer, 5 – electric heater, 6 – online gas chromatograph)

## 2.4 Analysis

GC and mass-spectroscopic analysis. The reactor was connected to a gas chromatograph, Kristall 2000M, equipped with the chromatographic column, Hayesep Q80/100 ( $l = 3$  m,  $d = 2$  mm, the maximum column temperature is  $275$  °C). The transport line temperature was maintained at  $80$  °C, the analysis valve temperature was  $150$  °C, the evaporator temperature was  $230$  °C, the temperature of flame ionization detector was  $250$  °C. The column temperature was maintained at  $40$  °C for the first 5 minutes of analysis, then it increased to  $245$  °C with a rate of  $10$  °C/min. The gas phase feed rate was  $20$  mL/min, the hydrogen feed rate was  $25$  mL/min, and the air feed rate was  $250$  mL/min.

For liquid phase analysis, a Shimadzu HPMSQP2010 GC-MS spectrometer was used to analyze samples. The sample was analyzed using a capillary column (MS-1), with a length of  $100$  m and a diameter of  $0.32$  mm. The maximum column temperature was set to  $310$  °C. The initial thermostat temperature was set at  $50$  °C, the evaporator temperature set at  $300$  °C, and the gas pressure set at  $182.9$  kPa. The helium flow rate was set at  $81.5$  mL/min, and the carrier gas flow rate was set at  $1$  mL/min. The gas velocity was  $19.9$  cm/s, and the purge gas flow rate was  $5$  mL/min. Gas split ratio was set at  $1:1$ , evaporator pressure was set at  $200$  kPa, and sampling time was set at  $5$  s. The column temperature was maintained at  $50$  °C for  $10$  min, then it was increased to  $310$  °C at a rate of  $10$  °C/min. Ion source and interface temperatures were set at  $260$  °C and  $280$  °C respectively. The initial measured mass was  $10$  amu, and the final mass was  $100$  amu. Peak identification was made using the NIST library, and concentration of reaction products was made using the calibration curves.

X-ray fluorescence analysis was made using a Spectroscan-Maks-GF1E spectrometer equipped with a Mo anode and LiF crystal analyzer and SZ detectors. The analysis was based on the Co K $\alpha$  line. A series of standards containing metals was prepared by mixing  $0.1$ – $0.2$  g of matrix with  $10$ – $20$  mg of standard metal compound.

Liquid nitrogen physisorption was made at the normal boiling point of liquid nitrogen, using a Beckman Coulter SA3100 instrument. Before the analysis, the samples were degassed using a Beckman SA-PREP instrument for sample preparation at  $120$  °C in a vacuum for  $1$  h.

Hydrogen and carbon dioxide chemisorption was performed using the Micromeritics AutoChem 2910. Prior to analysis, the samples were purified in-situ at  $500$  °C for  $2$  hours in a continuous stream of Ar and He, then the temperature was decreased to  $105$  °C and the samples were flushed with active gases for an hour. After that, the samples were again flushed with Ar or He in order to reduce the amount of physically adsorbed gases, and then the temperature was increased to  $500$  °C at a rate of  $10$  °C/min, and gas adsorption curves were recorded.

## 3. Results and Discussion

The initial sample of silica was characterized by a nitrogen physisorption isotherm (Figure 3), the obtained isotherm curve is typical for micro-mesopores samples. The incorporation of metal over silica surface results in some decrease of hysteresis loop, from the other side, micropore region remains unchanged.

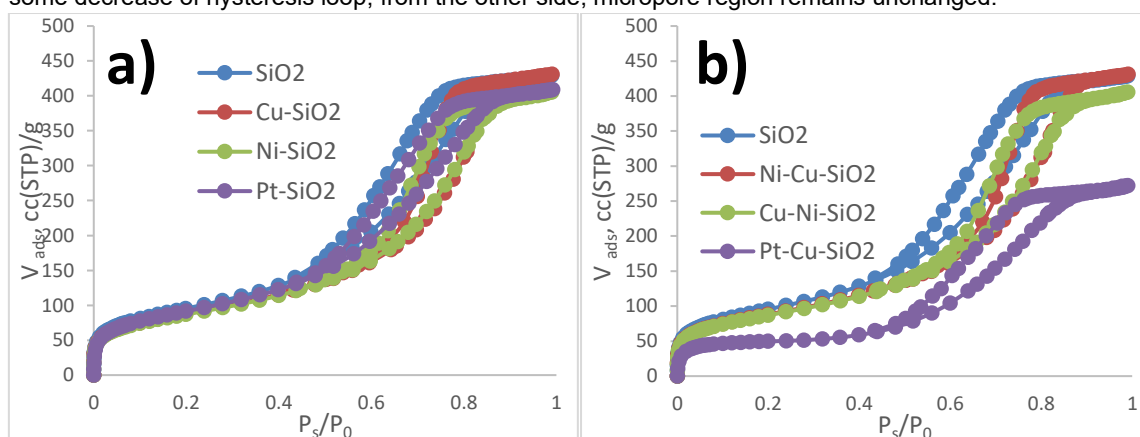


Figure 3: Nitrogen physisorption isotherms for a) monometallic and b) bimetallic samples

