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

ҚАЗАҚСТАН РЕСПУБЛИКАСЫ
ҰЛТТЫҚ ҒЫЛЫМ АКАДЕМИЯСЫНЫҢ

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

ХАБАРЛАРЫ

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 (442)

JULY – AUGUST 2020

PUBLISHED SINCE JANUARY 1947

PUBLISHED 6 TIMES A YEAR

ALMATY, NAS RK

Clarivate
Analytics

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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. Webof 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.

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«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 Ақпарат және қоғамдық даму министрлігінің Ақпарат комитетінде 29.07.2020 ж. берілген **№ KZ66VPY00025419** мерзімдік басылым тіркеуіне қойылу туралы куәлік.
Мерзімділігі: жылына 6 рет.
Тиражы: 300 дана.

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

Редакцияның мекенжайы: 050100, Алматы қ., Қонаев к-сі, 142, «Д. В. Сокольский атындағы отын, катализ және электрохимия институты» АҚ, каб. 310, тел. 291-62-80, факс 291-57-22, e-mail:orgcat@nursat.kz

Типографияның мекенжайы: «NurNaz GRACE», Алматы қ., Рысқұлов көш., 103.

«Известия НАН РК. Серия химии и технологий».
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 Министерства информации и общественного развития Республики Казахстан **№ KZ66VPY00025419**, выданное 29.07.2020 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

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

Адрес типографии: «NurNaz GRACE», г. Алматы, ул. Рыскулова, 103.

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 periodical printed publication in the Committee of information of the Ministry of Information and Social Development of the Republic of Kazakhstan **No. KZ66VPY00025419**, issued 29.07.2020.
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

Editorial address: JSC «D.V. Sokolsky institute of fuel, catalysis and electrochemistry», 142, Kunayev str., of. 310, Almaty, 050100, tel. 291-62-80, fax 291-57-22, e-mail: orgcat@nursat.kz

Address of printing house: «NurNaz GRACE», 103, Ryskulov str, Almaty.

OF THE NATIONAL ACADEMY OF SCIENCES OF THE REPUBLIC OF KAZAKHSTAN
SERIES CHEMISTRY AND TECHNOLOGY
ISSN 2224-5286 **https://doi.org/10.32014/2020.2518-1491.72**
Volume 4, Number 442 (2020), 112 – 119

UDC 544.478; 542.97; 665.612.3; 546.264-31
IRSTI 31.15.28

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BIMETALLIC Co-Pd CATALYSTS FOR DRY AND BIREFORMING OF METHANE

Abstract. Carbon dioxide reforming of methane represents a promising method to effectively convert both greenhouse gases – CH_4 and CO_2 into valuable energy resources *via* syngas. Adding steam to a feed allow to adjust syngas composition that is important for its following application. This work considers the bimetallic Co-based catalyst modified with additive of noble metal – Pd and supported on alumina tested in the dry (DRM) and combined steam-dry (CSDR) reforming so-called bireforming of methane (BRM) to produce synthesis gas with a controllable ratio of H_2/CO. The addition of small amount of noble metal (2-5% from total metal mass) to the Co-based catalyst caused an increase in efficiency of the catalyst in the both processes. The bimetallic 5%Co-Pd/Al_2O_3 catalyst revealed the high stable activity and selectivity during its long-term continuous testing. Thus, in BRM the extent of conversion of CH_4 and CO_2 are 93 and 84% respectively at t = 700°C, CH_4:CO_2:H_2O = 1:1:0.5 under atmospheric pressure. No losses of activity and selectivity of the 5%Co-Pd(4.9:0.1)/Al_2O_3 catalyst were observed during for 100 hours of its continuous operation. The catalysts were characterized by BET, SEM, TEM, and TPR methods. The catalysts studied can be considered as a prospective base to develop the effective catalysts for methane conversion into valuable syngas with controllable ratio.

Key words: Dry Reforming of Methane, Bireforming of Methane, Syngas, Bimetallic Co-Pd supported catalysts.

1. **Introduction.** It is known that the reserves of dominantly used fossil fuel (crude oil) are depleting. On the other hand, natural gas, which is primarily composed of methane, is expected to last longer than oil reserves. Current industrial processes utilize methane as a main feedstock for converting it to the valuable synthesis gas (syngas, a mixture of CO and H_2) which is further used in diverse downstream processes, such as production of oxygenated compounds, methanol synthesis, Fischer-Tropsch (FT) synthesis for production of liquid hydrocarbons and numerous other carbonylation and hydrogenation or reduction processes [1-2].

