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RESEARCH ARTICLE

The effects of Al_2O_3 and Cr_2O_3zeolites during the dynamic regime hydrotreating reaction for Tarfaya oil shale (Morocco). Duality of energy and conversion

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Abstract

Catalyzed hydropyrolysis has been the subject of several studies. These studies are based on thermal reactions under hydrogen aided by catalysts that facilitate the diffusion of heat and matter through their pores. Supercritical extraction **(J. Triday and J.M. Smith. 1988)** of solid compounds are reactions influenced by interparticle position, pore diffusion, interphase mass, heat transfer and flow in the differential reactor. Zeolites include Al_2O_3 and Cr_2O_3.In this study, we monitored the effects of these zeolites during the decomposition of Tarfaya oil shale (Morocco) under dynamic hydrogen conditions (21°C/min), using thermogravimetry and calorimetry. The results obtained using Al_2O_3 (alumina) can be summarized as an increase in the rate of pyrite conversion, invariability for calcite and dolomite, and a decrease for quartz, kaolinite and chlorine compounds. When chromium oxide Cr_2O_3 was used, however, energetic deactivation was observed. The techniques used in this study include dispersive XRD coupled with scanning electron microscopy, thermogravimetry with amplified differential calorimetry (DCA), a precise and reproducible calorimetric technique.

Introduction:-

Among the zeolite compounds, which are oxides of the elements Na, Al, Si, Ca....ranked in order of importance, we have alumina Al_2O_3. As in oil refining, catalysis using active agents impregnated in inert or low-activity matrices is considerable. The predominant examples are catalytic cracking and hydrocracking using high-activity zeolites dispersed in shielded, "inactive" compounds such as alumina. Increased dilution activity can cause physical and chemical changes, such as transfer phenomena in samples **(V.T. John and P. Varghese: 1986).** Chemical changes in the transfer of the aluminum atom from the armor to the internal crystal sites of the zeolite can cause high activity **(Chu et al: 1985).**Norton Zeolon zeolites **(Wen and Cain: 1984),** like natural zeolites, show high catalytic activity for the cracking of bituminous coal. Clays and kaolinite enhance catalytic activity in the same way as small-pore zeolites. The process of fine migration and fine injection into pores has been studied, the first problem frequently encountered being the reservoir of oils that are formed as well as the pores produced by the departure of fine particles and their physico-chemical interactions as well as the injection of fluids into these pores. The second problem is the relative filtration of large particles
(M.M Sharma and Y.C. Yortos: 1987). The solutions found by the proposed model derive from the expression

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containing the particle concentration profile, the pore opening and density, as well as the pore size distribution profile, as well as the reducing permeability.

1/ Literature Review:-

The conductance (mass-energy) for the pore chain, as well as the first main physical effect for determining beginning diffusion, have been studied by medium theory **(V.N. Burganos and S.V. Sotirchos: 1987)**. Observations of this pore chain for uniform conductance satisfy the uniform application of the approximation field. This medium theory also makes it possible to determine the fluid flow distribution in the pore chain and calculate the permeability**(M.M Sharma and Y.C. Yortosos 1987).** A model based on the pore's convergence, divergence, structure, blockage and inner cavity has been studied **(Y. Chang and D.D .Perlmutter: 1989).**This study is applied to regenerative catalysis. The results show that the presence of pores undergoing occlusion reduces the reaction at its onset. For a high level of coke loading, the reaction behavior is affected by a fraction of the pores. A qualitative model has also been developed to predict the effects of non-uniformity of metal activity and distribution during catalytic hydromethylation**(K.W. Limbach and J. Wei: 1988).** Thermal analysis of alumina prepared by two methods, PFHS (precipitation of homogeneous solution) and the conventional method have been described and indicate that alumina obtained by PFHS has a monophasic nature, whereas that obtained by the conventional XRD method has a microspheroidal shape **(B.S. Mruthiprasad et al: 1988**). Absorbing chemical species play a dominant role in determining the dehydration characteristics of alumina trihydrate**(S.J. Puttock et al: 1985).** The addition of small amounts of active surface improves dehydration remarkably. The active surface, N beta alumina ceramic, reacts on the surface with CO_2 to eliminate the formation of carbons and bicarbonates **(B. Berbenni et al: 1988).**The diffusion rate of polyaromatic compounds in alumina decreases as the ratio of solute molecular diameter to pore diameter increases **(A. Chantaong and F.F. Mossoth: 1983).** An empirical correlation between effective apparent diffusion and the ratio of molecular diameter to pore diameter has been obtained. Alumina reacts with carbon tetrachloride in the temperature range from 563 to 643K and at pressures ranging from 4 to 10MPa.

