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# RECYCLING OF PLASTIC MATERIALS EMPLOYING ZEOLITE AND MCM-41 MATERIALS

# RECICLADO DE MATERIALES PLÁSTICOS EMPLEANDO ZEOLITAS Y MATERIALES MCM-41

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**Abstract**

We report on the catalytic and the thermal decomposition of low density polyethylene resulting in several fuel products (LP gas, gasoline, gas oil). We built a continuos, fixed-bed reaction system. We employed Ga-MCM-41, Al-MCM-41, commercial FCC Y zeolite (fresh and equilibrium) and natural mordenite as catalysts. We set the following reaction conditions: 450 °C reaction temperature, constant feed flow and 30 min reaction time at atmospheric pressure. We analyzed the gas and liquid products by gas chromatography and simulated distillation (ASTM D-2887), respectively. The highest selectivity towards liquid products (60.7% w/w) 85% w/w of which consisted of gasoline, was obtained with natural modernite.

*Keywords*: catalytic cracking, MCM-41, natural mordenite, LDPE, plastic recycling.

**Resumen**

En el presente trabajo reportamos la descomposición térmica y catalítica de polietileno de baja densidad para la producción de combustibles (gas LP, gasolina, gasóleo). Se construyó un sistema de reacción contínuo de lecho fijo. Se emplearon materiales Ga-MCM-41, Al-MCM-41, catalizadores FCC comerciales basados en zeolita Y (fresco y de equilibrio) y zeolita mordenita natural. La temperatura de reacción fue de 450 °C y el tiempo de reacción 30 min. Se analizaron los productos por cromatografía de gases y destilación simulada (ASTM D-2887). La mayor selectividad hacia productos líquidos, de los cuales el 85% en peso correspondió a gasolina, se obtuvo con la mordenita natural.

*Palabras clave:* desintegración catalítica, MCM-41, mordenita natural, polietileno, reciclaje.

## 1. Introduction

The environmental hazards of plastic waste, a major component of urban solid residues arise from the substitution of previously employed materials such as glass, metals, ceramics, wood, paper, cardboard or cotton, from a huge increase in consumer products and from the indifference from large sectors of the population. In a large number of countries, plastic waste is disposed without any control or processing and left to accumulate on the ground, pits or along the shore of rivers.

The generation of solid residues in Mexico City is of almost 12 thousand tons per day (Compendio de Estadísticas Ambientales, 2002**)** and the major component in the plastic waste is low density polyethylene, LDPE. A promising alternative for recycling plastic materials is catalytic decomposition (commonly classified as a Tertiary Recycling method) obtaining useful added value products such as LP gas, gasoline, light cyclic oils and olefins, therefore contributing to reduce the depletion of petroleum reserves and biological sources of fuel, helping to preserve our environment. Plastic waste can

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be considered a cheap source of raw material.

In recent years, several reports have shown the feasibility of recycling plastic materials employing a wide range of catalysts**:** zeolite Y, zeolite ZSM-5, FCC, MCM-41, SBA-15 and mesoporous silica (Aguado *et al*., 2002; Arandes *et al*., 2003; Bockhorn *et al*., 1999; Cardona *et al*., 2000; De la Puente *et al*., 2002; Grieken *et al*., 2001; Serrano *et al*., 2003; Serrano *et al*., 2004; Sánchez *et al*., 2003; Takuma *et al*., 2001; Uemichi *et al*., 1998a,b). Some of them have also studied the thermal cracking of polymers (Grieken *et al*., 2001; Serrano *et al*., 2003; Cardona *et al*., 2000; Bockhorn *et al*., 1999). We have previously reported the catalytic decomposition of LDPE with commercial FCC catalysts by adding the polymer into the industrial FCC refinery feedstock (Sánchez *et al*., 2003). The aim of this work was to study the performance of different catalysts (natural mordenite, MCM-41 materials and FCC catalysts) in the cracking of LDPE in a fixed-bed reaction system.

## 2. Experimental

MCM-41 materials were synthesised according to a previously reported procedure (Noreña, 1993), employing cetyltrimethylammonium chloride, tetrabutylammonium hydroxide, fumed silica and gallium nitrate, as gallium source. The gel of synthesis was kept at 100 ºC for 48 hours, then extensively washed, filtered, dryed and calcined. Commercial FCC catalysts were supplied by the Mexican Petroleum Institute (IMP). These catalysts were: FCC-Fresh, (25-35% zeolite and 2.4% w/w rare earth content, with 84 and 108 ppm of Ni and V, respectively) and FCC-Equilibrium (18-24% zeolite and 2% w/w rare earth content, with 389 and 1532 ppm of Ni and V, respectively). The natural mordenite was obtained from a mine in Tamaulipas, Mexico. The natural mordenite was exchanged with $NH_4Cl$. The main properties of these catalysts are indicated in Table 1.

