Solid Acid Catalyst From Biedillite Intercalated by mixed cohydrolysis (Ti-Zr)Improve their acidity and stability thermic.

Abbas Matrood Bashi

department of chemistry college of science/university of Kerbala .

الخلاصة:

الطين المعدني من نوع البدلايت يتميز بخاصية الامتزاز بين طبقاته مما يجعل عملية التحكم بالمسامية والمساحة السطحية له ممكنة بواسطة ادخال اكاسيد لاعضوية وكذلك زيادة الحامضية, مما يجعله في التطبيقات الصناعية من نوع الامتزاز او السحق الحراري موازيا للمادة الصناعية المستوردة.

Introduction:

Clays of smectite type have long been used as adsorbent material (1) , intercalated clays are anew class of calalyst . in which an homogeneous distribution of microspores can be obtained with porosity varying from 6 A° to 18 A° according to the type of intercalating agents.

The activity catalytic and adsorbents were attracted the tension to this type of clay .

R.M Barrer (2) prepared expanded clay which act as molecular sieves for the adsorption of organic molecules from the uses of Tetraalkyl ammonium as intercalating agent with clay.

A moutmorillonite intercalated by1.4 – diazobicylo (2,2,2) octane was found to posses molecular sieve properties and good catalytic activity (3) for the esterfication of carboxylic acids (4,5) , the thermal stability at 300c° of the resulting clays was limited there applications to catalysis.

The introduction of polyoxocation (6 – 8) were improved the stability thermic up to 650 c° , which is the base of most catalytic process.The preparing of pillared – clay is based on the phenomenon of swelling which is a typical property of smectites .The polar species able to penetrating between the sheets causing an expanding the structure (3 , 9).

The basic phenomenon used in the preparation of pillared clays is the ion exchange of inter lamellar cation by bulky cation species which act as props to keep the structure open .

The use of organic reactants has been recently reviewed by Barrer (3) pinnavia(28), has reviewed the intercalation of smectites by organometallic complexes (10) with stability thermic of these structure reaches 450c°.

A polynuclear hydroxyl metal cations yield higher free spacing which can reach 15A° with reasonable stability nearly 650 c° -700c° , intercalating Ti^{+4} , the chemistry of the solution used for intercalation is very important in the explanation of the catalytic properties .

According to the method used to determine the x-ray diffraction spectrum by evaporating a thin film of pillared -clay on a glass slide at room temperature , this film has a good orientation in the direction of (c) coordination of the crystal , this shows a better resolved (001) spacings , any small anomaly in the orientation of the film resulting in broader lines and slightly lower spaceings .

The results reported for silica (12 , 14) , chromia (28,29) show large differences which should be attributed to a different type of pillaring agent.

Only a few cases are well understood from the point of view of the chemistry of the solution including Al , Zr , Si hydroxides .The chemistry of the solution of Al is well known (11) using potentiometer techniques who suggested the formation of oligomers like $Al_6(OH)_{15}^{=3}$ or $Al_8(OH)_{20}^{+4}$ using a small–angle x-ray scattering , Rausch & Bale (30) suggested for $\dfrac{OH}{Al}$ ratios between 1 and 2.5 , the formation of a polymer species $[Al_{13}O_4(OH)_{24}\ (H_2O)_{12}\ ]^{+7}$ its

structure has been previously described in the solid state by Johansson (12) this polymer species is composed of 12 octahedral Al and central Al tetrahedron .

In the case of $ZrOCl_2$ it is general a greed .That the partial hydrolysis of the salt produces the tetrameric cation $[Zr_4(OH)_8(H_2O)_{16}]^{+8}$ (13).

The analysis of solution by small-angle x-ray scattering supports the proposal (14) this tetramer is also found as a structural unite of the solid (15) , Lewis et al (16) proposed that the use of organosilcon compounds producesa positive charge .

Three-dimensional silicate structures are known as a polyhedral oligosilsesquioxanes (17) .

They are composed of polyhedral silicon- oxygen skeleton which has bears organic or in organic substitutions attached to the silicon atoms .

