Catalytic conversion of polyethylene into fuels over mesoporous MCM-41

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Tetrahedral Al-containing MCM-41, prepared under ambient conditions, exhibits suitable catalytic properties for the conversion of low-density polyethylene into hydrocarbon feedstocks.

Recycling of plastic wastes is currently an environmental requirement and several alternatives are being considered. Chemical methods are quite promising for commercial applications since they allow the polymeric wastes to be removed by conversion into valuable chemicals.[1–3] At present, four different chemical processes are being investigated for recycling of polyolefinic wastes: pyrolysis, gasification, hydrogenation and catalytic cracking. In this way, catalytic conversion has been reported to lead to hydrocarbon mixtures with potential applications as synthetic fuels.[4,5]

Catalytic cracking of polyolefins usually proceeds over solid-acid catalysts, such as amorphous silica–alumina and zeolites.[6–8] Due to the bulky and polymeric nature of plastic molecules, the catalytic activity is mainly governed and limited by the catalyst pore size. It is difficult to adjust this in amorphous silica–alumina and a wide distribution of pore sizes is usually present in these materials. In addition, zeolite pores are too small for the plastic molecules to gain access into the channels; hence the initial stages of cracking are supposed to take place over a small portion of the total acid sites (those located on the external zeolite surface or at the pore entrances).

The synthesis of a new family of silicate/aluminosilicate molecular sieves has been recently reported.[9,10] The most studied member, designated as MCM-41, is a material characterized by the presence of uniform mesopores with sizes that may be tailored in the range 15–100 Å by changing the synthesis conditions. Consequently, MCM-41 is a potential catalyst for reactions involving bulky molecules. In this way, as reported here, we have found it exhibits interesting catalytic properties for the degradation of polyethylene, usually the major component of plastic wastes.

The sample of Al-containing MCM-41 used in this work was prepared following a simple room-temperature method, which is based on a procedure developed by Tanev *et al.*[11] for the synthesis of Ti-containing mesoporous materials. The latter has been modified in order to allow Al species to be incorporated in tetrahedral positions of the network. Thus, solution A was prepared by dissolving tetraethylorthosilicate (TEOS, Alfa 99%) and aluminium isopropoxide (AIP, Aldrich 98%) in ethanol (Panreac) whereas solution B was obtained by mixing cetyltrimethylammonium chloride (CTMACl, Aldrich 25%) and HCl (Panreac, 35%) in distilled water. After adding solution A to solution B, the resulting acidic homogeneous mixture was slowly stirred at room temperature for *ca.* 2 days. Thereafter, the formation of a gel was observed, which was separated by filtration, washed several times with distilled water, dried at 110 °C overnight and finally calcined at 550 °C in air for 14 h. The molar composition of the initial synthesis mixture was: 1 TEOS : 0.034 AIP : 0.27 CTMACl : 0.02 HCl : 6.54 EtOH : 36 H_2O.

The XRD pattern of the as-synthesized MCM-41 sample presents an intense peak with *d*-spacing at 45.3 Å, typical of this material. TG analysis of this sample in flowing air leads to a mass loss of 50% with a peak in the differential curve centred at 254 °C due to the decomposition and removal of the surfactant occluded in the MCM-41 pores. The cyclohexane adsorption isotherm of this material, measured at 25 °C in a thermobalance, shows an inflection point at *ca.* p/p_0 = 0.3, whereas its adsorption capacity for $p/p_0 \geqslant 0.6$ is >50 mass%. XRD, TG and adsorption data compared to those reported in the literature[10,12] indicate high purity of this MCM-41 sample. Its Al content (Si/Al = 32.6, determined by XRF) is nearly the same as that of the starting synthesis mixture (Si/Al = 29.4). ^{27}Al MAS NMR spectra of both as-synthesized and calcined MCM-41 present an intense peak with a chemical shift at δ 53, assigned to tetrahedral Al species, whereas a very small shoulder is observed at *ca.* δ 3, indicating essentially the absence of octahedral Al even after calcination.

NH_3 TPD measurements have been performed on the calcined sample. The outgassed MCM-41 was first saturated with an ammonia stream and subsequently the physisorbed NH_3 was removed by treatment at 180 °C in an He flow. By increasing the temperature at a constant rate of 15 °C min^{-1}, a single desorption peak was observed at *ca.* 310 °C (Fig. 1), which is in agreement with the presence of medium-strength acid sites in the MCM-41. These sites are weaker than those usually present in zeolites such as ZSM-5 (NH_3 desorption peak at 470 °C, Fig. 1). The amount of ammonia desorbed between 180 and 550 °C was 0.275 mequiv. g^{-1}, clearly lower than the theorical value of 0.5 mequiv. g^{-1} if it is assumed that each Al atom is associated with an acid site. This MCM-41 acidity is not increased even after repeated ion exchange with 1 mol dm^{-3} NH_4Cl aqueous solution, followed by calcination. The discrepancy between the amount of ammonia desorbed between 180 and 550 °C and the aluminium content of MCM-41 may be due to the location of a part of the Al atoms within the pore walls, being inaccessible to the NH_3 molecules, and to the possible presence of very weak acid sites which release NH_3 below 180 °C. It should be pointed out that the MCM-41 sample prepared by the room-temperature method described here, presents, after calcination, suitable acid properties. These are