Table 1. Catalysts properties

| CATALYST | Si/Al ratio[1] | Unit Cell Parameter (nm)[1] | Specific Area (m$^2$/g)• |
|---|---|---|---|
| FCC-F | 24.5* | 24.30 | 300.34 |
| FCC-Eq | 25.0* | 24.46 | 166.15 |
| Al-MCM-41 | 9 | 41.75 | 800 |
| Ga-MCM-41 | 25** | 46.18 | 900 |
| Natural Mordenite | 5.5 | 18.1 | 280 |

*of the zeolite. **Si/Ga ratio. [1] X-ray diffraction analysis ($Cu_\lambda$=1.5406 nm).
• B.E.T. analysis.

We built a reaction system (Fig. 1) based on a design by (Uemichi *et al*., 1998b). The system consists of a loading deposit where the polymer melts, a capillary tube for controlling the plastic feed, a fixed bed reactor (descendent vertical flow), a condenser and recipients for gas and liquid products. We modified the dimensions of the reaction system, longer than that reported by Uemichi (350 mm length, 6 mm reactor diameter). The material used in all the reaction system was stainless steel. We employed electric resistors in a ceramic material for heating. There are 3 heating zones, automatically controlled from a PC computer with a *labview* graphic software. For the automatic control of the system, we calculated the power passing through the resistors and we employed several National Instruments Field Point Modules (FP), such as RS -232 interfaces, TC-120 temperature controllers and PWM-520 power registers, and other components, such as thermocouples, electric relevators and fuses.

Prior to the reaction, the catalysts were dried at 100 °C for 1.5 h in a NEYTECH Qex oven (94-94-400 model, Degussa-Ney dental, INC, USA). For the thermal decomposition test (pyrolysis) the reactor was filled with inert SiC in order to keep the same pressure drop. We loaded 0.4 g of LDPE in small pieces in each test. The polymer was melted at 290 °C and fed into the reactor (0.04 cc/min). The capillary tube was kept at 330 °C and the reactor at 450 °C. The LDPE was forced into the capillary tube and the reactor with 10 cc/min $N_2$ UAP generating a pressure differential. After several preliminary tests and in order to keep stable the reaction conditions, we employed a constant catalyst volume inside the reactor (1.47 cc) and we kept a constant LHSV. Table 2 summarizes the experimental conditions.

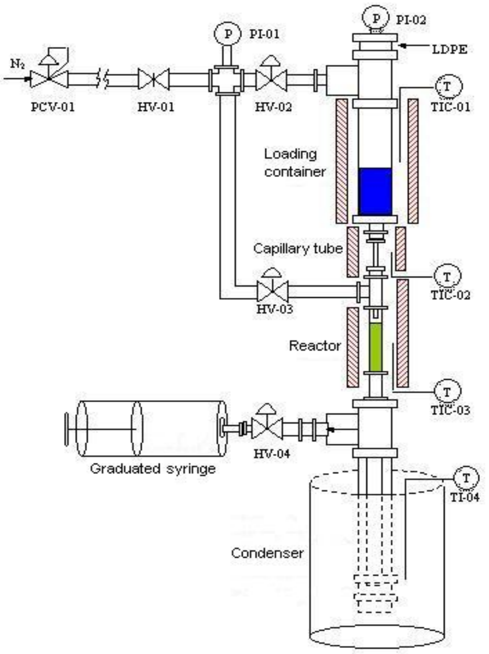

Fig. 1. Reaction system employed in the experimental procedure. HV-valves, TIC-termocouples, PI-manometers.

Table 2. LDPE decomposition reaction conditions

| LDPE feed | 0.3100-0.446 g |
|---|---|
| **LHSV** | 0.033 $min^{-1}$ |
| Reaction time | 30 min |
| Loading container temperature (TIC-01) | 290 °C |
| Capillary tube temperature (TIC-02) | 330 ° C |
| Condenser Temperature (TI-04) | 1.57 °C |
| Reactor Temperature (TIC-03) | 450 °C |
| $N_2$ flow (carrier) | 10 ml/min |

The products obtained were divided into four groups: gas products (C1-C4), liquid products (C5 and higher), solid-like products as a yellowish wax (only produced by pyrolysis) and carbonaceous deposits remaining on the catalyst (residues). The liquid products were quantified by weighing the condenser (kept at 1.5 °C), analyzed by simulated distillation (ASTM D-2887) and classified as gasoline, turbosine, kerosene, gas oil and fuel oil, according to Table 3. The gas products were collected by means of a graduated syringe and analyzed by gas chromatography (refinery gas analysis) employing a HP 6890 PLUS+ chromatograph.

