WATER-GAS SHIFT REACTION OVER THE POLYMETALIC Fe-CONTAINING SUPPORTED CATALYSTS

Abstract. The water-gas shift reaction over the polymetallic iron-containing catalysts modified by additives of the transition metals and supported on alumina was studied in the work. The effects of process temperature and nature of additives (Co or Cu) on behavior of the iron-containing catalysts in the process of interaction between water and carbon monoxide were investigated. It was observed that the synthesized iron-based catalysts modified by additives of copper/cobalt and transition metal of the 8th group of elements as the third component and supported on alumina perform the high activity and selectivity on hydrogen formation in the water-gas shift reaction. The optimum conditions for producing hydrogen by the water shift reaction over the synthesized catalysts are determined.

Keywords: Water-Gas Shift Reaction, Fe-containing Supported Catalyst, Hydrogen, Carbon Oxides.

1. INTRODUCTION

The water-gas shift reaction (WGSR) discovered by Italian scientist Felice Fontana as early as 1780 [1] became well-known in the 1912 due to process of ammonia synthesis [2,3]. At present time, WGSR is widely used for hydrogen production from fossil and renewable carbonaceous raw materials – biomass. Hydrogen is used to enrich gas mixtures, production of ammonia, and also in oil refining and petrochemistry, and more recently in fuel cells [1, 4-5]. Hydrogen is considered as one of the most attractive types of future clean fuels, because it can be effectively stored and transported. Only water is formed as a side product when hydrogen is burned [6]. Water-gas shift reaction as well as the steam reforming of methane/other hydrocarbons is the most industrially developed method for hydrogen production. Overall reaction of water-gas shift is described by the following equation (1):

\[ \text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \quad \Delta H^{\circ}_{298} = -41.09 \text{ KJ/mol} \] (1)

The same amount of carbon dioxide is formed in water-gas shift reaction and hydrocarbon fuel combustion; however carbon dioxide produced can be captured and then can be either stored or utilized. This fact permits to classify this reaction as a process with zero CO₂ emission [7].

WGSR reaction (Eq.1) runs with the release of heat and without changing the volume, therefore an increase in temperature will help to reduce the degree of CO conversion. There is no possibility to shift the reaction equilibrium to the right due to the pressure change. Nevertheless, growing the total pressure leads to an increase in the rate of reaching the equilibrium state. An increase in H₂O/CO ratio enhances carbon monoxide conversion, however for reasons of cost reduction, a large excess of steam should be avoided. As for the iron-based catalysts, the minimum excess of steam is needed to prevent excessive catalyst reduction, which leads to methanation [8,9], for the copper catalysts this fact is not critical.

With taking into account the opposite effect of temperature on both the reaction completeness and rate, the various types of catalysts operating at different temperature ranges are used. They are divided on the high temperature (HT) and low temperature (LT) catalysts [10]. Traditionally, the iron-chromium and copper-zinc catalysts were used for facilitation of reaction in high and low temperature regions.
respectively [1]. The typical composition of high temperature catalysts operating in temperature region within 310–450°C: 74.2% Fe₂O₃, 10% Cr₂O₃, 0.2% MgO and balance of variable composition. It is supposed that the active phase is the magnetite (Fe₃O₄) is formed during partial reduction of the initial catalyst, while Cr₂O₃ improves the catalyst stability and prevents sintering the iron oxide. By using the high temperature catalysts it is possible to achieve residual concentration of CO in amount of 3%, which corresponds to the equilibrium concentration at 450°C [3,11]. Because of risk of leakage of toxic Cr(VI), the chromium-free catalysts should be developed. Aluminum was considered as an alternative, because it is textural promoter. Introduction of Al³⁺ ions into iron oxide is easily feasible because they have similar ionic radii: 0.675Å and 0.690Å for Al³⁺ and Fe²⁺ respectively [12].

