

Kinetic study of carbon dioxide catalytic methanation over cobalt–nickel catalysts

Alla G. Dyachenko, Olena V. Ischenko, Snizhana V. Gaidai,

Tetiana M. Zakharova, Andrii V. Yatsymyrskyi, Vladyslav V. Lisnyak

Department of Chemistry, Taras Shevchenko National University of Kyiv, Volodymyrska Street, 64/13, Kyiv 01601, Ukraine

vladyslav_lisnyak@yahoo.com, lisnyak@chem.univ.kiev.ua

Keywords: *Sabatier process, bimetallic catalysts, catalytic methanation of CO₂, kinetic patterns.*

Based on the data of the thermoprogrammed desorption and using mass-spectroscopic analysis of desorbed products and on the kinetic patterns of the methanation process for cobalt–nickel catalysts, we suggested a mechanism for the reaction which passes through forming intermediate formyl compounds: CHO*, HCOH*, and HCOOH*. Because of the high stability of the carbon dioxide molecule, the step of adding the first hydrogen atom is the limiting step. Such a mechanism is in good agreement with the proposed kinetic equations.

Introduction

The electrolytic splitting water into hydrogen is one of the remarkable solutions at conversing surplus electricity into fuels [1]. The resulting gas reserves can be effectively stored for further use in fuel cells.

These fuel cells will generate electric energy at the highest point of seasonal consumption of electricity by customers [2]. In addition, the Sabatier process that can be shown by equation

$$\text{CO}_2 + 4\text{H}_2 = \text{CH}_4 + 2\text{H}_2\text{O} \quad (1)$$

accumulate the energy by converting electrochemically generated hydrogen into methane [3].

Methane, the main component of synthetic natural gas, has several advantages over

hydrogen, for example, higher volumetric energy content [4]. Using methane is lowering the risk of the gas leakage and explosion of gas-oxygen mixtures. The undoubted plus is also that the infrastructure of the existing gas networks can be used for methane consumption.

Alternatively, the methane production can be done by a combined Sabatier reaction/water electrolysis process [5]. A mixture of gases H₂, CO, CO₂ (syngas) obtained from alkaline water electrolysis using graphite electrodes (1 kW
COBE
ad of producing just
oxygen and hydrogen as in the common alkaline
electrolysis process. The syngas has been
subjected to methanation over Ni/CaO-Al₂O₃
catalyst at 1 bar and different temperatures.

In the reported installation [5], one can achieve a CH₄ yield of 25.5% and 44.2% CO₂ conversion into CH₄ at 96.5% selectivity towards CH₄. In this way, one can produce methane fuel on-line in remote locations.

The complete CO₂ methanation in hydrogen is an exothermic reaction. It has a negative enthalpy of -164.7 kJ mole⁻¹. This methanation of CO₂ is an eight-electron process with significant kinetic difficulties [6–8]. Therefore, an efficient catalyst is required to achieve high selectivity towards methane at acceptable reaction rates. In recent years, to develop thermostable catalysts with high activity at low temperatures, extensive researches have been conducted, as evidenced by the growing number of publications [9–11].

For industrial usage, cobalt and nickel catalysts have been extensively investigated because of their low cost and availability. However, the active Ni catalyst can be deactivated even at low temperatures because of the sintering of metal particles as a result of nickel carbonyls formation [12]. Many methods have been tested to increase the stability and activity of Ni-based catalysts, for example, by adding different catalytic systems or oxides, as well as changing types of carriers and methods of the catalyst preparation [13, 14].

Carbon dioxide is a source of carbon for not only methane but alcohols and other organic compounds synthesis. The catalytic reactions occur at low reaction temperature and not

require additional energy. Among the wide range of combinations of transition metals, the particular interest arouses that of Ni and Ni–Co having high selectivity towards methane [15, 16]. At this moment, there is no consensus on the mechanism for the reaction of hydrogenation of CO₂ [17, 18] and also remains unexplored a significant part of potentially effective combinations of the active phase, promoter, and carrier. Consequently, the search for new methanation catalysts and the study of the reaction mechanism remains the actual task.

