# Application of Modified Clay Catalysts in Oligomerization of Light Olefins

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#### ABSTRACT

The oligomerization of light olefins to high-octane clean engine fuels is one possible way to solve increased requirements for motor fuels. This paper presents a study of catalytic oligomerization of  $C_2$ - $C_4$  olefins on Ru-Fe supported pillared clay catalyst with different metallic quantity. The prepared catalysts were characterized by X-ray diffraction, N<sub>2</sub> adsorption-desorption at 77K, BET and BJH methods. The BET and BJH methods showed the pillared clay had significantly increased surface area and when an appropriate amount of Ru and Fe were added, the bimetallic alloys were uniformly dispersed on the modified clay surfaces and had an average mesopore size of 4.1 nm. It is indicated that excess metal oxides blocked the surface of bimetallic RuFe/MMC system, resulted in decreased catalytic activity. The low metal content catalysts showed higher oligomerization activity and increasing the Fe content gave selectivity to isomerization reactions.

Key word: pillared clay catalyst, oligomerization, selectivity, light olefin, isomerization

#### **INTRODUCTION**

Oligomerization of light olefins ( $C_2$ - $C_4$ ) to high octane motor fuel is an important topic in the petrochemical industry. Because it can produce more valuable products less harmful to the environment and the feedstock of the process will derive from many other industrial byproducts (fluid catalytic cracking, steam cracking, and Fischer-Tropsch synthesis). The oligomerization has already been studied by variety method of such as solid phosphoric acid [1-3], ion exchange resins [4-10], zeolites [11-19], ionic liquids [20-23] and metal oxide [24-25] catalysts.

In recent years clay or clay modified catalysts are also used in the petroleum refining industry as a green catalyst. Its expandable properties give the clay large surface area and porous volume, which opportunity to obtain large basal spacing. Pillared clays are one of the porous materials which can be synthesized by exchanging interlayer cations of clays with inorganic polyoxocations followed by thermal treatment. Al-pillared clay was the first and the most studied one. The chromium(III) pillared clay is also alternative to obtain catalytically active pillars with high selectivity. Chromium(III) pillared interlayered clays are used in the conversion of hydrocarbons [26], hydrocracking of heavy liquid fuels [27, 28], propene oxidation [29], chlorinated hydrocarbon oxidation [30], hydrodesulphurization [31] reactions.

As well as, the group VIII metals are catalytically active for petroleum refining processes. The Ni, Co and Fe based catalysts are widely used as olefin polymerization and

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oligomerization. But deactivated upon coke formation, therefore adding noble metals are less sensitive to coke and perform the high activity. In our previous work noble metal-doped Ga and Cr-pillared clays to be an efficient catalyst for the oligomerization of  $C_2$ - $C_4$  olefins [32, 33]. In continuation of our work, the present paper is to study the effect of doped metal cations to the activity and selectivity of the pillared clay catalyst over oligomerization reaction

#### EXPERIMENT

#### **Chemicals and instrumentation**

The materials used in this study are bentonite from the Republic of Kazakhstan, rich in montmorillonite (>90%). CrCl<sub>3</sub> (99%, Sigma-Aldrich), NaCl, Ruthenium(III) chloride-RuCl<sub>3</sub>·3H<sub>2</sub>O (99.99%, Alfa-Aesar) and hexahydrate of iron(II) chloride – FeCl<sub>3</sub>·6H<sub>2</sub>O (97 %, Sigma-Aldrich). All materials are used without further treatment.

Textural properties of the samples were obtained from nitrogen adsorption-desorption isotherm, measured at 77K using an ASAP 200 Micrometric 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. The phase identification was carried out by X-ray diffraction spectroscopy (XRD).

Table 1. Main properties of the parent carrier and metal supported catalysts		
Samples	Specific surface	Pore size,
	area, S <sub>BET</sub> $(m^2/g)$	(nm)
MM*	60	1.0
MMC**	237	3.8
0.5% RuFe/MMC	239.0	4.0
1.0% RuFe/MMC	240.0	4.1
1.5% RuFe/MMC	229.0	4.2
2.0% RuFe /MMC	164.0	4.3

MM\* - montmorillonite

MMC\* - chromium pillared montmorillonite

#### **Catalyst preparation**

For the preparation of RuFe/MMC\* catalytic system with atomic ratio Ru:Fe = 0.6:0.4, the aqueous solutions of ruthenium(III) chloride-RuCl<sub>3</sub>·3H<sub>2</sub>O and hexahydrate of Iron chloride - FeCl<sub>3</sub>·6H<sub>2</sub>O were used. The wt. % of impregnated metals were varied from 0.5 to 2.0%. Pillared clay preparation carried out by the method proposed in [32]. 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<sub>3</sub>. Then 0.1 M NaOH solution added to the required amount of 0.1M CrCl<sub>3</sub> solution under vigorous stirring at room temperature. This mixture added to the aqueous clay suspension and stirred 4 h. 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 8 h under air with the heating rate of 2 °C/min. The bimetallic catalyst system was synthesized by wet impregnation of Cr-pillared clay with Ru and Fe salts. The RuCl<sub>3</sub>·3H<sub>2</sub>O and FeCl<sub>3</sub>·6H<sub>2</sub>O dissolved in water and added to the certain mass of pillared clay by dropwise and this suspension continuous mixed under water bath until obtaining the shape of the dough. Then the 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.

