Selective Methanation of Carbon Monoxide to Purify Hydrogen for Fuel Elements

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Abstract

The possibility of fine purification of hydrogen from CO by means of preferable hydrogenation of carbon(I) monoxide into methane till the residual CO content of 1000 ppm is investigated. In order to develop a compact device intended for hydrogen preparation for fuel elements, an efficient nickel-containing catalyst was proposed that provides the required purification degree (not more than 1000 ppm CO at the outlet), selectivity (not less than 70 % of methane is formed from CO) and the level of activity (contact time is not more than 6000 h^{-1}).

INTRODUCTION

For the purpose of energy resource saving and in order to solve ecological problems, intense research and developments are carried out in the world in the area of electrochemical power engineering. Efforts are aimed at the creation of highly efficient and ecologically safe power installations based on fuel elements (FE). In order to achieve broad introduction of the FE technology, it is necessary to make a compact and not very expensive fuel processor to treat fuel in order to obtain hydrogen-containing gas mixture and make it suitable for the necessary technical requirements. The catalytic activity of modern anode catalysts of fuel elements with a proton exchange membrane (PEMFE) decreases substantially if CO content of the gas mixture rises above 10–100 ppm (depending on tolerance of the anode catalyst). At the same time, the mixture after hydrocarbon fuel reforming contains a substantial amount of CO (10 % and more). Therefore, it is necessary to purify the hydrogen-containing mixture from CO before supplying it to PEMFE. At the stage of CO conversion with water vapour (the first stage of purification), CO content can be decreased to 0.5–1 %. For further profound purification, it is proposed to use selective oxidation of CO and selective methanation.

In order to carry out selective methanation of CO, no addition of oxygen (air) is required. So, the engineering arrangement of the reactor may be simplified; substantial dilution of the mixture with nitrogen can thus be avoided. It was shown in [1] that a two- or three-fold excess of oxygen is necessary for fine purification from CO (to 10 ppm); the amount of hydrogen to be oxidized should be equal to or larger than the initial CO content). This decreases the general efficiency of the process. Indeed, to oxidize 1 % of residual CO, it is necessary to add 2–3 % of oxygen into the reaction mixture (that is, 10–15 vol. % of air). Since the gas enriched with hydrogen after passing through the electrochemical battery enters the burner of the first stage of the process, which is steam reforming of methane, it is more preferable to use undiluted and higher-calorie gas after methanation than the gas mixture after oxidation. According to our estimations, in comparison with oxidation (a three-fold oxygen content), the calorific value of the gas containing 1 and 1.5 % (vol.) CO is higher under methanation by 304 and 450 kJ/nm^3 of gas, respectively (assuming that the selectivity of hydrogenation of CO and CO_2 is 50 %).

However, according to the data reported in [2], fine purification from CO by means of hydrogenation is complicated not only by the unfavourable reaction of CO_2 hydrogenation but also the reverse reaction of CO conversion with water vapour.

The catalysts of CO methanation used to prepare hydrogen for FE were described in a number of patents [3–7]. Methanation is carried out in one or to stages with the catalysts based on Ru, Rh, Pt, Ni, Fe.

In the present work we investigate the possibility of fine purification of hydrogen from CO by means of preferable hydrogenation of carbon monoxide into methane till the residual content of 1000 ppm, followed by its selective oxidation till 10–100 ppm.

Hydrogenation of carbon oxides proceeds according to the reactions:

$$CO + 3H_2 = CH_4 + H_2O \quad (1)$$

$$CO_2 + 4H_2 = CH_4 + 2H_2O \quad (2)$$

Fine purification from CO by means of hydrogenation is hindered due to the formation of CO from CO_2 according to the inverse conversion reaction:

$$CO_2 + H_2 = CO + H_2O$$

A typical reaction mixture entering the stage of methanation after conversion of CO with water vapour has the following composition, vol. %: CO 1, CO_2 18–20, H_2O 10–20, H_2 – balance.

