

ISSN 2518-1491 (Online),  
ISSN 2224-5286 (Print)

ҚАЗАҚСТАН РЕСПУБЛИКАСЫ  
ҰЛТТЫҚ ҒЫЛЫМ АКАДЕМИЯСЫНЫҢ

Д.В.Сокольский атындағы «Жанармай,  
катализ және электрохимия институты» АҚ

# Х А Б А Р Л А Р Ы

## ИЗВЕСТИЯ

НАЦИОНАЛЬНОЙ АКАДЕМИИ НАУК  
РЕСПУБЛИКИ КАЗАХСТАН  
АО «Институт топлива, катализа и  
электрохимии им. Д.В. Сокольского»

## NEWS

OF THE ACADEMY OF SCIENCES  
OF THE REPUBLIC OF KAZAKHSTAN  
JSC «D.V. Sokolsky institute of fuel, catalysis  
and electrochemistry»

**SERIES**  
**CHEMISTRY AND TECHNOLOGY**

**4 (436)**

**JULY-AUGUST 2019**

PUBLISHED SINCE JANUARY 1947

PUBLISHED 6 TIMES A YEAR

ALMATY, NAS RK

---

*NAS RK is pleased to announce that News of NAS RK. Series of chemistry and technologies scientific journal has been accepted for indexing in the Emerging Sources Citation Index, a new edition of Web of Science. Content in this index is under consideration by Clarivate Analytics to be accepted in the Science Citation Index Expanded, the Social Sciences Citation Index, and the Arts & Humanities Citation Index. The quality and depth of content Web of Science offers to researchers, authors, publishers, and institutions sets it apart from other research databases. The inclusion of News of NAS RK. Series of chemistry and technologies in the Emerging Sources Citation Index demonstrates our dedication to providing the most relevant and influential content of chemical sciences to our community.*

*Қазақстан Республикасы Ұлттық ғылым академиясы "ҚР ҰҒА Хабарлары. Химия және технология сериясы" ғылыми журналының Web of Science-тің жаңаланған нұсқасы Emerging Sources Citation Index-те индекстелуге қабылданғанын хабарлайды. Бұл индекстелу барысында Clarivate Analytics компаниясы журналды одан әрі the Science Citation Index Expanded, the Social Sciences Citation Index және the Arts & Humanities Citation Index-ке қабылдау мәселесін қарастыруда. Web of Science зерттеушілер, авторлар, баспашылар мен мекемелерге контент тереңдігі мен сапасын ұсынады. ҚР ҰҒА Хабарлары. Химия және технология сериясы Emerging Sources Citation Index-ке енуі біздің қоғамдастық үшін ең өзекті және беделді химиялық ғылымдар бойынша контентке адалдығымызды білдіреді.*

*НАН РК сообщает, что научный журнал «Известия НАН РК. Серия химии и технологий» был принят для индексирования в Emerging Sources Citation Index, обновленной версии Web of Science. Содержание в этом индексировании находится в стадии рассмотрения компанией Clarivate Analytics для дальнейшего принятия журнала в the Science Citation Index Expanded, the Social Sciences Citation Index и the Arts & Humanities Citation Index. Web of Science предлагает качество и глубину контента для исследователей, авторов, издателей и учреждений. Включение Известия НАН РК в Emerging Sources Citation Index демонстрирует нашу приверженность к наиболее актуальному и влиятельному контенту по химическим наукам для нашего сообщества.*

Б а с р е д а к т о р ы  
х.ғ.д., проф., ҚР ҰҒА академигі **М.Ж. Жұрынов**

Р е д а к ц и я а л қ а с ы:

**Ағабеков В.Е.** проф., академик (Белорус)  
**Волков С.В.** проф., академик (Украина)  
**Воротынцев М.А.** проф., академик (Ресей)  
**Газалиев А.М.** проф., академик (Қазақстан)  
**Ергожин Е.Е.** проф., академик (Қазақстан)  
**Жармағамбетова А.К.** проф. (Қазақстан), бас ред. орынбасары  
**Жоробекова Ш.Ж.** проф., академик (Қырғыстан)  
**Иткулова Ш.С.** проф. (Қазақстан)  
**Манташян А.А.** проф., академик (Армения)  
**Пралиев К.Д.** проф., академик (Қазақстан)  
**Баешов А.Б.** проф., академик (Қазақстан)  
**Бүркітбаев М.М.** проф., академик (Қазақстан)  
**Джусипбеков У.Ж.** проф. корр.-мүшесі (Қазақстан)  
**Молдахметов М.З.** проф., академик (Қазақстан)  
**Мансуров З.А.** проф. (Қазақстан)  
**Наурызбаев М.К.** проф. (Қазақстан)  
**Рудик В.** проф., академик (Молдова)  
**Рахимов К.Д.** проф. академик (Қазақстан)  
**Стрельцов Е.** проф. (Белорус)  
**Тәшімов Л.Т.** проф., академик (Қазақстан)  
**Тодераш И.** проф., академик (Молдова)  
**Халиков Д.Х.** проф., академик (Тәжікстан)  
**Фарзалиев В.** проф., академик (Әзірбайжан)

