

**NEWS****OF THE NATIONAL ACADEMY OF SCIENCES OF THE REPUBLIC OF KAZAKHSTAN  
SERIES CHEMISTRY AND TECHNOLOGY**

ISSN 2224-5286

Volume 5, Number 419 (2016), 211 – 215

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E-mails: kusanova\_sholpan@mail.ru, s.itkulova@ioce.kz**CO<sub>2</sub> HYDROGENATION OVER BIMETALLIC  
Co-Mo/Al<sub>2</sub>O<sub>3</sub> CATALYSTS**

**Abstract:** This work deals with carbon dioxide hydrogenation over the bimetallic Co-Mo/Al<sub>2</sub>O<sub>3</sub> catalysts, where the second metal is Mo – metal from the VI Group of elements. The effect of temperature on the CO<sub>2</sub> hydrogenation over the synthesised catalysts has been studied depending on the amount of the second metal. Carbon dioxide hydrogenation have been investigated under atmospheric pressure, GHSV= 2710 h<sup>-1</sup>, and varying the process temperature within range of 400-700°C. It has been observed that the synthesized Co-Mo bimetallic catalysts provide the production of methane by CO<sub>2</sub> hydrogenation at the certain temperature region. Increase in the content of the second metal up to 2 mas.% is accompanied with the raising of the catalyst activity. Thus, extent of carbon dioxide conversion reaches 62.0% at 700°C. The main product is carbon oxide under these conditions. The number of physico-chemical methods such as BET, SEM, and TPR has been used to characterize the catalysts.

**Keywords:** CO<sub>2</sub> hydrogenation, iron catalyst, methane, conversion, selectivity

УДК 542.941.7, 546.264-31, 546.73

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**ГИДРИРОВАНИЕ CO<sub>2</sub> НА БИМЕТАЛЛИЧЕСКИХ  
Co-Mo/Al<sub>2</sub>O<sub>3</sub> КАТАЛИЗАТОРАХ**

**Аннотация:** В данной работе рассмотрен процесс гидрирования диоксида углерода на биметаллических Co-Mo/Al<sub>2</sub>O<sub>3</sub> катализаторах, где второй металл – Мо относится к VI-ой группе элементов. Было изучено влияние температуры процесса и количества добавок второго металла на процесс каталитического гидрирования CO<sub>2</sub>. Гидрирование диоксида углерода проводилось при атмосферном давлении, объемной скорости – 2710 ч<sup>-1</sup>, соотношении H<sub>2</sub>/CO=3,5/1 и варьировании температуры в пределах 400–700°C. Было обнаружено, что разработанные катализаторы проводят процесс метанирования диоксида углерода в определенных условиях. Увеличение содержания второго металла до 2 мас.% способствует повышению активности катализатора. При 700°C степень конверсии диоксида углерода достигает 62,0%, а единственным продуктом в этих условиях является оксид углерода. Физико-химические свойства катализаторов были изучены рядом методов: БЭТ, СЭМ и ТПВ.

Greenhouse gas - carbon dioxide (CO<sub>2</sub>) can serve as an alternative carbon source. Disposal of carbon dioxide has become an important global issue because of the significant and continuous growth of its concentration in the atmosphere. In this regard, a great interest is the search for sustainable technologies based on the utilization of greenhouse gases.

**Ключевые слова:** Гидрирование CO<sub>2</sub>, катализатор, метан, конверсия, селективность.

In the past, several processes for the conversion of CO<sub>2</sub> and utilization as an energy source has been proposed [1-4]. One of the processes used in the present time on an industrial scale, is a Sabatier reaction (eq. 1)



Methanation of CO<sub>2</sub> have been devoted several works using catalysts based on metals such as Ru [5-9], Pd [10, 11], Rh [12-15], Ni [16-18], and Co [17-22] on various carriers. Catalysts based on noble metals are characterized by high reactivity, reduced coke formation and more stable. However, the low availability and high cost limit their use [23]. Therefore, in the best case, the noble metals can be used in small amounts as promoters [24]. Currently, the main focus is on creating cheap catalyst with high activity, stability, and resistance to coking. We used the Co-containing catalysts [22] showed that the CO<sub>2</sub> conversion and methane yield is 15% higher on a cobalt catalyst supported on Al<sub>2</sub>O<sub>3</sub>, than on MgO and SiO<sub>2</sub>, prepared by an impregnation method.

