

## Catalytic Aromatization of Methane

N.I.FAYZULLAYEV\*<sup>1</sup>, S.M.TUROBJONOV<sup>2</sup>

<sup>1</sup>Department of Natural Sciences, Division of Chemistry,  
Samarkand State University, Samarkand, Uzbekistan

<sup>2</sup>Tashkent chemistry-technology institute  
Email: fayzullayev72@inbox.ru

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### Abstract

*The catalytic conversion process of the mixture of natural gas and hydrocarbons with the composition of 40 % - CH<sub>4</sub>; 10 % - C<sub>2</sub>H<sub>6</sub>; 25 % - C<sub>3</sub>H<sub>8</sub>; 20,3 % - C<sub>4</sub>H<sub>10</sub>; 4,7 % - C<sub>5</sub>H<sub>12</sub> into aromatic hydrocarbons in bentonite modified by Zr, Zn and Mo has been studied. Depending on the composition of initial raw materials the formation selectivity of aromatic hydrocarbons makes 77,0-86,1 % in 550-750<sup>0</sup> C and 500-1000 hour<sup>-1</sup> of volumetric rate.*

**Keywords:** Methane, oil simultaneous gases, catalytic aromatization, flow reactor, bentonite, catalyst, kinetic objective laws, “sol-gel” method, volumetric rate, temperature, contact time, height of catalyst layer, mass ratio of the catalyst active components, GTL – technology, alternative energetics, gas refining in gasoline, synthetic oil.

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### Introduction

In the result of automobile transportation development using oil fuel in large quantities leads to fuel shortage and ecological problems on a world scale. It requires solving the global problems like using non-oil fuel products for automobile transportation, finding alternative energy sources and implementing them into industry.

Natural gas is the most perspective among the available non-oil sources of hydrocarbons – coal, natural gas, wood, biomass and others in liquid fuel production. Nowadays a number of scientific investigations are being carried out on obtaining motor fuels and aromatic hydrocarbons from natural gas, oil simultaneous gases and gas condensate in the presence of zeolite catalysts [1-2].

Following above mentioned the main purpose of the work is to synthesize ecologic pure liquid fuels by catalytic aromatizing natural and oil simultaneous gases directly [3-7].

### Experimental work

With the purpose of obtaining liquid fuels from natural and oil simultaneous gases the experiments were carried out in a flow reactor in the interval of 350-850<sup>0</sup> C, in usual atmosphere pressure, in 300-1500 hour<sup>-1</sup> volumetric rate. The reaction products have been analyzed by gas – liquid chromatography.

## Results and discussion

As the research object natural gas and artificial mixture with the composition: ethane – 20,0 %, propane – 40,0 %, normal and isobutanes – 32,3 %, pentanes – 7,7 % have been used. As a carrier a local raw material bentonite, which is rich for silicon was used. It is known from literature that Mo – containing catalysts possess a high catalytic activity in aromatization reaction of methane without oxidants. As initial researches have shown the formation of aromatic hydrocarbons has not been observed, when bentonite was used itself to aromatize the artificial mixture in 550<sup>0</sup> C and  $V_{\text{mixture}}=500 \text{ hour}^{-1}$ . The conversion of the artificial mixture into aromatic hydrocarbons was observed when molybdenum nanopowders have been brought in bentonite. As a result of the experiments it was determined that a conversion of the initial compounds, when an optimal concentration of Mo in bentonite was 4,0 %, the selectivity and productivity was high as compared with aromatic hydrocarbons. With the presence of bentonite, which has 4,0 % Mo a conversion of low alkanes into aromatic hydrocarbons begins at 400<sup>0</sup>C and the expected compounds (benzene, toluene, xylene) are formed, when the temperature reaches to 450-500<sup>0</sup>C. As an additional product methane and ethane, hydrogen in a small quantity and C<sub>2</sub> – C<sub>4</sub> alkenes are formed with the increase of temperature the conversion of the initial mixture and formation selectivity of aromatic hydrocarbons increases. The conversion of hydrocarbons and formation selectivity of aromatic hydrocarbons decreases, when the volumetric rate is increased from 500 to 600 hour<sup>-1</sup>.

