CATALYTIC ALKYLATION OF C_2-C_4 HYDROCARBONS

Bolysbek Utelbayev
Tasmagambetova Aigerim
Toktasyn Raila
Markayev Yergali
Myrzakhanov Maxat
Kazakh British Technical University,Kazakhstan

Abstract

The aim of this paper is development putting metals on pillar structured clay for catalytic alkylation of light hydrocarbons. The pillar structured bentonite obtained with modifying polyhydrocomplex of chromium (III) chloride. Pillar structured bentonite was used for preparation 0.5-1.0% Ru/Carrier (modifying bentonite) support catalysts where is realized alkylation of C_2-C_4 hydrocarbons. Process of alkylation is carried out at partial pressure of hydrogen 0.5-1.0MPa. The outcome of high octane number components 2.2.4 three-methylpentane and 2.2.3 three-methylpentane achieved about 40%. At alkylation butane-butene mixture yield of isooctane achieved 60%.

Keywords: Catalyst, bentonite, alkylation, butane, butene, motor fuels

Introduction

Gasoline, one of the major derivatives of crude oil, is used throughout the world as a motor vehicle fuel. The environmental protection requirements are stiffenning in the world, and a number changes have been made in the quality indexes of motor fuels. In particular, for gasoline the content of benzene and sulfur have been introduced – a maximum 0.1 wt. % and 10ppm respectively(Euro-5 standart).Decrease in the maintenance of aromatic hydrocarbons, especially benzene in motor fuel is an actual and urgent problem. Toxic action of benzene and a product of its incomplete oxidation benzpyrene- cancerogenic substance accumulated in an environment, renders negative influence on safety of ability to live of people and fauna[1]. Necessity to improve technology of oil refining and its separate stages for reduction of the maintenance of benzene and its derivatives.One of such processes is catalytic hydrodearomatization-transformations of aromatic hydrocarbons to cyclohexane and its derivatives . However, the maintenance in oil distillates heterocyclic compounds which deactivate catalysts, demand their perfection and more detailed studying of the mechanism catalytic transformation of hydrocarbons [2-4].

Besides it, there is a way to produce motor fuels by alkylation and oligomerization of light gases which does not contain aromatic hydrocarbons.Intensive development of secondary processes of destructive processing of crude oil has led to occurrence at oil refining plants resources of C_2-C_4 hydrocarbons. Except for oil gases also contain basically C_1-C_4hydrocarbonic gases where some of amount are burned. All these data has induced interest to study of producing alkylatebeing as components of motor fuels from hydrocarbons C_2-C_4 .

One of such processes is alkylation isoalkaneswith light olefinic hydrocarbons, typically C_2 and C_4 olefins, in the presence of an acid catalyst, usually sulphuric acid (H_2SO_4) or hydrofluoric acid (HF). The quality of gasoline as a fuel in internal combustion engines is measured by its octane rating. Gasoline is produced in several grades of octane rating. The product, alkylate has a high-octane value and is blended into motor and aviation gasoline to improve the antiknock value of the fuel. Alkylate is one of the best gasoline blending components because it is a clean burning, very low sulphur component, with no olefinic or aromatic compounds and with high octane and low vapour pressure characteristics. The development of sustainable active and selective catalysts for the alkylation of light hydrocarbons to replace the unfriendly homogenous systems such as sulfuric, hydrofluoric acids and transition metal complexes currently applied in the industry still remains a challenge[5].

The purpose of this work was to study transformation of light gases C_2-C_4at presence of the ruthenium – chromic support catalyst where as carrier is served pillar structured montmorrillonite containing in native bentonite clay.