«ҚР ҰҒА Хабарлары. Химия және технология сериясы».

ISSN 2518-1491 (Online),

ISSN 2224-5286 (Print)

Меншіктенуші: «Қазақстан Республикасының Ұлттық ғылым академиясы» Республикалық қоғамдық бірлестігі (Алматы қ.)

Қазақстан республикасының Мәдениет пен ақпарат министрлігінің Ақпарат және мұрағат комитетінде 30.04.2010 ж. берілген №1089-Ж мерзімдік басылым тіркеуіне қойылу туралы куәлік

Мерзімділігі: жылына 6 рет.

Тиражы: 300 дана.

Редакцияның мекенжайы: 050010, Алматы қ., Шевченко көш., 28, 219 бөл., 220, тел.: 272-13-19, 272-13-18,  
<http://chemistry-technology.kz/index.php/en/arihiv>

© Қазақстан Республикасының Ұлттық ғылым академиясы, 2019

Типографияның мекенжайы: «Аруна» ЖК, Алматы қ., Муратбаева көш., 75.

Главный редактор  
д.х.н., проф., академик НАН РК **М. Ж. Журинов**

Редакционная коллегия:

**Агабеков В.Е.** проф., академик (Беларусь)  
**Волков С.В.** проф., академик (Украина)  
**Воротынцев М.А.** проф., академик (Россия)  
**Газалиев А.М.** проф., академик (Казахстан)  
**Ергожин Е.Е.** проф., академик (Казахстан)  
**Жармагамбетова А.К.** проф. (Казахстан), зам. гл. ред.  
**Жоробекова Ш.Ж.** проф., академик (Кыргызстан)  
**Иткулова Ш.С.** проф. (Казахстан)  
**Манташян А.А.** проф., академик (Армения)  
**Пралиев К.Д.** проф., академик (Казахстан)  
**Баешов А.Б.** проф., академик (Казахстан)  
**Буркитбаев М.М.** проф., академик (Казахстан)  
**Джусипбеков У.Ж.** проф. чл.-корр. (Казахстан)  
**Мулдахметов М.З.** проф., академик (Казахстан)  
**Мансуров З.А.** проф. (Казахстан)  
**Наурызбаев М.К.** проф. (Казахстан)  
**Рудик В.** проф., академик (Молдова)  
**Рахимов К.Д.** проф. академик (Казахстан)  
**Стрельцов Е.** проф. (Беларусь)  
**Ташимов Л.Т.** проф., академик (Казахстан)  
**Тодераш И.** проф., академик (Молдова)  
**Халиков Д.Х.** проф., академик (Гаджикистан)  
**Фарзалиев В.** проф., академик (Азербайджан)

«Известия НАН РК. Серия химии и технологии».

ISSN 2518-1491 (Online),

ISSN 2224-5286 (Print)

Собственник: Республиканское общественное объединение «Национальная академия наук Республики Казахстан» (г. Алматы)

Свидетельство о постановке на учет периодического печатного издания в Комитете информации и архивов Министерства культуры и информации Республики Казахстан №10893-Ж, выданное 30.04.2010 г.

Периодичность: 6 раз в год

Тираж: 300 экземпляров

Адрес редакции: 050010, г. Алматы, ул. Шевченко, 28, ком. 219, 220, тел. 272-13-19, 272-13-18,  
<http://chemistry-technology.kz/index.php/en/arhiv>

---

© Национальная академия наук Республики Казахстан, 2019

Адрес редакции: 050100, г. Алматы, ул. Кунаева, 142,  
Институт органического катализа и электрохимии им. Д. В. Сокольского,  
каб. 310, тел. 291-62-80, факс 291-57-22, e-mail:orgcat@nursat.kz

