

Research Article

Preparation of Solid Catalysts and Its Application for Conversion of Heavy Petroleum Fractions

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Abstract

Solid catalysts for petroleum refining and catalytic transformations have been developed starting from local Algerian materials, mainly "bentonite" [1]. These catalysts are used for the transformation of the heavy fractions and the residues of the oil by the catalytic processes leading to obtaining clean and environmentally friendly petrol (fuel) as well as petroleum fractions that are considered as important raw materials for petrochemical, pharmaceutical, and cosmetic industry. The preparation of modified catalysts using Algerian local bentonite enriched by oxides to give them a better performance for the validation of certain fractions of oil and condensate is described.

Keywords: Heterogeneous catalysis; Heavy petroleum fractions; Solid Catalysts.

Introduction

Heterogeneous catalysis has considerably influenced the refining and petrochemical industries. The 30s of the 20th century have seen the development of three main types of processes, which were intended for primary refining, namely the catalytic cracking, alkylation and dehydrogenation [2,3]. This is also valid for other important industrial process named the Fischer-Tropsch process using Co / Fe catalysts which converts coal into synthetic gas that is processed into cuts C5-C11-rich olefins and paraffin's. This method is widely used in Japan, Germany and South Africa. Nowadays heterogeneous catalysis dominates and determines the great advances in refining and petrochemical industries [4]. It is noted that the sales of catalysts for refineries reached \$ 2.7 Billion in 2005 with an annual increase of 3.24% and still in progress [5]

Taken together, the industrial catalysts are the heart of the refining processes and they determine their future. The catalytic processes are increasingly developing and the discovery of new

catalysts still represents urgent need. Heterogeneous catalysis or contact catalysis is to achieve a transformation of liquid or gaseous reagents by using a solid catalyst; the chemical process takes place at solid-fluid interface by adsorption of reagents at specific sites of the solid surface, which are capable of contracting with reactive chemical bonds more or less strong. The adsorbed species are better and strongly formed if the catalyst is properly selected for the desired reaction according to the Sabatier principle [6]. Therefore the introduction of surface atoms or ions plays an important role. In the present work, the preparation of modified catalysts using Algerian local bentonite enriched by oxides to give them a better performance for the validation of certain fractions of oil and condensate is described [7-9].

Different stages of the catalytic cycle

The reaction taking place not in the whole volume of the fluid, but only at the solid-fluid interface, the formation of adsorbed species involves carriage of active molecules to the surface followed by adsorption. The surface reaction gives products followed by desorption from the catalytic surface, then migration into the fluid. Thus we can say that a catalytic cycle takes place in the following steps:

- Transfer of reagents to the solid surface.
- Adsorption of reactants on the catalyst.
- Interaction between reactants adsorbed to the surface.
- Desorption of products from the catalytic surface.
- Transfer of products leaving the catalyst.

Results and Discussion

The importance of the catalytic processes and needs to refining

are constantly changing as more and more oil is processed into fine products: fuels, base for petrochemicals, lubricants. The transport industry plays a leading role in this development: the steady progress of processes and catalysts. Due to environmental reasons, changes in fuel specifications are becoming severe challenge. In terms of processes and catalysts, the applications are shown in (Table 1). We can say that the overall objective of the use of catalysts is to produce quality products at lower cost through technologies and processes leading to emissions and discharges with minimum harmfulness.

Objective	Processes involved	Targets
Purify expenses and income	Hydrotreating	Reduction of sulfur, nitrogen, metals and asphaltens
Convert residues	Hydroconversion of vacuum residue and FCC and hydrocracking	Catalysts more active and selective in reducing their production costs
Improving the quality of products (petrol, diesel)	Catalytic reforming,	A cetane Name nor
	FCC Increases cetane Name nor	Reduction of benzene, sulfur, nitrogen and aromatics
	Reduction of benzene, sulfur, nitrogen and aromatics	
Lower investment and operating costs	All the existing processes, mainly hydrocracking and hydroconversions of residues	Reduced operating pressure, increased activity, selectivity and lifetime of catalyst
Improving existing processes	FCC and downstream processes	New Catalysts decyclization of naphthenes and aromatic-naphthenics
	Aliphatique alkylation	
Control émissions and redué émissions	Claus process, purification of effluents, fumes and thermal FCC	increased sulfur recovery and conversion of SOx and NOx
		Reduced émissions of particulate
Producing Hydrogen	Partial oxidation of residues	Redue soot, Redue temperature,
	Steam reforming gas	Increasing selectivity H2