The most common methane reforming processes for hydrogen production are known as: “steam reforming (SRM)”, “partial oxidation (POM)”, “dry reforming (DRM)” or combination of the exothermic POM process with endothermic ones – SRM or DRM “autothermal reforming (ATR)” and are still developed [2-9]. All processes represent itself oxidative reactions that collectively named in the literature as oxyforming processes [10].

In various reforming processes, biogas can be used as a methane source, which directly depends on its composition. In general, syngas and H_2 from syngas can be produced by methane or biogas reforming in a wide temperature range of 600-1000°C (endothermic and reversible reactions), involving predominantly catalytic processes that are often combined. Both reforming processes can be performed under low pressure (in most cases under atmospheric pressure) in tubular fixed-bed or fluidized reactors [11-13].

In DRM and SRM, methane, the most abundant hydrocarbon, is reformed through the reactions (1)-(4) to H_2, CO and CO_2. These reactions take place catalytically at temperatures as high as 800 °C for satisfactory methane conversion [1, 14-15].

$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2$ $\Delta H°_{298}$= 247.3 kJ mol^{-1} (Eq. 1)

$CH_4 + H_2O \leftrightarrow CO + 3H_2$ $\Delta H°_{298}$ = 206.1 kJ/mol (Eq. 2)

$CO + H_2O \leftrightarrow CO_2 + H_2$ $\Delta H°_{298}$ = -41.17 kJ/mol (Eq. 3)

$CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2$ $\Delta H°_{298}$ = 165.0 kJ/mol (Eq. 4)

Although SRM producing CO and H_2 (Eq. 2) has great energy expenditure, this is the most widespread industrial route to obtain H_2. The H_2/CO ratio produced in SRM is equal to three, therefore this way is the most appropriate one from the H_2 generation point of view [11]. The Water-Gas Shift Reaction, commonly known as "Shift Reaction" (Eq. 3), occurring in DRM and SRM processes enables to produce an additional amount of H_2. Equation 4 shows the reaction of methane SR associated with the Shift Reaction [2, 11, 16-17].

Currently, a combination of SR with DR of methane has attracted much attention. The H_2/CO product ratio can be controlled by changing the H_2O/CO_2 ratio in the reaction feed [18-19], thus it is feasible to produce synthesis gas with the H_2/CO ratio of about 2, which is suitable for the methanol and Fisher–Tropsch syntheses [1-2]. Addition of steam to the feed has some practical benefits over CH_4 reforming with CO_2 alone: (i) the carbon formation is reduced because of the oxidation of carbonaceous species, and (ii) syngas with a broader range of H_2/CO ratios can be produced by alteration of the relative concentrations of steam and CO_2 in feed stream based on the final FT products [1-2, 18-19].

Transition metals such as Ni, Pt, Rh or Pd possess the catalytic activity in SRM, among them the Ni catalysts have the advantage of having lower costs. On the other hand, Ni has greater deactivation susceptibility by the coke formation due to the high temperatures used, which makes the Pt and Pd catalysts interesting with regards to stability. The most active catalysts for DRM, reported in literature, are those that use the transition metals of the group 8 of the Periodic Table, particularly Pt, Rh, and Ru. These metals have been used as catalysts for the DRM because of their excellent catalytic reactivity and anti-coking property [7-8]. However, these metals are expensive and less abundant and are therefore not suitable for commercial applications. More affordable transition metals such as Ni and Co have been studied as alternative catalysts for the DRM because of their low cost and good catalytic performance [20-21]. Addition of noble metals in small amount can be used to enhance the catalyst stability.

Earlier we have studied the 5%Co-Pd system supported on alumina demonstrated activity in dry conversion of methane with producing syngas and oxygenates under elevated pressure and relatively low temperature [22]. Interaction in a bimetallic Co-Pd system supported on a solid support material can play an important role in determining the catalytic performance to achieve high effective catalysts for syngas production either by dry or combined dry-steam reforming of methane. In this paper we report the experimental results on testing the bimetallic Co-based alumina supported catalyst modified with a low amount of noble metal – Pd (2-5% from total metal content) in DRM and BRM.