Low temperature process (LTS – Low Temperature Shift) is carried out in temperature range of 200-250°C. Because of water condensation negatively effects on catalyst activity, a lower limit of process temperature is determined by condensation temperature of water under specific pressure. The typical catalysts for LTS have the following composition: 32-33% CuO, 34-53% ZnO, 15-33% Al₂O₃ [2]. The active centers in these catalysts are crystallites of CuO, while ZnO provides the structural stability and Al₂O₃, mainly inactive, provides dispersion of an active phase and prevents shrinking of catalyst granules [1]. Using the low temperature catalysts allows reaching the residual concentration of CO is 0.1% [8]. Another advantage of low temperature water gas shift catalysts is their low activity toward the side reactions. That has importance under elevated pressures [13,14]. Disadvantages of the low temperature catalysts are their susceptibility to poisoning by sulfurous compounds, halogens, and unsaturated hydrocarbons, pyrophoricity, low thermal stability, and complexity of their activation [15,16].

Despite of industrial development of WGS process, search for more active and efficient catalysts and optimal process parameters is still ongoing. In recent years, the technologies of catalysts preparation have been significantly improved. The catalysts are modified in order to provide the reaction in the middle range of temperatures and to achieve both high conversions of CO and selectivity [1,17]. As a rule, the middle temperature catalysts are the low temperature catalysts modified usually by iron oxide. They operate at higher temperatures – 275-350°C [18]. The catalysts supported on alumina contain sulfides of cobalt and copper or cobalt and nickel as the active ingredients. The feature of the catalysts is their sulfur resistant [19-20].

In addition to these types of catalysts, the acid gas shift catalysts and catalysts containing noble metals are developed [9]. The latter mainly include gold or platinum and are used in fuel cells.

In general, there is significant progress in the water-gas shift reaction including approaches to the methods of preparation and characterization, doping, improvement and evaluation of catalysts, in particular the nanocatalysts [1,6]. The data concerning WGS studies permanently published demonstrate a significant variety of the novel catalysts compositions and continuous interest in this field [7].

This work deals with testing the novel chromium-free, polymetallic alumina supported catalysts based on iron as main component of high temperature catalysts and modified by additives of cobalt or copper as the main components of low temperature catalysts and a noble metal – M₁ as a promoter. The catalysts were tested in the water-gas shift reaction under atmospheric pressure and varying temperature, gas hourly space velocity (GHSV), and steam to CO ratio (H₂/CO).

2. EXPERIMENTAL

The WGS process – water-gas shift reaction was carrying out in a quartz flow reactor with fixed bed catalyst under atmospheric pressure. Volume of catalyst was 6 ml. Water was supplied with well-controlled rate using the syringe pump “Perfusor FM BRAUN” plugged to an unit via connecting tube equipped by heating system aimed for evaporating water. Steam was mixed with carbon monoxide (99.9% vol. purity) and argon (99.9% vol. purity) used as balance-gas (10 vol %) incoming from cylinders. Gas velocities (carbon monoxide and argon) were regulated and controlled by means gas the mass-flow rate regulators (F201CV, series EL-FLOW). Gas hourly space velocity (GHSV) of inlet mixture of carbon monoxide and steam was varied within a range of 500-1500 h⁻¹. Steam to carbon monoxide ratio – H₂O/CO was varied from 1.0 to 1.6. Temperature was varied in the range of 200-400°C. Duration of catalysts testing was 8-20 hours.

Composition of inlet and outlet gas streams was determined by gas chromatograph Chromatec Crystal 5000.1 equipped with two TCD and with two packed columns, NaX 60/80 and Haysep R 80/100, to detect CO, H₂, CO₂, CH₄, C₂-C₆ hydrocarbons.
The catalysts with the following composition were prepared: 10%Fe-Cu(1:1)-0.25%Mₓ/AlₓOᵧ and 10%Fe-Co(1:1)-0.25%Mₓ/AlₓOᵧ (wt. %), where Mₓ – metal of the Group VIII. The catalysts were prepared by the impregnation method.