The conversion of low alkanes and productivity of aromatic hydrocarbons increases, when the temperature is increased up to 550<sup>0</sup>C. At the same time the selectivity of cracking products (C<sub>1</sub> – C<sub>2</sub> alkanes) and low olefins is decreased, when the temperature is increased higher than 550<sup>0</sup>C the reaction productivity and the formation selectivity of aromatic hydrocarbons are decreased.

The influence of different factors to aromatization reaction productivity of low alkanes has been studied and the following optimal condition chosen: T=550<sup>0</sup>C, the volumetric rate 500 hour<sup>-1</sup>. In formation of aromatic hydrocarbons the catalyst activity is increased, while the catalyst that contains 4,0 % molybdenum has been modified by different metals. Therefore by adding metals like zinc, gallium, zirconium, manganese, iron their catalytic activity was studied. It has been determined that the formation productivity of aromatic hydrocarbons from C<sub>2</sub> – C<sub>5</sub> hydrocarbons is high, when bentonite was modified with zirconium, zinc and gallium.

Spending high energy and raw material with heterogenic catalysts to available technologies is requiring to find new methods of fulfilling abovementioned processes. One of the ways to solve the problem is a fulfillment of the process in aerosol nanocatalysts. Zeolites are carrier compounds with nanosize active center. For direct aromatization reaction of C<sub>2</sub> – C<sub>5</sub> hydrocarbons the catalyst has been prepared on “sol-gel” method. For “sol-gel” synthesis of nanosize particles the aqueous solutions of salts Zr(NO<sub>3</sub>)<sub>4</sub>, ZrO(NO<sub>3</sub>)<sub>2</sub>, Zn(NO<sub>3</sub>)<sub>2</sub> were used. The reagents in a required amount were weighed and they

were dissolved in bidistilled water then additions forming gel: citric acid and ethylene glycol have been added. Formed mixture was well stirred in 80<sup>0</sup>C. Then it has been thermally processed for 2 hours at 200<sup>0</sup>C, for 3 hours 500-1000<sup>0</sup>C.

The space composition of formed catalyst was studied using CuK – ray source in X-ray structure method in “DRON – 3M ” diffract meter. The promoting influence of different metals in the presence of chosen high performance catalyst to the formation productivity, selectivity of aromatic hydrocarbons and to the conversion of initial mixture has been studied and obtained the following results:

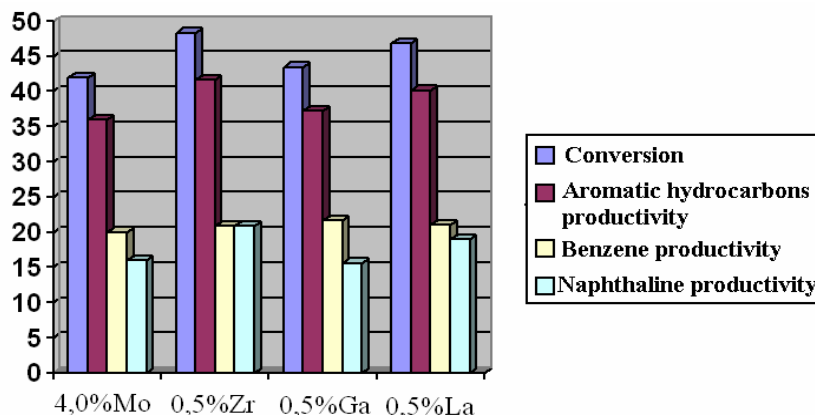


Figure 1. Activity comparison indices of Mo/bentonite and the catalysts prepared based on it.

In chosen optimized condition 550<sup>0</sup>C and  $V_{mix}=500 \text{ hour}^{-1}$  and conversion of artificial mixture reaches to 48,3 %, aromatic hydrocarbons productivity 41,6 %. The selectivity makes 86,1 % as compared with aromatic hydrocarbons. It is shown from the figure that the highest result was obtained in a catalyst with the presence of zirconium. As a result of the researches it was determined that the reaction yield and conversion of the initial substances get the highest value, when zirconium amount in bentonite composition is 0,5 %. When zirconium amount increases further an aromatizing property of the catalyst decreases and cracking property increases.