Experimental

Materials and apparatus

The raw bentonite clay was collected in South Kazakhstan. The weigt% chemical composition was measured as (SiO_2) 54.0-60.0, (Al_2O_3) 13.0-16.0, (Fe2O3) 4.0-6.0, (MgO) 2.0-3.0, (Na_2O) 1.0-2.0, (H_2O) 8.0-11.0, and other ingredients 6.0-9.0. Cation-exchange is 66.4mmol/100.0g clay. Chromium (III) chloride, sodium hydroxide were of analytical grade, and used without further purification to prepare chromium polyhydrocomplex. Other chemical reagents $HClH_2SO_4$,H_3PO_4 and $RuOHCl_3{\cdot}4H_2O$ were of analytical grade. Acidity of environment supervised by means of digital pH meter OP-208/1. Concentration of HCl acid is varied from 1.0% up to 15.0%. X-ray diffraction samples were measured using a Rigaku D/Max 2200 VPC powder diffractometer with CuKα radiation, accelerating voltage of 40 kV, emission current of 30mA, and scanning speed of 10^0/min was used to determine the crystal phase composition of the prepared carrier at 20^0C. The acidity of the bentonite , pillar-structured montmorillonite and catalysts was investigated by FTIR spectroscopy. For the IRstudies, the calcinedRu/ Pillar-structured montmorillonite sample was pressed into self-supported wafers and introduced in an IR cell allowing in situ treatments in controlled atmospheres and temperatures from -176^0C to 550^0C and connected to a vacuum system with gas dosing facility. Before to the adsorption measurements the sample of catalyst was pretreated in the IR cell at 350^0C for 2h in flowing Ar about flow rate $30cm^3$ per minute.Afterwards, the catalyst was evacuated at 350^0C during the 3h under dynamic vacuum of $1{\cdot}10^{-3}$Pa, cooled down to -30^0C, and NH_3dosed at increasing pressures about 10- 100Pa. TheIR spectrum was then recorded after each dose.The textural properties of the support catalysts were evaluated from the N_2adsorption-desorption isotherms obtained at 77K over the whole range of relative pressures, using a Micromeritics ASAP-2000 apparatus. Specific surfaces of catalysts calculated from these isotherms using the BET method in the 0.005-0.25 P/P_0 range. Temperature – programmed study catalysts were carried out in a semiautomatic Micromeritics TPD/TPR 2900 apparatus interfaced to a computer. Amount of Ru on support catalysts were determined using a Perkin-Elmer 3030 atomic absorption spectrophotometer. The determination of the composition of feeds and products was carried out by chromatograph Chrom-4with a Flame Ionization Detector(FID). The conditions were the following: columns: 3m x 3mm, filled by «Chromaton –N» processed with liquid phase «Polyethylenglycoladipate» (15 wt.% of the carrier). Temperature of a column 373K, temperature of the evaporator 423K. Carrier gas: argon, with 50 cm^3/min flow rate.

Synthesis of pillared clays and catalyst

Preparation of pillared clays carried out as in [6, 7, 8]. Suspension of bentonite clay prepared in water and mixed up during 4 h, pH-water extract of clay makes ~ 8-9. The polyhydroxocomplex of chromium obtained by adding gradually the solution of sodium hydroxide to aqueous solution of chromium(III) chloride. Concentration of chloride chromium change from 5.0 to 30.0 mmole Cr^{3+} per gram clay. For prevent from coagulation of the solutionpolyhydroxocomplex of chromium it slowly added to suspension of clay. After endurance this system during the 24 h at room temperature, excess water was removed in a rotary evaporator. Subsequently the impregnate was dried at 120^0C in air for 6 h and finally calcined in air 500^0C for 4 h. After cool off it to the room temperature obtaining mass was pounded to a powder and sifted. Powder of pillar structural bentonite particles about the size 2.0 mm was impregnated by aqueous solutions of $RuOHCl_3{\cdot}4H_2O$ at room temperature. Subsequently, excess water was removed at mixing, was dried at 110^0C in air for 6 h and finally calcined in air at 400^0C for 4 h. Chemical analysis revealed chlorine contents were changed from 0.5 to 1.0 wt % respectively.

Reduction of catalyst and alkylation

Catalytic alkylation butane- butylene fraction(15% isobutylene 30% butylene ,10 % n-butane and 40% isobutane) was carried out in a continuous flow fixed-bed reactor at the range of temperature 130-180^0C and pressure of gas fraction 0.2-2.0MPa. Prior to alkylation catalyst were heated in a stream of hydrogen ($50cm^3$/min) at a rate 5^0C/min up to a final temperature 300^0C and kept at that temperature for 2 h. Typically, the reactor was loaded with 10.0g of catalyst with a pellet size of 2.0mm diluted with ceramic particles the same pellet size (mass catalyst: mass ceramics = 1:1).Then, the catalysts were cooled to temperature of alkylation in the same flow of hydrogen. The optimum of the applied process parameters – temperature, pressure and amount of catalyst based on the results of preliminary experiments.

