

NEWS

OF THE NATIONAL ACADEMY OF SCIENCES OF THE REPUBLIC OF KAZAKHSTAN

SERIES CHEMISTRY AND TECHNOLOGY

ISSN 2224-5286

Volume 2, Number 422 (2017), 5 – 11

UDC 541.128

B.T. Utelbaev¹, R. Toktassyn^{1*}, Michele O. de Souza², M. Myrzahanov¹¹Department of Chemical Engineering, Kazakh-British Technical University, Tole bi 59, Almaty, Kazakhstan;²Institute of Chemistry, UFRGS, Av. Bento Gonçalves 9500, 91501-907 Porto Alegre, Box 15003, Brazil*E-mail address: rai_t@mail.ru**STUDY OF THE BUTANE-BUTYLENE FRACTION
ON MODIFIED RU-CO SUPPORTED CLAY CATALYSTS**

Annotation. The metal (Ru and Co) doped on chromium pillared montmorillonite was have been prepared by wet impregnation method. The prepared bimetallic catalysts were characterized by N₂ adsorption-desorption isotherm, Brunauer-Emmett-Teller (BET) and Scanning Electron Microscopy (SEM) methods. The activity of the catalysts was evaluated by using conversion of C₄ fractions at different reaction temperature and pressure. Amount of metals in the catalyst, temperature and gas pressure revealed to a significant impact on the catalyst activity and selectivity. Experimental results show that the 1.5%Ru-Co/MMC system has a best selectivity towards C₈ olefins.

Key words: montmorillonite, butane-butylene fraction, motor fuel, ruthenium, cobalt.

1. Introduction

Butane-butylene fraction is the main part of gaseous products from the Fluid catalytic cracking (FCC) process. C₄ fraction dimerization, trimerization and oligomerization products will be used in a wide range of chemical and petrochemical industry. For example, C₈= olefins are the main component of high-octane gasoline and C₁₂= olefins are the raw material of production of plastic substances [1], dodecylbenzene, lubricants and gasoil additives [2, 3]. A variety of solid catalysts: zeolites [4, 5], sulfated zirconia [6, 7], sulfated titania [8], WO_x/ZrO₂ [9], NiO-W₂O₃/Al₂O₃ [10], silica supported chloroaluminate ionic liquid [11], HNaNi-ZSM-5 [12] have been studied for C₄ fraction oligomerization reactions. However, all of them appeared low selectivity and/or conversion.

Actually, in industry for the oligomerization of C₄ fractions used solid phosphoric acid catalyst [13]. Because of polluting and easily deactivation disadvantage, requires modification of catalyst environmentally safe direction. According to the afford mentioned, clay minerals represent a available source to prepare catalysts because of low cost and environmentally friendly porous materials. As well as it has good swelling, high specific surface area and ion exchangeable properties. The most used modification techniques include cation exchange and pillaring. Clays or clay modified catalysts have been used for petroleum refining and petrochemical industries [14, 15]. An earlier paper reported that nickel or cobalt layered clays are highly active for hydroisomerization and hydrocracking to light hydrocarbons [16] and oligomerization of C₃-C₄ hydrocarbons [17]. In the resent paper reported that Co, Na, Ca-Y [18] and carbon supported cobalt catalysts [19] showed good dimer selectivity for C₄ fraction oligomerization. Also an aluminum pillared montmorillonite and aluminum pillared saponite were used as catalyst for 1-pentene oligomerization [20]. In our previous work we investigated new oligomerization Cr-pillared supported clay catalyst and tested it for C₂-C₄ oligomerization reaction. It was showed highly selective towards C₈ hydrocarbons [21].

In this report we describe the synthesis and characterization of Cr-pillared Ru-Co supported montmorillonite and their catalytic behavior in the conversion of C₄ fractions. Obtained products identify and quantify by GC.