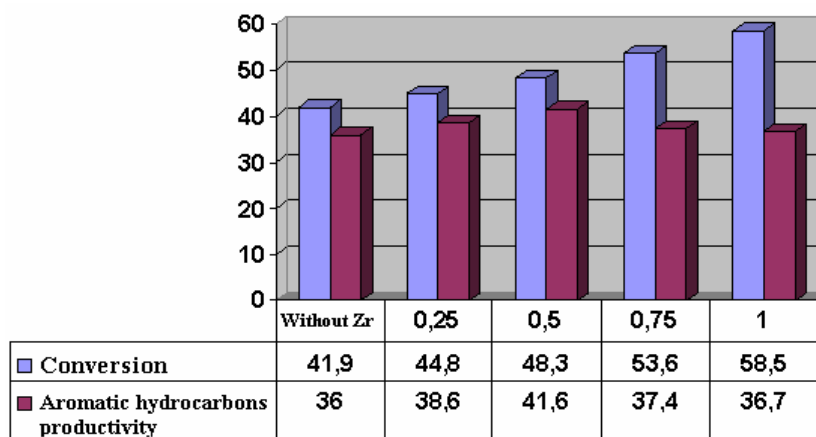


Figure 2. Dependence of natural gas conversion and reaction products yield in Mo/bentonite catalysts on zirconium concentration (T=550<sup>0</sup>C).



Catalytic activity of the catalyst depends not only on its composition, but also on the condition of processing it thermomechanically. When the catalyst is processed thermomechanically high disperse particles that possess extra energy are formed more. When the catalyst that contain 0,5 % zirconium had been thermomechanically processed at 500-600<sup>0</sup>C during 2-3 hours its aromatizing property was not changed. When the temperature was increased up to 700-750<sup>0</sup>C an increase of aromatizing activity of the catalyst has been observed. At the same time the formation productivity of the products of cracking and dehydrogenating reaction decreases. Side by side with the activity and selectivity of the catalyst one of its important parameters is its ability to work longer without changing its high aromatizing property. In the process of aromatizing hydrocarbons coke is formed in the surface of the catalyst, it influences negatively to effective catalytic interaction of the catalyst and decreases gradually its activity. Therefore regeneration of the catalyst is required. The catalyst regeneration is performed in air at 650<sup>0</sup>C in air flow during 8 hours by increasing gradually the volume concentration of oxygen. After regeneration the catalyst restores its initial activity completely.

In aromatization reaction of low alkanes the preparation technology of a catalyst also influences more to the activity and productivity of a catalyst. Bentonite was thermically processed at 500-650<sup>0</sup>C for 2 hours after absorption of zirconyl nitrate to it and its catalytic activity was studied. At the same time any changes has not been observed. When the catalyst has been thermically processed at 700-750<sup>0</sup>C for 3 hours a sharp increase in its aromatizing activity was observed. When the reaction temperature was 550<sup>0</sup>C the productivity of aromatic hydrocarbons increased to 5,2 % as respect with initial state. When the temperature was 550<sup>0</sup>C and the volume rate 300 hour<sup>-1</sup> the conversion of initial substances reached to 99 %. The formation productivity of aromatic hydrocarbons decreases, when volume rate increases two times.

The main component of natural gas composition – methane is thermodynamically stable and of great endurance for many reagents influence. C-H bond energy in methane molecule makes 439 kJ/mol. Direct synthesis based on methane is very difficult, but its products are active comparing to methane and reacts well. When we used the catalyst that has high catalytic activity, which was used to aromatize artificial mixture for aromatizing natural gas in T=550<sup>0</sup>C, in volume rate 500 hour<sup>-1</sup> change of methane to aromatic hydrocarbons has not been observed. In the presence of chosen catalyst the influence of some factors to the reaction rate (volumetric rate, temperature, contact time, height of catalyst layer, mass ratio of catalyst active components) was studied and as a result the following optimal condition of the reaction chosen: T=750<sup>0</sup>C, volumetric rate V<sub>CH<sub>4</sub></sub>=1000 hour<sup>-1</sup>, height of the catalyst layer 10 cm.

When the effect of active components mass ratio to catalytic activity and productivity of the catalyst was studied and up to 5,0 % on mass Mo added to the catalyst an increase of natural gas conversion and aromatic hydrocarbons productivity has been determined. With the increase or decrease of

Mo amount from 5,0 % in the bentonite composition its catalytic activity decreases sharply. When volumetric rate increases from 1000 to 1500 hour<sup>-1</sup> conversion of initial substances and productivity of aromatic hydrocarbons decreases. After that the promoting property of different metals to catalyst based on molybdenum has been observed. As a result the highest results were achieved, when zirconium added to the catalyst based on molybdenum. The experiment results are presented in fig.3.