$2Al_2O_3(s) + 2CCl_4(g) \longrightarrow 4ALCl_3(g) + CO_2(g)$ **(D.E.Herrick et al: 1988)**

Alumina has been used as a support for CO hydrogenation in the presence of bimetallic Mo - Fe and Mo - Co sulfide **(L.T. Thompson: 1989).** By adding methane (CH_4), a significant amount of dimethyl ether was produced. Changes in alumina-supported platinum activity and acid function are controlled by the rate of hydropyrolysis and hydrocracking respectively **(J.N. Beltramini: 1991).** Al_2O_3 has also been used as a support for molybdenum during heat treatment, exhibiting similar pore size distributions **(P.R. Duncombe and S.W. Weller: 1985).** Redistribution is minimal at 625°C and maximum at 750°C. The maximum is observed for a radial distribution of the catalyst. Molybdenum vaporization at 750°C is not appreciable, but it is at 875°C. Redistribution is minimal at 625°C and maximum at 750°C.The maximum is observed for a radial distribution of the catalyst. Molybdenum vaporization at 750°C is not appreciable, but it is at 875°C. The effects of alumina or carbon support type for Co and Ni catalysts in activity and Mo, are compared in parallel for the hydrodenitrogenation and hydrodesulphurization (HDN, HDS) of pyridine and thiophene at 320°C and 2MPa hydrogen pressure **(Z. Vit :1993).** The formation of piperidine is lower for carbon as a catalyst support (Mo) than for alumina as a support for Co, Ni or Mo catalysts. Regardless of the support, the presence of Co or Ni accelerates the HDS reaction. The (Mo) catalyst is more selective for HDN/HDS than CoMo and NiMo. Catalysis of bitumen or petroleum residue for the hydrocracking reaction was studied using Al_2O_3 as support. Carbon was considered as a support in competition with Al_2O_3 for two reasons **(M.A. Altajam and M. Terman:1989).** Firstly, the metal from the crude catalyst is easily recovered when the carbon is fully combusted; secondly, carbon support sometimes produces higher conversion rates than alumina. It should also be remembered that reactions occurring during the hyroprocess (HPR) improve oil production and properties by 90-95% **(D. Tsamatsoulis et al: 1991).**

The use of copper chromite and copper aluminate for hydrotreatment depends on the nature of the active sites, depending on the spinel nature of the oxidized elements Cr^{3+} and Al^{3+}. Hydrogen supply plays an important role in hydrogenation **(L. Jalwiecki et al :1987).** We also note the usefulness of chlorine for the regeneration of the various cokes during Pt/ catalysis. Al_2O_3 for methylcyclohexane dehydrogenation **(A. Parmaliana et al: 1988),** a concentration of 0.5% Cl shows complete regeneration for hydrotreating in the dynamic or statistical regime. Hydrogenation and hydrodesulfurization of thiophene under Ru/ Al_2O_3 and CoMo/ Al_2O_3 as catalysts were carried out. The HDS of thiophene has a higher rate for Ru/Al_2O_3 than for $CoMo/Al_2O_3$ **(Y.J. Kvo et al: 1988),** and is also selective in the presence of RuS_2, which results from surface sulphuration of Ru. Hydrodesulphurization (HDS) by alumina-supported Co and Mo has been monitored by EXAFS spectroscopy of Mo and Co and proves from the

HDS test that the reference compounds Co/S and Co/O are dominant. When Co loading is high, Co9S8 appears as the phase (N.S. Chiu et al: 1988).

TheXraydiffractionanalysisindicatedthatzeolitesampleisamixtureofclinoptiloliteandmordenite,whilethevermiculitesampleispure–identifiedinbyreflectionsat1.4,0.98,0.48,0.36,and0.29nmintheMg-saturatedsample,reflectionat1.4nminsamplesaturatedwithethyleneglycol(indicatingnochange in the basalplane),andreflectionat1nminthe K-saturatedsampleheatedat350and550^{o}Cduetothecollapseofthebasalplane**(Chen: 1977**).

The action of Cr_2O_3-Al_2O_3 solid solutions for isobutane dehydrogenation has been studied**(J. Besson and M. Abouaf: 1991)**, showingthat the intrinsicactivitydefined as isobutane conversion per catalyst surface area is maximum for a Cr_2O_3 -richsolid solution. For an Al_2O_3 -richsolid solution, itisalmost inactive. The mechanism of dehydrogenation and deactivationwasdiscussed in terms of the C ion, whichisprobablyresponsible for the high initial activitythatwasrapidlyinhibited.