In this work, to suggest the reaction mechanism, we considered the methanation kinetics and thermal desorption from the surface of Co–Ni catalysts.

Experimental part

Material and methods

The gases used at kinetic experiments are hydrogen taken from a hydrogen generator, carbon dioxide (99.8%) and helium (99.995%) taken from gas cylinders.

We studied high active Co₈₀Ni₂₀ and low active Co₃₅Ni₆₅ catalysts. For them, the methane yield reaches 65% and 40% at 325 °C. To prepare Co₃₅Ni₆₅ and Co₈₀Ni₂₀ catalysts, mixtures of pure metal powders of Ni and Co were taken in the nominal ratio of 35:65 and 80:20 mass% Co:Ni. They were dissolved in 50 ml of concentrated 55 vol.% HNO₃ and refluxed using a sand bath for 30 min. When both metals dissolved, the nitrate solution was cooled and

then poured into 25 ml of 18% (w/v) NH_4OH . The prepared solution was adjusted to pH 7 then stirred for 10 min and concentrated at 100 °C for 4 h. Precipitated solids obtained by the evaporation was calcined at 350 °C for 4 h to yield a mixture of NiO and CoO powders. These oxide mixtures were reduced to Co–Ni metal catalysts in a gas flow of 50 vol% H_2 rest He at 375 °C for 4 h, at atmospheric pressure.

Kinetic studies were conducted in a gradientless reactor at a pressure of 0.1 MPa and the constant concentration of selected reagent ($C(\text{CO}_2)$ or $C(\text{H}_2)$). This reactor was operated under a continuous flow of reagents mixture diluted by helium gas-carrier. At $C(\text{CO}_2) = 0.6 \times 10^{-3}$ mol/L, $C(\text{H}_2)$ varied from 3×10^{-3} to 3.2×10^{-2} mol/L; at $C(\text{H}_2) = 8.17 \times 10^{-3}$ mol/L, $C(\text{CO}_2)$ varied from 0.7×10^{-3} to 3.0×10^{-2} mol/L. The constant concentration of reagent was selected in such a way to maintain the conversion of CO_2 below 20%. A gas sample was taken from the reactor outlet to be analyzed.

The chromatographic analysis for CO_2 , CO, and CH_4 was performed with a thermal conductivity detector on a Shimadzu 2014 GC. A column packed with 5A molecular sieves was used for gas separation. Kinetic regularities of methanation were determined by measuring the rate of

formation of CH_4 and CO against the reactant concentration. The reaction rate (r , $\text{mol} \times \text{s}^{-1} \text{m}^{-2}$) was calculated by the formula

$$r = CU/gS \quad (2)$$

where C is the CO_2 concentration at the outlet of the reactor, $\text{mol} \times \text{m}^{-3}$, U is the volume rate of gas flow of $1.67 \times 10^{-6} \text{ m}^3 \times \text{s}^{-1}$, g is the catalyst mass of 1 g, and S is the specific surface area of the catalyst in $\text{m}^2 \times \text{g}^{-1}$.

The reaction temperature was selected for each sample in such a way to maintain the CO_2 conversion below 20%. The reaction orders with respect to reactants were calculated by the Van't Hoff method, at a fixed concentration of the selected component of the reaction mixture.

Thermodesorption studies after catalysis were performed by thermoprogrammed desorption mass spectrometry (TPD MS). The thermal analysis was carried out in the temperature range of 30–800 °C, at a heating rate of 10 °C/min [19].

Results and discussion

For $\text{Co}_{35}\text{Ni}_{65}$ catalyst, the reaction order of CO formation towards H_2 showed an increase with reaction temperature (**Figure 1a**).

Thus, the reaction order is 0.09 at 225 °C, 0.13 at 240 °C, and 0.52 at 255 °C.

