Chemical Engineering Journal 134 (2007) 235–238

Chemical Engineering Journal

www.elsevier.com/locate/cej

Permeable composite material for compact apparatus for hydrogen-rich gases deep cleaning from CO

T.P. Minyukova [a,*,1], I.Sh. Itenberg [a,1], A.A. Khassin [a,1], A.G. Sipatrov [a,1], E.V. Dokuchits [a,1], V.Ya. Terent'ev [b,2], A.P. Khristolyubov [b,2], O.F. Brizitskii [b,2], T.M. Yurieva [a,1]

[a] *Boreskov Institute of Catalysis, 5, Pr. Lavrentieva, Novosibirsk 630090, Russia*

[b] *Russian Institute for Experimental Physics (VNIIEF), 37, Mira Ave., Sarov, 607190 Nizhegorodskoi obl., Russia*

Abstract

In order to provide a wide application of the proton exchange membrane fuel cell (PEMFC) technology, reduce cost and improve characteristics of PEMFC-based power plants, it is necessary to create a compact and economic apparatus for deep cleaning of converted fuel from carbon monoxide. The obstacle of preferential CO hydrogenation is the presence of about 20 vol.% of CO_2 and the same amount of H_2O along with 1 vol.% of CO. The compact apparatus for deep purification from CO can be only created basing on the highly active (providing 10–20 ppm CO in the outlet gas at GHSV above 6000 h^{-1}) and selective catalyst (at least 30% of CH_4 and higher hydrocarbons is to be formed by CO hydrogenation). In the present paper, we study the process of preferential CO hydrogenation over the nickel-chromium catalyst, which was found earlier to be efficient in the CO hydrogenation over fine catalyst fraction: outlet CO content below 20 ppm and the selectivity not less than 0.3 at GHSV above 6000 h^{-1}. We report on the effect of the catalyst grain size on the CO hydrogenation selectivity and consider the possibility of using permeable composite materials for weakening the intraparticle diffusion constrains and for efficient performing the reaction under the study close to the kinetic region.

Keywords: Hydrogen-rich gas purification; CO preferential hydrogenation; Permeable composite material; Ni-containing catalyst

1. Introduction

In order to provide a wide application of the proton exchange membrane fuel cell (PEMFC) technology, reduce cost and improve characteristics of PEMFC-based power plants, it is necessary to create a compact and economic apparatus for deep cleaning (to 20 ppm) of converted fuel gas from carbon monoxide.

WGSR and deep purification by preferential CO oxidation (PROX) or preferential CO hydrogenation follow the stage of hydrocarbon steam reforming in many existing technologies of hydrogen conditioning for fuel cells. Method of preferential CO hydrogenation for deep purification does not demand the air addition, eliminates the fuel gas dilution with nitrogen and provides more high-calorie hydrogen fuel that leads to the higher overall efficiency of electric power plant. Despite that, the process of preferential CO hydrogenation was not studied so extensively comparing to preferential oxidation. In some early works (see e.g. [1]), it was shown that the presence of CO in gas phase inhibits undesirable CO_2 hydrogenation over commercial Ni-containing catalysts, when concentration of CO in the gas feed is only above 200 ppm. Lower CO content does not suppress CO_2 conversion. Similar conclusions were made by Solymosi and Erdohelyi basing on the study of a wide series of supported metallic catalysts [2]. The authors of this paper concluded that CO can be efficiently hydrogenated down to residual CO content of 400–1000 ppm.

However, in last decade, several publications and patents have reported the possibility of selective CO hydrogenation down to 100 ppm and even less [3–7]. The hydrogenation is carrying out in one or two stages on the catalysts based on Ru, Rh, Pt, Fe. In these studies the necessary depth of purification is not reached and so a problem is solved by the subsequent selective oxidation. In Ref. [8] the required purity of 20 ppm is achieved on Ni/Al_2O_3 catalyst at GHSV 300 h^{-1}. A compact apparatus for hydrogen deep purification cannot be designed on the basis of such a low active catalyst. The most encouraging data on the preferential CO hydrogenation were recently published by Takenaka et al. [9], who showed that preferential CO hydrogenation to residual CO limit of 20 ppm can be selectively performed in the

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[*] Corresponding author. Tel.: +7 383 3309109; fax: +7 383 3308056.
E-mail addresses: min@catalysis.ru (T.P. Minyukova), trn@aven.visa44.vniief.ru (V.Ya. Terent'ev).

[1] Tel.: +7 383 3309109; fax: +7 383 3308056.

[2] Fax: +7 831 3040032.