2. **Experimental.** The bimetallic 5%Co-Pd/Al_2O_3 catalysts were synthesized by co-impregnation method and tested in dry and combined dry-steam reforming of methane. The total content of Co and Pd metals was equal to 5% of the catalyst mass. Ratio of Co:Pd is varied from 98:2 to 95:5 that corresponds to 4.75÷4.9/0.1÷0.25 mas.%. The processes were carried out in a tubing quartz reactor equipped with a heating furnace, a syringe pump, and mass flow controllers. Prior to the reaction, the catalyst sample in the amount of 6 ml was loaded into the reactor and pretreated by H_2 at 300°C for 1 h.

Testing the catalysts in DRM, CSDRM and SRM have been carried out using a feed – $CH_4:CO_2:H_2O=1/0\div1/0.5\div1$, varying temperature within 300-800°C, P_{atm} and gas hourly space velocity (GHSV) varying within 1000-2000 h^{-1}. "Pure" feed without diluting by inert gas have been used. The duration of each test under the certain conditions (temperature, feed ratio, and GHSV) was 10-12 hours. With an aim to determine the catalyst stability, the continuous long-term test of the catalyst 100 hours was carried out in bireforming of methane, because of it has high level conversion of methane.

Initial and final gas products were analyzed using on-line the GCs with a TCD (Chromatek-Krystall-5000 and Chromatek-Gazochrom-2000 using columns: Hayesep N, NaX, CaX and activated carbon;

carrier gases are Ar and air). The CH_4 and CO_2 conversion and H_2/CO ratio were calculated using the following formulas (1-3):

$$X(CH_4) = \frac{[CH_4]_{in} - [CH_4]_{out}}{[CH_4]_{in}} \times 100 \qquad (1)$$

$$X(CO_2) = \frac{[CO_2]_{in} - [CO_2]_{out}}{[CO_2]_{in}} \times 100 \qquad (2)$$

$$^{H_2}/_{CO} = \frac{[H_2]_{out}}{[CO]_{out}} \qquad (3)$$

where $X(CH_4)$ is conversion of methane (%), $X(CO_2)$ is conversion of carbon dioxide (%).

The conversion of water was not calculated because of the difficulties in differentiating unreacted water and water formed by the secondary reaction. The yields of the reaction products, hydrogen ($Y(H_2)$) and carbon oxide ($Y(CO)$), expressed in micromoles formed by 1 gram of the catalyst per second (μmol/g/s) were calculated, and thus selectivity and productivity of the catalyst were assessed and compared.

To understand the effects of the reaction feed and process conditions on the catalyst characteristics, the physico-chemical properties of the catalysts were characterized by BET, SEM, TEM, and TPR methods before and after reaction.

3. Results and discussion

3.1 Catalyst characterization

XRD analysis of fresh and spent samples of 5%Co-Pd/Al_2O_3 catalysts did not reveal phases except γ-alumina characterized by reflexes of 1.39, 1.98 and 2.42 (ASTM 10-425). This can be caused by a high dispersion of the metal phase and/or their X-Ray amorphous state. The TEM analysis confirmed the high dispersion of metallic particles: their sizes were less than 3 nm. No sintering of the particles was observed after the catalyst operation.

The BET surface area of the 5%Co-Pd(4.9:1)/Al_2O_3 catalyst was markedly decreased from 159.1 to 89.3 m^2/g after its long-term operation in both DRM and BRM processes. One of the possible reasons for this may be the presence of the residual reaction products adsorbed on the catalyst surface, which was not treated after testing and prior BET study.

The addition of a noble metal, Pd, has a significant effect on the reducibility of cobalt oxides. This has been demonstrated by means of TPR-study. Figure 1 shows the effect of Pd additive on Co reduction. There is a two-step reduction *via* $Co_3O_4 \rightarrow CoO \rightarrow Co^\circ$ as it was proposed earlier for a similar Co-based catalyst [23]. It is clear from Figure 1 that the reduction temperatures of the Co oxides are significantly shifted to lower values. The shift is enhanced with increase in Pd amount. Thus, the first and second peaks corresponding to the reduction of Co_3O_4 and CoO respectively are shifted in the following sequence of 230 → 210 → 190°C and 410 → 380 → 328°C, respectively, while the Pd content is increased from 0.25 to 1.5 mas.% (figure 1).