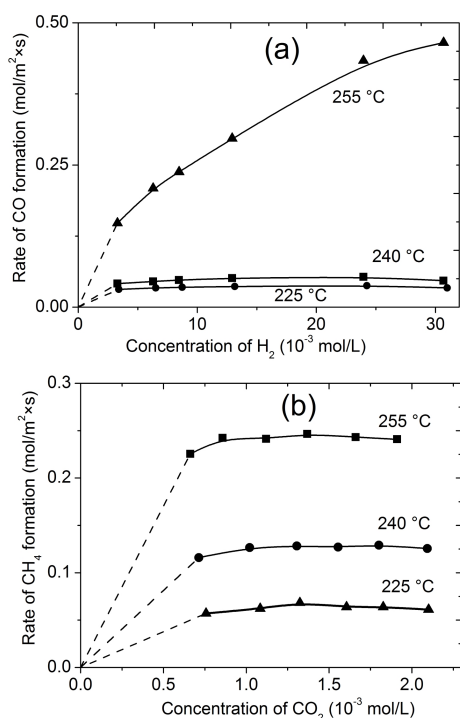


Figure 1. (a) CO and (b) CH₄ formation rate against H₂ concentration for Co₃₅Ni₆₅ catalyst.

Figure 1b shows the reaction order of CH₄ formation towards H₂ is markedly increased with temperature, e.g., 0.39 at 225 °C, 0.45 at 240 °C, and 0.52 at 255 °C.

For this catalyst, the reaction order of CO formation towards CO₂ shows a strong dependence on the CO₂ concentration. The reaction order of CO formation towards CO₂ is decreasing from 1.28 to 0.5 at 225 °C, see Figure 2a.

We observed the same decrease from 0.79 to 0.0 at 240 °C and from 1.58 to 0.23 at 255 °C. The reaction order of CH₄ formation towards CO₂ showed the same zeroth order at 225, 240, and 255 °C (Figure 2b).

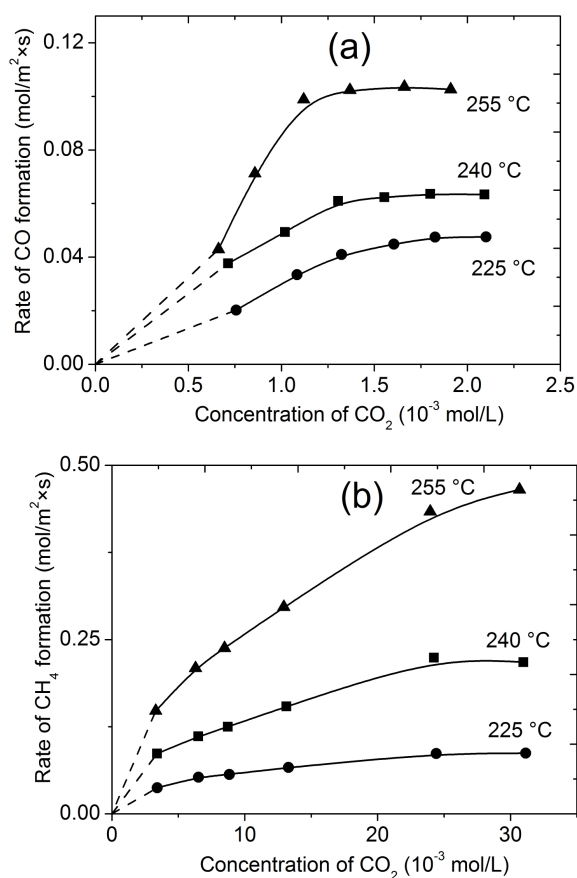


Figure 2. (a) CO and (b) CH₄ formation rate against CO₂ concentration for Co₃₅Ni₆₅ catalyst.