Conversion of CO (X(CO), %) was calculated by formula given below:

\[ X(CO) = \frac{V_{in}^{CO} - V_{out}^{CO}}{V_{in}^{CO}} \times 100\% \]

where \( V_{in}^{CO} \) – mole fraction of CO in inlet stream, \( V_{out}^{CO} \) – mole fraction of CO in outlet stream.

Conversion of water was not calculated.

Yields of reaction products: hydrogen, carbon dioxide and methane, \( Y_{H₂}, Y_{CO₂} \) and \( Y_{CH₄} \) respectively) expressed as its amount (µmol) formed by gram of the catalyst per second (µmol/(g·s)).

3. RESULTS AND DISCUSSION

The important parameters of WGSR process are reaction temperature and steam/CO ratio. The effect of temperature and H₂O/CO on carbon monoxide conversion and products yields have been studied in WGSR under atmospheric pressure over the synthesized catalysts.

During testing the 10%Fe-Cu(1:1)-0.25%Mₓ/AlₓOᵧ catalyst in reaction of water-gas shift under atmospheric pressure, H₂O/CO=1 and GHSV=1000 h⁻¹ it was observed that dependence of carbon monoxide conversion degree on temperature is characterized by maximum at 290°C (Fig.1). Conversion degree of CO at this temperature is 96.4%. Further increase in temperature to 310°C leads to slight decrease of carbon monoxide conversion to 95.0%, while at 340°C the degree of CO conversion is markedly decreased: X(CO)=88.0%. It is predictable taking into account the tendency of copper to thermal sintering at higher temperatures [2]. The reaction products are hydrogen and carbon dioxide only. Their yields and carbon monoxide conversion degree are symbatically changed. The yields of hydrogen and carbon dioxide reach at maximum 1.33 and 1.30 µmole/(g·s) respectively at temperature 290°C (Fig.1). The formation of methane was not detected in the whole investigated range of temperatures.

![Figure 1 – Effect of temperature on WGSR process parameters over 10%Fe-Cu(1:1)-0.25%Mₓ/AlₓOᵧ catalyst, H₂O/CO=1/1, P=1 atm, GHSV=1000 h⁻¹](image)

Testing the catalyst modified by cobalt – 10%Fe-Co(1:1)-0.25%Mₓ/AlₓOᵧ under the same conditions showed that the maximum conversion degree is 94.6% was reached at 315°C. In contrast to copper containing catalyst, there was no significant decrease in degree of CO conversion with increase in temperature (Fig. 2). Yields of hydrogen and carbon dioxide are almost equal and get at maximum 1.29 µmole/(g·s) at t=315-320°C (Fig. 2). At temperature ≥ 320°C, the formation of insignificant amount of methane was occurred (less than 0.03%). At temperatures below 320°C, the formation of methane was not observed.
For the both catalysts, the effect of steam amount on water-gas shift reaction was studied. In industry, the water-gas shift reaction is carried out at the excessive H₂O/CO ratios. Decreasing operating temperature and increasing steam/carbon ratio stimulate the growth of conversion degree regardless to operating pressure. It is well-known that the low steam/CO ratios can result in epy metallic iron formation, which causes increasing of methanation, carbon deposition, and Fischer – Tropsch reaction [6].

It was observed that a character of dependence of carbon monoxide conversion on molar ratio of H₂O/CO was the opposite to the expected one. That requires the further study. However, the high value of feed conversion at a low steam to carbon monoxide ratio may indicate that the 10%Fe-Co(1:1)-0.25%M₀/Al₂O₃ is a perspective one to be used as the middle temperature catalyst for water-gas shift reaction accompanied with the steam economy.

At Fig. 3 the dependence of carbon monoxide conversion degree on H₂O/CO ratio over the iron-copper catalyst at t=310°C and GHSV=1000 h⁻¹ is presented. With increase in H₂O/CO ratio from 1 to 1.4 the conversion degree is decreased from 95.0 to 91.9% and accordingly the yields of hydrogen and carbon dioxide decreased from 1.27 and 1.28 to 1.22 μmol/(g·s) respectively.

