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Carbon Dioxide Conversion of Real Associated Gases in Presence of Water Over the KMR-8 Catalyst

Sholpan S. Itkulova and Gaukhar D. Zakumbaeva*

*D.V. Sokolsky Institute of Organic Catalysis & Electrochemistry
142 Kunaev st., Almaty, 050010 Republic Kazakhstan¹*

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The new supported zeolite-containing catalyst has been investigated in the reaction of interaction between carbon dioxide and real associated petroleum gases (APG) in presence of water steam at varying experiment temperature within a range of 300-900 °C and space velocity from 1000 to 6000 hr⁻¹. It has been shown that the catalyst performs the high activity in reforming of APG. At 800 °C, the complete conversion of C₂₊ hydrocarbon fraction is occurred, degree of methane conversion gets 92.2 and carbon dioxide conversion – 93.4 %. The main product of reaction is synthesis-gas (mix of carbon oxide and hydrogen) with a ratio of H₂/CO=1.4 at 800 °C. Also water and traces of oxygenates (basically acetic acid) are produced at T ≤ 600 °C. The catalyst works with practically the same activity at increasing space velocity by 4 times. The advantages of the synthesized catalyst are its activity, selectivity, stability, ability to work in water presence, and resistance to coke formation.

Keywords: carbon dioxide conversion, associated gases, synthesis-gas.

Introduction

Associated petroleum gas (APG) is still burned in Kazakhstan. Kazakhstan ranks the fifth place on amount of burned APG (Russian Federation is in the lead). Information on total amount of burned gases in Kazakhstan is not complete and has an inconsistent character. In 2008 according to the official data the gross output was 33.5 bln. m³ at that volume of burned associated gases was decreased to 1.8 bln. m³ [1].

From 25 to 1000 m³ of associated gases is extracted at producing 1 ton of oil at the Kazakhstan's oil and oil-gas condensate fields. In a best case they are squeezed into oil reservoir. This approach does not solve the problem of

utilization of associated gases. Moreover as a rule it leads to raising the gas amount at the following oil extraction and increase in cost for re-squeezing.

At APG combustion, the high value hydrocarbon raw material is aimlessly burned that is accompanied with carbon dioxide and hazardous sulfur and nitrogen oxides formation. Carbon dioxide among these anthropogenic gases is a main greenhouse gas. The amount of carbon dioxide formed exceeds twice the amount of burned fuel.

Obviously that burning of APG is unacceptable from a point of view of environment protection and resource-saving. One of decisions

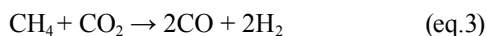
* Corresponding author E-mail address: itkulova@nursat.kz

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of this problem is creation of infrastructure for APG collection, their transportation, purification, separation, and squeezing into main pipe line that requires the huge investments [2].

Other way is processing of APG into motor fuel, methanol, and other high value products directly at the oil fields [2-4]. The light hydrocarbons in composition of APG can be converted into liquid products by so called GTL process (Gas-To-Liquid) [4], and also they can be a source for hydrogen production [5]. The GTL process has been considered as a clean and alternative process in an environmental respect.

Light hydrocarbons can be converted into syngas. Syngas, a mixture of H₂ and CO is a major feedstock for methanol, ammonia and Fischer–Tropsch (F–T) synthesis. There are three main catalytic ways for syngas production from hydrocarbon feed with involving: 1) water – steam reforming (equation1), 2) half oxygen – partial oxidation (equation2); and 3) carbon dioxide – dry reforming (equation 3). The last one attracts interest because of allows utilizing greenhouse gases – methane and carbon dioxide with producing syngas with a ratio of H₂/CO = 1 [6-10].



Also the combination of these methods is possible. For example, combined steam and carbon dioxide reforming of methane is a suitable process for the direct control of the H₂/CO ratio by regulating the H₂O/CO₂ feed ratio [11]. This process allows using the real petroleum gases

containing water and carbon dioxide without their extraction and drying.

The aim of this study was the development and test of the new catalyst – KMR-8 for converting the real associated gases by involving into the process carbon dioxide in presence of water (carbon dioxide – steam reforming or bi-reforming).

Experimental

The catalyst – KMR-8 with total metal content – 5 weight % supported on alumina promoted with zeolite has been synthesized and tested in conversion of real associated gases (APG) from one of the Kazakhstan’s oil field. The reforming of APG by carbon dioxide at presence of water (bi-reforming process) was carried out in a flow quartz reactor at atmospheric pressure and varying experiment temperature from 300 to 900 °C and space velocity from 1000 to 6000 hr⁻¹. The catalyst loading was 10-30 mL. Ratio of CO₂:APG:H₂O was constant – 1:1:0.1.

The composition of associated gases extracted from one of oil wells of the West Kazakhstan is presented in Table 1.