2 / Les techniques expérimentales

2.1 : Rayon X dispersifs

A Quanta200Fegscanningelectronmicroscope(SEM)coupledtoanX-rayspectrometer(EDX)wasusedtostudythemorphologyandqualitative chemicalcompositionofthesamplesurfaces

Scanning electronmicroscopyis a technique based on the analysis of "electron-matter" interactions. The surface ofthesampleissubjected to a bombardment of electrons. Some radiation (backscatteredelectrons, secondaryelectronsand X-rays) isemitted as a result of the multiple collisions between the electronsthat scan the surface and the atomsof the materialunder test. This radiation isanalyzed by different detectors to build an image of the surface and toobserve the presence of elements in the analyzed area. The emission of backscatteredelectrons (electronsfromtheincidentbeamdeflected by elastic interactions) is sensitive to the atomicnumber of the chemicalelementspresentinthesample. Secondaryelectrons are electronsfromatomsthat have been ejected by the incident beam. Theselowenergyelectrons are representative of the topography of the sample.Atomsthat have lostthesesecondaryelectronswill regain theirstabilitythroughelectron transitions that cause the emission of electromagnetic and X-ray radiation.This radiation ischaracteristic of the original atoms and provides information on the chemical composition of thesample.

2.2: Thermogravimetry and differential amplified calorimetry(DCA)

In thisstudywe have used the thermobalancefrom the SetaramseriescalledRed-Croft, whichisaflailthermobalancewith a compensation system based on a photoelectric source to keep the sampleat the samepositionintheoven,avoiding the temperaturegradientduetoadisplacementofthesampleintheoven.

The technique of calorimetric thermal analysissuffersfrom a number of shortcomingsconcerningreproducibility, makingitdifficult to deduce quantification. This studyaddresses the significant variables responsible for removingtheseshortcomings and exploring the possibility of accuratedetermination of reactionenthalpy. Thesemethodsincludeamplifieddifferential scanning calorimetry (DCA) and differential scanning calorimetry (DSC). The latter uses an electricalconverter circuit to transformheatevolved or absorbed, isindependent of temperature or otherexperimental conditions and canmeasure enthalpies directly**(B. Rejai and R.D. Gonzalez :. 1990).**

In ourwork on non-isothermalcatalyzedhydropyrolysis of oil shale, we have used DCA, a precise and reproduciblecalorimetric technique thatenables us to deduce and discussreaction enthalpies aftertesting. This technique iscoupledwiththermogravimetry on the RedCroft STA 780. DCA peaks are recordeddirectly and simultaneouslywith the TG.

3/ Experimentalresults of thisstudy.

3.1 :Thermogravimetricstudy.

Weused the Red-Croftapparatus in dynamicregime (21°C/min).samples of oil shale from the Z2, Z3 and Z4 layers of the Tarfaya deposit (formed in the UpperCretaceousat the Senonian, Turonian and Cenomaniangeological stages respectively**(A. Attaoui et al: 2022)**werehydropyrolyzedfrom ambient to 750°C, first aloneand thenwith the

addition of well-defined proportions of zeolite Al_2O_3 or zeolite Cr_2O_3. The thermograms are shown in the following figures:

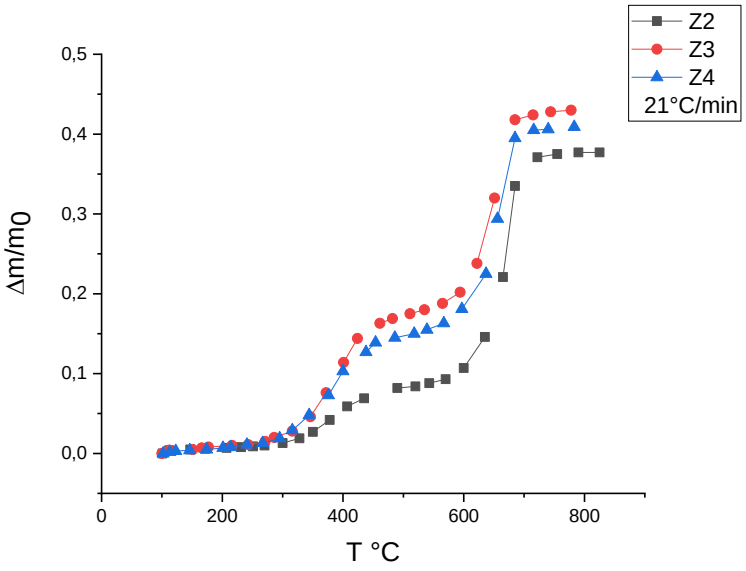

Fig 1:-Hydropyrolysis of layers alone.