Table 1: Employment of catalysts in refining

Methods of Preparation of Solid Catalysts

There are different protocols for the preparation of solid catalyst. The final properties of the catalyst depend strongly on each stage of preparation and on the purity of raw materials used. Small changes in the drying temperature, the solvent composition or the curing time can affect the performance of the catalyst. In refining we are dealing with two types of catalysts: The bulk catalysts; and the impregnated catalysts. The bulk catalysts are prepared by precipitation, hydro-thermal synthesis or fusion with mixtures of metals or metal oxides as their name implies. They consist of an active material: alumino silicates or zeolites. Catalytic synthesis of ammonia with ran metals belong to this class. Impregnated Catalysts are used when one is forced to use precious metals or sensitive compounds and in this case the precursor of active metal is

deposited on a porous support which may be an oxide (for example silica, alumina), activated charcoal or even a resin.

The media used are themselves prepared by the same method of preparation of bulk catalysts. As examples of supported catalysts: Pd / C used in hydrogenation processes and Pt/ Sn/Al₂O₃ for dehydrogenation processes. Sometimes a method of preparation that combines the two previous methods is used; for example the active precursor powder is mixed with the substrate and the mixture is then agglomerated. Figure 1 shows an outline of the Key Steps for preparing a solid catalyst. This technique is performed at high temperature; it combines metal oxides and gives a good clean with a good dispersion of solids for example V₂O₅-MoO₃. The drawback of this method is the complexity of the material used because it requires special equipment in case of high temperatures required.

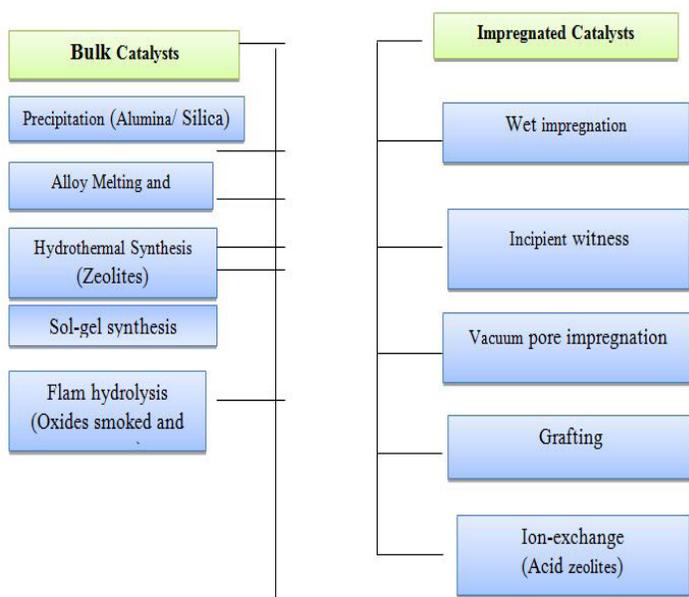


Figure 1: Key Steps for preparing a solid catalyst

Technique of alloys leaching

In 1924 the American engineer Murray Raney discovered that the metal alloys used in leached hydrogenation give better results, he built a Ni / Al 50: 50 Then he removed the aluminum with Na OH and the result is called a “nickel sponge” also known as “skeletal catalyst”. These catalysts are ready to use without pre-activation and have a large surface area. Figure 2 shows an outline for the preparation a Nickel sponge

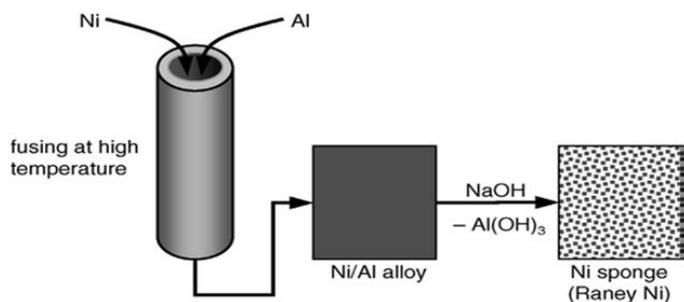


Figure 2: Preparation of nickel sponge (Raney/ Nickel (

Precipitation technique

The precipitation techniques are widely used for the preparation of several important catalysts, including silica, alumina and Cu/Zn O/Al₂O₃ catalyst used in the synthesis of methanol. This method produces high purity materials, but it requires solvent or precipitating agent which causes loss during the preparation of the catalyst and extra costs for the separation of the solvent compared to the previous method. This method generally comprises mixing

aqueous solutions of salts and the desired salt is precipitated as a gel with the addition of a base or an acid or other precipitating agent. It passes through three stages which are super saturation, nucleation and crystal growth. Cooling the obtained material till it is matured, filtered, washed, dried and finally calcinated. For example Ni/Al₂O₃ catalysts used in steam cracking process are prepared by co precipitation of a precursor of nitrate in the presence of Na OH.