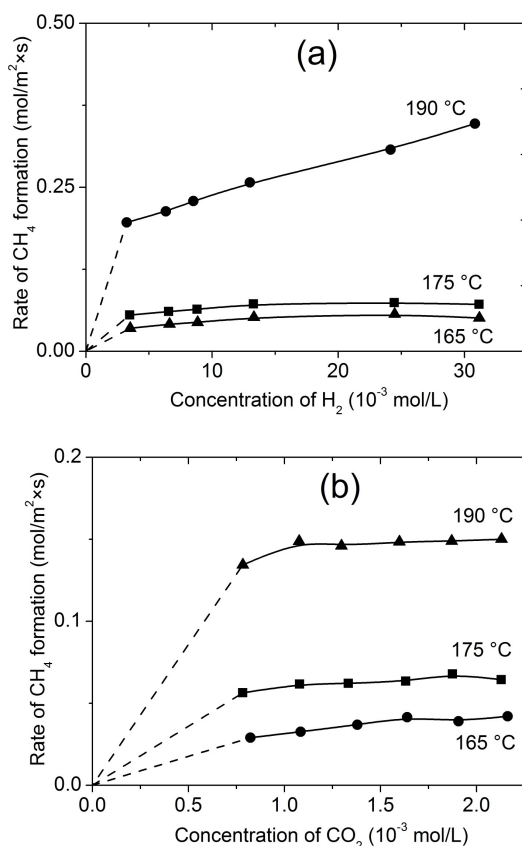


Figure 3. CH₄ formation rate against (a) H₂ and (b) CO₂ concentrations for Co₈₀Ni₂₀ catalyst.

For the most active Co₈₀Ni₂₀ catalyst, CO was not observed within the reaction products. The reaction order for CH₄ formation with respect to H₂ is 0.19 at 165 °C, 0.13 at 175 °C, and 0.25 at 190 °C (Figure 3a). The reaction order for CH₄ formation with respect to CO₂ is 0.22 at 165 °C, 0.12 at 175 °C and 0.02 at 190 °C (Figure 3b).

Data from TPD MS analysis showed the presence on strongly and weakly bonded HCO*, HCOH*, and HCOOH* intermediates of the gradual hydrogenation of CO₂ molecule at the active catalyst site (Figure 4).

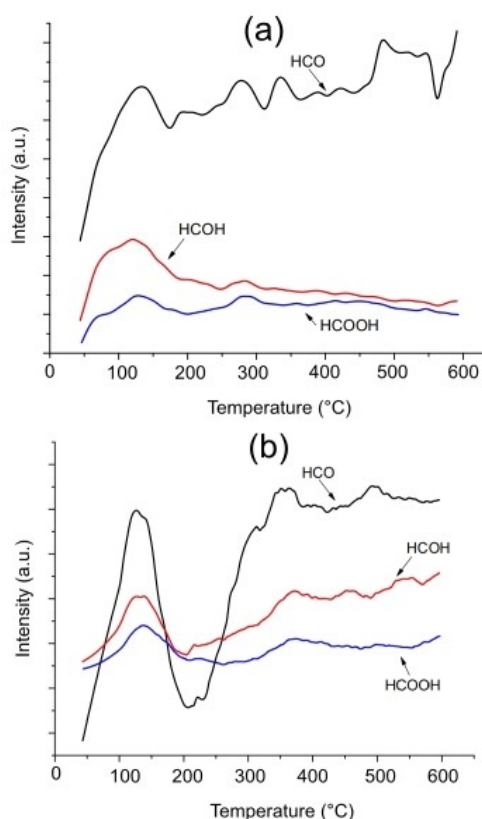
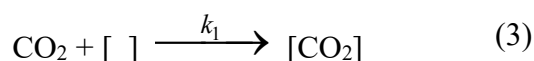


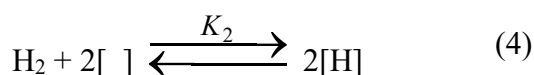
Figure 4. TPD MS profiles of HCO*, HCOH*, and HCOOH* for (a) Co₃₅Ni₆₅ and (b) Co₈₀Ni₂₀ catalysts.