The set was combined with gas chromatographs (GC) equipped with thermal conductivity detector for on-line analysis of H₂, Ar, CO, CH₄, O₂, CO₂ (columns: molecular sieves and activated coal) and flame-ionization detector (FID) for on-line analysis of hydrocarbons (column: modified alumina). Liquid phase was collected in a special cooled trap (separator) and then analyzed by GC equipped with FID on columns: Carbowax/Carbopak and Poropak N, as well as by IR-spectroscopy. The carbon formation was controlled by thermogravimetric

Table 1. Hydrocarbon composition of real associated gas extracted from one of oil well of the West Kazakhstan

Hydrocarbons	C ₁	C ₂	C ₃	C ₄	C ₅	C ₆	C ₇
Content, vol. %	52.1	20.1	14.0	8.1	4.4	1.1	0.2

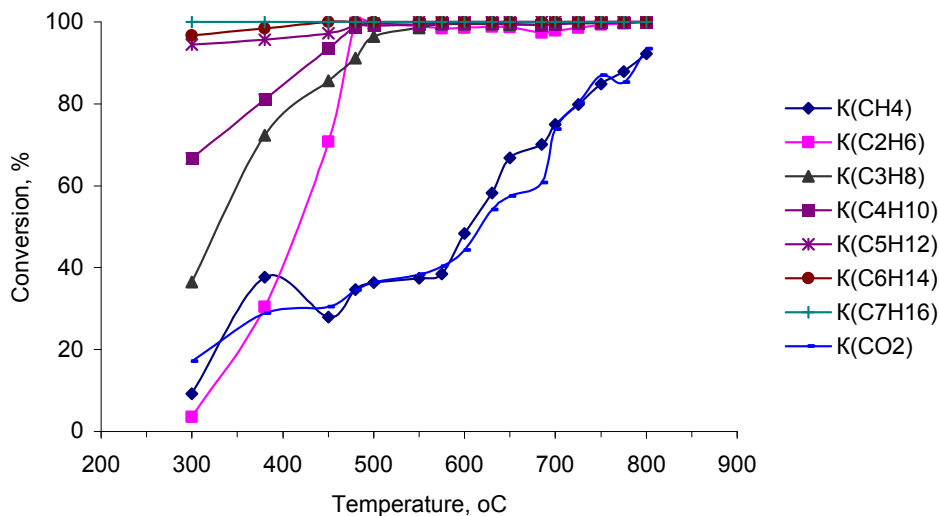


Fig. 1. Effect of temperature on conversion degree of hydrocarbons and CO₂ at bi-reforming of associated gases over the KMR-8 catalyst

analysis (TGA), thermo-programmed reduction (TPR) and electron microscopy.

The catalyst was studied with using BET, IR-spectroscopy and electron microscopy.

Results and discussion

The hydrocarbons are converted with noticeable activity in carbon dioxide – steam reforming (bi-reforming) over the KMR-8 catalyst already at $T=300$ °C. Under these conditions, the C₇ hydrocarbons (heptanes) are completely converted, the conversion degree for C₆ (hexane) is 96.7, C₅ (pentane) – 94.5, C₄ (butane) – 66.7, C₃ (propane) – 36.5, C₂ (ethane) – 3.5, C₁ (methane) – 9.2 and carbon dioxide – 17.1 %. Increase in temperature is accompanied with raising conversion degree of all initial components as it shown in Fig. 1. The hydrocarbons with higher molecular weight are converted first. For example, if the 100 % conversion of pentane is occurred at 550 °C, ethane is completely converted at 800 °C (Fig. 1).

Methane and carbon dioxide are not completely converted within temperature region of 300 – 800 °C. With temperature increase the

conversion degrees of CH₄ and CO₂ are increased from 9.2 to 92.2 and from 17.1 to 93.4 % respectively (Table 2).

The main product of APG conversion by carbon dioxide is syngas. The formation of hydrogen is occurred at 300 °C while carbon oxide is produced at higher temperature – 400 °C. The total yields of hydrogen and carbon oxide are constantly grown with increase in conversion of hydrocarbons. At lower temperature – 400 °C syngas is reached with hydrogen. In temperature region of 450-600 °C the yield of hydrogen and carbon oxide becomes relatively equal and ratio of H₂/CO=0.9-1. At higher process temperatures 650-800 °C, the hydrogen production is prevailed and maximum ratio of H₂/CO=1.4 is observed at 800 °C.

Except synthesis-gas traces of oxygenates are formed over the KMR-8 catalyst at bi-reforming of APG at $T \leq 600$ °C. Acetic acid is prevailed among them. There is no oxygenates at higher temperature – 800 °C (Table 3).