The iron-cobalt catalyst is less sensitive to the effect of steam excess in comparison with the Fe-Cu. Nevertheless, the observed insignificant extremal dependence of carbon monoxide conversion and
products yields on H₂O/CO ratio indicates a negative impact of steam excess for this catalyst too (Fig. 4). The optimal ratio H₂O/CO=1.2 at temperature of 320°C when degree of CO conversion is 95.2% and yields of hydrogen and carbon dioxide are equal to 1.31 μmol/(g·s) each.

![Graph showing H₂O/CO ratio impact on WGS process parameters](image)

The effect of gas hourly space velocity on WGS process parameters was studied over the 10%Fe-Co(1:1)-0.25%M/Al₂O₃ catalyst. The optimal value of GHSV in terms of products yields is 1000 h⁻¹, when the carbon monoxide conversion is 91.0% that is slightly lower than 93.6% at GHSV=500 h⁻¹. The yields of hydrogen an carbon dioxide are equal to 1.2 μmol/g·s, that is twice higher in comparison with GHSV=500 h⁻¹ (Table 1). Increase in GHSV to 1500 h⁻¹ is accompanied with decrease in both carbon monoxide conversion and products yields (Table 1).

<table>
<thead>
<tr>
<th>GHSV, h⁻¹</th>
<th>X(CO)%,</th>
<th>Yield of products, μmol/(g·s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Y(H₂)</td>
</tr>
<tr>
<td>500</td>
<td>93.6</td>
<td>0.5</td>
</tr>
<tr>
<td>1000</td>
<td>91.0</td>
<td>1.2</td>
</tr>
<tr>
<td>1500</td>
<td>60.4</td>
<td>0.8</td>
</tr>
</tbody>
</table>

Thus, the testing of 10%Fe-M(1:1)/Al₂O₃ catalysts, where M is Co or Cu, demonstrate their high activity in water-gas shift reaction. The comparison of catalysts under the following conditions: H₂O/CO=1/1, P=1 atm, GHSV = 1000 h⁻¹, is given in Table 2. It needs to note that the cobalt-containing catalyst has lower but quite sufficient activity. The catalyst has not a tendency to significant decrease in activity with increasing temperature.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>X(CO)ₘₙₜ, %</th>
<th>t°C</th>
<th>Yield of products, μmol/g·s</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Y(H₂)</td>
</tr>
<tr>
<td>10%Fe-Cu(1:1)-0.25%M/Al₂O₃</td>
<td>96.4</td>
<td>290</td>
<td>1.33</td>
</tr>
<tr>
<td>10%Fe-Co(1:1)-0.25%M/Al₂O₃</td>
<td>94.6</td>
<td>315</td>
<td>1.29</td>
</tr>
</tbody>
</table>
Both catalysts worked without loss of stability for 20 hours of their exploitation. The values of specific surface area and pore volume of the fresh and spent catalyst are given in Table 3. Insignificant decreasing of both parameters is occurred, that can be explained by blocking of surface by reaction products, which were not removed from the surface after reaction running for 20 hours.

**Table 3 – Specific surface area (BET) and pore volume of catalyst samples**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Specific surface area, m(^2)/g</th>
<th>Pore volume, ml/g</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fresh</td>
<td>Spent</td>
</tr>
<tr>
<td>10%Fe-Cu(1:1)-0.25%M/Al(_2)O(_3)</td>
<td>132.2</td>
<td>123.9</td>
</tr>
<tr>
<td>10%Fe-Co(1:1)-0.25%M/Al(_2)O(_3)</td>
<td>156.2</td>
<td>141.9</td>
</tr>
</tbody>
</table>

**CONCLUSIONS**

On the base of data obtained the following can be concluded.