#### **Procedure reaction**

The oligomerization of C<sub>2</sub>-C<sub>4</sub> hydrocarbons that the basic compositions consist of ethylene (4%), propylene (29%) propane (8%), butylene (39%), isobutane (11%) and others was evaluated within the temperature range of 110-170 °C by using continuous flow fixedbed reactor. Reaction duration was for 1 hour, pressure 3 MPa and space velocity is 1.492 h<sup>-1</sup>. Prior to experiment1 g of catalyst was pre-treated in situ in a stream of hydrogen (50 cm<sup>3</sup>/min) at 300 °C at atmospheric pressure for 2 h. Then the reactor cooled to room temperature in a flow of argon (Ar, 50 cm<sup>3</sup>/min) and the gas mixtures were fed to the reactor. Once the reaction pressure stabilized, the reactor temperature increased to the desired reaction temperature and start the reaction. The liquid products condensed until -2 °C, then weighed and analyzed by DANI Master GC Fast Gas Chromatograph.

# **RESULT AND DISCUSSION**

# **Catalyst characterization**

The N<sub>2</sub> adsorption-desorption isotherms for raw and pillared clay samples at 77K are shown in Figure 1. According to the IUPAC classifications [34-36], the shape of isotherms of the raw and pillared clays corresponded to type IV and the hysteresis loops corresponded to H3-H4 type in relative pressure ( $P/P_0$ ) range of 0.4-0.8, indicating a microporous and mesoporous structure. The BJH-adsorption pore size distribution curve of the pillared sample is shown in the top of the isotherm curves. MMC clay displayed different mesopore size distribution ranging from 2 to 35 nm. The average diameters of the mesopores are at about 4.1 nm and 13.5 nm belong to low-density area.



Figure 1. N<sub>2</sub> adsorption-desorption isotherms of the calcined montmorillonite and MMC (Cr-pillared montmorillonite) sample

The surface area and mesopore volume of the raw and synthesized all samples are shown in table 1. The starting clay has a small surface area of 60 m<sup>2</sup>/g and on the modified clay it is increased to 237 m<sup>2</sup>/g. This is indicated that the pillaring process had executed

successfully. The surface areas and pore volume of the metal-doped pillared clays were slightly increased with increasing metal content until 1.0% after decreased sharply to 164 and 0.14 respectively. This behavior was explained that during the impregnation period active metal ions full fill the interlayer space and the extra ion particles collapse each other and narrowing the gap between the layers then this can cause reduce the specific surface area [37-38].

Figure 2 are shown the XRD pattern of modified clays MMC and Ru-Fe/MMC. There was no considerable change in the intensity patterns of pillared clay and supported samples. It indicates that the ion exchange does not affect the layer structure. Diffraction peaks at  $38.4^{\circ}$  (Ru<sup>3+</sup>) and  $58^{\circ}$ (Fe<sup>3+</sup>) were observed in the Ru-Fe/MMC pattern due to ions Ru<sup>3+</sup> and Fe<sup>3+</sup> respectively.[45] Diffraction peaks were also observed in the MMC sample at  $65^{\circ}$  due to Cr<sub>2</sub>O<sub>3</sub> [39]. The XRD results show that the bimetal loading had no significant effect on peak position and intensity of the Ru-Fe/MMC in comparison with MMC.



**Figure 2.** XRD patterns of pillared clay and metal-supported pillared clay catalyst. MMC: pillared montmorillonite; Ru-Fe/MMC: metal supported pillared montmorillonite