Table 3. Composition of the liquid products

| DISTILLATION FRACTION | CARBON NUMBER | BOILING POINT (°C) |
|---|---|---|
| Gasoline | C5 – C12 | 39 – 220 |
| Turbosine | C13 – C14 | 221 – 254 |
| Kerosene | C15 – C17 | 255 – 300 |
| Gas oil | C18 – C28 | 301 – 431 |
| Fuel oil | C29 – C44 | 432 - 545 |

## 3. Results and discussion

The catalyst samples were characterized by X-Ray Diffraction, (Fig. 2), all showing their corresponding characteristic phase. The diffraction pattern of the commercial FCC-Fresh and FCC- Eq catalysts show the diffraction peaks of a Y zeolite (Fig. 2a). The main diffraction features of the natural zeolite in Fig. 2b belong to mordenite (approximately 85% w/w content) with a smaller proportion of other components, such as quartz and calcite. Fig. 2c shows the diffraction pattern of the Al-MCM-41 and Ga-MCM-41 samples, exhibiting the typical profile of a hexagonal array of pores, with the characteristic (100) diffraction peak.

All the catalysts showed catalytic activity in this reaction. Fig. 3a shows the total conversion at 30 min reaction time to gas and liquid products obtained with the catalysts studied (in varying weights), ranging from 52% (with Ga-MCM-41) to

72.7% total conversion (with FCC-Fresh) The design of the reaction system does not allow to measure the conversion at initial conditions (t=0) that would determine the initial activity. Fig. 3b shows the turnover (grams of polymer converted by gram of catalyst) for each catalyst, indicating that the more active cracking materials by weight unit are Al-MCM-41 and Ga-MCM-41. These catalysts are probably more active because their wide pores facilitate the diffusion of the polymer chains.

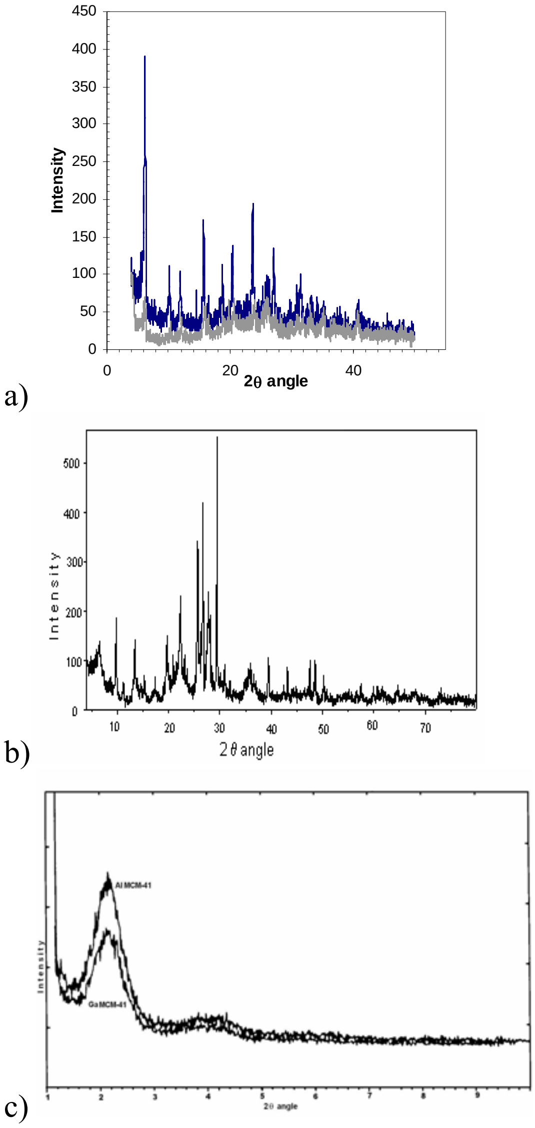

Fig. 2. XRD pattern of a) the fresh and equilibrium commercial FCC catalyst, b) the natural mordenite and c) Al-MCM-41 and Ga-MCM-41.

A much larger proportion of gas and liquid products was obtained with the catalytic decomposition if compared to the thermal decomposition (pyrolysis). Pyrolysis produced 90.67 % w/w of solid product as a yellowish greasy wax.