Based on the obtained results, the following kinetic description of the reaction on the Co–Ni

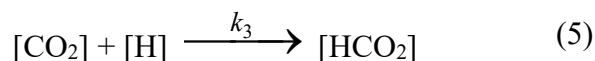
catalysts can be done, and the CO₂ methanation reaction mechanism can be suggested. Here below [...] is the free adsorption site, r is the rate reaction of CH₄ formation from CO₂, θ_{\emptyset} is the fraction of free adsorption sites, θ_H , θ_{CO_2} , and θ_{HCO_2} are fractions of the adsorption sites occupied by H, CO₂, and [HCO₂], respectively, $p(H_2)$ and $p(CO_2)$ are partial pressures of H₂ and CO₂.



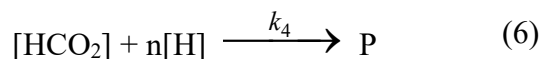
where k_1 is the CO₂ adsorption constant.



where K_2 is the equilibrium reaction constant.



k_3 is the CO₂ methanation constant. This is a slow process since $\theta_{HCO_2} \rightarrow 0$.



where P means products, here is realized the fast process of [H₂COO], [H₂CO], ..., and CH₄ formation. According to the literature [20], CH, CH₂, and CH₃ are formed very quickly; therefore, they forming are not presented as separate stages of the mechanism.

From the aforementioned assumptions, we have

$$\frac{d\theta_{CO_2}}{dt} = 0; \quad (7)$$

$$k_1 p_{CO_2} \theta_{\emptyset} - k_3 \theta_{CO_2} \theta_H = 0$$

$$\theta_{CO_2} = \frac{k_1 p_{CO_2} \theta_{\emptyset}}{k_3 \theta_H} \quad (8)$$

$$K_2 = \frac{\theta_H^2}{p_{H_2} \theta_\emptyset^2} \quad (9)$$

$$\theta_H = (K_2 p_{H_2})^{1/2} \theta_\emptyset \quad (10)$$

$$\theta_{CO_2} = \frac{k_1 p_{CO_2}}{k_3 (K_2 p_{H_2})^{1/2}} \quad (11)$$

$$1 = \theta_\emptyset + \theta_H + \theta_{CO_2} \quad (12)$$

$$\theta_\emptyset + \theta_\emptyset (K_2 p_{H_2})^{1/2} + \frac{k_1 p_{CO_2}}{k_3 (K_2 p_{H_2})^{1/2}} = 1 \quad (13)$$

$$\theta_\emptyset = \frac{1 - \frac{k_1 p_{CO_2}}{k_3 (K_2 p_{H_2})^{1/2}}}{1 + (K_2 p_{H_2})^{1/2}} \quad (14)$$

$$r = k_3 \theta_{CO_2} \theta_H = \frac{k_1 p_{CO_2} - \frac{(k_1 p_{CO_2})^2}{k_3 (K_2 p_{H_2})^{1/2}}}{1 + (K_2 p_{H_2})^{1/2}} \quad (15)$$

From these equations, the following relations can be derived for the reaction order of CH₄ formation with respect to CO₂

$$p_{CO_2} \gg p_{H_2} \Rightarrow r = k_1 p_{CO_2} \quad (16)$$

This means that the reaction order of CH₄ formation with respect to CO₂ is in the range from 0.0 to 1.0. For the reaction order of CH₄ formation with respect to H₂, we get

$$p_{H_2} \gg p_{CO_2} \Rightarrow r = \frac{k_1 p_{CO_2}}{\sqrt{K_2 p_{H_2}}} \quad (17)$$

That is, the reaction order of CH₄ formation with respect to H₂ is in the range from -0.5 to 0.5, which does not contradict our experimental data.

Conclusions

Kinetic patterns of the methanation process for these catalysts showed a complex character. We proposed the mechanism which stages are based on data of kinetic measurements combined with TPD MS data. From TPD MS analysis, we found formyl intermediate compounds that are strongly and weakly bonded to the catalyst surface. We proposed the four-stage mechanism for the reaction considering the one atom hydrogenation of CO₂ as the limiting step. Such a mechanism is in good agreement with the data given.