Адрес типографии: ИП «Аруна», г. Алматы, ул. Муратбаева, 75

## E d i t o r i n c h i e f

doctor of chemistry, professor, academician of NAS RK **M.Zh. Zhurinov**

## E d i t o r i a l b o a r d :

**Agabekov V.Ye.** prof., academician (Belarus)  
**Volkov S.V.** prof., academician (Ukraine)  
**Vorotyntsev M.A.** prof., academician (Russia)  
**Gazaliyev A.M.** prof., academician (Kazakhstan)  
**Yergozhin Ye.Ye.** prof., academician (Kazakhstan)  
**Zharmagambetova A.K.** prof. (Kazakhstan), deputy editor in chief  
**Zhorobekova Sh.Zh.** prof., academician ( Kyrgyzstan)  
**Itkulova Sh.S.** prof. (Kazakhstan)  
**Mantashyan A.A.** prof., academician (Armenia)  
**Praliyev K.D.** prof., academician (Kazakhstan)  
**Bayeshov A.B.** prof., academician (Kazakhstan)  
**Burkitbayev M.M.** prof., academician (Kazakhstan)  
**Dzhusipbekov U.Zh.** prof., corr. member (Kazakhstan)  
**Muldakhmetov M.Z.** prof., academician (Kazakhstan)  
**Mansurov Z.A.** prof. (Kazakhstan)  
**Nauryzbayev M.K.** prof. (Kazakhstan)  
**Rudik V.** prof., academician (Moldova)  
**Rakhimov K.D.** prof., academician (Kazakhstan)  
**Streltsov Ye.** prof. (Belarus)  
**Tashimov L.T.** prof., academician (Kazakhstan)  
**Toderash I.** prof., academician (Moldova)  
**Khalikov D.Kh.** prof., academician (Tadjikistan)  
**Farzaliyev V.** prof., academician (Azerbaijan)

**News of the National Academy of Sciences of the Republic of Kazakhstan. Series of chemistry and technology.**  
**ISSN 2518-1491 (Online),**  
**ISSN 2224-5286 (Print)**

Owner: RPA "National Academy of Sciences of the Republic of Kazakhstan" (Almaty)

The certificate of registration of a periodic printed publication in the Committee of Information and Archives of the Ministry of Culture and Information of the Republic of Kazakhstan N 10893-Ж, issued 30.04.2010

Periodicity: 6 times a year

Circulation: 300 copies

Editorial address: 28, Shevchenko str., of. 219, 220, Almaty, 050010, tel. 272-13-19, 272-13-18,

<http://chemistry-technology.kz/index.php/en/arhiv>

---

© National Academy of Sciences of the Republic of Kazakhstan, 2019

Editorial address: Institute of Organic Catalysis and Electrochemistry named after D. V. Sokolsky  
142, Kunayev str., of. 310, Almaty, 050100, tel. 291-62-80, fax 291-57-22,  
e-mail: orgcat@nursat.kz

Address of printing house: ST "Aruna", 75, Muratbayev str, Almaty

**NEWS**

OF THE NATIONAL ACADEMY OF SCIENCES OF THE REPUBLIC OF KAZAKHSTAN

**SERIES CHEMISTRY AND TECHNOLOGY**

ISSN 2224-5286

<https://doi.org/10.32014/2019.2518-1491.36>

Volume 4, Number 436 (2019), 12 – 18

**K.A. Valishevskiy<sup>1</sup>, S.S. Itkulova<sup>1</sup>, Y.A. Boleubaev<sup>1</sup>**

D.V. Sokolsky Institute of Fuel, Catalysis and Electrochemistry, Almaty, Kazakhstan  
[s.itkulova@ifce.kz](mailto:s.itkulova@ifce.kz)

## **WATER-GAS SHIFT REACTION OVER THE POLYMETALLIC 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 8<sup>th</sup> 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 (WGS) 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, WGS 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):



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 CO<sub>2</sub> emission [7].

WGS 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 H<sub>2</sub>O /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% Fe<sub>2</sub>O<sub>3</sub>, 10% Cr<sub>2</sub>O<sub>3</sub>, 0.2% MgO and balance of variable composition. It is supposed that the active phase is the magnetite (Fe<sub>3</sub>O<sub>4</sub>) is formed during partial reduction of the initial catalyst, while Cr<sub>2</sub>O<sub>3</sub> 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 Al<sup>3+</sup> ions into iron oxide is easily feasible because they have similar ionic radii: 0.675Å and 0.690Å for Al<sup>3+</sup> and Fe<sup>3+</sup> 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% Al<sub>2</sub>O<sub>3</sub> [2]. The active centers in these catalysts are crystallites of CuO, while ZnO provides the structural stability and Al<sub>2</sub>O<sub>3</sub>, 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 – M<sub>1</sub> 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 (H<sub>2</sub>/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<sup>-1</sup>. Steam to carbon monoxide ratio – H<sub>2</sub>O/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 Hayesep R 80/100, to detect CO, H<sub>2</sub>, CO<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>-C<sub>6</sub> hydrocarbons.