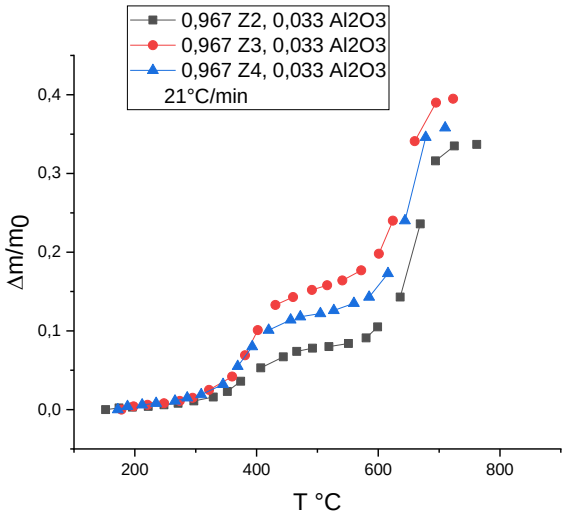

Fig 2:-Hydropyrolysis in the presence of 0.033 Al_2O_3

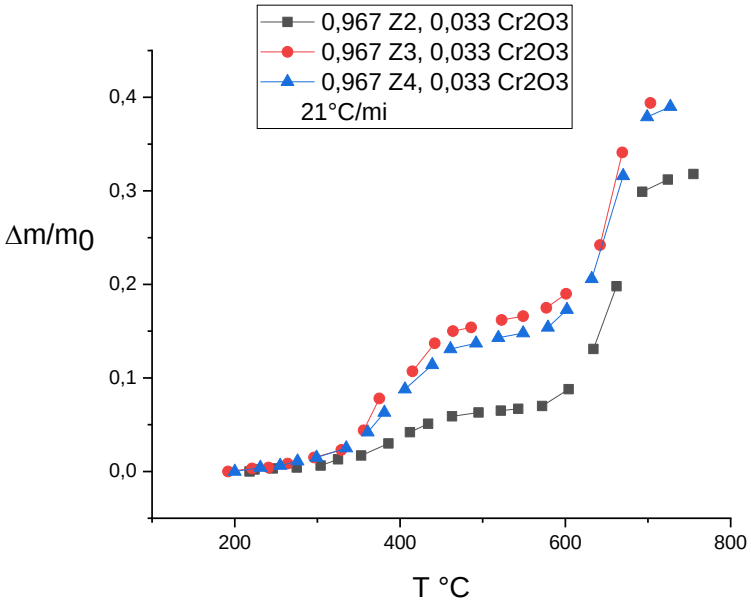

Fig 3:-Hydropyrolysis in the presence of 0.033 Cr_2O_3

We have also represented each layer alone and in the presence of the two zeolites.

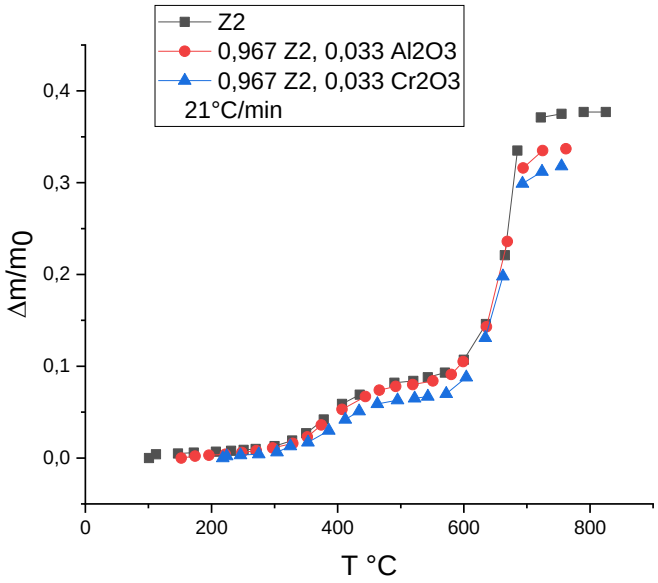

Fig 4:-Hydropyrolysis of Z2 in the presence of the tow zeolites.

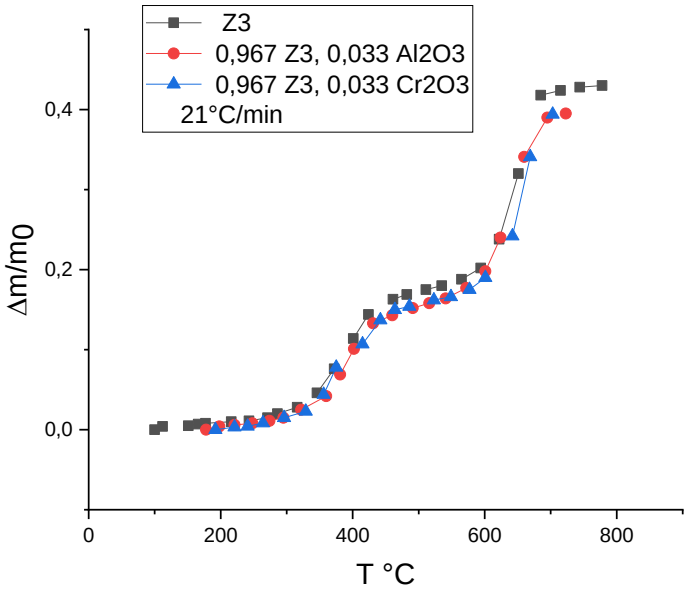

Fig 5:-Hydropyrolysis of Z3 in the presence of the two zeolites.

