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Y.Y. Nurmakonov¹, A.J. McCue², J.A. Anderson², S.S. Itkulova¹, S.K. Kussanova¹¹D.V. Sokolsky Institute of Fuel, Catalysis and Electrochemistry, 142, Kunaev str., Almaty, 050010, Republic of Kazakhstan;²Surface Chemistry and Catalysis Group, Materials and Chemical Engineering, School of Engineering, University of Aberdeen, AB24 3UE, Scotland, United KingdomMETHANE REFORMING BY CO₂ OR CO₂-H₂O
OVER Co-CONTAINING SUPPORTED CATALYSTS

Abstract: Co-containing catalysts promoted by noble metal and supported on alumina modified with rare earth metal have been studied in dry and combined dry-steam reforming of methane. The effect of the amounts of additive – noble and rare earth metals on the catalyst performance in both dry and combined reforming of methane have been assessed. With this aim, the activity and stability of supported cobalt catalysts Co/ γ -Al₂O₃ modified with various amounts of M and R additives have been investigated under atmospheric pressure, GHSV= 1000hr⁻¹, varying the process temperature within 300-800°C. It has been shown that modified catalysts exhibit a high stable activity for the production of syngas with a variety of H₂/CO ratios depending on a type of process and its conditions.

Keywords: methane dry reforming, combined dry-steam reforming, Co-containing catalyst, syngas.

Introduction

The considerable use of fossil fuels dictates the development of alternative technologies based on non crude oil feedstock with minimum environmental impact. Syngas (a mixture of hydrogen and carbon monoxide) seems to be an important step of manufacturing chemicals, as well as liquid fuels *via* Fischer-Tropsch (FT) synthesis [1]. Methane, mostly, is a main raw material and its price and availability affect the economics of syngas production [2]. Therefore, methane containing feedstock as natural gas, biogas etc. is becoming a critical carbon-based energy source. Methane is a major constituent of natural gas, making up to 98% of the gas depending on its source, also it is a main component of biogas and processes based on them will become more vital in the near future [3]. The most common processes to convert methane into syngas are steam reforming (1), partial oxidation (2), and dry reforming (3) [4, 5]:



Among these processes, dry reforming is more attractive because it produces syngas with the H₂/CO ratio close to unity which suitable for oxo-synthesis, and FT synthesis [6, 7]. From environmental point of view, methane and carbon dioxide are two main greenhouse gases their involving to process contributes to carbon footprint reduction.

The dry reforming of methane is typically followed by reverse water-gas shift reaction (4), and it appears to be the most important because of its dependence on the product hydrogen [8]:



Due to the DRM works in presence of high concentrations of carbon-containing compounds which lead to deactivation of the catalyst as carbon deposition, originating from methane decomposition (5) and the Boudouard's reaction (6) [9]:





The coke deposition problem can be overcome either by developing catalysts that minimize coke formation, by adding steam or oxygen and working at low temperatures; the reaction (5) is thermodynamically limited under these conditions [10].

Research on the catalyst development for the dry reforming of methane deals with the exploration of catalysts, which are highly effective and stable to carbon deposition, sintering and forming of inactive chemical species. DRM was first studied by Fischer and Tropsch on Ni- and Co-based catalysts [11], afterwards a large number of catalysts have been tested and it has been demonstrated that all members of group VIII metals with the exception of osmium, perform activity towards this reaction, among these metals Rh and Ru have superior activity and stability, as respects, high cost of these catalysts, noble metals on the whole, prevents their industrial application [12, 13].

Numerous studies of supported cobalt catalysts have been published for developing high active and stable catalyst, factors as the preparation technique, the addition of promoter, the choice of support were investigated to improve efficiency.

Supported cobalt catalysts have good stability against temperature changes. Also the mechanism of carbon deposition on Co is probably different from that on Ni [12]. Co-based catalysts are potential alternative catalysts.

In the present study, the effect of various amounts of noble metal – M and R – rare earth metal on Co-based catalyst was investigated.

Experimental

The polymetallic Co-containing catalysts were prepared by impregnating alumina with a solution containing metal salts followed by thermal treatment. The total content of Co+M metals was 5 wt.%. The amount of noble metal – M is indicated as a percentage by mass based on metal content (Co+M). The mass ratio of Co: M varied from 95:5 to 9:1. The amount of rare earth metal (R) was 2 and 5 wt.%.