The catalysts with the following composition were prepared: 10%Fe-Cu(1:1)-0.25%M<sub>1</sub>/Al<sub>2</sub>O<sub>3</sub> and 10%Fe-Co(1:1)-0.25%M<sub>1</sub>/Al<sub>2</sub>O<sub>3</sub> (wt.%), where M<sub>1</sub> – metal of the Group VIII. The catalysts were prepared by the impregnation method.

Conversion of CO (X<sub>CO</sub>,%) was calculated by formula given below:

$$X(\text{CO}) = \frac{V_{in}^{CO} - V_{out}^{CO}}{V_{in}^{CO}} \times 100\%,$$

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<sub>H<sub>2</sub></sub>, Y<sub>CO<sub>2</sub></sub> and Y<sub>CH<sub>4</sub></sub> 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 WGS process are reaction temperature and steam/CO ratio. The effect of temperature and H<sub>2</sub>O/CO on carbon monoxide conversion and products yields have been studied in WGS under atmospheric pressure over the synthesized catalysts

During testing the 10%Fe-Cu(1:1)-0.25%M/Al<sub>2</sub>O<sub>3</sub> catalyst in reaction of water-gas shift under atmospheric pressure, H<sub>2</sub>O/CO=1 and GHSV=1000 h<sup>-1</sup> 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.

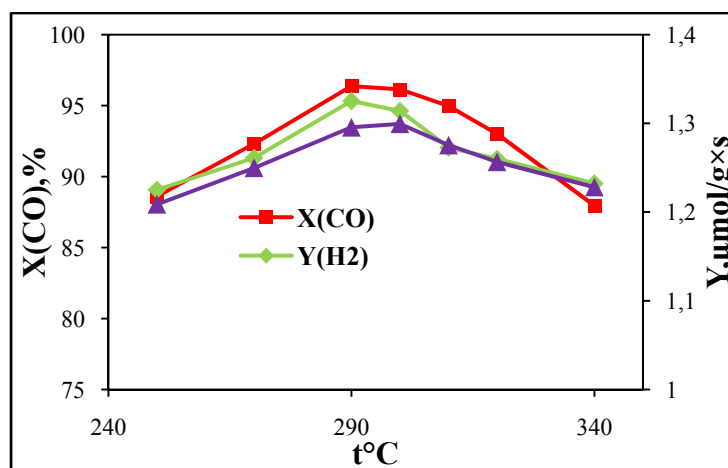


Figure 1 – Effect of temperature on WGS process parameters over 10%Fe-Cu(1:1)-0.25%M<sub>1</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst, H<sub>2</sub>O/CO=1/1, P=1 atm, GHSV=1000 h<sup>-1</sup>

Testing the catalyst modified by cobalt – 10%Fe-Co(1:1)-0.25%M<sub>1</sub>/Al<sub>2</sub>O<sub>3</sub> 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.



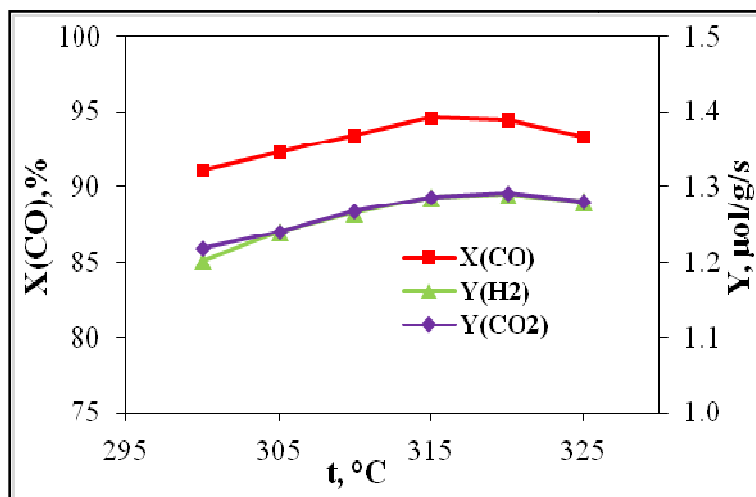


Figure 2 – Effect of temperature on WGSR process parameters over 10%Fe-Co(1:1)-0.25%M<sub>1</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst, H<sub>2</sub>O/CO=1/1, P=1 atm, GHSV=1000 h<sup>-1</sup>