Technique for impregnating pores

It is a common method for preparing supported catalysts as the catalyst Pt/Al₂O₃ used in catalytic reforming. If impregnation of a wet ‘wet impregnation’ support is immersed in a solution of catalyst precursor it can be spontaneously adsorbed by the catalyst or it will precipitate by a change in pH or by the intervention of another chemical reaction and the resulting catalyst will be filtered, dried and calcinated. Taking the example of Pt/Al₂O₃ catalyst which is prepared by mixing porous alumina with an acid solution chloroplatinic, the solvent is evaporated leaving 6 Pt ions on the support where they will suffer reduction using hydrogen, the reaction is illustrated below.

The disadvantage of this method is the large volume of waste liquids, but you can avoid this problem by using the method called “incipient wetness» that is to gradually moisten the powder from the support by the precursor solution until the mixture becomes slightly sticky which indicates that the pores of the support are filled with the liquid. It can also be done by vacuum impregnation method is “Vacuum impregnation pore” where the medium is first dried and placed under vacuum to clear the air ports, then the support volume of precursor is added equivalent to pore volumes. It can happen to charge the pores by the active agent, repeating several times.

Figure 3: shows photograph and schematic outline of a laboratory reactor for vacuum impregnation of the pores [10, 11].

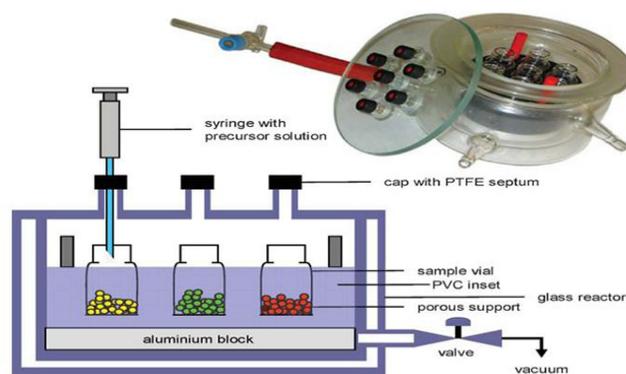


Figure 3: Vacuum impregnation of the pores

Hydrothermal synthesis

As its name suggests it involves heating the precipitates, gels, or flocks in presence of water, this treatment is carried out in an autoclave at temperatures of 100-300 ° C. it follows from the textural and structural changes leading to a transformation from amorphous to crystalline state. This part is illustrated by the manufacture of zeolites.

Hydrothermal synthesis of zeolites

RM Barrer pioneered the synthesis of zeolites, trying to duplicate the crystallization (very slow) of natural zeolites, but he found that acceptable crystallization times (about a day) can be achieved by performing the synthesis under conditions of much more severe temperatures and alkaline mineral solutions used. The first synthesized zeolites were Al / If low (1 to 1.5) zeolites LTA, FAU type X. Subsequently zeolites average ratio (from 2-5) as the FAU zeolites Y type were synthesized. It is noted that the addition of organic compounds (structural) to the synthesis solution allowed obtaining zeolites Si / Al with very high ratio ($\approx 10-100$).

Milestones synthesis

The synthesis process of zeolites also called zeolitization corresponds to the transformation of a mixture of aluminum compounds and silica, alkali metal cations, possibly of organic molecules and water in a micro-porous crystalline aluminosilicate (zeolites) using an alkaline solution super saturated. The mixture is quickly converted to an aluminosilicate hydro gel. The aging of the gel at room temperature (or slightly higher) allows slow dissolution of solid treated in the solution of monomers and oligomers silicates and aluminates in the latter leading to condense forming a crystalline phase. The crystallization is conducted at temperatures of 60-160 ° C The zeolitization involves three stages: super saturation of the solution, nucleation and crystal growth.