An efficient catalyst of methanation for a compact reactor of hydrogen preparation for FE should meet the following requirements:

1) purification degree: CO content at the outlet should be not higher than 1000 ppm;

2) selectivity: CO_2 should be transformed into methane by not more than 70 %;

3) Activity level: contact time should not exceed 0.4 s (9000 h^{-1}).

On the basis of these criteria, keeping in mind the catalyst price, we studied three series of catalysts based on transition metals Ni, Co, Cu.

EXPERIMENTAL

The catalysts were obtained by co-precipitation followed by thermal decomposition of the resulting hydroxocompounds. Before catalytic measurements, the catalysts were activated with hydrogen.

Catalytic measurements were carried out in a flow set-up at atmospheric pressure within temperature range 170–300 °C for the reaction mixture of the composition, vol. %: CO 1, CO_2 20, H_2O 18, H_2 – balance. Contact time was varied from 1.2 to 0.06 s (3000–55 000 h^{-1}). Analysis of the initial gas mixtures and reaction products was carried out with the help of gas chromatograph "Tsvet" with a flame-ionisation detector equipped with a methanating unit. Selectivity of CO hydrogenation was characterized as a ratio of CO consumption rate to the rate of methane formation.

RESULTS AND DISCUSSION

Preliminary experiments showed that the catalysts based on nickel and cobalt exhibit high activity in hydrogenation reactions. Copper-containing catalysts were less active with respect to CO hydrogenation to form methane but they promoted the formation of CO in the inverse conversion of CO with water vapour. For further investigation, we chose Co and Ni based catalysts. The use of samples optimised in composition allowed us to obtain the required parameters: purification degree, selectivity and time of contact.

The results of tests of the most promising Ni and Co containing catalysts are shown in Figs. 1–4. The data shown in Fig. 1 indicate that both catalysts provide the necessary degree of

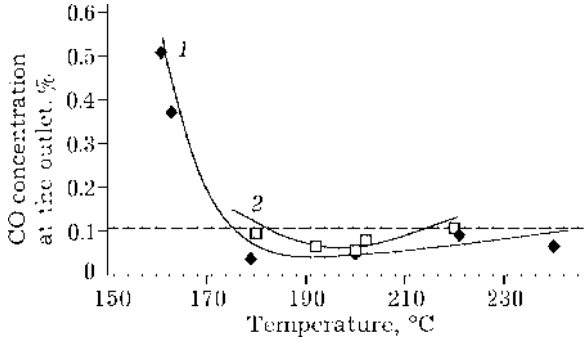

Fig. 1. Dependence of CO concentration in the reaction mixture at the outlet of the reactor of methanation on reaction temperature for contact time 0.2 s (17000 h^{-1}) for the catalysts containing nickel (*1*) and cobalt (*2*). Here and in Figs. 2–4: dashed line shows the maximal permissible CO content (1000 ppm).

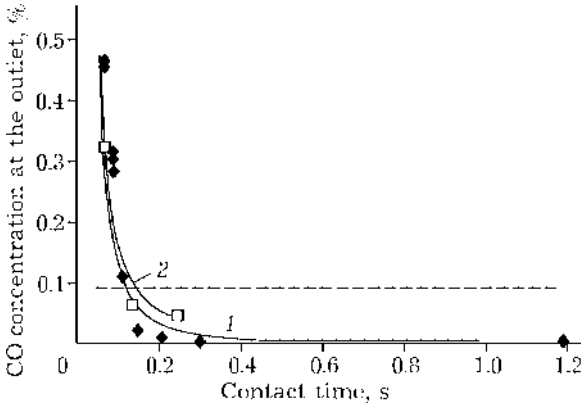

Fig. 2. Dependence of CO concentration at the outlet on contact time at 200 °C for the catalysts containing nickel (NM-1) (*1*) and cobalt (*2*).