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 H<sub>2</sub>O/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 H<sub>2</sub>O/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%M<sub>1</sub>/Al<sub>2</sub>O<sub>3</sub> 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 H<sub>2</sub>O/CO ratio over the iron-copper catalyst at t= 310°C and GHSV=1000 h<sup>-1</sup> is presented. With increase in H<sub>2</sub>O/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.

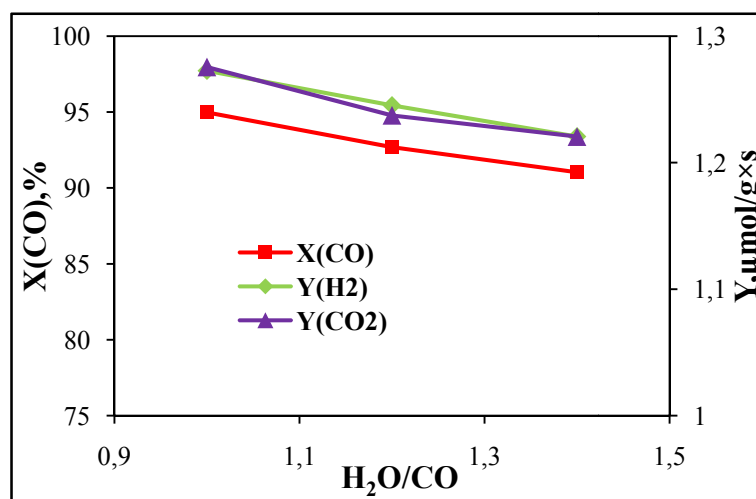


Figure 3 – Effect of H<sub>2</sub>O/CO ratio on WGSR process parameters over 10%Fe-Cu(1:1)-0.25%M<sub>1</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst, P=1 atm, t=310°C, GHSV=1000 h<sup>-1</sup>

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 H<sub>2</sub>O/CO ratio indicates a negative impact of steam excess for this catalyst too (Fig. 4). The optimal ratio H<sub>2</sub>O/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.

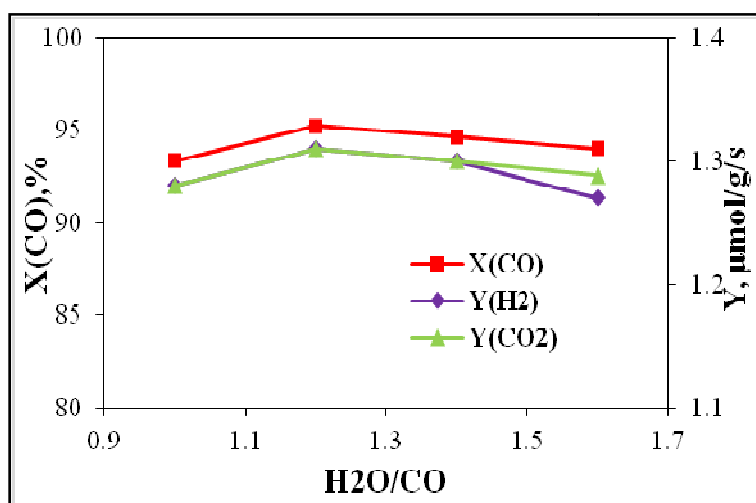


Figure 4 – Effect of H<sub>2</sub>O/CO ratio on WGS process parameters over 10%Fe-Co(1:1)-0.25%M<sub>1</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst, P=1 atm, t=320°C, GHSV = 1000 h<sup>-1</sup>

The effect of gas hourly space velocity on WGS process parameters was studied over the 10%Fe-Co(1:1)-0.25%M/Al<sub>2</sub>O<sub>3</sub> catalyst. The optimal value of GHSV in terms of products yields is 1000 h<sup>-1</sup>, when the carbon monoxide conversion is 91.0% that is slightly lower than 93.6% at GHSV=500 h<sup>-1</sup>. The yields of hydrogen and carbon dioxide are equal to 1.2 μmol/g·s, that is twice higher in comparison with GHSV=500 h<sup>-1</sup> (Table 1). Increase in GHSV to 1500 h<sup>-1</sup> is accompanied with decrease in both carbon monoxide conversion and products yields (Table 1).