#### **Catalytic activity**

The objective of our test was to select a catalytic system which suitable for oligomerization of light olefins to gasoline range products. The effect of the amount of loaded metal to the catalytic activity and product distribution of all synthesized catalysts under the same reaction conditions (P=3.0 MPa, WHSV =  $1.483 \text{ h}^{-1}$ ) were shown in Figure 3. Based on the result the increasing temperature from 110 to 130 °C, increase the selectivity of C<sub>4</sub>-C<sub>6</sub>, except for the catalyst 2.0%Ru-Fe/MMC. Continued rise the temperature up to 170 °C decreased the selectivity (Figure 3A). It implies that at higher temperature the formation of long-chain hydrocarbons increases. In this regard, the C<sub>4</sub>-C<sub>6</sub> selectivity is reduced. The 0.5 and 1.0% of Ru-Fe/MMC catalysts showed good selectivity to C<sub>10+</sub> with increasing temperature. It is due to the desorption of C<sub>4</sub> and C<sub>6</sub> olefins from the catalyst surface and cooligomerized to form C<sub>10+</sub> olefins. And the catalysts 1.5 and 2.0% of Ru-Fe/MMC in the same temperature range had shown low selectivity to  $C_{10+}$  (Figure 3B). Although depending on the nature of the support, in the case of too many adsorbed particles on the catalyst surface overlapping with each other and reduce specific surface area, in the end, can cause decrease catalytic activity. The results in Figure 3C show that the C<sub>8</sub> selectivity also greatly depends on nature of the catalyst and reaction temperature. For this reason, major product  $(C_8)$ selectivity decreased by increasing amount of loaded metal. The best selectivity has shown on The journal homepage www.ipacr.ub.ac.id 193 p-ISSN : 2302 - 4690 | e-ISSN : 2541 - 0733

the catalyst 1.0%Ru-Fe/MMC at 170 °C in about 33.0%.

Moreover, increasing the temperature has a positive effect on the olefin conversion. As shown in figure 3D the conversion increased in all samples. Compared to the obtained results, the low metal content catalysts showed significantly higher oligomerization activity than high metal content catalysts. The gas conversion increased from 38% (2.0%Ru-Fe/MMC) to 80% (1.0%Ru-Fe/MMC) with increase temperature from 110 °C to 170 °C.



**Figure 3.** The effect of temperature and metal loading amount on the conversion and product selectivity of  $C_2$ - $C_4$  olefin oligomerization:  $A - C_4$ - $C_6$  selectivity;  $B - C_{10}$  selectivity;  $C - C_8$  selectivity; D - conversion;

As we mentioned the results obtained in Figure 3A, when the metal content increased the selectivity of  $C_4$ - $C_6$  was increased too. At 130 °C the selectivity was 13.0% on the catalyst 1.5%RuFe/MMC and most of them consisted of iso- $C_4$  olefins. It may be closely related to the presence of iron in the catalyst [40]. According to the results, it is possible to obtain more iso- $C_4$  olefins by changing the ratio of active metals in the catalyst. In some studies, it can be seen that iron has the olefin isomerizes ability along with oligomerization and polymerization. Moronta et al. have reported several studies that butene isomerization over ion exchanged/pillared clay catalysts with different cations (Al<sup>3+</sup>, Cr<sup>3+</sup>, Fe<sup>3+</sup>, and Ni<sup>2+</sup>)

[41-42]. At this point of view, it is important to observe that the acidity of the clays increases by the pillaring process [45] and high polarizing species of  $\text{Fe}^{3+}$ . This makes the catalyst favorable for isomerizing activity [43-44].

In the further experiment, we determined the isomer selectivity of the catalyst by changing of Ru:Fe ratio. Figure 4 shows the iso- $C_4$  fraction selectivity over the catalysts of 1.5%Ru-Fe/MMC (The catalytic properties depend on the ratio Me<sup>+</sup>/Me<sup>0</sup>) with different Ru:Fe ratio. Concerning the selectivity to the desired product, the share of Fe increases in the Ru:Fe ratio, the reaction has been exerting intense on  $C_4$  isomers (mainly cis and trans butene) than other oligomer products and increased due to leading to the reaction temperature. When the catalyst composition was converted from bimetallic to monometallic, that contains only Fe, the temperature did not have the significant impact on selectivity and the reaction strives to stable and at 170 °C the iso- $C_4$  selectivity was reached 18.0%. (It is our experimental data)



**Figure 4.** Effect of Ru:Fe ratio and temperature to the iso-C<sub>4</sub> fractions selectivity on the catalyst 1.5%RuFe/MMC

# CONCLUSION

In the course of experiment with pillared clay, we performed the oligomerization of light olefins on the different amount of metal loaded catalysts. The highest olefin conversion and  $C_8$  selectivity were showed on the catalyst 1.0%Ru-Fe/MMC as about 80.0% and 33.0% respectively. It is important to indicate that at a constant pressure the reaction temperature and the amount of loaded metal in the catalyst significant effect on the catalyst activity and selectivity. It is also noteworthy that at a low Ru:Fe ratio the catalysts showed good selectivity to iso-C<sub>4</sub> olefins accompanied by increasing temperature. This will allow us to open a new direction for continued investigation into the appropriate reaction.

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