Experimental work

1-Clay type Biedillite was washed several times and separating the particules less than 1 μ by sedimentation process.

10 g Biedillite was dispersed in 2 L water with continuous stirring to get better dispersion before intercalating.

2- a solution of 0.5 M mixed hydrolysis constitute of 10% Ti^{+4} 90% Zr as molar ratios Ti^{+4} from $TiCl_4$ and from $ZrOCl_2 8H_2O$ droping the cohydrolysis solution drop by drop on the clay suspension during 2 hours with continuous stirring .NH_4 added as competitors cation.

Filtering the resulting suspension-washed with distill water until free chlorine , drying at 25c° .

A sampling of each 0.5g of the pillared-clay was preheated at 200c° , 300c° , 400c° ,500c° ,600c° ,700c° ,800c° each sample was examined by the technique of IR , X -ray scattering , organic molecules adsorptions and cracking test applications .

Determination surface area (S.S.A) & pores size

We used the adsorption of N2 at the temperature of N2 liquid 77K° to determine the S.S.A and then the distribution of pores size using the equation of BET .

To determine the quantity of N_2 adsorbed , and using the relation $N=\delta^{D/2}$ attempted by Van Damme & Fripait (18) .

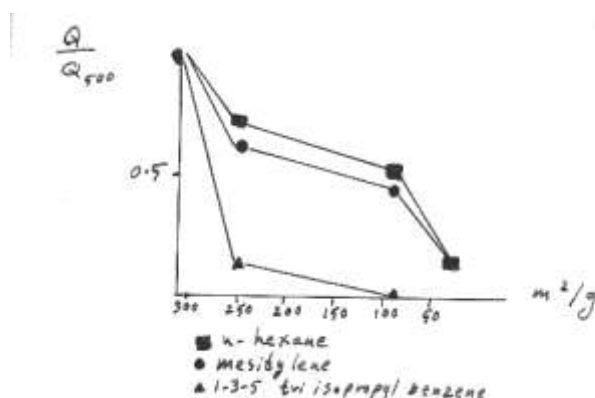Where D= Fractal dimension of pillared -clays

N = the adsorption $\dfrac{mmol}{g}$

σ = cross section of adsorbed molecule.

The D value is close to 2 whether the solid is air or freeze dried .

Results and Discussion

The adsorption capacities ($\dfrac{cm^3}{g}$)for several adsorbents of increasing kinetic diameter σ for pillared- clay calcined in different condition .Table(1).

Fig(1)Rate of diffusions of hydrocarbons adsorbed on the surface of pillared-clay.

Table(1)Quantities of Adsorbed organic molecules of differents diameter on the surface of Pillared-Clay.

Sample N2($\sigma = 4A°$)	500 Air dry	680c° Air dry	550 steam	650c° Steam 20 h
n-hexanc($\sigma = 4.6A$)	0.29	0.2	0.11	0.04
1.3.5 trimethylbenzen ($\sigma = 7.6A°$)	0.150	0.092	0.068	0.02
1.3.5 triisoprobyl Benzene ($\sigma = 9.2$)	0.030	0.005	0.011	0

When these results are compared with the surface of commercial Y-zeolite calalyst we found that the thermal stability of the pillared- clays is reasonably good.
It is also remarkable that the Zeolite -like character of the adsorption of hydrocarbons is retained upon steaming .
Table (2) shows the hydrocarbons quantity adsorbed on the surface of pillared –clay. The rate of adsorption of 1.3.5 trimcthyl benzene and n-hexan were 100 times rapid than the 1.3.5 trisoprpyl benzene over the sample precalcined at 700c° that n-hexan defuse to the interior porosity more easily than 1.3.5 trimethyl benzene that the diffusion coefficient reduce 10 times with the adsorption of 1.3.5 triispopyl benzene ,than the n-hexan & 1.3.5 trimethy benzene.Fig(1).
Dn-hexan = 2.18×10^4 sec^{-1}
D1.3.5 trimethbenzen = 0.014×10^4 sec^{-1}
This is calculated from the equation .

$$\frac{M_{(t)}}{M_d} = \frac{6}{11}(\frac{D_{(t)}}{L_2})^{\frac{1}{2}}$$

Md ,Mt =hydrocarbon quantity adsorbed at time (t) & final time (d)
D= diffusion coefficient .
L=average diameter of the clay aggregates.