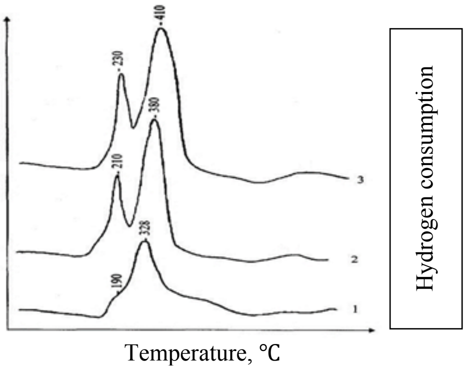

Figure 1 – H_2-TPR profiles of the 5%Co-Pd/Al_2O_3 catalysts with varying content of Pd:
1– Co-Pd(3.5:1.5); 2 – Co-Pd (4.5:0.5); 3 – Co-Pd(4.75:0.25)

3.2 Catalyst test

The Co-containing alumina supported bimetallic catalysts – 5%Co-Pd/Al_2O_3 were examined in dry (DRM) and bireforming (BRM) of methane. Due to the highly endothermic nature of reforming reactions (Eqs.1-2), the temperature has the most significant effect on methane reforming. Conversion CH_4 and CO_2 as well as yields of H_2 and CO in DRM and BRM as a function of temperature are exhibited in figures 2 and 3, respectively. In DRM, the yields of hydrogen and carbon oxide are grown with increase in temperature and are almost the same over the entire temperature range studied. Their values reach 15.03 and 15.3 μmol/g·s respectively at 700℃ (figure 2). Whereas in BRM under the same conditions: t=700℃ and ratio C/O=1 in a feed the yield of hydrogen is slightly higher – 15.5 and Y(CO) decreases to 11.1 μmol/g·s (figure 3). These results may be explained by lower content of C and higher H in a feed: CH_4:CO_2=1:1 (DRM) and CH_4:CO_2:H_2O=1:0.5:0.5 (BRM). Accordingly, the ratio of H_2/CO is higher in BRM – 1.4 in contrast to DRM – 1.0. Extents of methane and carbon dioxide conversion are 82.7 and 85.6% and 91.1 and 78.3% in DRM and BRM, respectively. Enhanced conversion of CO_2 is caused by its twice lower content in the BRM feed.

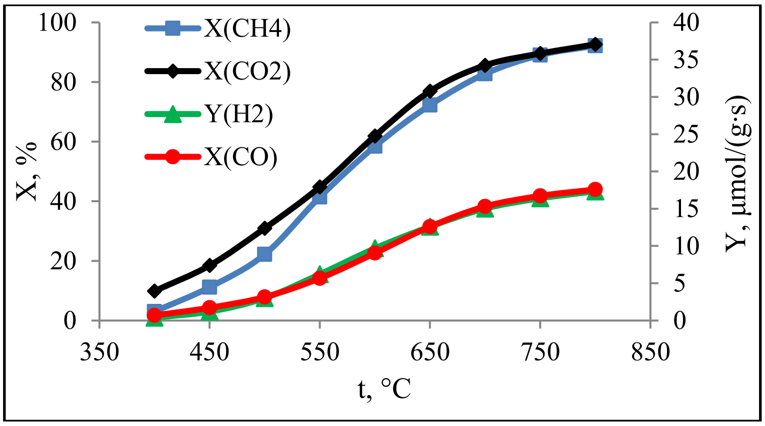

Figure 2 – Effect of the temperature on the DRM over 5%Co-Pd(4.9:0.1)/Al_2O_3 under P=1 atm, CH_4:CO_2=1:1, GHSV=1000 h^{-1}

