مجلة القادسية للعلوم الصرفة المجلد 13 العدد 1 لسنة 2008
المؤتمر العلمي الاول لكلية العلوم المنعقد في 26-27 اذار لسنة 2008

Cracking Catylists from Hectorit intercalated with mixed cohydrolysis La-Zr).

Abbas M. Bashi, J.H.Ali, S.M.Haddawi
College of science /department of chemistry/kerbala university

الخلاصة:

المعدن الطيني من نوع هكتورايت يمتلك تركيب على شكل طبقات يمكن ادخال اكاسيد من مجموعة اللنثنايد مثل السريوم، اللنثانيوم بالتميؤ المشترك مع عنصر الزركونيوم مما يؤدي الى تحسين المقاومة الحرارية للطين المعدني، يمكن ستخدامه كعامل مساعد في عمليات السحق الحراري، له مسامية ومساحة سطحية كافية

Abstract:

College of science /department of chemistry/kerbala university

Hectorite clay laminated structure bridged by metallic oxides selected from oxides of Lanthanum & Zirconium containing 25 to 40% of an oxide of metal of the group of Lanthanum like cerium ,La,Gd, the presence of Lanthanum and cerium improves the thermal resistance during a dry calcinations or even under humid air the clays can be used as catalyst during conversion of hydrocarbons.

Introduction:

Hectorite clay laminated structure bridged by metallic oxides selected from oxides of Lanthanum & Zirconium containing 25 to 40% of an oxide of metal of the group of Lanthanum like cerium the presence of Lanthanum and cerium improves the thermal resistance during a dry calcinations or even under humid air the clays can be used as catalyst during conversion of hydrocarbons.

Introduction : Clays are among the most important constituents of the earth crust .clays of smectite type such as bentonite montmorillionite , beidellite and hectorite have layered structure.

The sheet that constituents the mineral is called dioctahedral , and comprises an octahedral layer of aluminum surrounded by tow tetrahedral layers of silicon the cohesion between the layers is ensured by pooling oxygen atoms.

The layered structure is characterized by inter foliar spacing that is the distance that separates two layers, or by the basal spacing which represents the sum of the inter foliar spacing and thickness of a layer.
The inter foliar spacing can be increased by introduce between the layers polar molecules such as water, alcohol .The thermal stability of the clays thus obtained is not sufficient for allowing their use as catalyst , In fact , at a temperature of 100 c° ,the clay expels the polar molecules adsorbed and closes again that their inter layered distance became 9A°.

This clay layers can be kept separate in amore durable manner by introducing bridges of metallic oxides .These bridges or pillars of metallic oxides are introduced between the layers by means of metallic complexes.

The synthesis of bridged clays has been described in Graces(1)he describes the synthesis of clays bridged by metallic oxides by reacting the clay with an aluminum or zirconium containing complex in aqueous medium .

The inter foliar spacing is between 6 to 16 A° .the aluminum complex is used in polymerized form the Aluminum bridge clay a cording to this process maintains from 50 to 90 % of its initial surface after heating at 760c°, but only form 50 to 70% after heating at 675c° in the presence of water vapor according to Lahav (2) Amoutmorillonite aqueous suspension is contacted with an oligomer of aluminum hydroxide, The basal spacing of the solid obtained is of 18A°.

European patent No 130 , 055 of British petroleum co.(4) describes the synthesis of clays bridged in an anhydrous medium by reaction with boron trichloride or an organometailic compound another European pat. No 73718 describes abridging method by dialysis of a mixture of an aqueous solution of a metallic hydroxide and an aqueous clay suspension .

The thermal stability of the products thus obtained dose not exceed 500c° .

D.Tichit (5) describes the intercalation of moutmorillonite with aluminum hydroxides with a different ration $\frac{OH}{Al}$ and he obtains a pillared – clay , of inter foliar distance of 18.7 A° after calcinations at 750c°.

F. Cotton &al. as a metal of the group of the lanthanides (6) Ym can be considered as a lanthanide and will be included in the phase lanthanide group as used.

Experimental work : Hectorite clay was washed several times after sedimentation as stock law for 16h and kept 10g clay as a suspension in two liters of distal water cohydolysis oxide ($\frac{lauthnum}{Zircounum}$)of a 10% ration atom $\frac{La^{+3}}{Zr^{+4}}$ the metal salts most commonly used are chlorides a ,competitor cation the of small charge $ volume like NH_4^+ obtains from NH_4NO_3 , a several quantities of this competitor cation used with the cohydrolysis oxide of $\frac{La^{+3}}{Zr^{+4}}$,0% , 4% , 10% , 20% .