Results and discussion

Textural Properties of bentonite

Natural bentonite clay has a little specific surface about 60 m^2 per gram and lose their porosity at heating above 110^0C to $20m^2$/g. Preliminary experiments treatment bentonite clay with HCl, H_2SO_4 andH_3PO_4 gave to conclude that more effective render hydrochloric acid. Using hydrochloric acid with concentration about 6.0-8.0%wt changed the ratio SiO_2/Al_2O_3 from 4.0 up to 21.0.Inccrease the concentration of HCl from 4.0% up to 15.0% lead to destruction of the crystalline lattice structure of montmorillonite (fig. 1 curve 6). It means transformation of aluminum to the solution. The treating samples of bentonite clay with HCl (C=6.0-8.0%) not increase their termostability. One of the way giving termostability to native clay is to modify with a large ions for support between the layers of the mineral. Modifying bentonite clay by polyhydroxocomplexes Cr(III) leads to growth of a specific surface from 64 up to $260m^2$/g, total volume of porous from 0,18 cm3/g up to.0,54cm3/g, interlaminar distances from 0.90 up to 2.04nm(table 1,fig 2).

The maximal distance 2,00 - 2,04 nanometers corresponds to concentration of chromium about 15-20 mmole per gram of clay where between the layers settle down polyhydroxocomplex ions of chromium [8].

Increase the concentration of chromium above 20 mmole per gram of clay does not lead to the further growth of distance. It is probably connected by that in a solution there are not hydrolized forms of chromium chloride which do not influence formation pillar structures. The similar phenomenon with polyhydroxocomplex ions of iron (III) also was revealed in [9].

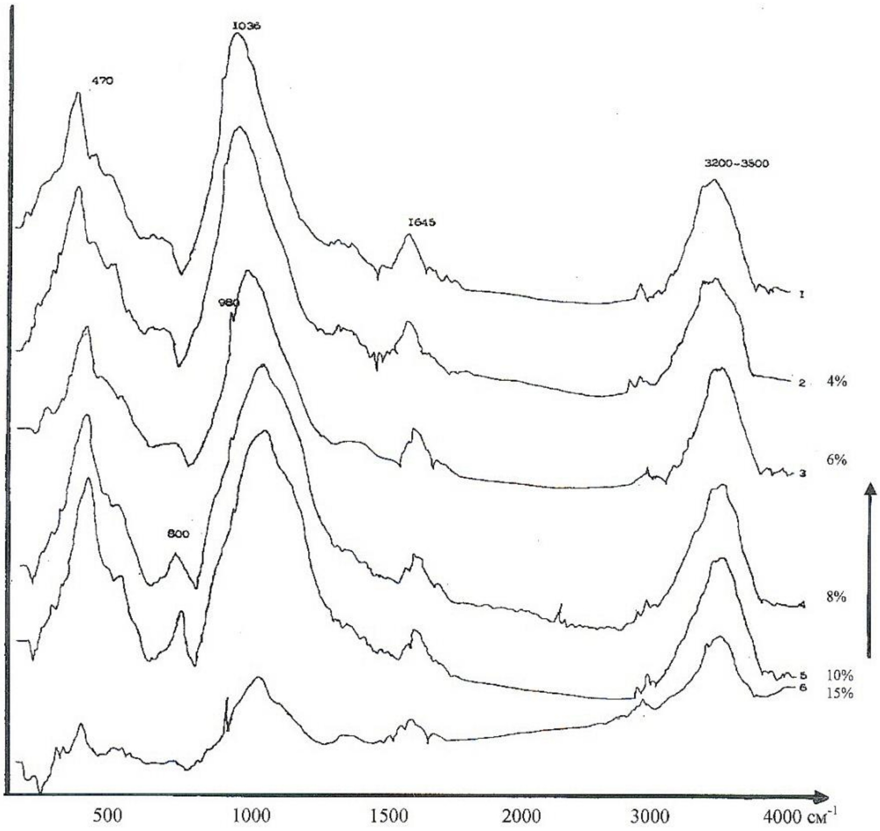

Fig.1 IR spectrum bentonite clay by treating with HCl:1-native clay; 2- sample treated with 4%HCl; 3- 6%; 4- with 8%HCl;5- with 10%HCl;6- with 15%HCl;