The aim of this work was to study the new bimetallic Co-containing catalyst with the addition of a second metal, not belonging to the group of noble metals in the hydrogenation of carbon dioxide. it was studied the effects of process temperature and the amount of the second metal additives on CO<sub>2</sub> methanation process over the synthesized catalysts. Physico-chemical properties of the catalysts were studied by a number of methods.

### Experimental procedure

Bimetallic Co-M<sub>8</sub> / Al<sub>2</sub>O<sub>3</sub> catalysts, where Mo - the 6th group metal, have been synthesized in IFCE n/a D.V. Sokolsky. The number of second metal Mo was varied from 0.25 to 4 wt.% of the weight of the catalyst, and the amount of Co remained constant - 4 wt.%.

The specific catalysts surface area was determined by the BET method. To determine the recoverability of supported metal oxide catalysts were studied by TPR-H<sub>2</sub> methods. The morphology of the catalysts was examined by scanning electron microscopy.

The hydrogenation of carbon dioxide was conducted in the IOC RAS in a flow reactor at atmospheric pressure with a ratio H<sub>2</sub> / CO<sub>2</sub> equal to 3.5 / 1, the volume hourly space velocity (V<sub>0</sub>) 2710 hr<sup>-1</sup> and the process temperature is varied from 400 to 700°C. Analysis of the reaction starting and final products was carried out by gas chromatography in "on-line" mode.

### Results and their discussion

#### Testing the catalysts

The CO<sub>2</sub> hydrogenation over 4%Co-0,75%Mo/Al<sub>2</sub>O<sub>3</sub> catalyst was carried out in the temperature range 400-700°C. It was studied the effect of temperature on the conversion of carbon dioxide and methane selectivity. Figure 1 presents data on the extent of CO<sub>2</sub> and CH<sub>4</sub> conversions on the catalyst selectivity 4%Co-0,75%Mo/Al<sub>2</sub>O<sub>3</sub>.

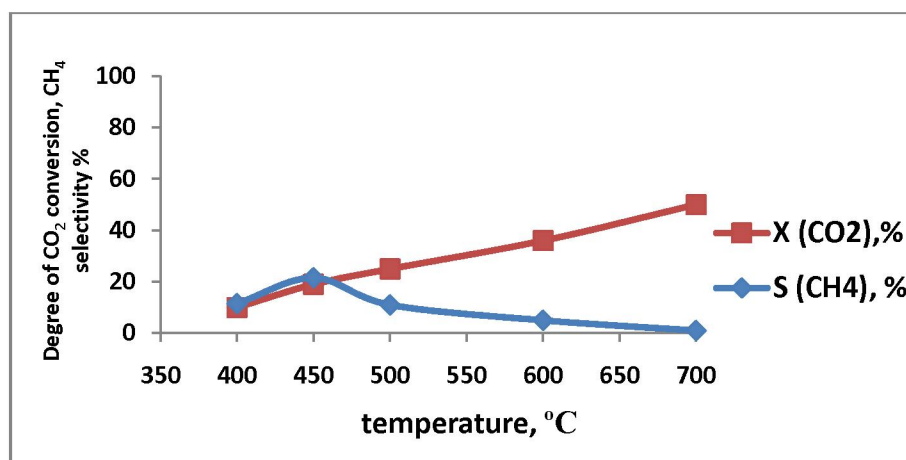


Figure 1 - The effect of temperature on the degree of CO<sub>2</sub> conversion and the CH<sub>4</sub> selectivity on 4%Co-0,75%Mo/Al<sub>2</sub>O<sub>3</sub> catalyst at H<sub>2</sub>:CO<sub>2</sub>=3.5/1, P=0.1 MPa, V<sub>0</sub>=2710 h<sup>-1</sup>

As the temperature increases from 400 to 700°C, conversion degree of carbon dioxide increases from 10.0 to 50.0%. The reaction product is methane, selectivity of which at a temperature of 400°C is equal to 11.5%. At 450°C the CH<sub>4</sub> selectivity reaches its maximum - 21.5%. With a further rise in the temperature its formation is reduced and almost negligible at 700°C.

Under the same conditions the catalyst with a high content of the second metal Mo (2%) was tested. Figure 2 graphically presents the effect of temperature on the degree of CO<sub>2</sub> conversion and the CH<sub>4</sub> selectivity on 4%Co-2%Mo/Al<sub>2</sub>O<sub>3</sub>.