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doi:10.1016/j.cej.2007.03.043

presence of CO_2 over Ni-containing catalysts in the wide range of temperatures (260–320 °C) at GSHV of 50,000 h^{-1}. Over Ru-containing catalysts even better performance was achieved. These data are manifold higher, than any other published in literature and evidence in possibility to purify $H_2 + CO_2$ mixtures from CO. It is, however, worthy to note that the authors of Ref. [9] studied the catalytic reaction over fine catalyst grain fraction, which is very important for the process selectivity, as we will show below.

In the present paper, we study the process of preferential CO hydrogenation over the nickel-chromium catalyst NM-1, which was found earlier [10] to be efficient in the CO hydrogenation over fine catalyst fraction (in kinetic region): outlet CO content below 20 ppm and the selectivity not less than 0.3 at GHSV above 6000 h^{-1}. We report on the effect of the catalyst grain size on the CO hydrogenation selectivity and consider the possibility of using permeable composite materials for weakening the intraparticle diffusion constrains and for efficient performing the reaction under the study close to the kinetic region.

CO hydrogenation occurs by the reaction (1) forming methane (and some amounts of higher hydrocarbons) and is complicated by reactions (2) and (3):

$$CO + 3H_2 = CH_4 + H_2O, \quad \Delta H_r^\circ = -49\,\text{kcal/mol CO} \tag{1}$$

$$CO_2 + 4H_2 = CH_4 + 2H_2O, \quad \Delta H_r^\circ = -39\,\text{kcal/mol}\,CO_2 \tag{2}$$

$$CO_2 + H_2 = CO + H_2O, \quad \Delta H_r^\circ = 10\,\text{kcal/mol} \tag{3}$$

The following criteria were adopted for estimation of the effectiveness of the catalysts for selective CO hydrogenation for the compact apparatus of hydrogen-rich gas conditioning for fuel cells:

(1) *depth of purification*: CO outlet gas content not higher than 20 ppm;
(2) *selectivity* 0.3; i.e. not more than 70% of methane may be formed from CO_2;
(3) *activity*: GHSV not less than 6000 h^{-1}.

Reactions (1) and (2) are strongly exothermal, so maintaining the isothermal regime in the catalyst's bed may also play important role in the selectivity of target reaction.

2. Experimental

The catalysts were obtained by the thermal decomposition of nickel-chromium hydroxycarbonate with pyroaurite structure. The atomic ratio of Ni:Cr was selected as 7:3. Before catalytic tests the catalysts were activated in hydrogen at 300 °C. The catalytic tests were carried out in the unit with flow reactor at 0.1 MPa at 180–230 °C, GHSV 6000–30,000 h^{-1}. Gas flow composition was analysed by the GC Crystall-2000 equipped with the activated carbon packed column and a thermal-conductivity detector using helium as a carrier gas. The threshold of sensitivity by CO was 10 ppm. Inlet gas composition was $CO:CO_2:H_2O:H_2 = 1:21:18:60$.

Two main parameters monitored were: the residual CO partial pressure and the CO hydrogenation preference (or CO hydrogenation selectivity, as it is often referred in literature). The selectivity was considered as the ratio of CO conversion rate to that of hydrocarbons formation.

3. Results

In our previous study [10] the series of nickel- and cobalt-containing catalysts with different composition, thermal treatment and activation parameters have been prepared and tested in preferential CO hydrogenation. Nickel-chromium containing catalysts NM-1 occurred to be the most promising one. The detailed study of CO hydrogenation over fine grain fraction of this catalyst has shown that in the kinetic region, when diffusion constrains are mild, NM-1 catalyst provides CO hydrogenation down to 10–20 ppm of residual CO with selectivity about 0.7 in a rather wide temperature and GHSV ranges (190–210 °C and 2000–17,000 h^{-1}). Fig. 1 shows the impact GHSV to the residual CO concentration at 200 °C for 0.25–0.5 mm granules of NM-1 catalyst. However, the preference of the hydrogenation sharply decreases, when the reaction is performed over larger grains of catalyst, i.e. 2–3 mm granules or 5 mm × 5 mm pellets. The effect of the catalyst grain size on the process selectivity is shown in Fig. 2 for the reaction temperature of 200 °C and GHSV of 9000 h^{-1}. The rate of CO_2

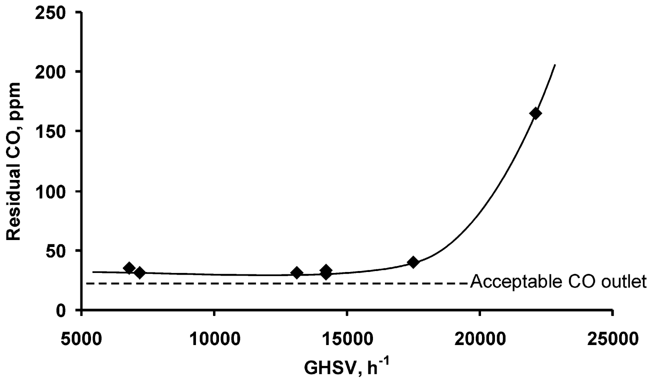

Fig. 1. Impact of gas flow rate to the residual CO concentration at 200 °C, NM-1 catalyst, 0.25–0.5 mm grain size.