In the case of bimetallic samples, Ni-Cu-SiO<sub>2</sub> and Cu-Ni-SiO<sub>2</sub> a decrease in mesopore loop is rather noticeable. In the case of platinum containing Pt-Cu-SiO<sub>2</sub> sample, some decrease in the micropore slope region can be determined. Introduction of Cu on silica support results in some shift in the pore diameter dispersion from  $5$  nm to  $7$  nm (Figure 4a), that can be subscribed to the Cu species formation in the pores with a diameter of  $3$ – $4$  nm. While Ni incorporation over silica results in a drastic shift of the pore dispersion to  $10$  nm, that can be explained

by Ni species formation in the pores with a diameter from 3 to 10 nm. From the other side, Pt incorporation over support results only in a small decrease in the pore volume in the 4-6 nm region that can be subscribed to Pt species formation in these pores.

Incorporation of a second metal onto a silica support results in a drastic change in the distribution of pore volumes (Figure 4b). In the case of the Ni-Cu sample, there is a decrease in pore volumes in the 3-7 nm range and the appearance of additional pore volumes in the range of 7-15 nm, which can be explained by the partial formation of Ni-Cu species in the pores of 3-7 nm in diameter and on the external surface of silica. For the Cu-Ni species, there is some shift in pore volumes from the 4-5 nm range to the 7-8 nm region, which can also be explained by Cu-Ni species formation in the pores of 4-5 nm in diameter. In the presence of Pt-Cu species, there is an even more drastic reduction in the pore volumes between 3 and 9 nm, as well as the addition of new mesopores in the 10-20 nm region. This can be attributed to Pt-Cu species formation in small pores of silica with a diameter of 3-9 nm and over the silica surface, forming additional pores in the 10-20 nm region.

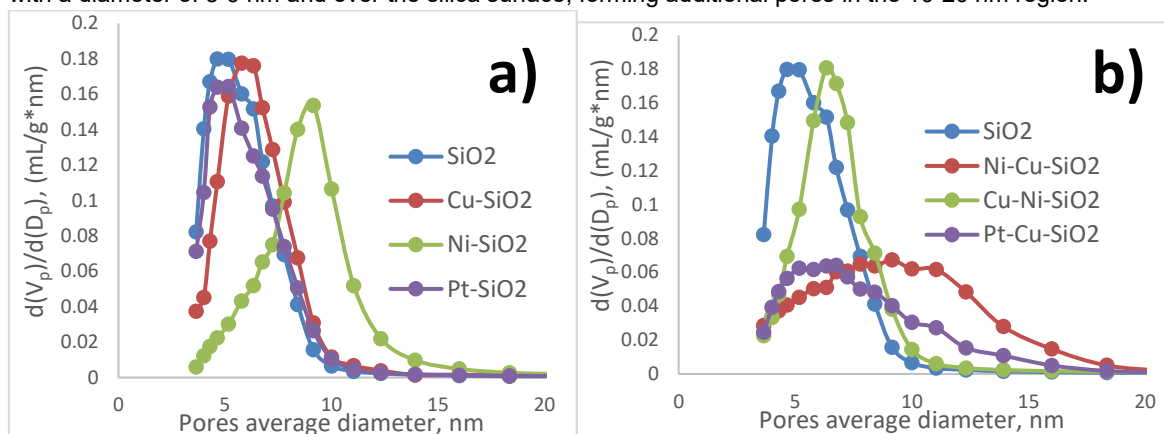


Figure 4: Pore volume distribution for a) monometallic and b) bimetallic samples

BET surface area values for monometallic samples (Table 1) are slightly lower compared to pure silica, with the lowest value being 332 m<sup>2</sup>/g for a platinum monometallic sample. The addition of a second metal leads to a further decrease in BET surface area compared to monometallic ones. A bimetallic platinum-copper sample has the lowest BET area of 173 m<sup>2</sup>/g, which can be attributed to the formation of platinum and copper species in the mesopores, resulting in a decrease in catalyst surface area. The active metal concentration (see Table 1) ranges from 0.72 to 0.98 wt. %.