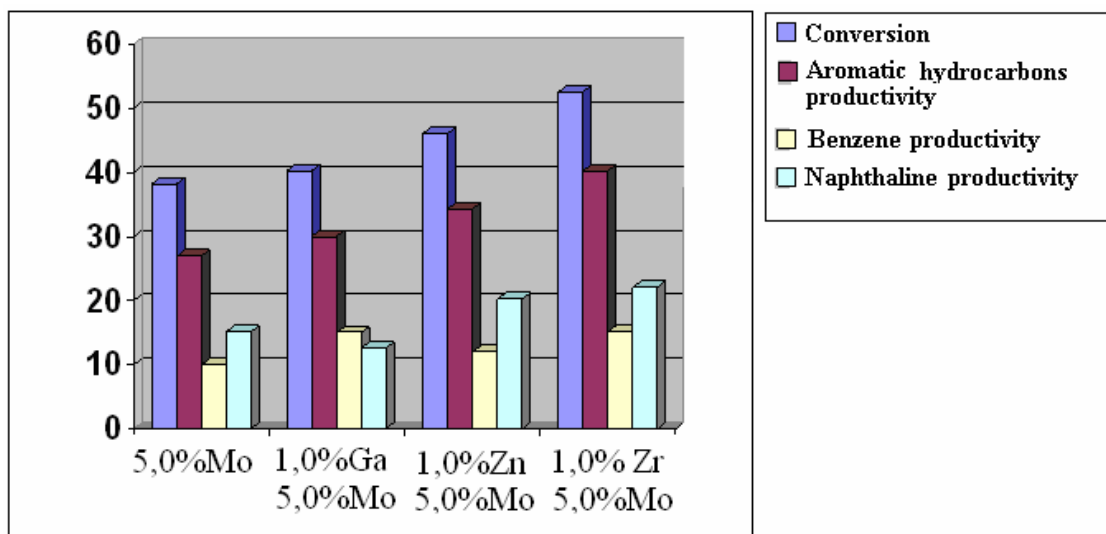


Figure 3. The promoting influence of different metals to the catalyst based on molybdenum

It is shown from the figure that a bentonite catalyst that possess 1,0 % Zr and 5,0 % Mo has high catalytic activity. When zirconium amount in the composition of prepared catalyst based on molybdenum had been changed from 0,25 % to 2,0 % the highest result obtained, when zirconium amount was 1,0 %. The reaction was carried out by adding Ga and Zn metals to chosen catalyst to increase the reaction productivity further. The catalyst catalytic activity increases with addition of Zn and Ga to the catalyst with Zr-Mo. The productivity of aromatic hydrocarbons was the highest in the presence of a catalyst with composition 5,0 % Mo, 1,0 % Zn, 1,0 % Zr. As a result of investigations was chosen an optimal catalyst with the following composition: 5,0 % Mo, 1,0 % Zn, 1,0 % Zr. An influence of the temperature to aromatizing reaction rate of natural gas without oxidizer, to the productivity and selectivity of aromatic hydrocarbons, as well as to the conversion of initial substances has been studied.

Maximum amount of aromatic hydrocarbons forms in the presence of a catalyst with the composition 5,0 % Mo, 1,0 % Zr, 1,0 % Zn. Aromatic hydrocarbons productivity makes 40,4 % at  $V_{CH_4}=1000 \text{ hour}^{-1}$ ,  $T=750^{\circ}\text{C}$  on this catalyst. As the researches show the formation of coke increases with the increase of the temperature and volumetric rate and the catalytic activity of the catalyst decreases coating the active centers of the catalyst with coke. In order to decrease coke formation and to prevent it the coke formation decreases sharply increased working period of the catalyst, when cobalt was added up to 0,2 % to bentonite containing Mo.

The experimental results are presented in the table.