Table 1 – Effect of space velocity on WGS process parameters over 10%Fe-Co(1:1)-0.25%M<sub>1</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst at H<sub>2</sub>O/CO=1/1, P=1 atm, t=310°C

GHSV, h <sup>-1</sup>	X(CO), %	Yield of products, μmole/(g·s)	
		Y(H <sub>2</sub> )	Y(CO <sub>2</sub> )
500	93.6	0.5	0.6
1000	91.0	1.2	1.2
1500	60.4	0.8	0.81

Thus, the testing of 10%Fe-M(1:1)/Al<sub>2</sub>O<sub>3</sub> catalysts, where M is Co or Cu, demonstrate their high activity in water-gas shift reaction. The comparison of catalysts under the following conditions: H<sub>2</sub>O/CO=1/1, P=1 atm, GHSV = 1000 h<sup>-1</sup>, 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 2 – Comparative characteristics of the catalysts in WGS process at H<sub>2</sub>O/CO=1/1, P=1 atm, GHSV=1000 h<sup>-1</sup>

Catalyst	X(CO) <sub>max</sub> , %	t, °C	Yield of products, μmole/g·s	
			Y(H <sub>2</sub> )	Y(CO <sub>2</sub> )
10%Fe-Cu(1:1)- 0.25%M/Al <sub>2</sub> O <sub>3</sub>	96.4	290	1.33	1.30
10%Fe-Co(1:1)-0.25%M/Al <sub>2</sub> O <sub>3</sub>	94.6	315	1.29	1.29

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

Catalyst	Specific surface area, m <sup>2</sup> /g		Pore volume, ml/g	
	Fresh	Spent	Fresh	Spent
10%Fe-Cu(1:1)- 0.25%M/Al <sub>2</sub> O <sub>3</sub>	132.2	123.9	n/d	n/d
10%Fe-Co(1:1)-0.25%M/Al <sub>2</sub> O <sub>3</sub>	156.2	141.9	146.1	126.6

## 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.

**Acknowledgement:** This research was supported by the Ministry of Education and Science of the Republic of Kazakhstan through the Programme # BR05236739 MES RK.

### Information about the authors:

Valishevskiy 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>;

Itkulova S.S. - D.V. Sokolsky Institute of Fuel, Catalysis and Electrochemistry, Almaty, Kazakhstan, s.itkulova@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>

**К.А. Валишевский<sup>1</sup>, Ш.С.Итқұлова<sup>1</sup>, Е.А. Болеубаев<sup>1</sup>**

<sup>1</sup>АҚ «Д.В. Сокольский атындағы жанармай, катализ және электрохимия институты», Алматы, Қазақстан

## ПОЛИМЕТАЛДЫ Fe-ҚҰРАМДЫ ҚОНДЫРЫЛҒАН КАТАЛИЗАТОРЛАРДА СУДЫҢ КЕРІ ЫҒЫСУ РЕАКЦИЯСЫ

**Аннотация.** Бұл жұмыста ауыспалы металдар қоспасымен модифицирленген және алюминий тотығына қондырылған полиметалды темірқұрамды катализаторларда судың кері ығысу реакциясы зерттелді. Көміртек тотығымен судың әрекеттесуі процесінде темірқұрамды катализаторлар сипатына процесс температурасы мен қоспа (Со немесе Си) табиғатының әсері, сонымен қатар H<sub>2</sub>/CO қатынасы мен көлемдік жылдамдық әсері қарастырылған болатын. Кобальт немесе мыс қоспасымен модифицирленген, сондай-ақ үшінші компонент ретінде 8-ші топ элементінің ауыспалы металын құрайтын және алюминий тотығына қондырылған темір негізіндегі синтезделген катализаторлар судың кері ығысу реакциясында сутегі бойынша жоғары белсенділік пен талғамдылықты көрсетті. Синтезделген катализаторларда судың кері ығысу жолымен сутегі алудың тиімді жағдайы анықталды.