References

- [1] Petipas F. Conception et conduite de systèmes d'électrolyse à haute température alimentés par des énergies renouvelables. Paris: MINES ParisTech; 2013, p. 180.
- [2] De Saint Jean M, Baurens P, Bouallou C, Couturier K. Economic assessment of a power-to-substitute-natural-gas process including high temperature steam electrolysis. *Int J Hydrogen Energy* 2015;40(20):6487-6500.
- [3] Rönsch S, Schneider J, Matthischke S, and et.al. Review on methanation – From fundamentals to current projects. *Fuel* 2016;166:276-296.
- [4] Sherif SA, Yogi Goswami D, (Lee) Stefanakos EK, Steinfeld A. *Handbook of Hydrogen Energy*. Boca Raton: CRC Press; 2014, p. 1058.
- [5] Guerra L, Rossi S, Rodrigues J, Gomes J, Puna J, Santos MT. Methane production by a combined Sabatier reaction/water electrolysis process. *J Environ Chem Eng* 2018;6:671-676.
- [6] Prieto G. Carbon dioxide hydrogenation into higher hydrocarbons and oxygenates: thermodynamic and kinetic bounds and progress with heterogeneous and

- homogeneous catalysis. *ChemSusChem* 2017;10(6):1056-1070.
- [7] Miguel CV, Soria MA, Mendes A, Madeira LM. Direct CO₂ hydrogenation to methane or methanol from post-combustion exhaust streams—A thermodynamic study. *J Natural Gas Sci Eng* 2015;22:1-8.
- [8] Swapnesh A, Srivastava VC, Mall ID. Comparative study on thermodynamic analysis of CO₂ utilization reactions. *Chem Eng Technol* 2014;37(10):1765-1777.
- [9] Meshkini Far R, Ischenko OV, Dyachenko AG. and et al. CO₂ hydrogenation into CH₄ over Ni–Fe catalysts *Funct. Mater. Lett.* 2018;11:1850057.
- [10] Zh ludenko M, Dyachenko A, Bieda O, and et.al. Structure and catalytic properties of Co–Fe systems in the reaction of CO₂ methanation. *Acta Phys Polonica A* 2018;133:1084-1087.
- [11] Su X, Xu J, Liang B, and et.al. Catalytic carbon dioxide hydrogenation to methane: A review of recent studies. *J Energy Chem* 2016;25:553-565.
- [12] Agnelli M, Kolb M, Mirodatos C. CO Hydrogenation on a Nickel Catalyst. *J Catal* 1994;148:9-21.
- [13] Aziz MAA, Jalil AA, Triwahyono S, Ahmad A. CO₂ methanation over heterogeneous catalysts: Recent progress and future prospects. *Green Chem* 2015;17:2647-2663.
- [14] Kustov LM, Tarasov AL. Hydrogenation of carbon dioxide: a comparison of different types of active catalysts. *Mendeleev Commun* 2014;24:349-350.
- [15] Alrafei B, Polaert I, Ledoux A and et al. Remarkably stable and efficient Ni and Ni-Co catalysts for CO₂ methanation *Catal Today* 2019, in press. <https://doi.org/10.1016/j.cattod.2019.03.026>
- [16] Martínez J, Hernández E, Alfaro S; and et al. High Selectivity and Stability of Nickel Catalysts for CO₂ Methanation: Support Effects. *Catalysts* 2019;9:24.
- [17] Miao B, Ma SSK, Wang X. et al. Catalysis mechanisms of CO₂ and CO methanation. *Catalysis Sci Technol* 2016;6(12):4048–4058.
- [18] Baraj E, Vagaský S, Hlinčík T and et al. Reaction mechanisms of carbon dioxide methanation. *Chem Pap* 2016;70:395-403.
- [19] Ishchenko EV, Boldyreva NA, Tsapyuk GG, Yatsimirskii AV. State of carbon monoxide adsorbed on the surface of Pd, Pd-Ag, and Ag catalysts deposited on Al₂O₃. *Russ J Phys Chem* 2000;74:S541-543.
- [20] Kwak JH, Kovarik L, Szanyi J. Heterogeneous catalysis on atomically dispersed supported metals: CO₂ Reduction on multifunctional Pd catalysts. *ACS Catal.* 2013;3:2094-2100.