The physico-chemical properties of the catalysts were studied using TPR and nitrogen adsorption/desorption isotherms.

TPR profiles of the samples were recorded with ThermoScientific TPDRO 1100 equipped with a TCD detector. The TPR profiles were obtained by exposing the samples to 5% H₂ in N₂ at a flow rate of 20 ml/min while the temperature was increased from ambient to 800°C at 5°C/min.

The processes were carried out in a laboratory flow quartz reactor with programmed heating and a controlled feeding velocity, operated at atmospheric pressure, the volume of catalyst was 6 mL. The temperature was varied from 300 to 800°C; the ratio of CH₄/CO₂ was 1, and the gas hourly space velocity (GHSV) was 1000 h⁻¹. Steam was added in amount 20% (vol.) in combined dry-steam reforming of methane (or biforming of methane). Duration of the catalyst test was 8-100 hours.

The initial and final reaction products were analyzed by on-line GC. The liquid products were collected in a special cooling trap and analyzed after the process.

The conversion degrees of methane (X_{CH_4} , %) and carbon dioxide (X_{CO_2} , %), calculated according to formulas 1 and 2, were used to determine and compare the catalysts activity.

$$X_{\text{CH}_4} = ([\text{CH}_4]_{\text{in}} - [\text{CH}_4]_{\text{fin}}) * 100\% / [\text{CH}_4]_{\text{in}} \quad (\text{formula 1})$$

$$X_{\text{CO}_2} = ([\text{CO}_2]_{\text{in}} - [\text{CO}_2]_{\text{fin}}) * 100\% / [\text{CO}_2]_{\text{in}} \quad (\text{formula 2})$$

Where $[\text{CH}_4]$ and $[\text{CO}_2]$ are the concentrations of CH₄ and CO₂ respectively, and the subscripts *in* and *fin* refer to initial feed and final products, respectively.

The conversion of water was not calculated because of the complexity resulting from differentiating between unreacted water and water formed due to the secondary reactions.

Results

1. Catalyst test

To identify the effect of additives on Co alumina supported catalyst, the monometallic 4%Co/Al₂O₃ was investigated in methane dry reforming. The effect of the temperature on the dry reforming of methane over 4%Co/Al₂O₃ is shown in Figure 1. The catalyst does not exhibit a high activity in the process at

temperature lower than 800°C. The conversion of methane and carbon dioxide grows from 5.8 to 13.0% while temperature increases from 400 to 750°C (Figure 1).

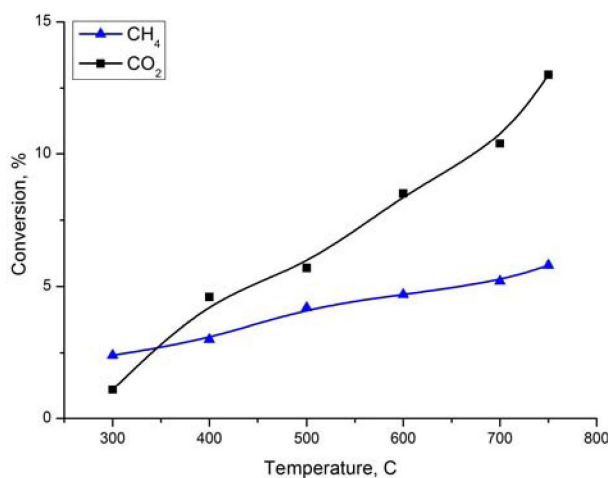


Figure 1 – Effect of the temperature on dry reforming of methane over the 4%Co/Al₂O₃ catalyst

The monometallic 4%Co/Al₂O₃ catalyst is not active in combined dry-steam reforming of methane. Methane conversion is not high at 5%. The possible reason of that is formation of inactive Co hydroxides observed by TEM [15].

To modify Co-containing catalysts the additives of noble metal and rare earth metal were introduced to the catalyst composition. Compared to the monometallic catalyst modified catalysts showed significant activity in the dry reforming of methane. It can be observed (Figure 2a) that all modified catalysts exhibited a methane conversion of above 93.3%. The superior activity among them 5%Co-M (9:1)/Al₂O₃-5%R and 5%Co-M(95:5)/Al₂O₃-5%R catalysts have shown in conversion of CH₄-CO₂.