2. Experimental

2.1. Materials

The starting material natural bentonit clay which containing montmorillonit (resource of bentonite clay is from Republic of Kazakhstan) used as carrier without further treatment. Modifying the natural clay to pillar structure used CrCl_3 (99%, Sigma-Aldrich) as a structuring agent. For improving the swelling properties of the clay used 1M NaCl solution. As support used Ruthenium (III) chloride- $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (99.99%, Alfa- Aesar) and hexahydrate of cobalt (II) nitrate- $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99.99%, Sigma-Aldrich).

2.2. Catalyst preparation

For preparation of RuCo/MMC* (atomic ratio Ru:Co=0.4:0.6) aqueous solutions of ruthenium(III) chloride- $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ and hexahydrate of cobalt (II) nitrate- $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were used. Pillared clay preparation carried out by method proposed in [22, 23]. The preparation of the Cr-pillared clay was analogues to that of the Ga-pillared clay [24]. Prior to pillaring process, the clay was saturated with sodium ions through exchange with 1M NaCl for 8 h, and then washed with deionized water in order to remove residues of NaCl as determined by the AgNO_3 . Then 0.1M NaOH solution added to the required amount of 0.1M CrCl_3 solution under vigorous stirring at room temperature. Then this mixture added to the aqueous clay suspension and stirred 4h. Obtained mass undergoes to dry in air at ambient temperature and left for a few days. Finally, the sample calcined at 450 °C during the 8h under air at heating rate of 2 °C/min. After cooling a certain mass of this sample is impregnated by cobalt and ruthenium salts. Then obtaining mass was dried at 80 °C for 8 h and calcined at 450 °C during 6 h in the air at heating rate of 2 °C/min.

2.3. Characterization techniques

Textural properties of the samples were obtained from nitrogen adsorption-desorption isotherm, measured at 77K using an ASAP 200 Mirometric instrument. The specific surface area and mean pore size diameter for the different synthesized solids were calculated by Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) - methods respectively. Scanning electron microscopy (SEM) - images of the sample previously gold-coated are performed using a Jeol JSM 5800 microscope (20 kv) equipped with a secondary electron images detector.

2.4. Catalytic tests

Oligomerization of C_4 hydrocarbons was carried out in a continuous flow fixed-bed reactor. The reaction temperature and gas pressures are range from 110-170 °C and 2.0-4.0 MPa respectively. Prior to experiment the catalyst (1g) was pre-treated in situ in a stream of hydrogen (50 cm^3/min) at 300 °C at atmospheric pressure for 2 h. Then the reactor cooled down until reaction temperature in a flow of argon (Ar, 50 cm^3/min) and the C_4 gas mixture were fed to the reactor. Reaction products analyzed by DANI Master GC Fast Gas Chromatograph.

3. Results and discussion

Textural properties of the starting clay and its derived catalysts are shown in Table 1. The montmorillonit have small surface area and pore diameter about 60 m^2/g and 1.1 nm respectively. After modifying with chromium they were 240 m^2/g and 3.9 nm respectively. This can be attributed to the pillaring agent successfully entered into the interlayer spacing of montmorillonite to create regular porosity, resulting effectively increase of it is surface area and pore diameter. After impregnation with Ru and Co to the clay, a decrease of specific surface area was observed. The metal content consist 2%, it was sharply decreased to 170 m^2/g . But the pore diameter still increased to 4.3 nm, then remain stable. This can be explained by the capacity of the career. In this case the more metal content less efficient for Cr modified montmorillonite, then measured the lower specific surface area.