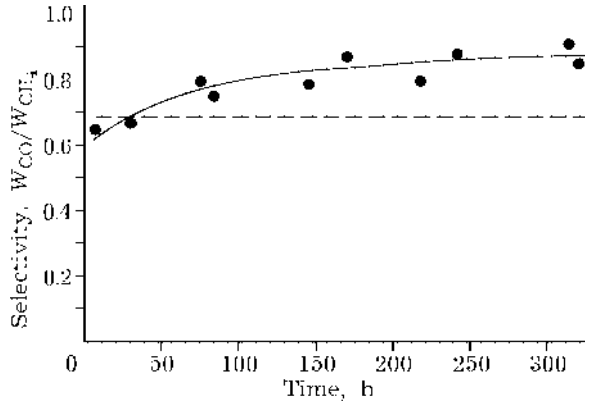

Fig. 4. Dependence of CO hydrogenation selectivity on performance time of the nickel-containing catalyst NM-1 at 200 °C and contact time 0.2 s (17 000 h^{-1}).

purification: within temperature ranges 180–240 and 180–210 °C, respectively, for Ni- and Co-containing catalysts the residual CO content is less than 1000 ppm. So, the required CO concentration at the outlet is achieved within rather broad temperature range, especially for the nickel-based catalyst. With both catalysts, in the temperature range for which the CO content at the outlet does not exceed 1000 ppm, methane formation from CO_2 accounts for not more than 40 %, that is, both catalysts possess high selectivity with respect to CO hydrogenation.

It follows from the dependencies shown in Fig. 2 that for contact time not more than 0.12 s (30 000 h^{-1}) the necessary purification degree is achieved in both cases. With a decrease in contact time, a sharp increase in CO concentration at the outlet occurs; the process selectivity decreases.

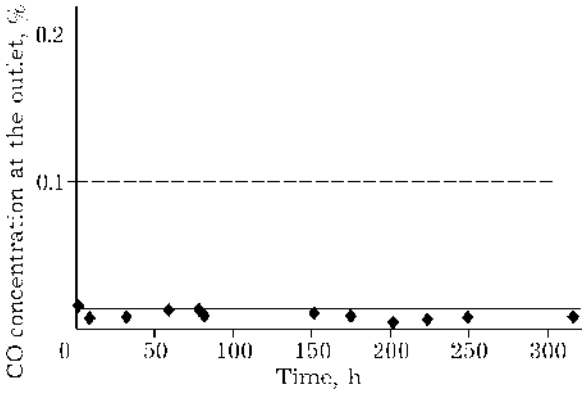

Fig. 3. Dependence of CO concentration at the outlet on performance time of the nickel-containing catalyst NM-1 at 200 °C and contact time 0.2 s (17 000 h^{-1}).

On the basis of the results obtained (see Figs. 1 and 2) it may be concluded that Ni-containing catalyst NM-1 possesses better catalytic properties with respect to preferable hydrogenation of CO in the presence of CO_2 in excess. So, detailed investigation of the effect of performance time on purification degree and selectivity of the process was carried out with the NM-1 catalyst. The duration of a continuous experiment was 14 days. The data shown in Fig. 3 demonstrate that CO content does not exceed 100 ppm during 320 h of performance of the Ni-containing catalyst; selectivity (Fig. 4) does not worsen and remains at the level above the required one.

CONCLUSIONS

It is shown that the use of Ni and Co based catalysts in methanation of CO in the presence of CO_2 in excess at a temperature within the range 180–240 °C and contact time 1.2–0.12 s (3000–30 000 h^{-1}) CO content at the outlet is essentially lower than the maximal required value (1000 ppm). With the nickel-containing catalyst NM-1, the achievable degree of purification is 100–30 ppm for contact time from 1.2 to 0.2 s. In this situation, methane formation as a result of hydrogenation accounts for less than 70 %.

So, the investigation demonstrated the promising character of fine purification of hydrogen fuel for FE from CO by means of preferential methanation of CO followed by oxidation. This process can be carried out with a nickel-containing catalyst NM-1.

Acknowledgement

The work was carried out within the ISTC (Project No. 2327).

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