In Figure 2b, it is shown that complete conversion of carbon dioxide was observed over all the catalysts in the dry reforming of methane. It should be noted, CO₂ conversion is higher compared to methane conversion. The syngas with a ratio H₂/CO close to unity is a main feature over all the tested polymetallic catalysts.

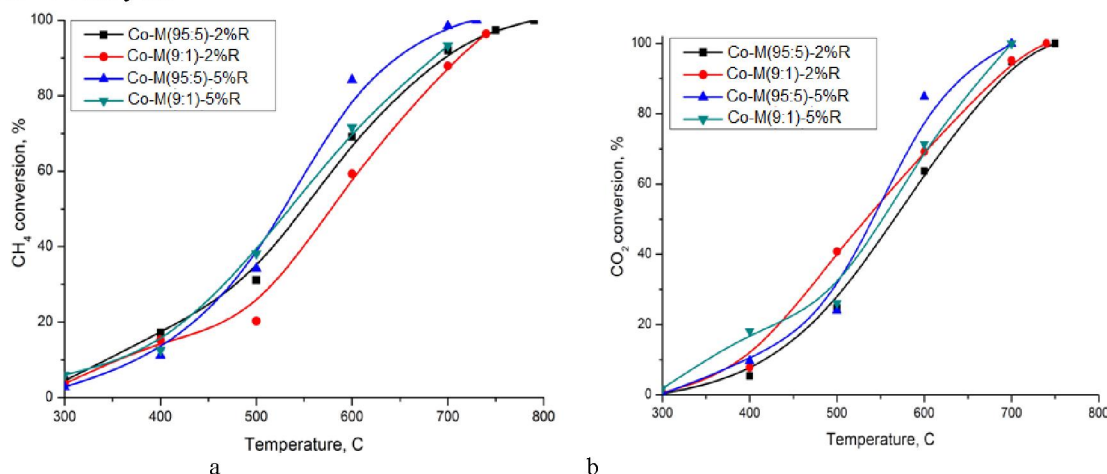


Figure 2 – Effect of the temperature on the degree of conversion of methane (a) and carbon dioxide (b) in the dry reforming

The same effect of the temperature on combined dry-steam reforming was observed over the catalysts (Figure 3). Comparison of the dry reforming and bireforming of methane over the catalysts demonstrates that complete methane conversion is achieved at lower temperature in bireforming. For instance, the complete conversion of both CH₄ and CO₂ over the Co-M(95:5)-2%R/Al₂O₃ in the dry reforming of methane was achieved at 790°C while in the bireforming the complete conversion was lower

by 90°C. Also, this pattern can be seen on the Co-M/Al₂O₃-R catalysts with a higher content of rare earth metal – 5% and ratio of Co-M varied within 90-95:5-10, where difference between temperatures of complete methane conversion in DRM and bi reforming is 20°C. Syngas enriched in hydrogen formed during bireforming of methane, and the ratio of H₂/CO reached a value is 2.1. Syngas with such a ratio is suitable for FT synthesis.