Adsorptions of n-Hexan on (Ti-Zr)Biedillite
a- sample calcined at 500C
b- sample calcined at 680C
c- sample calcined at 550C
d-sample calcined at 650C

Amount adsorbed
(m.moles/g)

Time (Sec)
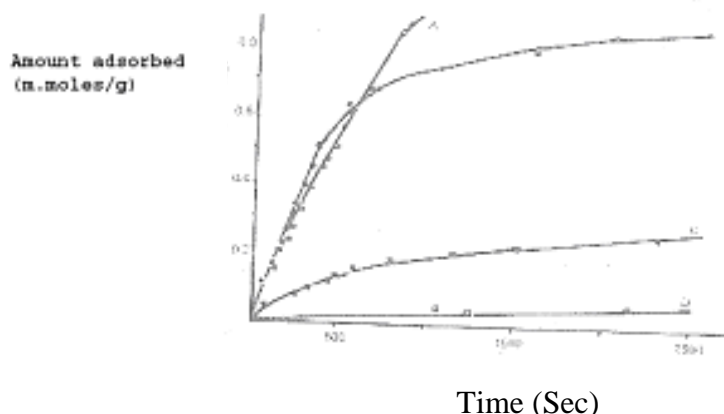
Determination of acidity:

There is an agreement on the existence of both Lewis and Bronsted sites on pillared – clay calcined at 400 C° with a higher proportion of Lewis acid sites (19 , 20 , 21 , 22). The number of acid sites of

[$\dfrac{Ti^{+4}}{Zr}$ – Biedillite] evacuated from NH$_3$ adsorption increases with the number of pillars and is

comparable to the number of sites measured on ceY – Zeolite namely 1.7-2.9 μ mol $\dfrac{NH_3}{m^2}$ versus

3 μ $\dfrac{mole}{m^2}$ for the Zeolite(19).

By adsorption of ammonia on ($\dfrac{Ti^{+4}}{Zr}$ -Biedillite) calcined at 500 c° the total adsorption of ammonia

at 25 c° was evaluated 2 μ mol/m^2 (23).

The acid sites of solid were found to be strong because 0.1 μ mol/m^2 of ammonia were still retained after evacuation at 500c° .The acid strength of the pillared – clay was also found higher than that of Zeolite by IR – technique since the spectrum of adsorbed ammonias still detected after out gassing at 500c° (20) while on Y-zeolite ammonia bands disappear after evacuation around 350c° (24)similar result have been reported for Al, Zr – montmorillonite (25-29) .

Bronsted acidity appears to be weaker than Lewis acidity .

Transmittance

Transmissions%

S   c

800 760 1400   1600 1400
e numbers   wave numbers
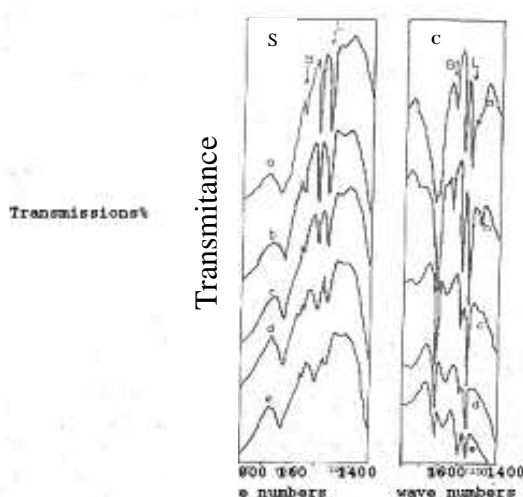
Fig(3)IR.spectrum of adsorption of ammonia on the surface of two samples(s)=steaming at $550C^0$,sample(c)=calcined at a=at room temp.,b-e at 180C^0, b=300C^0 ,d=400C^0 ,c=480C^0 ,Bronsted, L=lewis.

The element analysis reported in table(2).