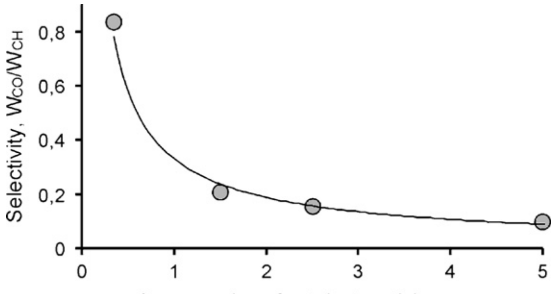

Fig. 2. Impact of the average Ni-Cr catalyst grain size to the CO hydrogenation selectivity at 200 °C, GHVS = 6000 h^{-1}.

hydrogenation increases manifold at increasing catalyst grain size. Such a noticeable fall of selectivity could be a result of the CO depletion in the catalyst grain bulk due to intraparticle diffusion constrains. As it is mentioned above, CO is well known to be inhibitor of hydrogenation reactions due to its strong adsorption over active metal surface [1,2]. Depletion of CO in the catalyst grain bulk leads to decrease in nickel surface coverage with CO and increases the rate of CO_2 hydrogenation. Therefore, to achieve high selectivity of the process, one should perform the reaction close to kinetic region, i.e. over the fine catalyst grain fraction.

Obviously, the fine grains of the catalyst cannot be used in a traditional fixed bed reactor due to high pressure drop and probable inhomogeneity of the catalyst bed. The problem of the trade between reasonable catalyst bed permeability and high catalytic performance could be solved by using the permeable composite materials, which were recently proposed for Fischer-Tropsch synthesis [11–13]. These materials have reasonable permeability of 100–200 mDarcy, high mechanical strength of 70 MPa at the PCM base and high thermal conductivity of above 4 W m^{-1} K^{-1}. At that the catalyst grain size within the composite is less that 0.2 mm, providing occurrence of the catalytic CO hydrogenation close to the kinetic region, while uniform distribution of pores within the composite ensures the absence of zones of gas stagnation. Such composites can be prepared from the powders of catalytic active component (nickel-chromium catalyst in our study), reinforcing and heat-conductive metal (electrolytic copper of dendrite morphology), and porophore component. PCM may be prepared in the form of the plates or hollow cylinder. In the latter case the gas flow is radially directed. The details on the PCM preparation, physical properties and its catalytic performance in Fischer-Tropsch synthesis are reported in the above quoted articles [11–13]. It is noteworthy, that a similar approach to performing exothermic heterogeneous reactions by using the monolithic catalysts with high thermal conductivity is developed in Ref. [14,15].

Fig. 3 shows the appearance of PCM-NM-1 of 18 mm in diameter in the form of a hollow cylinder. This PCM-NM-1 was tested in CO preferential hydrogenation. The impact of the reaction temperature to the residual CO content and the CO hydrogenation selectivity at GHSV 12,000 h^{-1} is shown in Fig. 4. One can see that PCM-NM-1 has high selectivity at below 220 °C, while the residual CO content is below 10 ppm at 200 °C and higher. The similar dependencies on GHSV at constant temperature of 200 °C are presented in Fig. 5. PCM-NM-1 provides 10–30 ppm residual CO and very high selectivity—above 0.6 in the GHSV range of 5000–17,000 h^{-1}.

Thus, permeable composite material based on NM-1 catalyst (PCM-NM-1) can be efficiently used for preferential CO hydrogenation in a wide range of GHSV and temperature. It is noteworthy, that the above estimated GHSV range is wider than that reported for the nickel-containing catalyst in Ref. [8]. Also, it is important to mention, that another (e.g. more active) catalyst can be used as an active component of PCM, showing even higher performance in the preferential CO hydrogenation.

The stability of the catalyst is of the high importance. Fig. 6 shows the performance of the PCM-NM-1 catalyst during three

Fig. 3. Hollow cylinder of permeable composite material based on the NM-1 catalyst.