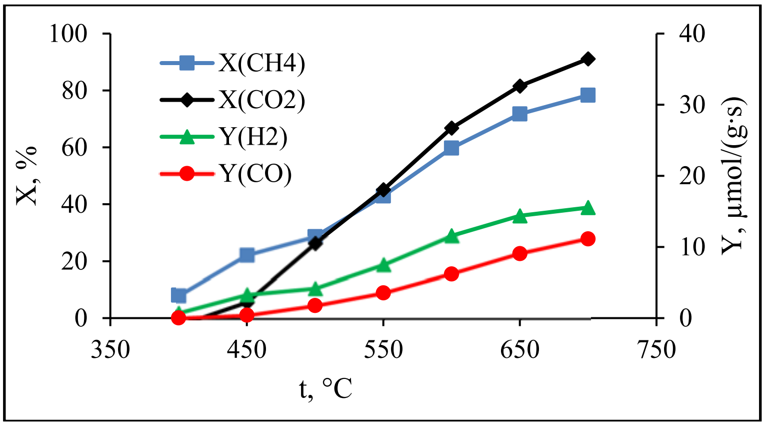

Figure 3 – Effect of the temperature on the BRM over 5%Co-Pd(4.9:0.1)/Al_2O_3 under P=1 atm, CH_4:CO_2:H_2O=1:0.5:0.5, GHSV=1000 h^{-1}

The 5%Co-Pd(4.9:0.1)/Al_2O_3 has been long-term tested in BRM in order to determine the catalyst stability. During 100 hours of testing, the catalyst retained its activity: X(CH_4)≈93 and X(CO_2) ≈84% on average and produced syngas with the same yield and consequently selectivity: Y(H_2) ≈18.5 and Y(CO)≈15.4 μmol/g*s under the following conditions: CH_4:CO_2:H_2O=1:1:0.5, P=0.1 MPa, T=700°C, GHSV=1250 h^{-1} (Fig.4). The ratio of H_2/CO=1.2.

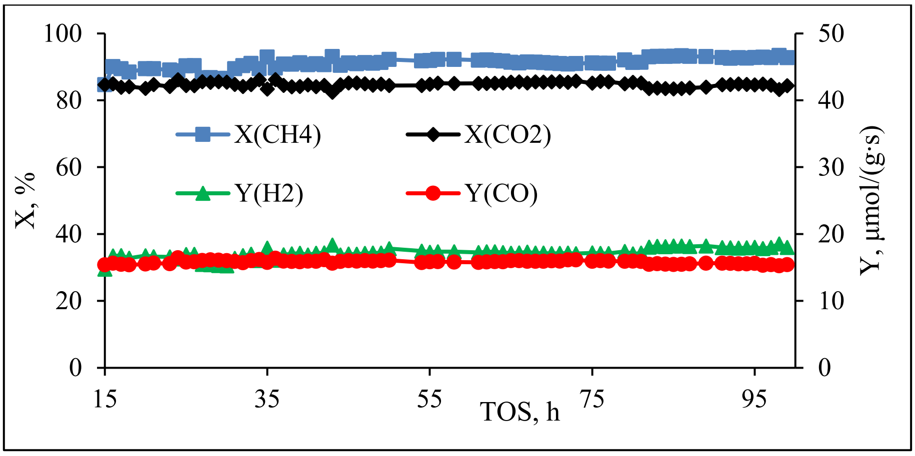

Figure 4 – Effect of time on stream on BRM over the 5%Co-Pd(4.9:0.1)/Al_2O_3 catalyst under P=1 atm, CH_4:CO_2:H_2O=1:1:0.5, GHSV=1250 h^{-1}, t=700°C

In table 1, the comparison of DRM and BRM is presented at varying ratios of reagents (CH_4, CO_2, H_2O) in a feed. In terms of high methane conversion and hydrogen yield, the content of both O and H in a reagent mix should be higher. Both CO_2 and H_2O facilitate carbon removal from the catalyst surface.

Table 1 – Effect of feed composition on methane conversion and yield of products over 5%Co-Pd(4.9:0.1)/Al_2O_3 catalyst under P=1 atm and t=700°C

Process	Feed: ratio, vol.				Conversion, %		Yield, µmol/g*s		Ratio of H_2/CO
	reagents	C/O/H	O/C	H/C	CH_4	CO_2	H_2	CO	
DRM	CH_4:CO_2=1:1	2/2/4	1	2	82.7	85.6	15.03	15.3	~ 1
BRM	CH_4:CO_2:H_2O=1:0.5:0.5	1.5/1.5/5	1	3.3	78.3	91.1	15.5	11.1	1.4
BRM	CH_4:CO_2:H_2O=1:1:0.5	2/2.5/5	1.25	2.5	93	84	18.5	15.4	1.2

The synthesized Co-Pd/Al_2O_3 catalysts have showed the high activity and stability in methane reforming. The high activity of the bimetallic catalysts is the result of the Co-Pd interaction demonstrated by H_2-TPR. Addition of Pd facilitates Co reproducibility. As well as metal-metal and metal-support interaction can prevent the sintering of small metal species into big particles and the coke formation. No visible coke formation was observed after long-term testing of the catalyst. No coke and metal sintering were revealed by TEM-study too.