Table 1: Initial catalysts characteristics

Sample	BET* surface area, m <sup>2</sup> /g	Metal concentration**, wt. %
SiO <sub>2</sub>	360	-
Cu-SiO <sub>2</sub>	349	0.72
Ni-SiO <sub>2</sub>	349	0.93
Pt-SiO <sub>2</sub>	332	0.95
Ni-Cu-SiO <sub>2</sub>	319	Ni-0.83 Cu-0.78
Cu-Ni-SiO <sub>2</sub>	314	Cu-0.87 Ni-0.92
Pt-Cu-SiO <sub>2</sub>	173	Pt-0.97 Cu-0.98

\* determined by the liquid nitrogen physisorption,

\*\* determined using X-ray fluorescence analysis.

Hydrogen programmed desorption from the silica surface (Figure 5a) and monometallic catalyst shows desorption of hydrogen at one type of active site with weak strength at a temperature range of 160–180 °C. Bimetallic samples (Figure 5b) of Ni-Cu and Cu-Ni show additional lines at temperatures of 290 °C and 340 °C, while the Pt-Cu sample shows a small peak at 280 °C. The desorption of carbon dioxide from the surface of silica and monometallic samples forms a line in the 160–190 °C region (Figure 5c). The copper sample additionally has a small reflection in the 340 °C region. The desorption of carbon dioxide from the bimetallic samples proceeded from the sites in the 160–190 °C range (Figure 5d). Additionally, copper-containing samples

have a small reflection at 340 °C. The presence of additional desorption peaks suggests the presence of additional active sites for carbon dioxide. Pure silica is characterized by the highest value of hydrogen desorbing from its surface, 0.004 mmol/g (Table 2). Comparable values of desorbing hydrogen were achieved with a Pt monometallic and Cu-Ni bimetallic samples. The copper-containing monometallic sample has the highest value of desorbed hydrogen from its surface, 0.03 mmol/g (see Table 2). Desorption sites are located in the 170–190 °C region for all samples, which suggests competitive adsorption of both hydrogen and carbon dioxide. The quantity of adsorbed CO<sub>2</sub> is 10–15 times higher than that for hydrogen, resulting in a higher adsorption of CO<sub>2</sub> over the sample surface compared to hydrogen.