The effect of space velocity on the process of APG conversion has been studied. The conversion degree of methane is slightly decreased from 98.9

Table 2. Effect of temperature on bi-reforming of associated gases over the KMR-8 catalyst (APG /CO₂ / H₂O=1/1/0.1, P= 1 atm, space velocity – 1500 hr⁻¹)

T, °C	Degree of conversion (K), %			H ₂ /CO
	K _{C1}	K _{C2+}	K _{CO2}	
300	9.2	3.5	17.1	*
400	37.7	30.4	28.9	3.8
450	27.9	70.8	30.4	1.0
500	36.3	99.6	36.3	1.0
550	37.4	99.0	38.4	0.9
600	48.4	98.6	44.3	1.0
650	66.8	98.7	57.4	1.1
700	75.0	97.9	73.8	1.2
750	84.8	99.3	86.9	1.3
800	92.2	100	93.4	1.4

* CO is not produced at this temperature

Table 3. Composition of products formed at conversion of associated gases (P=1 atm, S.V=1500 hr⁻¹)

T, °C	Degree of conversion, %			H ₂ /CO	Yield of oxygenates, %
	CH ₄	C ₂₊	CO ₂		
600	48.4	> 98	44.3	1.0	traces
800	92.2	100	93.4	1.4	not observed

Table 4. Effect of space velocity on bi-reforming of associated gases over the KMR-8 catalyst (APG/CO₂/ H₂O=1/1/0.1, P=1 atm, T=885 °C)

S.V.*, hr ⁻¹	K _{CH4} , %	K _{C2-C7} , %	K _{CO2} , %	Selectivity on syngas production, %	H ₂ /CO
1500	98.9	100	95.1	100	1.3
2250	98.7	100	95.0	100	1.2
3600	98.7	100	94.3	100	1.2
4500	97.7	100	93.4	100	1.2
6000	96.7	100	93.1	100	1.2

* S.V. – space velocity

to 96.7 % with increasing space velocity by 4 times (from 1500 to 6000 hr⁻¹) at T=885 °C. C₂-C₇ hydrocarbons are completely (100 %) converted under these conditions. The CO₂ conversion degree is not significantly decreased too: from 95.1 to 93.1 % (850 °C). At increasing space velocity, the contact time is shorted but it did not cause any substantial decreasing the activity of

the catalyst. The yield of syngas is not changed too. Ratio of H₂/CO is also constant 1.2. By other words, the KMR-8 catalyst performs the high productivity.

The catalyst demonstrates the high resistance to coke formation. We consider that water positively effects on suppression of coke formation over the catalyst. By electron microscope it was

shown that the catalyst keeps its high dispersed state after reaction. The catalyst worked with the stable activity during all period of its exploitation (more than 50 hours).

Conclusions

The KMR-8 catalyst performs the high activity ($X_{\text{CH}_4} = 92-98\%$ and $X_{\text{CO}_2} \sim 93\%$) and productivity: up to $\sim 12,000$ L of syngas can be produced from 3,000 L of APG by 1 L of the catalyst per hour. Syngas produced has an appropriate ratio for Fisher-Tropsch synthesis – $\text{H}_2/\text{CO}=1.2-1.4$. The advantages of the synthesized catalyst also are stability and resistance to coke

formation. Ability to work in water presence allows to use the real APG and to avoid the additional stages of their drying that reduces the investment costs.

The catalyst can be recommended for the industrial application to produce syngas from APG. In whole, the introduction of the technology of APG utilization into practice will promote also the mitigation of carbon dioxide emissions.

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Углекислотная конверсия реальных попутных газов в присутствии воды на катализаторе КМР-8

Ш.С. Иткулова, Г.Д. Закумбаева

*Институт органического катализа и электрохимии
им. Д.В. Сокольского (ИОКЭ)*

Республика Казахстан 050010, Алматы, ул. Кунаева, 142

Новый цеолитсодержащий катализатор исследован в реакции взаимодействия между диоксидом углерода и реальным попутным нефтяным газом (ПНГ) в присутствии воды при варьировании температуры в интервале 300-900 °С и объемной скорости – 1000-6000 ч⁻¹. Показано, что катализатор обладает высокой активностью в риформинге ПНГ. При 800 °С происходит полная конверсия фракции углеводородов C₂₊, степень конверсии метана достигает 92.2, а диоксида углерода – 93.4%. Основным продуктом реакции является синтез-газ (смесь оксида углерода и водорода) с отношением H₂/CO=1.4 при 800 °С. Также образуются вода и следы кислородсодержащих продуктов (в основном уксусная кислота) при T ≤ 600 °С. Катализатор работает практически с одинаковой активностью при увеличении объемной скорости в 4 раза. Достоинствами катализатора являются высокая активность, селективность, стабильность, способность работать в присутствии воды и устойчивость к коксообразованию.

Ключевые слова: углекислотная конверсия, попутные газы, катализатор, синтез-газ.