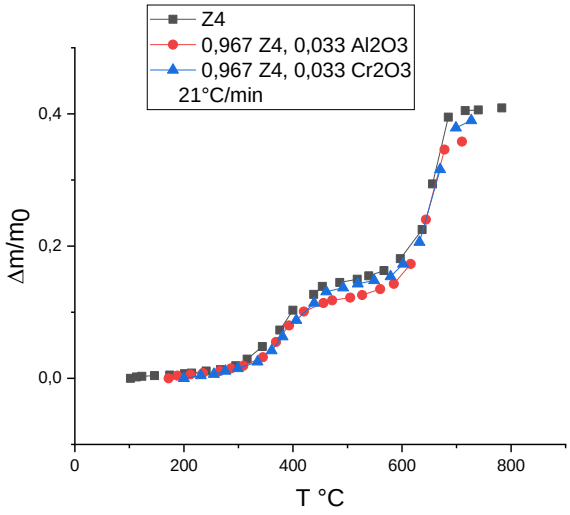

Fig 6:- Hydropyrolysis of Z4 in the presenceof the two zeolites.

When we observe the thermpgrams, we notice a decrease in the total conversion rate when zeolites are added. This decrease is selective, occurring for organic matter in the Z2 layer in the presence of Cr_2O_3, for organic matter in the Z3 layer in the presence of both zeolites, and for organic matter in the Z4 layer in the presence of Al_2O_3.

We now turn to the amplified differential scanning calorimetry (DSC) technique, which is coupled with thermogravimetry in the Red-Croft.

3.2: Calorimetric study (DCE)

The nacelle has two crucibles, one containing alumina (Al_2O_3) and the other containing the product to be analyzed. The two crucibles contain two thermocouples, the two thermocouples reacting differently to give the DCE peak. The DCE peaks recorded during hydrotreatment under dynamic conditions (21°C/min) for the Z2, Z3 and Z4 layers alone are shown in Figures7, 8 and 9.

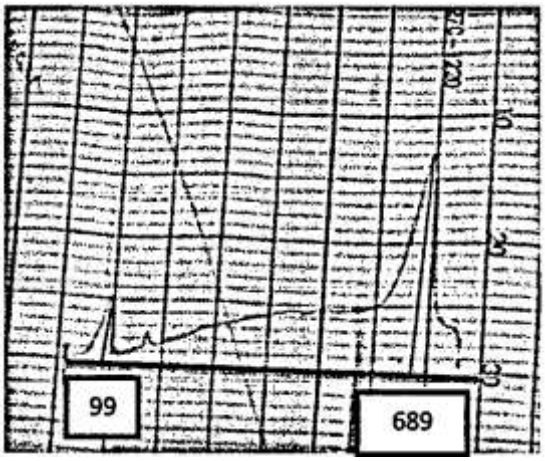

Fig 7:- Z2 DCE peaks.

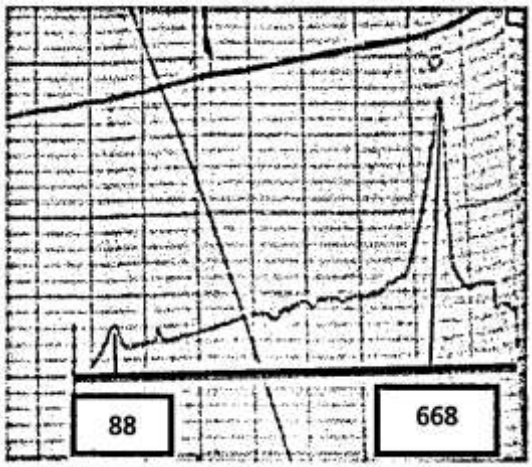

Fig 8:- Z3 DCE peaks.

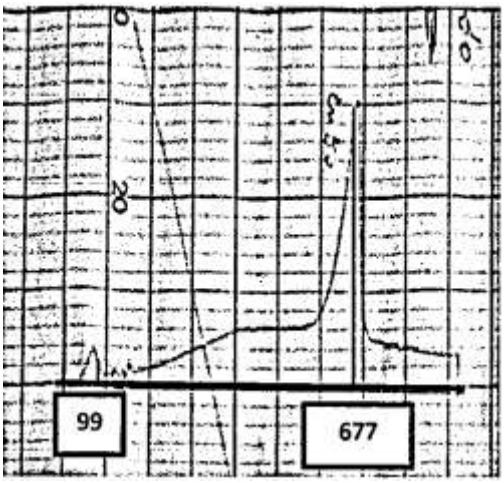

Fig 9:- Z4 DCE peaks.