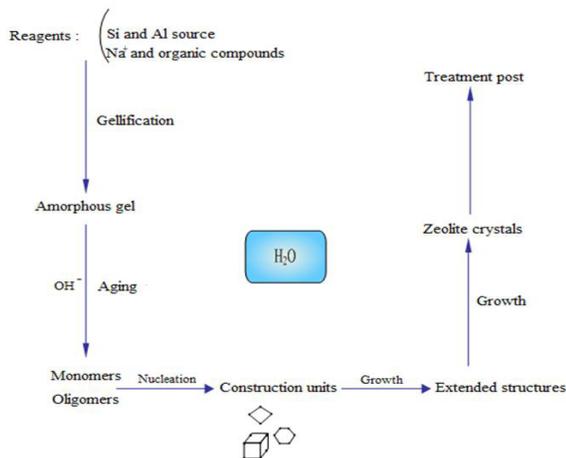


Figure 4: Stages of formation and ripening of the zeolites

a) The super saturation of the solution:

One solution may be under the conditions of concentration and temperature in three forms: stable, metastable or labile. The areas of stability and metastability are separated by the curve of solubility equilibrium concentration of component C * depending on temperature. The degree of super saturation S is defined as the ratio of actual concentrations and equilibrium concentration ($S = C / C^*$) in the field of stability or nucleation no crystal growth can occur, the crystal growth and nucleation can occur only in the field of lability, dominates in the meta stability only crystal growth is possible during aging conducted at constant temperature. The concentration of aluminosilicate species increases over time by dissolving the solid amorphous phase to shift from a stable solution to a metastable solution and labile in solution [12].

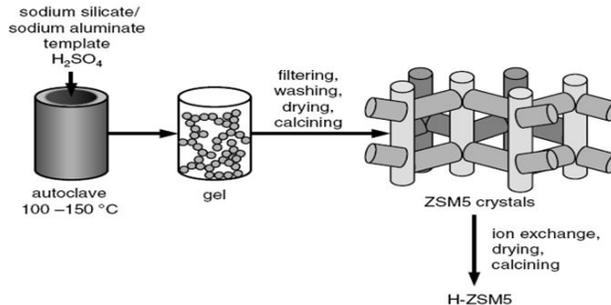


Figure 5: Schematic diagram of the synthesis of zeolites

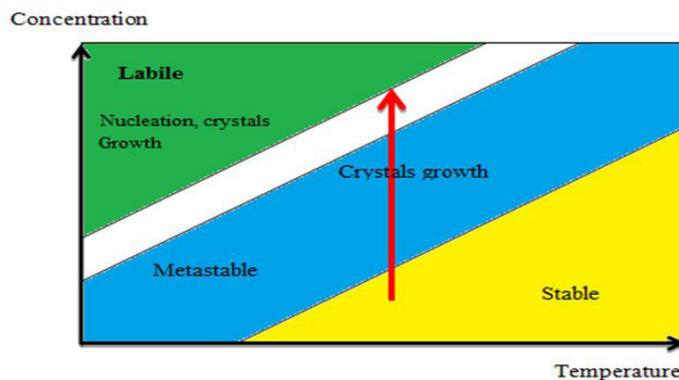


Figure 6: Solubility diagram

b) Nucleation

The initial nucleation (or primary) from the labile solution may be homogeneous (spontaneous formation) or heterogeneous (induced by impurities), the secondary nucleation is induced by crystals. Nucleation is an activated phenomenon, its rate increases with temperature (by Arrhenius) as well as the degree of super saturation S. The nucleation starts for a critical value of S, the velocity reaches a maximum for a larger value, the decrease observed at high values of S from limitations in the transport of species, caused by increased viscosity of the solution.

c) Growth of crystals

The crystal growth of zeolites occurs at the interface crystal-solution by condensation of dissolved species (secondary building units or larger species). The following figure illustrates the stages of manufacture of the synthetic zeolites is the most famous H-ZSM5 (figure 4).

Parameters determining the zeolitization:

The zeolitization depends on four main factors are:

The composition of the hydrogel: Each zeolite has a domain of well-defined composition, sometimes very large, sometimes very narrow, the composition of the hydrogel is a very important parameter for the synthesis of the desired zeolites. The composition of the zeolites is expressed in molar ratio of oxides: Al_2O_3 ; a Si_2O_2 ; b Na_2O : c H_2O

pH of the alkalinity of the solution: The pH of the alkaline so-

SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	P ₂ O ₅	Cr ₂ O ₃	SO ₃	Fire Los.
55,87	18,11	6,57	0,12	2,06	3,22	0,50	2,67	0,78	0,13	0,03	2,46	9,31

Table 2: Chemical composition of bentonite

Catalyst	1	2	3	4
SiO ₂	39.63	49.58	41.28	40.51
Al ₂ O ₃	13.67	16.87	12.83	10.34
Fe ₂ O ₃	6.82	4.03	2.51	2.47
CaO	3.87	2.87	1.97	1.76
MgO	4.36	2.66	1.66	1.63
SO ₃	2.46	1.48	0.92	0.91
K ₂ O	2.67	1.59	0.99	0.97
Na ₂ O	0.5	1.9	0.17	0.17
Cr ₂ O ₃	0.03	0.02	0.67	4.77
loss on ignition	13.56	8.29	8.88	7.81

Table 3: Chemical composition of 4 prepared catalysts

These catalysts were used in two main treatment processes namely: cracking and isomerization; which enabled the preparation of specific species with an octane rating around 100, without additives. Moreover, the pyrolysis gasoline is highly aromatic,

lution synthesis (usually between 9 and 11) has an essential importance, because the OH-anions are essential to depolymerize the amorphous gel at an appropriate speed (they are mineralizing agents). Temperature increasing the temperature allows for shorter times of crystallization.