The cohydrolsis oxides pored over the suspension of the clay drop by drops with continuous agitating for two hours the filtering the produce clay – metal oxide and washed several times until no chloride tested by ($AgN0_3$) .

The solid of a pillared – clay , heated in air and in the presence of water vapor of 0.5 bar.

The resulted samples with deferent condition of calcinations , was characterized by their basal spacing determined x- ray diffraction on CGR-60 Philips apparatus , and by their specific surface measured by the method B.E.T .

Decalin and diisoproylbenzen are used as a molecule model for the conversion .

Result $ Discussion :

Clays bridged have a basal spacing between 18 to 25 A° their specific surface area is between 200 and 400 m^2/g , the thermal stability is determined by the rate of change of the basal spacing and specific surface in the course of heating and or treatment with vapor .

The pillared – clay maintains100 % of their specific surface area after heating at 500 c° and from 20-50%of their specific surface after heating at 800c° in the presence of water vapor .

The basal spacing dose not change much when heated at a temperature exceeding 500c° .

That the bridges of metallic complexes formed are transformed to bridges of metallic oxide by heating above 550°c this indicating by the presence of the band ZrO_2 at 650 cm^{-1} after heating .

It is possible to introduce Lanthanum by exchanging part of Cations of already bridged clay between approximately 20 to 40% of the Cations are exchange between 200c° and 400c°.

The stability is better if the Lanthanum and Zirconium introduced by cohydrolsis that is starting from a mixed solution containing La^{+3} salt , as well as zirconium salts .

The mixed solution contain 10 to 50 % by atoms lanthanum at from 50 to 90 Zirconium .

The resulted hectorite – complexes can be used us catalysts or carriers of catalysts .

They can be associated with Zeolite , silica , alumina, magnesia , titanium oxides , specially used as catalysts for processes of conversion of hydrocarbons such as hydro treatment, isomerisation , reforming of a hydro cracking ,they are particularly useful as catalysts of catalytic cracking in fluidized bed .

They can be very advantageously used as catalyst in the treatment of the residues of refining such as described by Ritter(7).

The catalyst is subjected to a thermal treatment in the presence of water during which the hydrocarbon residues formed in the course of the reaction undergo a total or partial combustion .

But the bridged structure of clays is preserved after heating in the presence of water vapors at the used temperatures.

The results of catalytic cracking test as a function of the treatment with water vapor that thy have are summarizes in

	Catalyst	
% conversion	1 600c^{o} Ion air	2 650 In water – vapor
Conversion% By weight	46	86
Coke	8.5	17
H_2	0.2	0.3
C_1+C_2	2.5	4.3
C_3	1.2	6.84
i-c_4	0.1	5.9
t-c_4	4.3	4.7
i-c_4/t-c_4	21.3	1.23
Total gas	4	23.7
Total essence	14.2	44.9

table(1) .Microactivities test over Hectorite-Zr/La in two differents temperatures (600 ^{o}C in air,and at 650^{o}C with the present of vapour pressure.

This catalyst were subjected to a test of catalytic cracking for assessing their activity and their selectivity ,this test corresponds to the standard ASTMD 3907-80 and the

Specific gravity at 150 c^{o}	0.9226
Sulfur %	2.46
Carbon%	0.29
Refractions index 20c^{o}	1.5099
Aniline point c^{o}	77.8

Table (2) test ASTMD3907-80 characteristics of the treatment gas oil are set forth in table(2):

Distillation ASTMD11-60

P1	272c^{o}
10%befor	370c^{o}
50%before	442c^{o}
80%befor	491c^{o}

The catalytic activities are comparable for the pillared clays and REY and substantially higher than for the amorphous alumina silicate the gasoline yields are also comparable .

The octane number of the gasoline produced by the pillared-clays is higher than that yielded by Zeolitic catalyst , but the coke formation is higher on the clay.

The a mount of coke was reduced on the law Fe_2O_3 clay with concomittent increase of gasoline.

A lighter charge (27.9° API gravity)and low sulfur content 0.59% was used by occelli (8)is there for quite different in nature form the solid calcined at the same temperature since the acidity has been shifted form a strong Lewis to a strong Bronsted acidity some common features can be found between the acidities of clays and that of Zeolite, the most interesting being a large number of acid site strong bases like NH_3 or treatment by an alkaline solution can extract these protons and regenerate that exchange capacity of the clay .