Conclusions. The bimetallic 5%Co-Pd/Al_2O_3 catalysts with small amount of Pd – 0.1-0.25 mas.% have performed the high stable activity and selectivity in reforming of methane under atmospheric pressure and elevated temperatures producing syngas with H_2/CO ratio varied depending on the feed composition. Conversion of CH_4 and CO_2 is varied within 78-93% at 700°C. No loss of activity and selectivity of the 5%Co-Pd(4.9:0.1)/Al_2O_3 catalyst was observed during for 100 hours of its continuous operation.

The addition of Pd to the Co-based catalyst is accompanied with formation of the high dispersed state of metals as well as increasing in Co reducibility due to the Co-Pd interaction. In summary, the Co-Pd systems studied can be considered as a prospective base to develop the effective catalysts for methane conversion into valuable syngas with controllable ratio by regulating steam content in an initial feed CH_4:CO_2:H_2O.

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

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МЕТАННЫҢ СУСЫЗ ЖӘНЕ БИРЕФОРМИНГІНЕ АРНАЛҒАН БИМЕТАЛДЫ Co-Pd КАТАЛИЗАТОРЛАР

Аннотация. Метанның көмірқышқылды конверленуі қоспарникті газды (CH_4 және CO_2) синтез-газ арқылы бағалы энергия ресурстарына айналдыратын болашағы зор тиімді әдіс болып саналады. Шикізатқа су буының қосылуы синтез-газды алдағы уақытта қолдануда маңызды құрамының реттелуіне мүмкіндік береді, сонымен қатар кокс түзілісін төмендетеді. Бұл жұмыс Pd асыл металл үлесі негізінде модифицирленген Co құрамды биметалды катализаторды метанның көмірқышқылды (сусыз риформингі) және H_2/CO қатынасының реттелуі негізінде синтез-газ алуға мүмкіндік тудыратын булы көмірқышқылды (метан бириформингі) конверленуінде зерттеуге негізделген. Катализатор қасиеттері БЭТ, СЕМ, ЖЭМ және ТБТ әдістері арқылы сипатталды.

5%Co-Pd/Al_2O_3 биметалды катализаторлары біріккен сіңіру әдісі негізінде синтезделді және метанның көмірқышқылды және булы көмірқышқылды риформингінде сыналды. Co және Pd металының жалпы мөлшері катализатор массасының 5%-ын құрайды. Co:Pd қатынасы 98:2-ден 95:5-ке дейін ауытқиды, яғни 4,75÷4,9/0,1÷0,25 (%) массалық құрамына сәйкес келеді. Үдеріс қыздыру пеші, шприц сорғысы және газ шығынын бақылағыштармен жабдықталған құбырлы кварц реакторында жүргізілді.

5%Co-Pd/Al_2O_3 катализаторларының бастапқы қолданылған сынамаларының РФА талдамасы 1,39, 1,98 және 2,42 (ASTM 10-425) рефлекстері арқылы сипатталған γ-алюминий тотығынан басқа фазаларды көрсетпеді. Бұл металл фазасының жоғары дисперстілігіне немесе олардың ренгенді аморфтық күйіне байланысты болуы мүмкін. ЖЭМ талдамасы металдық ұсақ бөлшектердің жоғары дисперсті күйде екенін дәлелдейді: өлшемі 3 нм-ден кіші болып көрінді. Катализатор жұмысынан кейін ұсақ бөлшектердің бірігу үдерісі байқалмады. Co құрамды катализаторға аз мөлшерде Pd (металл массасының 2-5%-ы) қосылғандықтан, металдар жоғары дисперсті күйге келді, сонымен қатар Co-Pd өзара қатынас нәтижесінде Co тотықсыздануының артуы ЖБТ зерттеуі негізінде расталды.