Element	%percentage
Si	17.91
Al	7.43
Mg	0.95
Zr	12.69
Ti^{+4}	260ppm

Table(2),Elements analysis after intercalations with the cohydrolysis (Zr-Ti).

Applications to oil refining :

A lighter charge (27.9º API gravity) and low sulfur content (0.59wt%) was used the gasoline yield was lower on clay (54.5%) than on Zeolite catalyst (56.5%) at the same conversion of 70% the coke yield was higher 7% on clays table(4)(5), versus 3% on Zeolites at the same conversion .

The conversion of same gas oil has been investigated on pillared – Biedillite which gave the same selectivity for gasoline as Zeolite but produce a higher coke formation comparable to that obtained with the pillared clay (25-30) , pillared-Biedillite appeared less active at 515Cc^o, WHSV=15 and the conversion reached 65% as for Al-clay result reported in table (3) no clear difference appeared between Al-Zr- montmorillonite and pillared-Bedilites .These different clays have quite different cationic exchange capacity & different amount of Fe_2O_3.Biedillite is practically free of iron where is the pillared-bentonite contained 4.65 wt% F_2O_3.

Table(2) MAT test of gas-oil over (Ti^{+4}-Zr-Biedillite), (bentonite-Al-Ce) and commercial catalyst super D catalyst .

Table (3)

MAT test of gas oil over Biedillite intercalated catalyst with $\frac{Ti}{Zr}$, Bentonite(Al-Ce) and

commercial cat. Super D

Cat.	Biedillite - $\frac{Ti^{+4}}{Zr}$ Dry air	Biedillite-Ti/Zr Vap.water	Bent-Al-Ce Vap.water *	super vap.water**
T(c)º	680	550	550	775
Time of treat.	5h	17h	17h	17h
s.s.a m^2/g	260	93	80	62
Vol.cm^3/g	0.2	0.11	---	nd
p.p.H(h)$^{-1}$	30	26.4	30	30
Conv. %	73.1	81.6	86.7	72.5
Essence%	37.7	39.8	44.65	51.3
Coke %	17.6	19.3	17.6	3.3
Gas%	17.8	22.8	24.27	17.9
H$_2$%	0.6	0.64	0.32	0.03
(a) fule gas	4.6	5.98	4.91	2.06
(b) LCO+HCO%	26.9	18.4	13.48	27.5
C4=%	4.7	4.98	4.21	4.65
Essence/conv.	51.6	48.8	51.5	70.76

(a) fule gas +H$_2$+CO+CO$_2$+CH$_4$

(b)LCO+HCO>C$_{12}$

* result from reference (20)

** result from reference (31)

Table (4) coke deposion in function of conversion of gas oil .

Bedilite-(Ti/Zr)		Super D	
Conversion	Coke	Conv. %	Coke
45%	7.3%	70%	2.5%
65%	17%	75%	5%
80%	20%	80%	7%
90%	25%		

Table(5) test MAT selectivity in essence comparison on the Bedilte (Ti-Zr) & super D .

Bedilite-(Ti-Zr)		Super D	
Total Conversion%	Essence conversion %	Total conversion	essence conversion
65	40	65	55
75	43	75	56
80	45	80	51
90	45	90	46

Conclusion:

Pillared - clays prepared by cohydrolysis of (Ti-Zr) with the method of competion of cation NH^{+4}, are a new class of molecular sieves , the pore size of which can be adjusted by the choice of the preparations method up to 30 A° and there fore to higher values than those known as Zeolite.

The thermal stability of many of these pillared-clays reaches 700c° , high surface area are observed after steaming at 650c° for several hours which is comparable to the stability of protonic Y-zeolite . $\frac{Ti^{+4}}{Zr}$ - Biedillite has a large number of strongly acidic sites , and the distribution of acid strengths can probably be modified by ion exchanger or the methods of preparations , or steaming , then probably will find applications as wide-pore catalyst , in the processes in which both acidity and accessibility are required cracking catalysts would still be precluded by the excessive amount of coke deposited on the solid.

The technique of pillaring for the preparation of well-controlled porous structures is of general value with layered structure.

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