Table 1 - Physicochemical properties of the parent carrier and metal supported catalysts

Samples	Ru content, %	Co content, %	Specific surface area, m ² /g	Pore diameter, nm
MM*	-	-	60	1.1
MMC**	-	-	240	3.9
0.5%RuCo(Ru: Co=0.4:0.6)/MMC	0.2	0.3	235	4.1
1.0%RuCo(Ru: Co=0.4:0.6)/MMC	0.4	0.6	230	4.2
1.5%RuCo(Ru: Co=0.4:0.6)/MMC	0.6	0.9	218	4.3
2.0%RuCo(Ru: Co=0.4:0.6)/MMC	0.8	1.2	170	4.3

Note: *Montmorillonite, **Montmorillonite modified by compound Chromium

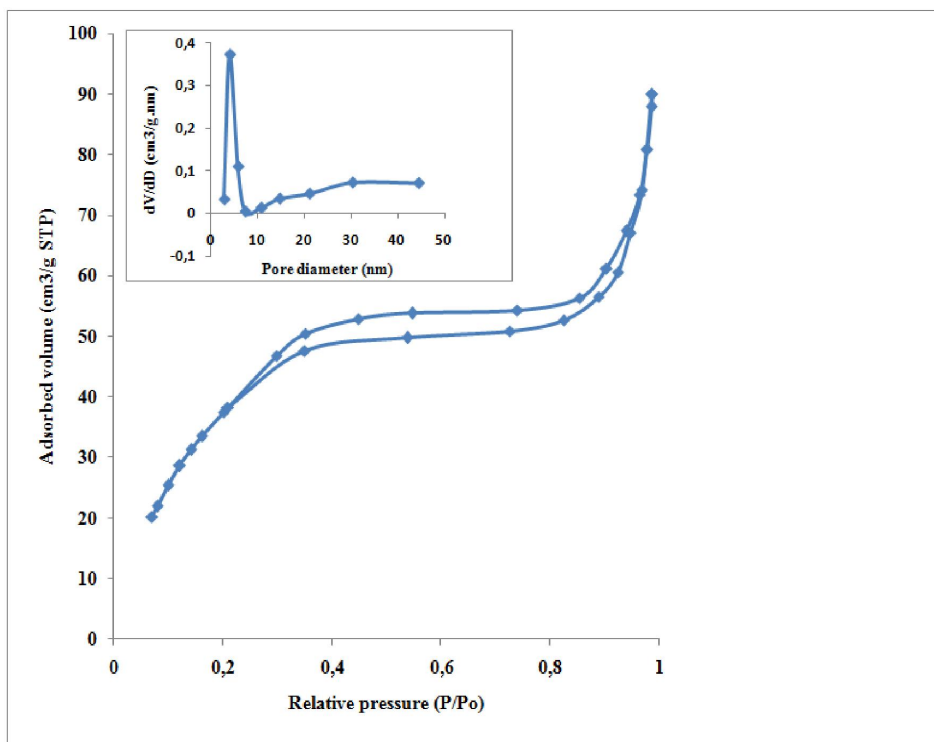
Figure 1 - N₂ adsorption-desorption isotherms of MMC

Fig. 1. shows the N₂ adsorption-desorption isotherms of Cr modified montmorillonite, which display a type IV curve with a adsorption region at 0.4-0.8 relative pressure (P/P_0) implying an uniform pore geometry and corresponding to mesoporous adsorbents. The hysteresis loops belong to type III, which is the same as IUPAC classification [25]. The pore size distribution of MMC is also shown in the inset in Fig. 1. The average pore size of MMC is calculated to be 4.0-5.0 nm from the BJH adsorption data, which is compatible the previous TEM result [20]. A gradual increase in nitrogen sorption observed at low to medium relative pressure ($P/P_0=0.4$) suggests the presence of micropores and small mesopores. While the increasing of the nitrogen adsorbed at higher relative pressure could be related to larger mesopores. In conclusion it can be seen the pillaring process improved its adsorption properties, led to create uniform mesoporosity structure.

The SEM images of chromium modified 1%Ru-Co/MMC are shown in Fig. 2. In Fig. 2A shows the raw montmorillonite particles remain united themselves. Fig. 2B reveals that the pillaring agent can affect

morphology and structure of the parent carrier. After pillaring process, the surface of MMC become more porosity and their morphologies are become more smooth, also appeared ordered parallel line (B,C) because of interlayer of clay binding with polyoxocations of chromium. It could positive influence for increasing specific surface area of parent clay mineral. The white spot observed in the Figure 2C is area of supported metals (Ru and Co) in the MMC carrier.