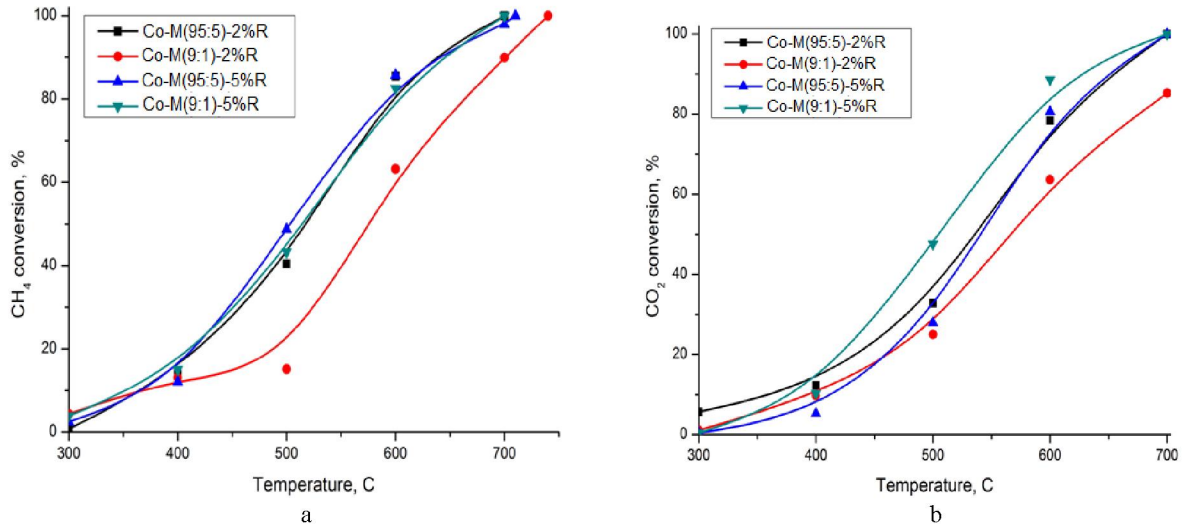


Figure 3 – Effect of temperature on the degree of conversion of methane (a) and carbon dioxide (b) in the combined dry-steam reforming of methane

To determine the stability, the catalysts with varied amount of noble metals: 5%Co-M(95:5)-5%R and 5%Co-M(9:1)-5%R catalysts have been taken. The results of the long-term study of the catalysts in both DRM and bireforming are presented for the catalyst with higher and lower content of noble metal in Figures 4 and 5 respectively. Temperature was increased from 300 to 700°C for the first 8 hours and then was held constant (700°C for more than 70 hours).

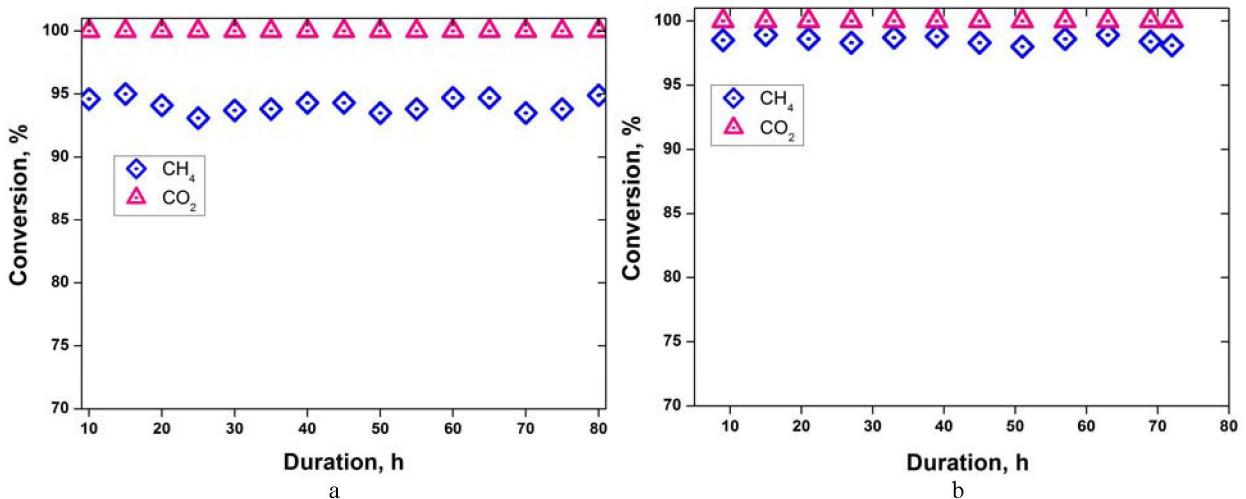


Figure 4 – Dependence of methane and carbon dioxide conversion on the time on stream in (a) DRM and (b) bireforming over the 5%Co-M(9:1)/Al₂O₃-5%R catalyst at CH₄/CO₂=1, GHSV=1000h⁻¹, t=700°C

During the test the catalysts retained its activity and produced syngas with the same selectivity. The average CH₄ conversion was higher in the bireforming than in the DRM over both the catalysts.