Co құрамды катализаторға аз мөлшердегі асыл металдың қосылуы екі үдеріс кезінде катализатор әсерін ұлғайтты. 5%Co-Pd/Al_2O_3 катализаторлары метанның көмірқышқылды және булы көмірқышқылды конверленуінде сыналды. Конверлеу реакцияларының жоғарғы эндотермиялық сипатына байланысты температураның метан конверленуіне айтарлықтай өте жоғары әсері бар. Реагенттердің конверлену дәрежесі және өнімдердің шығымы 400-ден 800°С-ге дейін температураның жоғарылау бойымен артады. Сутегі мен көміртек монототығының шығымы МКҚК-де зерттелген температураның барлық аумағында біркелкі болып келеді және сәйкесінше 800℃-де 15,03 мкмоль/г·с-ке тең. МБКҚК-де сутегінің шығымы 15,5-ке дейін артады, ал CO шығымы 11,1 мкмоль/г·с-ке дейін төмендеді (CH_4:CO_2:H_2O=1:0,5:0,5). Сәйкесінше, H_2/CO қатынасы МБКҚК үдерісінде МКҚК-іне – 1,0 қарағанда жоғары – 1,4-ке тең. Метанның және көміртек қос тотығының конверлену дәрежесі МКҚК жағдайында 82,7 және 85,6%-ды құрады, сәйкесінше, МБКҚК жағдайында 91,1 және 78,3%-ға тең.

5%Co-Pd/Al_2O_3 биметалды катализатор ұзақмерзімді үздіксіз сынау кезінде жоғары тұрақты белсенділікті және талғамдылды көрсетті. 5%Co-Pd(4,9:0,1)/Al_2O_3 катализатордың белсенділігі мен талғамының төмендеуі 100 сағат тұрақты жұмыс атқарғанда байқалмады. Орта есеппен $X(CH_4)\approx 92$ және $X(CO_2)\approx 84\%$ тең, ал келесі үдеріс (CH_4:CO_2:H_2O=1:1:0,5, P=0,1 МПа, T=700°C, GHSV=1250 $ч^{-1}$) жағдайында синтез-газ біркелкі талғаммен $Y(H_2)\approx 18{,}5$ және $Y(CO)\approx 15{,}4$ мкмоль/г·с алынады. H_2/CO қатынасы 1,2-ге тең. Ұзақмерзімді сынақтан кейін көрінетін кокс түзілусі байқалмады.

Сондықтан 5%Co-Pd/Al_2O_3 биметалды катализатор атмосфералық қысым кезінде және жоғары температурада шикізат құрамына байланысты өзгеріп отыратын H_2/CO қатынасы тән синтез-газ түзілісімен жүретін метанның конверлену үдерісінде жоғары және тұрақты белсенділікті көрсетті. Зеттелген катализаторларда МКҚК және МБКҚК үдерісінің салыстырылу жағдайы метанның конверлену температурасының төмендеуі тұрғысында қарағанда МБКҚК тиімді екендігі көрінді. Co-Pd қарастырылған жүйелерін метанды бақыланатын қатынасқа ие (берілетін шикізатқа су буының берілуін реттеу арқылы) синтез-газға конверлеуге арналған тиімді катализаторлар жасау үшін келешегі бар негіз ретінде қарастыруға болады.

Түйін сөздер: метанның сусыз риформингі, метан бириформингі, синтез-газ, Co-Pd биметалды орнатылған катализаторлар.

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БИМЕТАЛЛИЧЕСКИЕ Co-Pd КАТАЛИЗАТОРЫ ДЛЯ СУХОГО РИФОРМИНГА И БИРИФОРМИНГА МЕТАНА

Аннотация. Углекислотная конверсия метана является многообещающим способом эффективного преобразования обоих парниковых газов – CH_4 и CO_2 в ценные энергетические ресурсы через синтез-газ. Добавление паров воды в исходную смесь позволяет регулировать состав синтез-газа, что важно для его дальнейшего использования, а также снизить коксообразование. Данная работа посвящена исследованию биметаллического кобальтсодержащего катализатора модифицированного добавлением благородного металла – Pd, нанесённого на оксид алюминия, в процессах углекислотной (УКМ) и пароуглекислотной (ПУКМ) конверсии метана для получения синтез-газа с контролируемым соотношением H_2/CO. Свойства катализатора были охарактеризованы методами БЭТ, СЭМ, ПЭМ и ТПВ.

