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

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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
$$\text{CO}_2 + 4\text{H}_2 = \text{CH}_4 + 2\text{H}_2\text{O} \quad (1)$$
 is a more convenient and safe way to 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 prototype) was used instead 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) CH_4 formation rate against H_2 concentration for $Co_{35}Ni_{65}$ catalyst.

Figure 2. (a) CO and (b) CH_4 formation rate against CO_2 concentration for $Co_{35}Ni_{65}$ catalyst.

Figure 1b shows the reaction order of CH_4 formation towards H_2 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 CO_2 shows a strong dependence on the CO_2 concentration. The reaction order of CO formation towards CO_2 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 CH_4 formation towards CO_2 showed the same zeroth order at 225, 240, and 255 °C (**Figure 2b**).

Figure 3. CH_4 formation rate against (a) H_2 and (b) CO_2 concentrations for $Co_{80}Ni_{20}$ catalyst.

For the most active $\text{Co}_{80}\text{Ni}_{20}$ catalyst, CO was not observed within the reaction products. The reaction order for CH_4 formation with respect to H_2 is 0.19 at 165 °C, 0.13 at 175 °C, and 0.25 at 190 °C (**Figure 3a**). The reaction order for CH_4 formation with respect to CO_2 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 CO_2 molecule at the active catalyst site (**Figure 4**).

Figure 4. TPD MS profiles of HCO^* , HCOH^* , and HCOOH^* for (a) $\text{Co}_{35}\text{Ni}_{65}$ and (b) $\text{Co}_{80}\text{Ni}_{20}$ catalysts.

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

catalysts can be done, and the CO_2 methanation reaction mechanism can be suggested. Here below [...] is the free adsorption site, r is the rate reaction of CH_4 formation from CO_2 , $\theta_\emptyset$ 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, CO_2 , and $[\text{HCO}_2]$, respectively, $p(\text{H}_2)$ and $p(\text{CO}_2)$ are partial pressures of H_2 and CO_2 .

where k_1 is the CO_2 adsorption constant.

where K_2 is the equilibrium reaction constant.

k_3 is the CO_2 methanation constant. This is a slow process since $\theta_{\text{HCO}_2} \rightarrow 0$.

where P means products, here is realized the fast process of $[\text{H}_2\text{COO}]$, $[\text{H}_2\text{CO}]$, ..., and CH_4 formation. According to the literature [20], CH , CH_2 , and CH_3 are formed very quickly; therefore, they forming are not presented as separate stages of the mechanism.

From the aforementioned assumptions, we have

$$\frac{d\theta_{\text{CO}_2}}{dt} = 0; \quad (7)$$

$$k_1 p_{\text{CO}_2} \theta_\emptyset - k_3 \theta_{\text{CO}_2} \theta_{\text{H}} = 0$$

$$\theta_{\text{CO}_2} = \frac{k_1 p_{\text{CO}_2} \theta_\emptyset}{k_3 \theta_{\text{H}}} \quad (8)$$

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

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

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

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

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

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

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

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.

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