Fig.2 The pellet of ruthenium putting catalyst on the pillar structured montmorillonite

Table 1 Some parameters of pillar structural montmorillonite modified by chromium

The maintenance of ions chromium, mmol/g.clay	S, m^2/g	**d$_{001}$**nano meter	Total volume of porous, cm3/g	Loss of thermostability	
				T,°C	*SSP*,m^2/g
-	64	0,90	0,18	140	20
5	130	1,30	0,40	360	80
10	160	1,60	0,46	440	110
15	240	2,02	0,50	500	220
20	260	2,04	0,54	560	240
30	240	1,90	0,51	500	230

Modifying montmorillonite minerals (MM) containing in bentonite clay gives to them heat resistance. The specific surface of samples(containing 15-30 mmole Cr^{3+}) were defined after heat treatment at 180°C are 240-260 m^2/g and increasing the temperature up to 500-

560°C decreases this value insignificant to 220-240 м2/г, accordingly. Not modified bentonite clay lost their porosity at 140°C, and a specific surface made 20 m^2/g.

To elucidate the nature of Lewis and Bronsted acid sites studied of the South Kazakhstan bentonites held infrared spectroscopic study using the adsorption of molecules of ammonia (table 2).

Table 2 - Acidity of the South Kazakhstan bentonite according to the thermal desorption of ammonia molecules

Sample	Content of acid centers	Amount of acidic centers			
		weak 50-100^{0}C	medium 200-300^{0}C	strong > 300^{0}C	total
Horizon 1(depth 0.5-1.0m)	%	64	26	10	100
	micromoles NH_3/g	32	13	5	50
Horizon2(depth 1.0-2.0m)	%	66	25	9	100
	micromoles NH_3/g	33	13	5	51
Horizon 3(depth 3.0-4.0m)	%	65	25	9	100
	micromoles NH_3/g	32,5	8,5	5	50
Treated with 4%HCl	%	33	27	40	100
	micromoles NH_3/g	66	54	80	200
Treated with 8% HCl	%	30	30	40	100
	micromoles NH_3/g	69	69	92	230
Treated with 10%HCl	%	40	30	30	100
	micromoles NH_3/g	80	60	60	200

The bentonite clay containing montmorillonite has different types of acidic centers and used to prepare Ru support catalysts for alkylation.

The table 3 shows results of alkylation of butane-butylene fraction on the support catalyst containing ruthenium.

Table 3 Results of alkylation of butane-butylene fraction (15% iso-butene: 30% butene и 50 % n-butane and iso-butane) 0.5%Ru/MM (modified montmorrilonite) catalyst (25cm^3).

Parameters			Yield of liquid hydrocarbons, %об.				Unreacted gas,%	Selectivity by iso-octane,%
			2,2,3-trimethyl pentane	2,4,4-trimethyl pentane	2,5-dimethyl hexane	others,%vol.		
1			2	3	4	5		6
T,K	P, MPa	V,h^{-1}	0.5%Ru/MM					
403	0,2	100	8,0	12,0	3,0	6,0	71	23
	0,5		12,0	18,0	4,0	8,0	48	34
	1,0		13,0	21,0	6,0	10,0	50	40
	2,0		14,0	20,0	6,0	16,0	52	40
413	0,2	100	16,0	31,0	8,0	9,0	36	55
	0,5		18,0	38,0	7,0	10,0	27	63
	1,0		22,0	38,0	5,0	11,0	24	65
	2,0		21,0	38,0	5,0	12,0	25	64
423	0,2	100	17	34	11	9,0	25	66
	0,5		19	41	14	8,0	18	76
	1,0		20	44	13	7,0	16	77
	2,0		21	43	12	7,0	18	76
453	0,2	100	16,0	30,0	7,0	13,0	40	53
	0,5		18,0	31,0	7,0	15,0	34	56
	1,0		19,0	31,0	4,0	14,0	32	54
	2,0		19,0	30,0	4,0	13,0	34	53
423	1,0	150	18,0	26,0	6,0	16,0	30	50