Биметаллические 5%Co-Pd/Al_2O_3 катализаторы были синтезированы методом совместной пропитки и протестированы в процессах углекислотной и пароуглекислотной конверсии метана. Общее содержание металлов Co и Pd равнялось 5% от массы катализатора. Соотношение Co:Pd варьировалось от 98:2 до 95:5, что соответствует их массовому содержанию 4.75÷4.9/0.1÷0.25 (%). Процессы проводились в проточном кварцевом реакторе, оснащённом нагревателем, шприцевым насосом и регуляторами массовых потоков.

РФА анализ исходного и использованного образцов катализаторов 5%Co-Pd/Al_2O_3 не выявил наличия каких-либо фаз, кроме γ-оксида алюминия, характеризующегося набором рефлексов: 1,39, 1,98 and 2,42 (ASTM 10-425). Это может быть связано с высокой дисперсностью металлической фазы и/или её рентгеноаморфным состоянием. Исследование методом ПЭМ подтвердило высокую дисперсность металлических частиц: их размер составил менее 3 нм. Спекания частиц после проведения процессов не наблюдалось. Добавление небольших количеств Pd (2-5% от общей массы металлов) к кобальтсодержащему катализатору сопровождалось образованием высокодисперсного состояния металлов, а также увеличением восстанавливаемости Co в результате взаимодействия Co-Pd, что подтверждается данными ТПВ-исследования.

Добавление небольших количеств благородного металла в кобальтсодержащем катализаторе привело к увеличению его эффективности в обоих процессах. Катализаторы – 5%Co-Pd/Al_2O_3 были испытаны в процессах углекислотной и пароуглекислотной конверсии метана. В связи с высоко эндотермическим характером реакций конверсии температура имеет наиболее значительное влияние на конверсию метана. Степени конверсии реагентов и выходы продуктов растут с ростом температуры от 400 до 800°C. Выходы водорода и монооксида углерода практически одинаковы в процессе УКМ (CH_4:CO_2=1:1) во всём исследованном температурном интервале и равны 15.3 мкмоль/г·с при 700°C. В процессе ПУКМ при таких же температуре и соотношении C/O=1 в исходной смеси (CH_4:CO_2:H_2O=1:0,5:0.5) выход водорода несколько выше – 15.5, тогда как Y(CO) понижается 11.1 мкмоль/г·с. Соответственно соотношение H_2/CO выше в процессе ПУКМ – 1,4 по сравнению с УКМ – 1.0. Степени конверсии метана и диоксида углерода составили 82.7 и 85.6% в случае УКМ и 78.3 и 91.1% в случае ПУКМ, соответственно.

Биметаллический катализатор 5%Co-Pd/Al_2O_3 проявил высокую стабильную активность и селективность в течение продолжительных непрерывных испытаний. Снижения активности и селективности катализатора 5%Co-Pd(4.9:0.1)/Al_2O_3 не наблюдалось в течение 100 часов его постоянной работы. X(CH_4)≈92 и X(CO_2) ≈84% в среднем, синтез-газ образуется с одинаковым выходом: Y(H_2) ≈18.5 и Y(CO)≈15.4 мкмоль/г·с при следующих условиях: CH_4:CO_2:H_2O=1:1:0.5, P=0.1 MPa, T=700°C, GHSV=1250 h^{-1}. Соотношение H_2/CO=1,2. Видимого образования кокса после длительных испытаний не наблюдалось.

Таким образом, биметаллический катализатор 5%Co-Pd/Al_2O_3 проявляет высокую и стабильную активность в процессах конверсии метана при атмосферном давлении и повышенных температурах с образованием синтез-газа с соотношением H_2/CO, меняющимся в зависимости от состава сырья. Сравнение процессов УКМ и ПУКМ на исследованных катализаторах показывает, что ПУКМ более эффективен с точки зрения снижения температуры конверсии метана. Приведенные системы Co-Pd можно рассматривать как перспективную основу для разработки эффективных катализаторов для конверсии метана в синтез-газ с контролируемым соотношением посредством регулирования содержания паров воды в подаваемом сырье – CH_4:CO_2:H_2O.

Ключевые слова: сухой риформинг метана, бириформинг метана, синтез-газ, биметаллические Co-Pd нанесенные катализаторы.

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

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

Подписано в печать 06.09. 2020.
Формат 60x881/8. Бумага офсетная. Печать – ризограф.
9 п.л. Тираж 300. Заказ 4.

Национальная академия наук РК
050010, Алматы, ул. Шевченко, 28, т. 272-13-18, 272-13-19