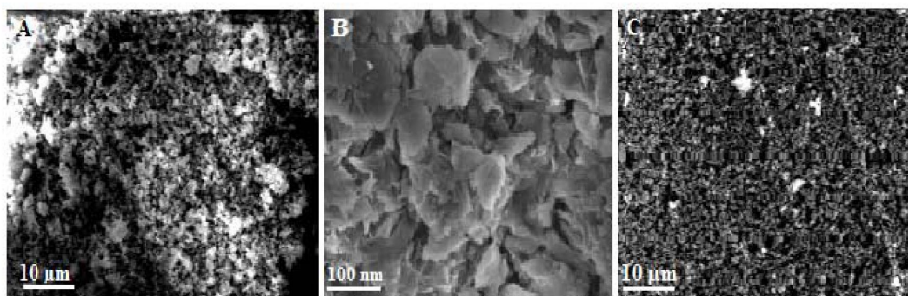


Figure 2 - SEM images of parent MM (A), Cr- pillared MMC (B), 1.5%Ru-Co/MMC (C)

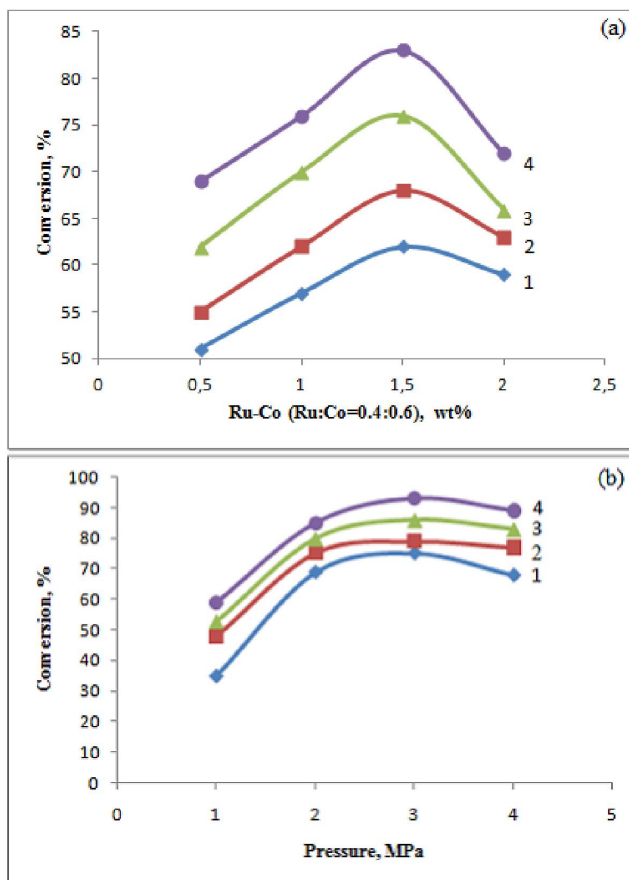


Figure 3 - Influence of amount of metals (a) and pressure (b) to the conversion of C₄ fractions on Ru-Co (Ru:Co=0.4:0.6)/MMC systems (1. 110 °C; 2. 130 °C; 3. 150 °C; 4. 170 °C)

Influence of amount of metals and pressure to the conversion of C_4 fractions on supported clay catalyst and product distribution at different reaction temperature were shown in Fig. 3 and Fig. 4. Increasing temperature and pressure have positive effect on gas conversion [26-28]. In Fig. 3a shows at constant pressure ($P=2$ MPa) conversion of gas went up at all temperature range when the amount of metal was increased from 0.5 to 1.5%, then decreased. The maximum value was achieved at 170 °C about 82%. In Fig. 3b showed the conversion of gas on 1.5% RuCo(Ru:Co=0.4:0.6)/MMC catalyst at different pressure and temperature. When the pressure and temperature climbed to 3 MPa and 170°C respectively, the gas conversion reaching the highest 90.0%, then tends to stabilize.