In the following table, we present the DCE peak temperatures for the three layers, specifying that the first peak corresponds to hydropyrolysis of the water in the oil shale and the second corresponds to hydropyrolysis of the mineral matrix.

Table 1:- DCE temperaturepeaks.

Sample	Z2	Z3	Z4
First T DCE peak (°C)	99	88	99
Second T DCE peak (°C)	689	668	677

3.3: Calorimetric study of oil shale hydrotreating in the presence of Al_2O_3 and Cr_2O_3

The present studies were carried out on the three shale samples hydrotreated in the presence of the metal oxides Al_2O_3 and Cr_2O_3. The technique used is amplified differential calorimetry at a constant heating rate of 21°C/min and a fixed hydrogen flow rate of 20 cm/min (pressure = 1atm). The temperature range explored is from 25 to 750°C.

3.3.1: Calculation of the heat capacity of the apparatus and the catalytic effect of Al_2O_3

Calibration of the apparatus was carried out using the energy of fusion or latent heat of fusion of aluminum. According to Awbery (Awbery. Phil. Mag: 1938), this value is 92.4 cal/g.

$$Q = Cp\Delta T = 92.4 \text{ cal/g} = 386.2 \text{ joule/g}$$

The melting temperature of the aluminum leaving the ambient (20°C) is 643°C detected by the thermocouple of the Red-Croft STA 780, which leads us to the calculation of the heat capacity of this microthermobalance, which is **Cp = 0.62 joule/gK.**

3.3.2: Effect of temperature on maximum energy exchange under Al_2O_3

Tests were carried out on 15mg of each sample and for the following Al_2O_3 fractions: 3.3%; 5.3% and 6.7%. The temperatures of the carbonate decompositionpeaks are as flow

Samples	Zi	Zi, 3,3% Al_2O_3	Zi, 5,3% Al_2O_3	Zi, 6,7% Al_2O_3
	Peak (°C)	Peak (°C)	Peak (°C)	Peak (°C)
Z2	689	687	693	683
Z3	668	661	669	669
Z4	677	671	674	669

According to these results, the DCA peak temperatures of alumina-containing samples are mostly lower than those of crude samples. In order to assess the **catalytic activity of Al_2O_3,** we determined the mean temperature deviation of the six tests (-3°C) and used the previously calculated heat capacity of the apparatus (Cp=0.62 J/gK). This activity translates into an energy gain of around 1.86 Joule/g.

3.3.3: Effect of temperature on maximum energy exchange under Cr_2O_3.

Again, the same shale samples were treated in the presence of Cr_2O_3. The decarbonation temperatures detected are slightly higher than those of the raw samples (next table).

Samples	Zi	Zi, 3,3% Cr_2O_3	Zi, 5,3% Cr_2O_3	Zi, 6,7% Cr_2O_3
	Peak (°C)	Peak (°C)	Peak (°C)	Peak (°C)
Z2	689	687	700	684
Z3	668	688	679	675
Z4	677	682	689	671

It should be noted that the presence of Cr_2O_3 at different percentages in shale increases the maximum temperature of the decarbonation peak. Statistically, this increase is of the order of 5.9°C. This value reflects the **deactivating role** played by chromium oxide, and the energy increase, determined by taking into account the heat capacity of the system and the thermal difference, is 3.7 Joule/g.

3.3.4: Study of reaction energy variation as a function of the added metal oxide mass fraction.

By varying the sample/oxide mass ratio, we calculated the average decomposition energy of the three samples and the average temperature deviation for each mass fraction, giving the following energies:

Presence of Al_2O_3

Mass fraction of Al_2O_3	0%	3, 3%	5, 3%	6, 7%
Energy (j/g)	408	404, 9	408, 4	405, 3

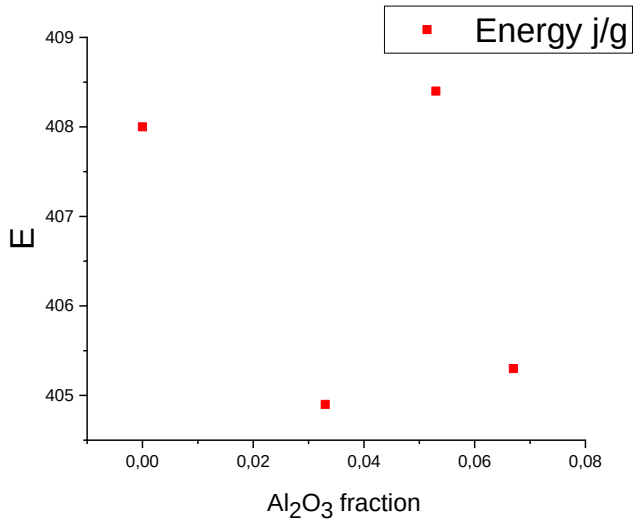

Fig 10:-Hydropyrolisis of mineral matter as fonction ofAl_2O_3mass fraction.