Table 1. Influence of the temperature to catalytic reaction products composition of natural gas in the presence of the catalyst modified with the nanoparticles of Mo, Zr, and Zn ( $V_{CH_4}=1000 \text{ hour}^{-1}$ )

T, <sup>0</sup> C	X <sub>gas</sub> , %	Products of the reaction						Y <sub>Ar</sub> , %	S <sub>Ar</sub> , %	
		H <sub>2</sub>	alkanes	alkenes	C <sub>6</sub> H <sub>6</sub>	C <sub>7</sub> H <sub>8</sub>	C <sub>8</sub> H <sub>10</sub>			C <sub>10</sub> H <sub>8</sub>
<b>5,0% Mo/bentonite</b>										
650	18,6	2,45	85,27	3,58	3,53	0,01	0,10	5,07	8,7	46,8
675	26,4	3,95	76,74	2,41	5,67	0,05	0,30	10,88	16,9	64,0
700	31,5	4,97	72,60	1,03	6,99	0,10	0,60	13,71	21,4	67,9
750	38,3	8,68	65,69	0,73	9,92	0,11	0,90	15,97	26,9	70,2
<b>5,0% Mo-0,5% Zr-1,0% Zn/bentonite</b>										
650	21,8	1,79	84,47	2,84	3,58	0,01	0,20	7,11	10,9	50,0
675	32,6	4,49	74,29	2,22	4,71	0,06	0,50	13,73	19,0	58,3
700	39,4	6,52	66,51	1,77	8,17	0,10	0,80	16,13	25,2	64,0
750	49,7	8,81	50,91	1,08	12,65	1,25	1,5	17,35	32,4	65,2
<b>5,0% Mo-1,0% Zr-1,0% Zn/bentonite</b>										
650	31,6	1,87	79,25	2,38	6,69	0,11	0,23	9,47	16,5	52,2
675	43,8	5,20	65,55	2,25	10,59	0,75	0,59	15,07	27,0	61,6
700	48,6	7,72	54,72	2,06	15,55	1,08	1,22	17,65	35,5	73,0
750	52,5	10,83	47,85	0,92	15,23	1,32	1,87	21,98	40,4	77,0
<b>5,0% Mo-1,5%Zr-1,0% Zn/ bentonite</b>										
650	21,6	1,57	85,82	2,21	3,87	0,12	0,20	6,21	10,4	48,2
675	28,3	2,86	75,27	2,07	8,65	0,59	0,30	10,26	19,8	70,0
700	36,7	5,27	66,63	2,20	9,8	0,72	0,50	14,88	25,9	71,0
750	44,6	6,57	59,57	2,06	11,38	0,96	0,70	18,76	31,8	71,3

Note: T-reaction temperature; X-conversion; Y<sub>Ar</sub>-aromatic hydrocarbons productivity; S<sub>Ar</sub>-formation selectivity of aromatic hydrocarbons.

With the increase of volumetric rate of starting substances the amount of benzene and naphthalene in the products of conversion and reaction decreases, the productivity of C<sub>3</sub> – C<sub>5</sub> olefines, as well as aromatic hydrocarbons increases. With the decrease of volumetric rate oligomerization of olefines and as a result of participation intensity increase in dehydrocyclization reaction their productivity decreases, it leads to the productivity increase of aromatic hydrocarbons.

### Conclusion

- i) The influence of different factors to the reaction productivity of low alkanes aromatization has been studied and chosen the following optimal condition. In chosen optimal condition the conversion of artificial mixture at 550<sup>0</sup>C and  $V_{\text{mixture}}=500 \text{ hour}^{-1}$  makes 48,3 %, aromatic hydrocarbons productivity 41,6 %. The selectivity as compared to aromatic hydrocarbons made 86,1 %.
- ii) As a result of the investigations was chosen a catalyst with the following composition: 5,0 % Mo, 1,0 % Zr, 1,0 % Zn.



- iii) Maximum amount of aromatic hydrocarbons in catalytic aromatization reaction of methane forms in the presence of a catalyst with the composition: 5,0 % Mo \* 1,0 % Zr \* 1,0 % Zn. Aromatic hydrocarbons productivity in the catalyst at  $V_{CH_4}=1000 \text{ hour}^{-1}$ ,  $T=750^{\circ}\text{C}$  makes 40,4 %.
- iv) The influence of some factors (volumetric rate, temperature, contact time, height of catalyst layer, mass ratio of catalyst active components) to the reaction rate in the presence of chosen catalyst has been studied and as a result chosen the following optimal condition:  $T=750^{\circ}\text{C}$ , volumetric rate  $V_{CH_4}=1000 \text{ hour}^{-1}$ , the height of the catalyst layer 10 cm.

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