**Түйін сөздері:** Судың Кері Ығысу Реакциясы, Fe-Құрамды Қондырылған Катализатор, Сутегі, Көміртек Тотығы

К.А. Валишевский<sup>1</sup>, Ш.С. Иткулова<sup>1</sup>, Е.А. Болеубаев<sup>1</sup>

<sup>1</sup>АО «Институт топлива, катализа и электрохимии им. Д.В. Сокольского», Алматы, Казахстан

## РЕАКЦИЯ ВОДЯНОГО СДВИГА НА ПОЛИМЕТАЛЛИЧЕСКИХ Fe-СОДЕРЖАЩИХ НАНЕСЕННЫХ КАТАЛИЗАТОРАХ

**Аннотация:** В данной работе была изучена реакция водяного сдвига на полиметаллических нанесенных на оксид алюминия железосодержащих катализаторах, модифицированных добавками переходных металлов. Было рассмотрено влияние температуры процесса и природы добавок (Co 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 – переходной металл из 8-ой 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

- [1] Pal DB, Chand R, Upadhyay SN, Mishra PK (2018) Performance of water gas shift reaction catalysts: A review. *Renewable and Sustainable Energy Reviews* 93: 549–565. DOI.org/10.1016/j.rser.2018.05.003
- [2] Rhodes C, Hutchings GJ, Ward AM (1995) Water-gas shift reaction: finding the mechanistic boundary. *Catal Today* 23: 43-58. DOI.org/10.1016/0920-5861(94)00135-0
- [3] Twigg MV (1989) In: Twigg MV (ed) *Catalyst Handbook*, 2nd edn. Wolfe Publishing Ltd, London. ISBN: 0-7234-08572
- [4] Muradov NZ, Veziroğlu TN (2008) “Green” path from fossil-based to hydrogen economy: an overview of carbon-neutral technologies. *Int J Hydrog Energy* 33: 6804-6839. DOI:10.1016/j.ijhydene.2008.08.054
- [5] Trimm DL (2005) Minimisation of carbon monoxide in a hydrogen stream for fuel cell application. *Appl Catal A-Gen* 296: 1-11. DOI:10.1016/j.apcata.2005.07.011
- [6] LeValley TL, Richard AR, Fan M (2014) The progress in water gas shift and steam reforming hydrogen production technologies – A review. *Int J Hydrog Energy* 39: 16983-17000. DOI.org/10.1016/j.ijhydene.2014.08.041
- [7] Gradisher L, Dutcher B, Fan M (2015) Catalytic hydrogen production from fossil fuels via the water gas shift reaction. *Appl Energy* 139: 335-349. DOI.org/10.1016/j.apenergy.2014.10.080
- [8] Saeidi S, Fazlollahi F, Najari S, Iranshahi D, Klemeš JJ, Baxter LL (2017) Hydrogen production: Perspectives, separation with special emphasis on kinetics of WGS reaction: A state-of-the-art review. *J Ind Eng Chem* 49: 1-25. DOI.org/10.1016/j.jiec.2016.12.003
- [9] Reddy GK, Smirniotis GK (2015) *Water gas shift reaction: Research developments and applications*, 1st edn. Elsevier, Amsterdam. ISBN: 978-0-12-420154-5
- [10] Jeong DW, Potdar HS, Roh HS (2012) Comparative Study on Nano-Sized 1 wt% Pt/Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub> and 1 wt% Pt/Ce<sub>0.2</sub>Zr<sub>0.8</sub>O<sub>2</sub> Catalysts for a Single Stage Water Gas Shift Reaction. *Catal Lett* 142: 439-444. DOI: 10.1007/s10562-012-0786-4
- [11] Newsome DS (1980) The water gas shift reaction. *Catal Rev Sci Eng* 21: 275-318. DOI: 10.1080/03602458008067535
- [12] Jeong DW, Subramanian V, Shim JO, Jang WJ, Seo YC, Roh HS, Gu JH, Lim YT (2013) High-Temperature Water Gas Shift Reaction Over Fe/Al/Cu Oxide Based Catalysts Using Simulated Waste-Derived Synthesis Gas. *Catal Lett* 143: 438-444. DOI: 10.1007/s10562-013-0981-y
- [13] Putanov PS, Jovanović ŽD (1970) The Effect of Additives on Catalyst Properties in Low-Temperature Carbon Monoxide Conversion. *Bull Soc Chim Beograd* 35: 279-284.
- [14] Rase HF (1977) In: *Chemical Reactor Design for Process Plants. Volume Two: Case Studies and Design Data*, John Wiley and Sons, 1977, 256. ISBN: 9780471018902
- [15] Spencer MS (1999) The role of zinc oxide in Cu/ZnO catalysts for methanol synthesis and the water–gas shift reaction. *Top Cat* 8: 259-166. DOI: 10.1023/A:101918171
- [16] Burch R (2006) Gold catalysts for pure hydrogen production in the water-gas shift reaction: activity, structure and reaction mechanism. *Phys Chem Chem Phys*. 8: 5483-5500. DOI: 10.1039/b607837k
- [17] Lucarelli C, Molinari C, Faure R, Fornasari G, Gary D, Schiaroli N, Vaccari D (2018) Novel Cu-Zn-Al catalysts obtained from hydrotalcite-type precursors for middle-temperature water-gas shift applications. *Appl Clay Sci* 155: 103-110. DOI: 10.1016/j.clay.2017.12.022
- [18] Ratnasamy C, Wagner JP (2009) Water Gas Shift Catalysis. *Catal Rev Sci Eng* 51: 325-440. DOI: 10.1080/01614940903048661
- [19] Nikolova D, Edreva-Kardjieva R, Goulieva G, Grozeva T, Tzvetkov P (2006) The state of (K)(Ni)Mo/γ-Al<sub>2</sub>O<sub>3</sub> catalysts after water–gas shift reaction in the presence of sulfur in the feed: XPS and EPR study. *Appl Catal A-Gen* 297: 135-144. DOI: 10.1016/j.apcata.2005.08.043
- [20] Li Y, Wang R, Chang L (1999) Study of reactions over sulfide catalysts in CO–CO<sub>2</sub>–H<sub>2</sub>–H<sub>2</sub>O system. *Catal Today* 51: 25-38. DOI: 10.1016/S0920-5861(99)00005-X