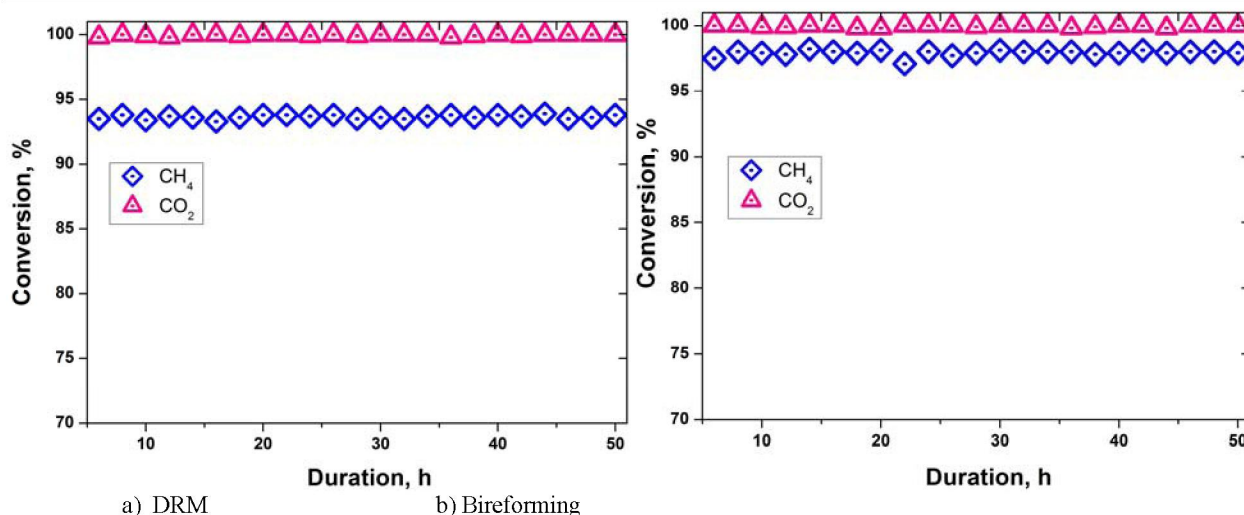


Figure 5 – Dependence of methane and carbon dioxide conversion on time on stream in the DRM and bireforming over the 5%Co-M(95:5)/Al₂O₃-5%R catalyst at CH₄/CO₂=1, GHSV=1000hr⁻¹, t=700°C

2. Catalyst characterization

Both additives – M and R has an effect on Co reproducibility.

The TPR profiles of the catalysts are shown in Figure 6. The area under the TPR curve is directly proportional to the amount of hydrogen consumed. According to the literature, the reduction of pure Co₃O₄ takes place as a two-step reduction process *via* Co₃O₄→CoO→Co⁰ [14]. The peak observed at 276-400°C for 4.5%Co/Al₂O₃ catalyst was attributed to the reduction of Co₃O₄→CoO/Co⁰ and the peak seen at 400-750°C was attributed to the reduction of CoO→Co⁰ or Co₃+ and CoO-Al₂O₃ to Co⁰.

Bimetallic samples exhibited a complex reduction profile. The addition of noble metal – M has a significant effect on the reducibility of cobalt supported alumina catalyst. The temperature of Co oxides reduction is shifted to lower values. This shift is increased with increasing amount of M. Two main reductive peaks were observed at 223, 344°C for 5%Co-M(9:1)/Al₂O₃ and 233, 362°C for the catalyst with less amount of M – 5%Co-M(95:5)/Al₂O₃.

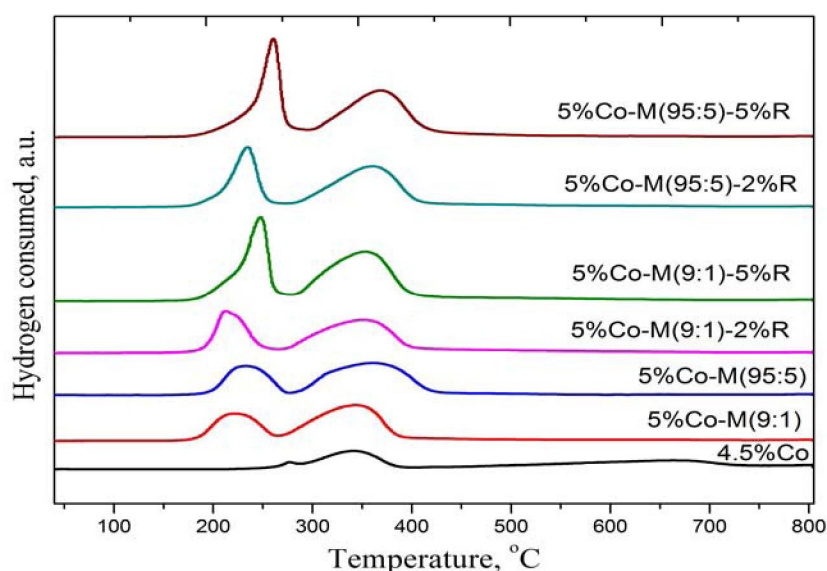


Figure 6 – H₂-TPR profiles of the catalysts

Introduction of rare earth metal to the Co-M/Al₂O₃ catalyst is accompanied with substantial increase in the hydrogen consumption.