The temperature also determines the type of zeolites formed, leading to the growth of denser phase. There is however a limit temperature for the formation of each zeolites.

Structuring agents added to the solution:

The structuring agents' role is to guide the synthesis of the wanted zeolites kinetically and thermodynamically. The oligomeric aluminosilicate organized around a particular geometry of structuring agents' molecules, precursors leading to species appropriate for nucleation and crystal growth. Bentonite extracted from the region Boghni (Algeria), and processed and analyzed and the results are in the table 2 below.

thereby obtaining BTX (Benzene, Toluene and Xylene) which are considered important raw material for petrochemicals [8]. Both processes have been conducted on a laboratory scale. An outline of the system is shown below and convincing results have been obtained.

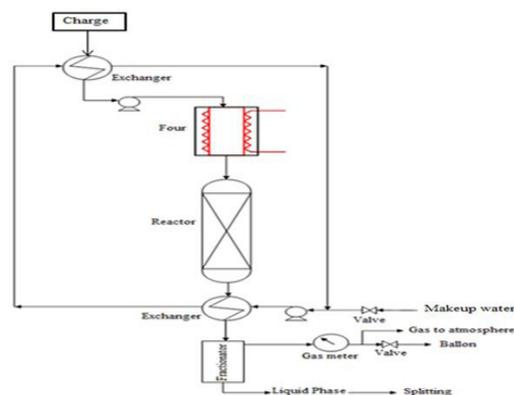


Figure7: Catalytic cracking plant.

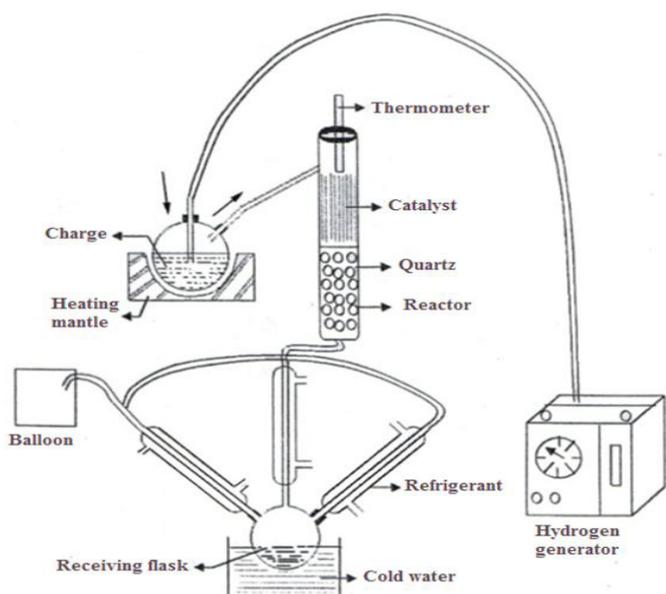


Figure 8: Installing catalytic isomerization

Conclusion

The catalysts prepared from local materials allowed us to conduct experiments on various charges compounding consisting of atmospheric residue and heavy diesel in the case of cracking and light fractions of condensate in the case of isomerization. The culmination of the work is the development of local bentonite by its application in industrial processes for obtaining oil from waste and light fractions of condensate, bases clean gasoline with high octane. In addition, the resulting gasoline is highly aromatic and can be used in the production of BTX necessary for the petrochemical industry. Moreover, the catalytic cracking process produces large quantities of gases consisting mainly of unsaturated fractions BTAN-butylenes-propylene and propane which is also much sought after for the manufacture of high octane gasoline.

It should be noted that to improve the desired product yields

it is necessary to recycle the residuals. The gas oil obtained is possibly consistent with commercial specifications and can overcome the deficits in this product during peak periods. The convincing results encourage us to reproduce the work in laboratory scale units before translating it to an industrial scale. In future research we recommend the use of catalysts of different compositions: for example the introduction of nickel compounds; whose properties are equivalent to the isomerizing ability of chromium.

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