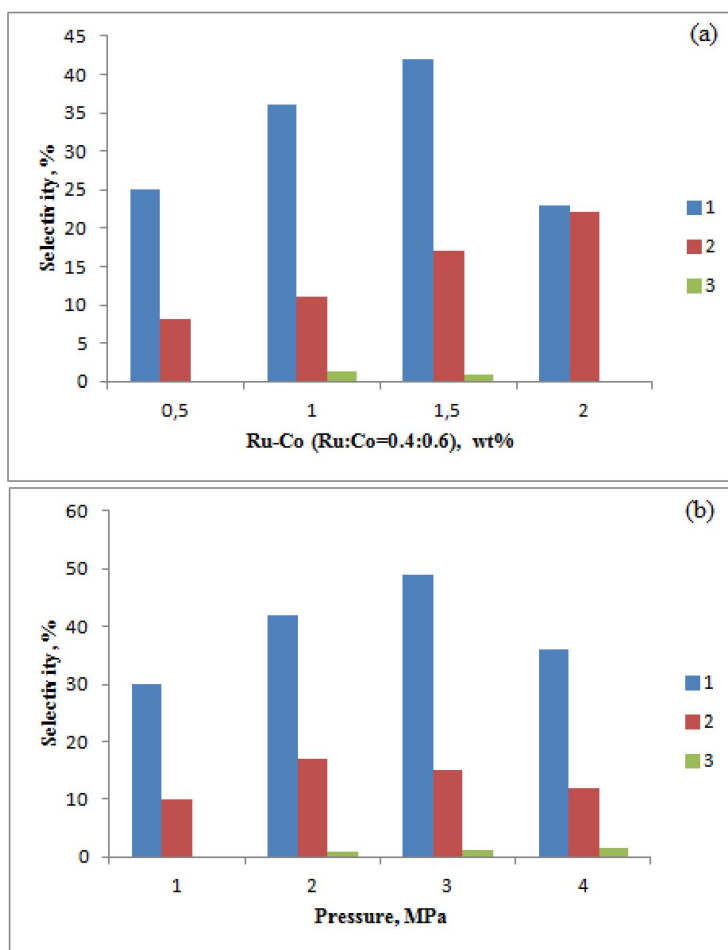


Figure 4 - Selectivity to C_8 , C_{12} and C_{16} (1. C_8 ; 2. C_{12} ; 3. C_{16}) for the transformation of C_4 fractions on Ru-Co (Ru:Co=0.4:0.6)/MMC systems as function of amount of metals (a) and pressure (b)

It is necessary to control amount of metal content, temperature and gas pressure to yield optimal productivity, which selective towards C_8 oligomers [29, 30]. The selectivity of catalyst with different amount of metal loading was evaluated for the same reaction conditions (170°C, 2 MPa) shown in Fig. 4a. Note that, the 1.5% RuCo (Ru:Co=0.4:0.6)/MMC catalyst exhibited the best selectivity for dimers product - C_8 , as about 42.0 % compared to among other synthesized catalysts. The C_{12} oligomer selectivity varied between 8.0 - 20% at all samples. The catalyst with 2.0% Ru-Co showed selectivities in the same order for

C₈ and C₁₂ fractions. It's worth pointing out, that the Ru-Co total content in the range of 1.0-1.5% gives much higher selectivity to C₈ fractions. This can be ascribed to the fact that in the reaction environment only the Ru-Co planted catalyst species will be active for dimerization C₄ fractions. In this case, increasing metal loading, all the Ru-Co species cannot be able to incorporate in the framework. In consequence, extra metal species will block the pores an active species and selectivity will reduce.