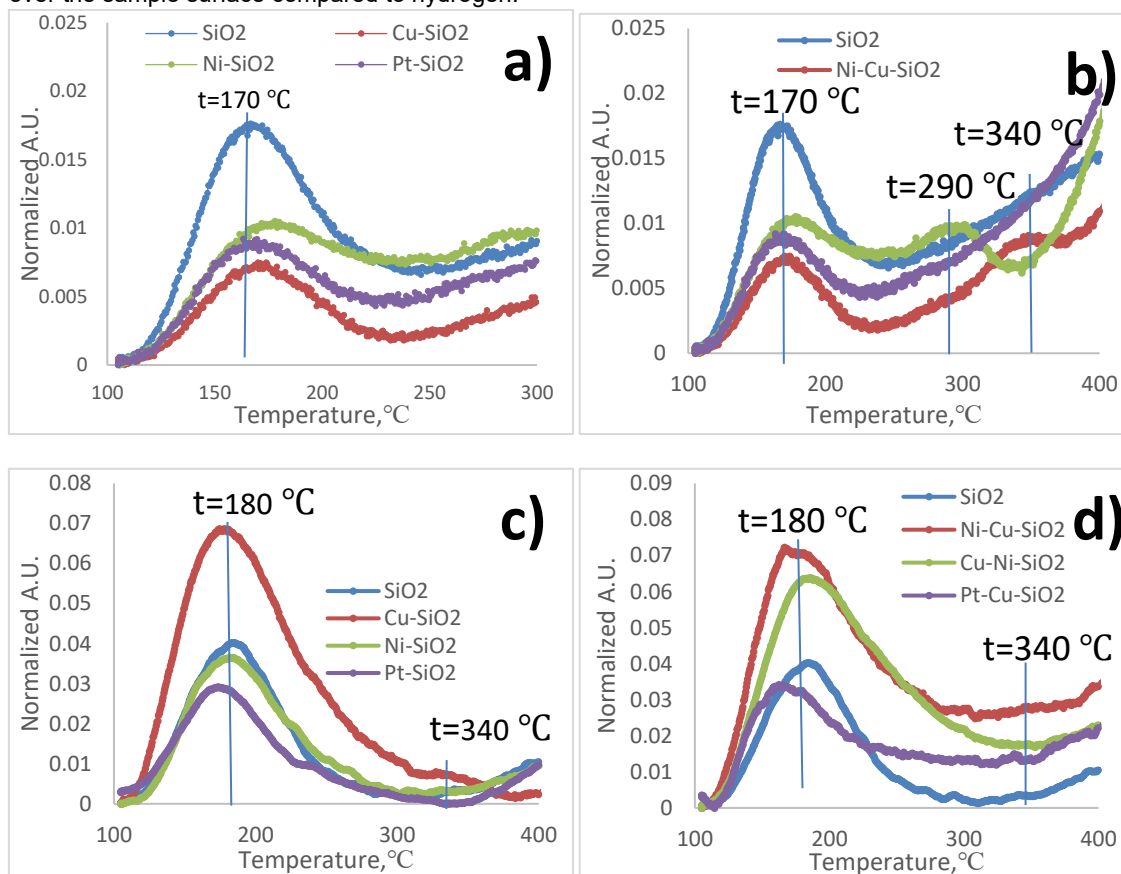


Figure 5: Hydrogen a), and b) carbon dioxide c), d) temperature programmed desorption curves for a) monometallic and b) bimetallic samples for c) monometallic and d) bimetallic samples

The partial pressure of hydrogen becomes a key reaction parameter in achieving high reaction rates, so it needs to be higher in magnitude than the partial pressure of carbon dioxide to provide a high rate of carbon dioxide transformation.

Table 2: Hydrogen and carbon dioxide adsorption values for synthesized catalysts

Sample	H <sub>2</sub> desorption, mmol/g	CO <sub>2</sub> desorption, mmol/g
SiO <sub>2</sub>	0.004	0.01
Cu-SiO <sub>2</sub>	0.001	0.03
Ni-SiO <sub>2</sub>	0.002	0.01
Pt-SiO <sub>2</sub>	0.003	0.007
Ni-Cu-SiO <sub>2</sub>	0.002	0.021
Cu-Ni-SiO <sub>2</sub>	0.004	0.022
Pt-Cu-SiO <sub>2</sub>	0.002	0.007

The developed catalysts' testing results (see Table 3) show that pure silica is nearly inactive in the carbon dioxide to formaldehyde transformation process. The copper-containing sample shows only 0.002 mmol(HCOH)/g(Cat), the nickel-containing sample shows 0.01 mmol(HCOH) /g(Cat), and the platinum result

was slightly higher, 0.2 mmol(HCOH)/g(Cat). It can be concluded that monometallic samples do not show activity in the transformation of carbon dioxide into formaldehyde, while bimetallic catalyst samples have a higher activity. Nickel and copper-containing samples showed a yield of 1.4–1.6 mmol(HCOH)/g(Cat), whereas platinum and copper-containing samples showed a yield of 2.4 mmol(HCHO)/g(Cat) (Table 3).

*Table 3: Catalyst testing results*

Sample	HCOH yield, mmol/g (Cat)	CO <sub>2</sub> conversion, %
SiO <sub>2</sub>	-	-
Cu-SiO <sub>2</sub>	0.002	0.004
Ni-SiO <sub>2</sub>	0.01	0.01
Pt-SiO <sub>2</sub>	0.2	0.7
Ni-Cu-SiO <sub>2</sub>	1.4	5.3
Cu-Ni-SiO <sub>2</sub>	1.6	6.4
Pt-Cu-SiO <sub>2</sub>	7.4	24.2

A comparison of the highest achieved yield of formaldehyde formation for the platinum-copper sample impregnated on silica showed an increase in the yield by 15–20 % compared to literature data (Chan et al., 2018).

#### 4. Conclusions

Synthesis of active nickel-, copper-, and platinum-containing samples of silica for direct carbon dioxide transformation into formaldehyde was provided. The developed samples were characterized by the nitrogen physisorption analysis, X-ray fluorescence spectroscopy, and hydrogen and carbon dioxide programmed desorption. The temperature-programmed desorption of hydrogen and carbon dioxide revealed the formation of primarily one desorption site for hydrogen and carbon dioxide at temperatures between 160 °C and 190 °C. The application of micro- and mesoporous silica for the formation of active metal species results in the formation of metallic species within the micro- and mesoporous areas of the silica. This leads to an increase in the formaldehyde yield by 15–20 % compared to literature data.

#### Acknowledgments

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