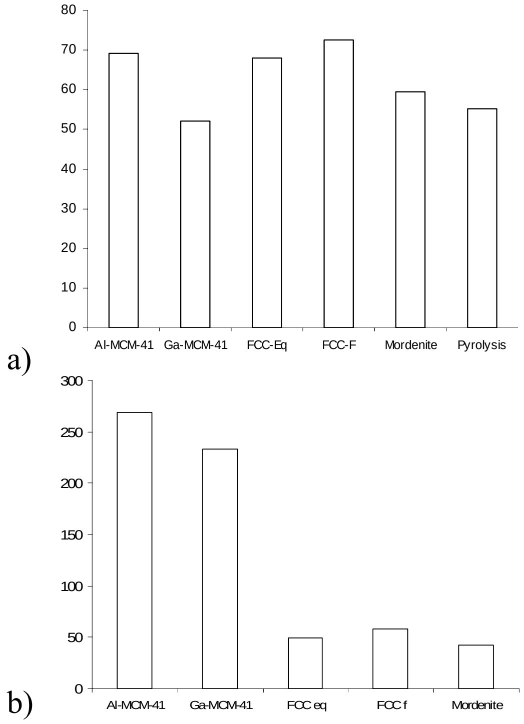

Fig. 3. a) Conversion of LDPE at 450°C, b) Turnover (grams of polymer converted by gram of catalyst).

Fig. 4 shows the amount of carbonaceous residues produced during the reaction. Ga-MCM-41 had a relatively small conversion to gas and liquid products and a high production of carbonaceous residues, such as coke. It is known that gallium promotes aromatization reactions (Serrano *et al*., 2004; Arendes *et al*., 2003) therefore, we consider that aromatic compounds and olefins, having low desorption rates, stay on the catalyst, promoting also the formation of carbonaceous deposits. Large amounts of residues were also obtained with the FCC-fresh catalyst (27% w/w), probably due to secondary hydrogen transfer reactions. The Ni and V content of commercial FCC (fresh and equilibrium) catalysts increase the coke yield.

It is known that the conversion of polymers over acidic catalysts leads to the production of a complex mixture of hydrocarbons, the composition of which depends on the polymer, the experimental conditions and the catalyst properties (De la Puente et al., 2002).

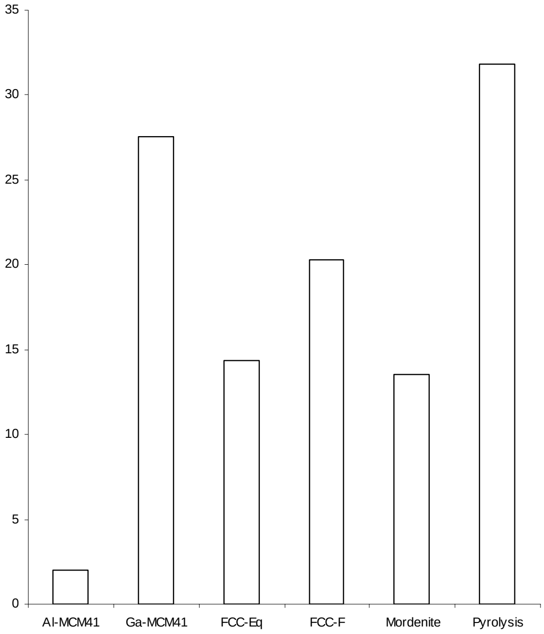

Fig. 4. Selectivity to liquid products obtained with the catalysts studied (%w/w).

Strong cracking catalysts produce small molecules (gases), while not so strong cracking catalysts produce relatively larger molecules (liquids). The gas products consisted of a complex mixture of molecules with a large proportion of isobutane and propylene. Fig. 5 shows the selectivity towards gas products. Catalysts of high acidity, such as the FCC-fresh catalyst, exhibit a large cracking activity, which is also increased by the rare earth oxides, resulting in a high gas yield. Al-MCM-41 which has a larger proportion of Broensted acid sites, if compared to Ga-MCM-41, also produced a high gas yield.

Fig. 6 shows the selectivity towards liquid products. The highest selectivity towards liquid products was obtained with the natural mordenite with a high composition of gasoline (85 % w/w). A high liquid yield was also obtained with Ga-MCM-41. The lowest selectivity towards liquid products was obtained with the FCC-Fresh catalyst, explained by the high rate of degradation to gas products during the 30 min reaction time.