Under constant temperature (t=170°C) the selectivity of 1.5%RuCo (Ru:Co=0.4:0.6)/MMC catalyst in function of pressure is presented in Fig. 4b. The selectivity of catalyst to C₈ fractions increased linearly when the gas pressure increase from 1 to 3 MPa, as about 30 to 49%, then decreased. On the contrary, the selectivity for C₁₂ fractions reduced. It was also observed that the catalysts exhibited a little selectivity to C₁₆ oligomers (< 2%), result of the tetramerization of the C₄ fractions. The reason for that the low pressure will increase spent time of the gas molecules in catalyst cavity, thereby increasing the formation of long-chain hydrocarbons.

Conclusion

In this work, the conversion of butane-butylene fractions on heterogeneous Ru-Co (Ru:Co=0.4:0.6)/MMC clay catalysts were studied. Temperature, pressure and metal content of the catalyst have great effect in controlling conversion and selectivity of the catalysts. Obtained results showed the gas conversion increase along with increasing temperature and pressure. The maximum conversion were found at 170 °C. According to the results, the best conditions that selectivity toward C₈ hydrocarbon products were found combination of higher partial pressure (3 MPa), lower content of metal (1.5% Ru-Co) and a temperature of 170 °C. Under these conditions the obtained highest volume of selectivity for C₈ oligomers was 49.0%.

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УДК 541.128

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ИЗУЧЕНИЕ БУТАН-БУТИЛЕНОВОЙ ФРАКЦИИ НА Ru-Co НАНЕСЕННЫХ ПИЛЛАРИРОВАННЫХ ГЛИНИСТЫХ КАТАЛИЗАТОРАХ

Аннотация. Металл (Ru и Co) нанесенный на хром пилларированной монтмориллонит был получен методом мокрой пропитки. Полученные биметаллические катализаторы характеризовались N₂ адсорбции-десорбции изотермой, методами Брунауэра-Эммета-Теллера (БЭТ) и Сканирующей электронной микроскопии (СЭМ). Активность катализаторов оценивали с использованием конверсии C₄-фракций при различных реакционных температурах и давлении. Количество металлов в катализаторе, температура и давление газа показали значительное влияние на активность и селективность катализатора. Экспериментальные результаты показывают, что 1,5% Ru-Co/ММС- система обладает лучшей селективностью к C₈-олефинам.

Ключевые слова: монтмориллонит, бутан-бутиленовая фракция, моторное топливо, рутений, кобальт.

ӨЖ 541.128

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Ru - Co ОТЫРҒЫЗЫЛҒАН ҚАБАТТАНҒАН ҚҰРЫЛЫМДЫ САЗ БАЛШЫҚТЫ КАТАЛИЗАТОРЛАРДА БУТАН-БУТИЛЕН ФРАКЦИЯСЫН ЗЕРТТЕУ

Аннотация. Металл отырғызылған (Ru және Co) хроммен қабаттық құрылымданған монтмориллонит дымқыл сіндіру әдісімен дайындалды. Алынған биметалды катализаторлар N₂ адсорбция-десорбция изотермы, Брунауэр-Эммет-Теллер (БЭТ) және сканерленген электронды микроскопия (СЭМ) әдістерімен сипатталды. Катализаторлардың белсенділігі C₄ фракциясының әртүрлі реакциялық температура мен қысым кезіндегі конверсиясы арқылы бағаланды. Енгізілген металдардың мөлшері, температура және газ қысымының өзгерісі катализатордың активтілігі мен талғамдылығына айтарлықтай әсер ететіндігі анықталды. Тәжірибелік нәтижелер 1,5% Ru-Co/ММС жүйесі C₈ олефиндерге жақсы талғамды екенін көрсетті.

Тірек сөздер: монтмориллонит, бутан-бутилен фракциясы, мотор отыны, рутений, кобальт.