We observe that the catalytic power of Al_2O_3 is maximum for Al_2O_3 mass fractions ranging from 3.3%.

Presence of Cr_2O_3

Mass fraction of Cr_2O_3	0	3,3%	5,3%	6,7%
Energy (J/g)	408	413	415	407

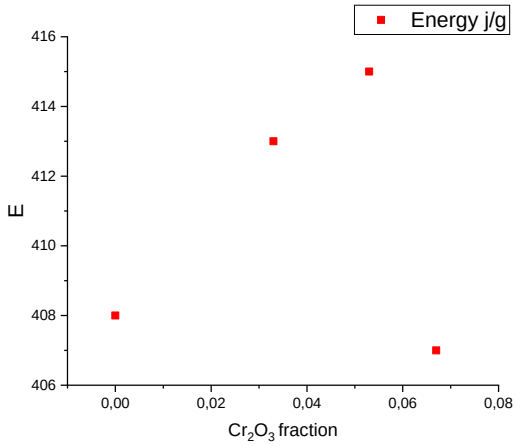

Fig 11:-Hydropyrolisis of mineral matter as fonction of Cr_2O_3mass fraction.

The maximum deactivating power is observed for a Cr_2O_3 fraction of 0.053.

4/ Morphological studies and dispersive X-ray diffractometry analysis.

The scanning electron microscope (SEM) gives us the morphology before and after the hydrotreating reaction, as well as dispersive X-ray diffractometry analysis.

4.1: Morphology study

The following SEM images show sample Z3 with an Al_2O_3 fraction after reaction, and sample Z3 with a Cr_2O_3 fraction after reaction.

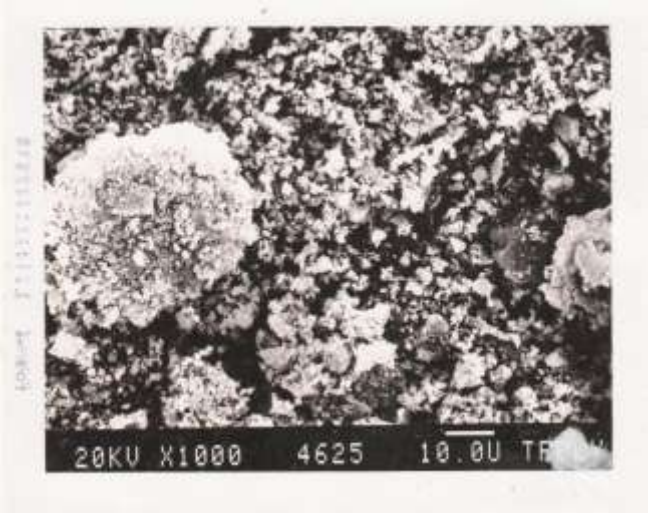

Fig 12:- Z3, 0,033 Al_2O_3hydrotreatedtill 750°C.

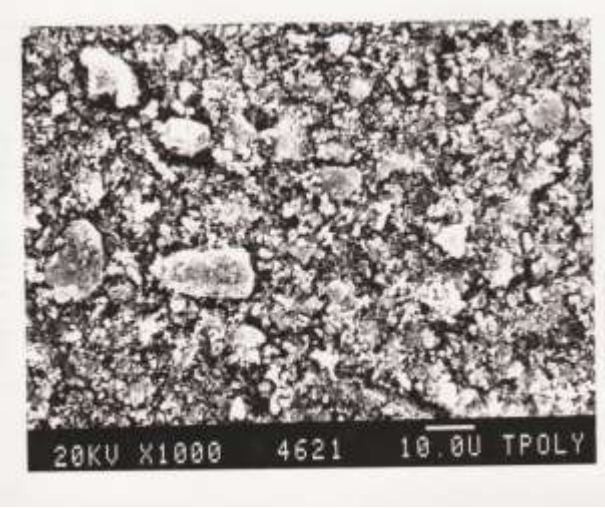

Fig13:- Z3, 0,033 Cr_2O_3hydrotreatedtill 750°C.

We observe the difference in grain size when hydrotreating in the presence of Al_2O_3 relative to Cr_2O_3, with the grains in the presence of Cr_2O_3 being smaller than those in the presence of Al_2O_3. The grain ratio is 0.75 between the two presences, showing that the morphological reaction proceeds kinetically faster in the presence of Cr_2O_3.

4.2: Dispersive X-ray analysis

The elements to be analyzed are calcium α, calcium β, silicon, chlorine and sulfur.

The following table represents the size of each peak in centimeters and the percentage of presence of each element..