The both iron-containing catalysts studied perform the high activity in water gas shift reaction with production of hydrogen. Conversion degree of carbon monoxide reaches 94.6 and 96.4% in maximum for Fe-Co and Fe-Cu catalysts respectively. The copper containing catalyst exhibit somewhat higher activity: higher carbon monoxide conversion (96.4% versus 94.6%) is achieved at lower temperature (290°C versus 315°C).

The both catalysts can be assigned as the middle temperature ones. The optimal temperatures of WGSR are within the temperature region of 290-320°C depending on the second metal nature – Cu or Co.

Further studies of catalysts are planned in particular to scale the water gas shift process - WGSR over the developed catalysts.

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**Information about the authors:**

Valishevsky K.A. - D.V. Sokolsky Institute of Fuel, Catalysis and Electrochemistry, Almaty, Kazakhstan, kirpitch83@yandex.ru, ORCID iD: https://orcid.org/0000-0001-5399-5791;
Ilikulova S.S. - D.V. Sokolsky Institute of Fuel, Catalysis and Electrochemistry, Almaty, Kazakhstan, s.ilikulova@ifce.kz, ORCID iD: https://orcid.org/0000-0001-7159-5249;
Boleubaev Y.A. - D.V. Sokolsky Institute of Fuel, Catalysis and Electrochemistry, Almaty, Kazakhstan, erzhan_bol@mail.ru, ORCID iD: https://orcid.org/0000-0001-5323-3623

K.A. Валишевский\(^1\), Ш.С. Иликулова\(^1\), Е.А. Болеубаев

\(^1\) АО «Д.В. Сокольский атындағы жаңа адамдар, каталитика және электролитика институты», Алматы, Қазақстан

**ПОЛИМЕТАЛДЫ Fe-КУРАМДЫ КОНДЫРЫЛГАН КАТАЛИЗАТОРЛАРДА СУДЫҢ КЕРІ БІГЫСУ РЕАЦИЯСЫ**

**Аннотация.** Бұл жұмыста ауыстырым металдар коспасымен модификациялған және алюминий төтімға қондырылған полиметалды темірқұрамдарынің каталитик ерекшеліктері сүйіп береді. Коміртекті коспасымен судың эркеттесуі процессінде темірқұрамдарынің каталитикалық арқылы қосына болады. Тұрмындаң ауыстырым модификациялған, сондай-ақ қолданыс компонент ретінде 8-ші топ қосынасын металдар құрылысы және алюминий төтімі қондырылған темір неғізінде сіңіргеннен каталитик ерекшеліктері судың кері бігысу реакциясында сүтегі бойынша жоғарғы белсенділік пен талғамдылықты көрсетеді. Сіңіргеннен каталитик ерекшеліктері судың кері бігысу қосынасын сүтегі алуына тінімді жағдайлары анықталды.

**Тұжір е сөзі:** Судың Кері Бігысу Реакциясы, Fe-Кұрамды Қондырылған Катализатор, Сүтегі, Коміртекті Төтімгі
РЕАКЦИЯ ВОДЯНОГО СДВИГА НА ПОЛИМЕТАЛЛИЧЕСКИХ Fe-СОДЕРЖАЩИХ НАНЕСЕННЫХ КАТАЛИЗАТОРАХ

Аннотация: В данной работе была изучена реакция водяного сдвига на полиметаллических нанесенных на оксид алюминия железо-содержащих катализаторах, модифицированных добавками переходных металлов. Было рассмотрено влияние температуры процесса и природы добавок (Сo или Cu) на поведение железо-содержащих катализаторов в процессе взаимодействия воды с оксидом углерода. Показано, что синтезированные катализаторы на основе железа, модифицированные добавками меди или кобальта, а также содержащие в качестве третьего компонента — переходный металл из 8-й группы элементов, нанесенные на оксид алюминия, обладают высокой активностью и селективностью по водороду в реакции водяного сдвига. Определены оптимальные условия получения водорода путем реакции водяного сдвига на синтезированных катализаторах.

Ключевые слова: Реакция водяного сдвига, Fe-содержащий Нанесенный Катализатор, Водород, Оксиды Углерода.

REFERENCES