Discussion

Temperature plays the most important role for CH₄ reforming, because of its endothermic characteristics. In both DRM and bireforming increasing temperature substantially enhances CH₄ conversion. Comparison of DRM and bireforming of methane over the studied catalysts shows that bireforming (combined dry-steam reforming) of methane is more effective process from the point of view of lower temperature of complete methane conversion. In the combined reforming higher CH₄ conversion can be achieved at the same temperatures that in accordance with our earlier work [16]. It should be noted that this is characteristic for the certain catalysts. Monometallic Co-containing catalyst is not active in combined reforming of methane.

The additional advantage of bireforming process is controlling a ratio of H₂/CO, which is a critical one for further syngas application.

Also, the positive effect of steam is in removal of surface carbon.

TPR data prove the promotion effect of noble metal on Co reproducibility. The temperatures of Co oxides reduction are significantly shifted to the lower values. That can be explained by formation of new type of active bimetallic Co-M particles.

The introduction of rare earth metal assists to the strengthening reduction of the Co-particles. That can be a reason of higher activity and stability of the studied catalysts in DRM and combined reforming in comparison with the monometallic catalysts.

Conclusions

The studied catalysts perform a high stable activity in both the processes – dry and combined dry-steam reforming of methane.

The addition of noble metal allowed increasing the activity and stability of Co/Al₂O₃ catalyst.

The role of the rare earth metal is in stabilizing the high dispersed and reduced state of Co over the alumina.

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СО-ҚҰРАМДЫ ҚОНДЫРЫЛҒАН КАТАЛИЗАТОРЛАРДА СО₂ НЕМЕСЕ СО₂-Н₂O КӨМЕГІМЕН МЕТАННЫҢ КОНВЕРСИЯСЫ

Аннотация. Бұл жұмыста алюминий оксидіне қондырылған сирек және асыл металдардың қоспала-рымен промотирленген Со-құрамды катализаторлардың активтілігі метанның көмірқышқылды және булы көмірқышқылды риформинг процесінде зерттелді. Көлемдік жылдамдығы – 1000 сағ⁻¹, температура ауытқуы 300-800°C шамасында және атмосфералық қысымда өткізілген метанның сусыз және біріктірілген риформинг процестерінде Со-құрамды катализатордың қасиетіне асыл металл мен сирек элемент қоспасы мөлшерінің әсері анықталды. Зерттелінген катализаторлар Н₂/СО қатынасы процестің түріне және ағу жағдайына тәуелді болатын синтез-газ өндірісінде жоғары тұрақты белсенділікті көрсететіндігі байқалды.

Түйін сөздер: метанның сусыз риформингі, біріктірілген көмірқышқылды риформинг, Со-құрамды катализатор, синтез-газ.

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КОНВЕРСИЯ МЕТАНА ДИОКСИДОМ УГЛЕРОДА ИЛИ СО₂-Н₂O НА СО-СОДЕРЖАЩИХ НАНЕСЕННЫХ КАТАЛИЗАТОРАХ

Аннотация. В данной работе изучена активность Со-содержащих катализаторов, нанесенных на оксид алюминия, промотированных добавками благородного и редкоземельного металлов, в процессах углекислотного и пароуг-лекислотного риформинга метана. Определено влияние количества добавок – благородного металла и редкоземельного элемента на поведение Со-содержащего катализатора в процессах сухого и комбинированного (СО₂-Н₂O) риформинга метана, проводившихся при атмосферном давлении, объемной скорости – 1000 ч⁻¹ и варьировании температуры в пределах 300-800°C. Обнаружено, что изученные катализаторы проявляют высокую стабильную активность в производстве синтез-газа, соотношение Н₂/СО, в котором зависит от вида процесса и условий его протекания.

Ключевые слова: сухой риформинг метана, комбинированный паро-углекислотный риформинг, Со-содержащий катализатор, синтез-газ.

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