		200	16,0	20,0	7,0	14,0	40	43
		300	11,0	14,0	8,0	11,0	41	33
		350	9,0	13,0	6,0	9,0	63	28
453	1,0	150	16,0	24,0	8,0	21,0	31	48
		200	13,0	18,0	9,0	18,0	42	40
		250	11,0	16,0	7,0	14,0	52	34
		300	8,0	12,0	6,0	8,0	66	26
		350	6,0	9,0	4,0	3,0	81	19

Experimental results shows that in the presence of supported ruthenium and rhodium catalysts formed 2,2,3-trimethylpentane, 2,4,4-trimethylpentane, 2,5-dimethylhexane and high octane motor fuel components. At 0.5% Ru / γ-Al_2O_3, 0.5% Ru / MM, 1,0% Rh / γ-Al_2O_3 and 1,0% Rh /MM at a temperature of 413-423 K and pressures of 1.0 MPa, an yield of iso-octane is 50-60% at a selectivity of 63-65%.

Conclusion

On the basis of theoretical and experimental studies of catalytic conversion of light hydrocarbons C2-C4 improve domestic natural aluminosilicates for alkylbenzene production, which can be qualified as new developments in the field of energy-saving technologies and harmless technology for petrochemical industry.

Using the South Kazakhstan bentonite, consisting mostly of montmorillonite, followed by modification to "pillar structure" in the petrochemical process of catalytic conversion of C4 -C6 alkanes of normal structure to the high-octane components of motor fuels It was established that the modification of bentonite comprising montmorillonite by polyhydroxocomplexes of aluminum, iron, chromium and zirconium lead to formation of a "pillar structure" exhibiting thermal stability to 500^{o}C. The study of light hydrocarbon conversion reactions revealed that bentonite treated by polyhydroxocomplexes of metals is very different in properties from the raw natural minerals. On the basis of the electronic spectra of acid-base indicators adsorbed on the surface of bentonite and study of the IR spectra of the ammonia molecule, established the presence of both Bronsted and Lewis acid sites in Keles bentonite. At 0.5% Ru / γ-Al2O3, 0.5% Ru / MM at a temperature of 413-423 K and pressures of 1.0 MPa, an yield of iso-octane is 50-60% with 63-65% selectivity.

Reference:

The Technical rules « About requirements to emissions by the automobile technics released in territory of the Russian Federation, harmful (polluting) substances» <http://www.gost.ru/wps/wcm/connect/fb6742004677b612aa3fbe8104aeacf2/.

Absi-Halabi, A.Stanislaus,and H. Qabazard, Hydrocarbon.Process. 76 (1997) 45-54.

A. Stanislaus,andB.H.L.Cooper, Catal. Rev. Sci. Eng. 36 (1994) 75-86.

G.Nagy, Z.Varga, D. Kallo, J. Hancsok, Hungarian Journal of Industrial Chemistry Veszprem. 37 (2009) 69-75.

Augustin Martinez,Maria A. Arribas, Patrica Concepcion, Sara Moussa.Applied Catalysis A:General 467(2013) 509-518.

V.S.Komarov, A.S. Panasjugin, N.E Trofimenko, Collodial magazine. 57 (1975) 51-56.

S. A. Korili, A.Gill, A.Korili, R.Trujillano, M.A.Vicente: Pillared clays and related catalysts, Springer (2010) 522p

P.Gallezot,“Catalysis by Zeolites” (B. Imelik, C. Naccache, Y. Ben Taarit, J. C. Vedrine, G. Coudurier, and H. Praliaud, Eds.), 5 Elsevier Science, Amsterdam, (1980) 227.

M. Koussathana, D.Vamvouka, M. Tsapatsis, and X.Verykios, Appl. Catal. 80, (1992) 99 - 104.