The creation of an Si-O-Zr linkage is probable similar to that of Zeolites this site could be a source of a strong acidity observed on such system.

Bronsted acidity was observed by adsorption of pyridine on the sample calcined at 480c° but the evolution of the spectrum as a function of pretreatment of the sample was quite different from that of Zeolites, which shows a decrease of a number of Bronsted sited and an increase of the number of Lewis sites ward(9).

But in the case of pillared -clays this is not observed Fig (1).

It is then necessary to invoke the presence of several types of acidsites , which indict are known to exist at the surface:

1- one type may connected with initial site of ion exchange, not occupied by the pillars, which represent a proximately 30% of the initial exchange capacity of the clay .
2- A second type can be the Si -O- Zr linkage proposed.
3- A third type can be connected with pillars since it is widely admitted that hydrolytic reactions can occur.

Bronsted acidity is restored and this acidity is then stable up to 500c° steaming at 650 c° decrease the number and the strength of the acid sites and this acid sites strength of pillared -clay was also found a higher than that of Y-Zeolites by IR spectrometry since the spectrum of adsorbed pyridine was still detected after out gassing at 500c°.

While on Y-Zeolites pyridine bands disappear after evacuation (10) similar results have been reported for Al-& Zr- Montmorillonite (11).

The disappearance of Bronsted acidity upon calcinations is often attributed to a migration of the protons from the interlayer space in to the octahedral layer where they neutralize the negative charge at the substitution atoms (10,11) .

The Element analysis was shown in table (3) before interaction and after and after intercalation with complex $\frac{\overset{+3}{La}}{\overset{+4}{Zr}}$

	before intercalating	After Intercalations
SiO_2	61.7	60.5
Al_2O_3	30.7	30.5
Fe_2O_3	3.1	0.3
CaO	<0.1	<0.1
MgO	3.9	0.3
Na_2O	0.2	1.6
K_2O	0.3	0.3
Zr	0	1.6
La	0	370ppm
Surface area m2/a	30	300

Table (3) micro analysis of elements>

The evolution of the surface and the inter foliar distance with the temperature illustrate the stability of this catalyst tab. (4)

	Temperature c^o			
Specific surface area $\frac{m^2}{g}$	$\frac{300}{340}$	$\frac{600}{265}$	$\frac{700}{250}$	$\frac{800}{130}$
d(001) A^o	25A^o	18.7	17.7	------

Table (4) Evolusion of surface area with calcinations temparatures

Table(5) The porosity of resulted pillared-clay was reported

Pore size distribution of $\frac{La^{+3}}{Zr^{+4}}$ -Hectorite as a function of the calcinations temperature

	Temperature c^o			
Pore diameter A^o	300	600	700	800
80			3.5	
80-60			0.6	1.5
60-40	10	6	9	24
40-30	7.6	20	18	26.5
30-20	4	0	5	5
20	78	74	64	43

Table (5) Evolusion of micropores with respect to calcinations temperature C^0

Conclusions:

Pillared clays offer a route for the preparation of new class of molecular sieves , the pore size of which can be adjusted by the choice of the pillars up to 40A^o , the thermal stability reaches between 500-700c^o which is comparable top Zeolite Y .

In this new technology we can improved the stability and the quality of this catalyst which have a cracking activity a slightly lower gasoline yield but a higher octane number than Y-Zeolite , this need for cheap row materials and cheap processes ,and this clay appear as possible catalysts for higher octane number.

References:
1-Grace s u.s . patent no. 4,248,739.
2-Lahav ,Clay Clays Mineral,26 107 (1978).
3-European Patent no. 130,055 of British Petroleom company.
4- European Patent no. 73,718.of British Petroleom company
5-D.Tichit Thesis d Etat university Montpellier II (1986).
6- F. Cotton and G.Wilkinson,Advanced Inorganic Chemistry,John Wiley p1055,(1972).
7-Ritter ,Annual meeting of the NPRA,(1981).
8-M.L Occelli and D.H.Finseth,J.Catal. 99,316,(1986).
9-J.W. Ward,Zeolite Chemistry and Catalysis,Acs monograph,171(J.A.Rabo,ed.)chap. 3,(1976).
10-J.D.Russell and A.R.Frazer,Clay Clays Mineral,13, 55(1971).
11-S.Yariv,and L.Hellere-Kallai, Clays Clay Mineral.,21,199,(1973).