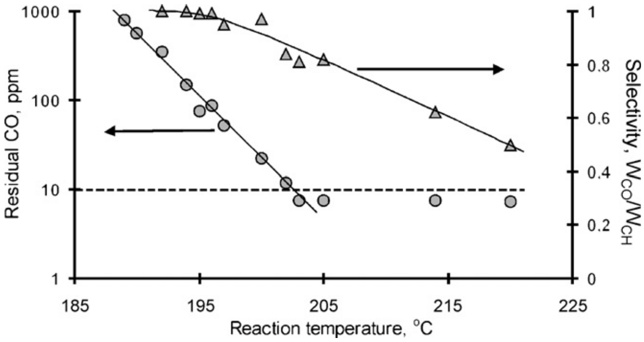

Fig. 4. Effect of the reaction temperature on the residual CO concentration and selectivity (W_{CO}/W_{CH}) at 12,000 h^{-1}. Eighteen millimetre hollow cylinder PCM based on nickel-chromium catalyst (PCM-NM-1). Inlet gas composition, $CO:CO_2:H_2:H_2O = 1:21:60:18$.

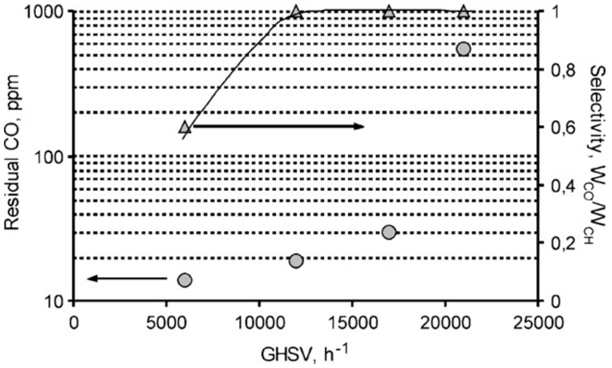

Fig. 5. Effect of the gas flow rate on the residual CO concentration and selectivity (W_{CO}/W_{CH}) at 200 °C. Eighteen millimetre hollow cylinder PCM based on nickel-chromium catalyst (PCM-NM-1). Inlet gas composition, $CO:CO_2:H_2:H_2O = 1:21:60:18$.

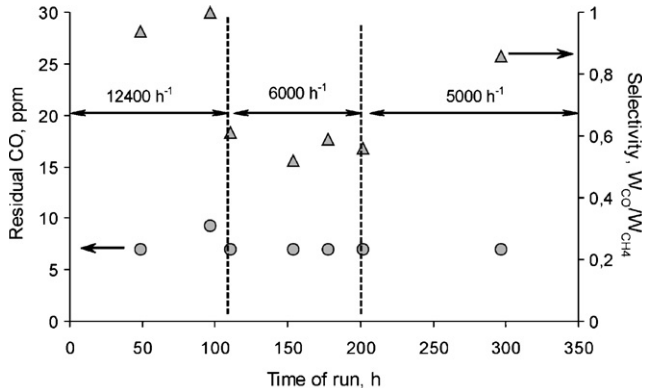

Fig. 6. Dependence of residual CO concentration (●) and selectivity (W_{CO}/W_{CH}) (▲) on the time of run for permeable composite material (PCM-NM-1). Inlet fuel gas composition, $CO:CO_2:H_2:H_2O = 1:21:60:18$. Reaction temperature is 200 °C. Gas flow rates: 0–48 h GHSV = 12,400 h^{-1}; 49–124 h GHSV = 6000 h^{-1}; 125–297 h GHSV = 5000 h^{-1}.

runs, which were performed with the breaks for 2 months between run 1 and run 2 and 7 months between run 2 and run 3. Run 1 was 48 h long and was performed at GHSV = 12,400 h^{-1}; run 2 was performed during 76 h at GHSV = 6000 h^{-1}; run 3 was 173 h long at GHSV = 5000 h^{-1}. The reactor temperature was maintained at 200 °C, inlet gas composition was $CO:CO_2:H_2O:H_2 = 1:21:18:60$. We observed no tendency to deterioration of both: the depth of purification and preference of CO hydrogenation. After experiment we observed no mechanical changes of the catalyst. Thus, we can expect steady work of the developed material and reproducibility of its properties after stops and restarts.

4. Conclusions

The permeable composite material (PCM) based on nickel-chromium catalyst provides the fine fuel gas purification by CO preferential hydrogenation down to residual CO concentration of 10–30 ppm and below in the wide range of GHSV from 6000 to 17,000 h^{-1} and ensures the selectivity above 0.5. We expect that the catalysts for compact apparatus for gas conditioning can be created on the basis of PCM using nickel-containing catalysts. Even higher performance in the preferential CO hydrogenation might be achieved if using another (e.g. more active) hydrogenation catalyst for producing permeable composite material.

Acknowledgement

This research is financed by the ISTC Project # 2327.

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