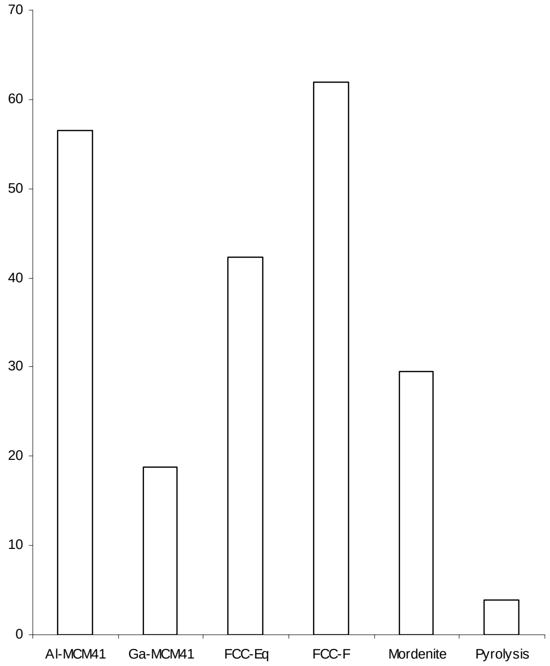

Fig. 5. Selectivity to gas products obtained with the catalysts studied (%w/w).

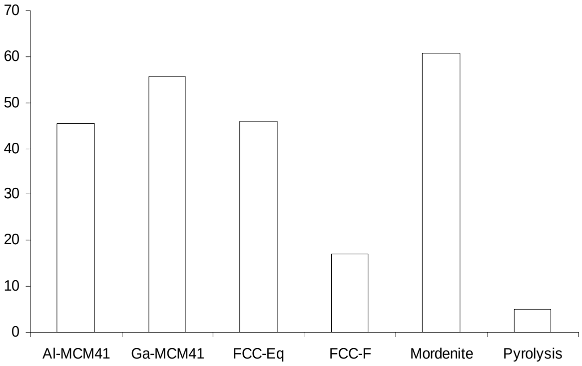

Fig. 6. Residues remaining on the catalysts (%w/w).

Fig. 7 shows the composition of the liquid product obtained by catalytic degradation of the polymer at 450 °C, consisting of a large proportion of C6-C12 fractions (gasoline). Ga-MCM-41 produced a relatively low gasoline yield and a particularly high gas oil yield, due to the aromatization properties of gallium, considering that gas oil is a mixture of alkanes, cycloalkanes and aromatic hydrocarbons of relatively high molecular weight.

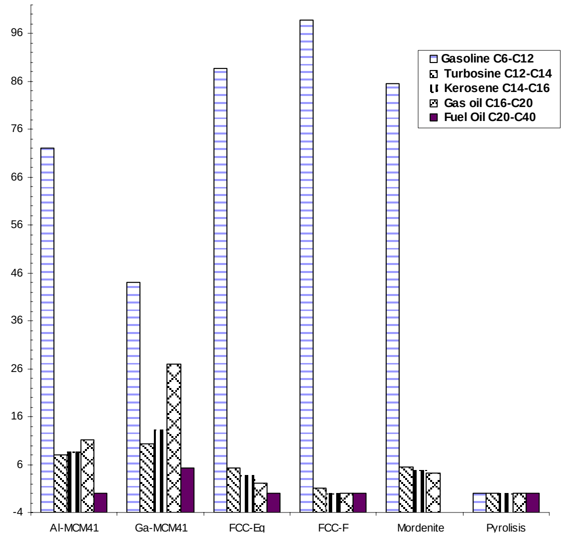

Fig. 7. % w/w composition of the liquid product.

It has been reported that the mechanism of the thermal decomposition is a free radical mechanism, considering there are no acid sites in this process. We obtained no methane or ethane in the pyrolysis test, which can be explained by the only partial decomposition of the polymer chains.

The high levels of parafins and branched olefins in the gas product of the catalytic decomposition can be explained by the formation of carbocations on Brönsted acid sites, by the protonation of the polymer molecule.

## Conclusions

Results obtained show that catalytic cracking is a promising route for obtaining clean fuel from LDPE (a cheap raw material) or intermediates for the chemical and petrochemical industries, reducing at the same time, the environmental problems arising from plastic waste.

Depending on the type of product wanted, a particular catalyst should be considered. A higher proportion of gas products was obtained with the commercial fresh FCC catalyst and Al-MCM-41, both of a relatively high cost. Al-MCM-41 also produced the smaller amount of residues. Interesting options for obtaining liquid products are natural mordenite and equilibrium FCC catalysts that produced a large proportion of gasoline and are cheap and widely available.

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