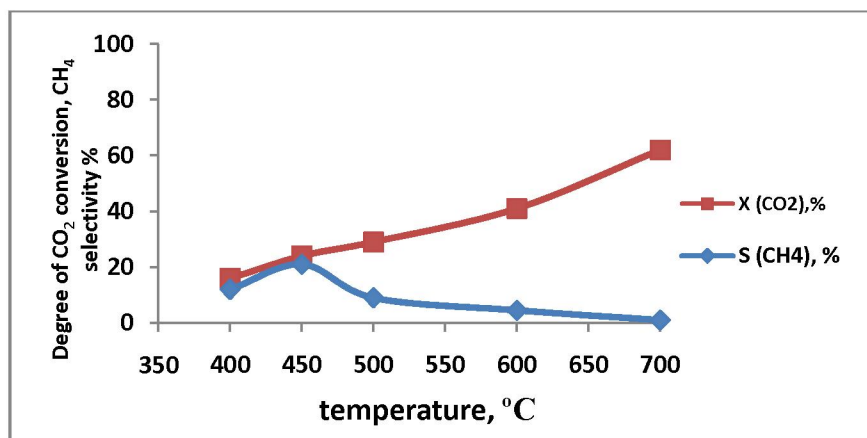


Figure 2 - The effect of temperature on the degree of CO<sub>2</sub> conversion and the CH<sub>4</sub> selectivity on 4%Co-2%Mo/Al<sub>2</sub>O<sub>3</sub> catalyst at H<sub>2</sub>:CO<sub>2</sub>=3.5/1, P=0.1 MPa, V<sub>0</sub>=2710 h<sup>-1</sup>

Catalyst with a higher content of the second metal exhibits greater activity in conversion of carbon dioxide. At a temperature of 700°C degree of conversion of carbon dioxide reaches 62.0%, which is higher than that for the catalyst with the addition of 0,75% Mo, where X(CH<sub>4</sub>) under the same conditions is 50.0%. With regard to the formation of methane it is maintained the same pattern: extreme dependence with a maximum at 450°C - 21.0%, and a decline in the temperature range 500-700°C.

Thus bimetallic Co-Mo/Al<sub>2</sub>O<sub>3</sub> are catalyzed predominantly backlash water shift:



#### Physico-chemical study of the synthesized catalysts

BET method determined specific surface area of the initial samples of catalysts.

Table 1 shows the specific surface areas on bimetallic Co-Mo/Al<sub>2</sub>O<sub>3</sub> catalysts. Specific surface areas of catalysts vary within 159,4-167,0 depending on the amount of the second metal - molybdenum.

Table 5 - The specific surface area of Co-Mo/Al<sub>2</sub>O<sub>3</sub> catalysts

Co:Mo ratio	initial sample
4:0,75	167,0
4:2	159,4

By scanning microscopy method it was studied a morphology of synthesized 4%Co-2%Mo/Al<sub>2</sub>O<sub>3</sub> catalyst, and it was conducted the elemental analysis and it was carried out metals distribution on the grain surface of catalysts. Figure 3 shows an SEM picture of the fresh sample of the catalyst. Elemental analysis obtained from three different places of this sample showed an uneven distribution of metal over the surface.

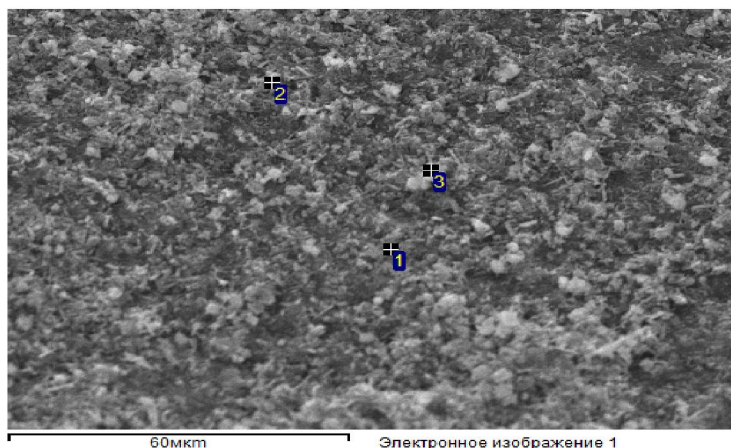


Figure 3 - SEM picture of the 4%Co-2%Mg/Al<sub>2</sub>O<sub>3</sub> catalyst (Fresh sample)

TPR-H<sub>2</sub> was studied on a bimetallic 4%Co-2%Mo/Al<sub>2</sub>O<sub>3</sub> catalyst. Data on bimetallic catalyst are given in Table 2.