Table2:- PercentageofchemicalelementsintheTarfayaoil shale.

Composition	Raw Z3	Z3, 0,033Al_2O_3hydrotreated till 750°C	Z3, 0,033Cr_2O_3hydrotreated till 750°C
Silicom (cm)	3,1	**3,5**	**1,3**
Silicom (%)	9,4	**9,9**	**8,9**
Sulphur (cm)	2,9	**2,3**	**1,4**
Sulphur (%)	8,9	**6,5**	**9,6**
Chlorine (cm)	2,3	**2,2**	**1,2**
Chlorine (%)	7,0	**6,3**	**8,2**
Calcium$_\alpha$ (cm)	21,2	**23,5**	**9,1**
Calcium$_\alpha$(%)	65	**66,7**	**62,3**
Calcium$_\beta$ (cm)	3,2	**3,7**	**1,6**
Calcium$_\beta$(%)	9,8	**10,5**	**10,9**

Itshouldbenotedthatthepercentagespresentarerelativetoeachotherforthesamesample.

A certain selectivityconcerning the effects of the zeolitesusedduringhydropyrolysis in the dynamicregimewasnoted.

Wefollowed the conversions of the different Z3 layersalone and in the presence of the zeolites Al_2O_3 and Cr_2O_3. The oil shale elements are Calcium α, Calcium β, SiliconChlorine and Sulfur.
Certain selectivityisobservedwhenweusedzeolites as additives. For the presence of Al_2O_3 alumina, we notice an improvement for sulfur and chlorine. A conversion increase of (100 - (6.5/8.9) × 100)% = 27% for sulfur, as well as a 10% increase for chlorine. In the presence of Cr_2O_3zeolite, Calcium β conversion isimproved by 4.2%, whileSilicon conversion isincreased by 5.3%.

Weconcludethat the mostremarkableadvantageis the improvement in sulfur conversion when alumina isused. Hydrodesulfurization (HDS) isimproved by **27%** in the presence of alumina, and calorimetric tests show that alumina reduces the energy input duringthis addition. Dechlorinationisalsoimproved by 10% in the presence of Al_2O_3.

Conclusion:-

Catalyzedhydropyrolysis has been the subject of severalstudiesusingzeolites. Thesestudies are based on thermal reactionsunderhydrogen, aided by catalyststhatfacilitate the diffusion of heat and matterthroughtheir pores. Zeolitesinclude Al_2O_3 and Cr_2O_3.

In thisstudy, wemonitored the effects of thesezeolitesduring the decomposition of Tarfaya oil shale (Morocco) underhydrogen in a dynamicregime (21°C/min),

In the thermogravimetricstudy, weobserved a decrease in the total conversion rate whenzeoliteswereadded. This decreaseisselective: itoccurs for organicmatter in the Z2 layer in the presence of Cr_2O_3, for organicmatter in the Z3 layer in the presence of bothzeolites, and for organicmatter in the Z4 layer in the presence of Al_2O_3.

According to theseresults, the DCA peaktemperatures (calorimetric) are lower for alumina-containingsamplesthan for crudesamples. In order to assess the catalyticactivity of Al_2O_3, wedetermined the averagetemperaturedeviation of the three tests and of-3°C for decarbonation.

Using the previouslycalculatedheatcapacity of the apparatus (Cp=0.62 J/gK). This activity (presence of Al_2O_3) results in an energy gain of the order of 1.86 Joule/g.

It shouldbenotedthat the presence of Cr_2O_3atdifferentpercentages in the shale increases the maximum temperature of the decarbonationpeak. Statistically, thisincreaseis of the order of 5.9°C. This value reflects the deactivatingroleplayed by chromiumoxide, and the energyincrease, determined by takingintoaccount the heatcapacity of the system and the thermal difference, is 3.7 Joule/g.

For the RXD analysis technique, whichis a SEM-coupled technique, wemonitored the conversions of the differentelements for the Z3 layer alone and in the presence of Al_2O_3 and Cr_2O_3zeolites. The elements in the oil shale are Calcium α, Calcium β, SiliconChlorine and Sulfur.

Certain selectivityisobservedwhenweusedzeolites as additives. For the presence of Al2O3 alumina, we notice an improvement for sulfur and chlorine. A conversion increase of (100 - (6.5/8.9) × 100)% = 27% for sulfur, as well as a 10% increase for chlorine.

In the presence of Cr_2O_3zeolite, Calcium β conversion isimproved by 4.2%, whileSilicon conversion isincreased by 5.3%.

Weconcludethat the mostremarkableadvantageis the improvement in sulfur conversion when alumina isused. Hydrodesulphurization (HDS) isimproved by **27%** in the presence of alumina, and calorimetric tests show that alumina reduces the energy input duringthis addition. Dechlorinationisalsoimproved by 10% in the presence of Al_2O_3.

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