## **Publication Ethics and Publication Malpractice in the journals of the National Academy of Sciences of the Republic of Kazakhstan**

For information on Ethics in publishing and Ethical guidelines for journal publication see <http://www.elsevier.com/publishingethics> and <http://www.elsevier.com/journal-authors/ethics>.

Submission of an article to the National Academy of Sciences of the Republic of Kazakhstan implies that the described work has not been published previously (except in the form of an abstract or as part of a published lecture or academic thesis or as an electronic preprint, see <http://www.elsevier.com/postingpolicy>), that it is not under consideration for publication elsewhere, that its publication is approved by all authors and tacitly or explicitly by the responsible authorities where the work was carried out, and that, if accepted, it will not be published elsewhere in the same form, in English or in any other language, including electronically without the written consent of the copyright-holder. In particular, translations into English of papers already published in another language are not accepted.

No other forms of scientific misconduct are allowed, such as plagiarism, falsification, fraudulent data, incorrect interpretation of other works, incorrect citations, etc. The National Academy of Sciences of the Republic of Kazakhstan follows the Code of Conduct of the Committee on Publication Ethics (COPE), and follows the COPE Flowcharts for Resolving Cases of Suspected Misconduct ([http://publicationethics.org/files/u2/New\\_Code.pdf](http://publicationethics.org/files/u2/New_Code.pdf)). To verify originality, your article may be checked by the Cross Check originality detection service <http://www.elsevier.com/editors/plagdetect>.

The authors are obliged to participate in peer review process and be ready to provide corrections, clarifications, retractions and apologies when needed. All authors of a paper should have significantly contributed to the research.

The reviewers should provide objective judgments and should point out relevant published works which are not yet cited. Reviewed articles should be treated confidentially. The reviewers will be chosen in such a way that there is no conflict of interests with respect to the research, the authors and/or the research funders.

The editors have complete responsibility and authority to reject or accept a paper, and they will only accept a paper when reasonably certain. They will preserve anonymity of reviewers and promote publication of corrections, clarifications, retractions and apologies when needed. The acceptance of a paper automatically implies the copyright transfer to the National Academy of Sciences of the Republic of Kazakhstan.

The Editorial Board of the National Academy of Sciences of the Republic of Kazakhstan will monitor and safeguard publishing ethics.

Правила оформления статьи для публикации  
в журнале смотреть на сайте:

[www.nauka-nanrk.kz](http://www.nauka-nanrk.kz)

<http://chemistry-technology.kz/index.php/en/arhiv>

**ISSN 2518-1491 (Online), ISSN 2224-5286 (Print)**

Редакторы: *М. С. Ахметова, Т. А. Апендиев, Аленов Д. С.*  
Верстка на компьютере *А. М. Кульгинбаевой*

Подписано в печать 05.08.2019.  
Формат 60x881/8. Бумага офсетная. Печать – ризограф.  
5,25 п.л. Тираж 300. Заказ 4.