Table 2 - H<sub>2</sub>-TPR cobalt catalysts

Catalyst	T <sub>max</sub> , °C			
	T <sub>1</sub>	T <sub>2</sub>	T <sub>3</sub>	T <sub>4</sub>
4%Co-2% Mo/Al <sub>2</sub> O <sub>3</sub>	190	365	460/600	795/945
4.5%Co/Al <sub>2</sub> O <sub>3</sub>	-	276/400	400/750	-

When recovering the cobalt-molybdenum catalyst there are additional peaks specific for the complex difficult to recover metal oxides in 700-945°C.

### Conclusions

The obtained data show that the bimetallic Co-Mo catalysts is carried out with moderate activity methanation of carbon dioxide. Maximum selectivity to 21.5% methane formation is observed in catalyst with a lower content of Mo - 4%Co-0,75%Mo/Al<sub>2</sub>O<sub>3</sub> at 20.0% degree of carbon dioxide conversion at temperature of 450°C, H<sub>2</sub>:CO<sub>2</sub>=3.5/1, P=0.1 MPa, V<sub>0</sub>=2710 hr<sup>-1</sup>. While the maximum conversion of the carbon dioxide - 62% is observed on the catalyst with a higher Mo additive - 4%Co-2%Mo/Al<sub>2</sub>O<sub>3</sub>, the selectivity for methane in this case is 1% at a temperature of 700°C, H<sub>2</sub>:CO<sub>2</sub>=3.5/1, P=0.1 MPa, V<sub>0</sub> = 2710 hr<sup>-1</sup>. At high temperatures (600 to 700°C) Bimetallic Co-M/Al<sub>2</sub>O<sub>3</sub> catalyze predominantly backlash water shift.

*The work was carried out with the financial support of MES RK within the framework of the project №5433/GF-4.*

### ЛИТЕРАТУРА

- [1] Zhag K., Kogelschatz U., Eliasson B. Conversion of greenhouse gases to synthesis gas and higher hydrocarbons // Energy & Fuel. – 2001. – Vol. 15. – P. 395-401.
- [2] Herzog H.J. Using Carbon capture and sequestration technologies to address the climate change // Am. Chem. Soc. Div. Fuel Chem. Prepr. – 2001. – Vol. 46. – P. 53-55.
- [3] Song C.S., Gaffney A.M., Fujimoto K. (eds). CO<sub>2</sub> conversion and utilization. // American Chemical Society, Washington, DC, ACS Symposium. – 2002. – Series 809, Chapter 3 – P. 39-47.
- [4] Schobert H.H., Song C.S. Chemicals and materials from coal in the 21st century // Fuel. – 2002. Vol. 81. – P. 15-20.
- [5] Marwood M, Doepper R, Prairie M, Renken A. // Chem Eng Sci – 1994. – V. 49. – P. 4801–4809.
- [6] Solymosi F, Erdohelyi A, Kocsis M. // J Chem Soc, Faraday Trans 1 – 1981. – P. 1003–1012.
- [7] Scire S, Crisafulli C, Maggiore R, Minico S, Galvagno S // Catal Lett – 1998 – V. 51. – P. 41–45.
- [8] Kondarides D.I., Panagiotopoulou P, Varykios X.E. // J Phys Chem C – 2011. – V. 115. – P. 1220–1230.
- [9] Behm R.J., Eckle S., Denkwitz Y. // J Catal – 2010. – V. 269. – P. 255–268.
- [10] McFarland E.W., Park J.N. // J Catal – 2009. – V. 266. – P. 92–97.
- [11] Erdohelyi A, Pasztor M, Solymosi F // J Catal – 1986. – V. 98. – P. 166–177.
- [12] Solymosi F, Erdohelyi A, Bansagi T // J Catal – 1981. – V. 68. – P.371–382.
- [13] Zhang Z.L., Kladi A, Varykios X.E. // J Catal – 1994. – V. 148. – P.737–747.