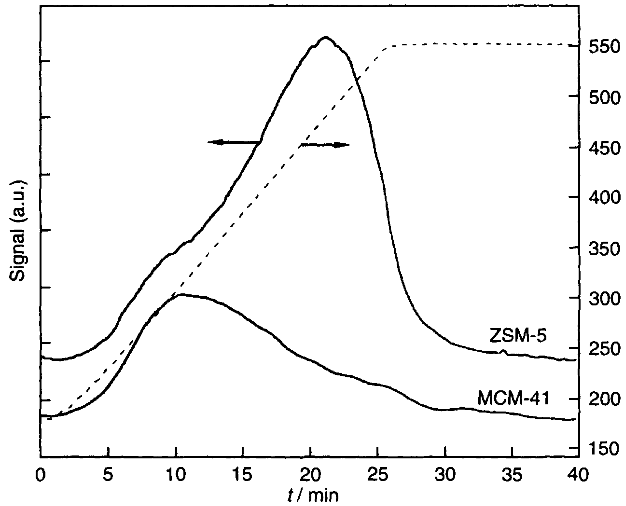

Fig. 1 NH_3 temperature programmed desorption (TPD) of MCM-41 and ZSM-5

not improved by subsequent ion exchange, *i.e.* this treatment is not necessary to generate acid sites.

Catalytic tests of cracking of low-density polyethylene (LDPE, REPSOL PE-033) have been carried out in a batch reactor at 400 °C, atmospheric pressure and under an N_2 flow. The mass of plastic loaded in each reaction was 1.2 g. The results obtained with the MCM-41 sample are shown in Table 1, and are compared with those corresponding to a commercial silica–alumina (Si/Al = 2, SÜDCHEMIE) and a ZSM-5 zeolite (Si/Al = 31, synthesized in our laboratory). The conversion is referred to in terms of cracking products with C_n ($n < 40$), whereas the residue remaining in the reactor is formed by partially cracked polyethylene. Under the conditions used here, polyethylene conversion into gaseous or liquid products simply by thermal cracking was found to be negligible.

Compared to the amorphous silica–alumina, the MCM-41 sample is more active despite its lower Al content. This difference is likely to arise from the higher mesoporosity of MCM-41 which favours the access of the plastic molecules to the acid sites. The most active catalyst for polyethylene cracking is ZSM-5 zeolite, even though the reaction is hindered by its small pore size (*ca.* 5.5 Å) and in the earlier reaction stages only acid sites located on or near the external catalyst surface are supposed to be involved. Therefore, the superior activity of ZSM-5 compared to MCM-41 is probably related to the higher strength of its acid sites. However, the product distribution obtained with MCM-41 reveals higher amounts of liquid hydrocarbons with boiling points in the range of gasolines (C_5–C_{12}) and middle distillates (C_{13}–C_{22}) relative to amorphous silica–alumina or ZSM-5 zeolite. Over 50 mass% of the product obtained with ZSM-5 consists of gaseous hydrocarbons, with a relatively high proportion of paraffins which are industrially less valuable chemicals. Moreover, the gasoline fraction obtained with MCM-41 shows a lower content of aromatic hydrocarbons than for ZSM-5. These differences are enhanced when the catalytic tests are carried out at lower plastic/catalyst ratios (Table 1): 7.69 mass% of aromatics in the MCM-41 gasoline *vs.* 17.86 mass% for ZSM-5 for a plastic/catalyst mass ratio of 4. The lower proportion of aromatics obtained with MCM-41 can be related to its lower acid strength and is beneficial in terms of environmental criteria.

Table 1 Cracking of LDPE over amorphous SiO_2–Al_2O_3, MCM-41, and ZSM-5

Catalyst	SiO_2–Al_2O_3		MCM-41		ZSM-5	
P/C[a]	18	4	18	4	18	4
Conv. (mass%)	5.11	35.18	62.83	95.87	95.4	94.32
Product selectivity (mass%)						
C_1–C_4 (paraffins)	25.81	12.47	11.05	9.48	19.77	24.75
C_2–C_4 (olefins)	27.85	20.16	15.39	10.44	32.76	32.98
C_5–C_{12}	46.34	52.84	56.35	58.80	44.61	39.35
Aromatic[b]	—	3.84	6.19	7.69	6.80	17.86
C_{13}–C_{22}	—	13.53	13.49	19.81	2.31	2.30
C_{23}–C_{40}	—	1.00	3.72	1.47	0.55	0.62

[a] P/C: plastic/catalyst mass ratio. [b] Aromatic content in the total C_5–C_{12} fraction (mass%). *Reaction conditions*: T = 400 °C, t = 30 min, atmospheric pressure, N_2 flow 23 ml min^{-1}.

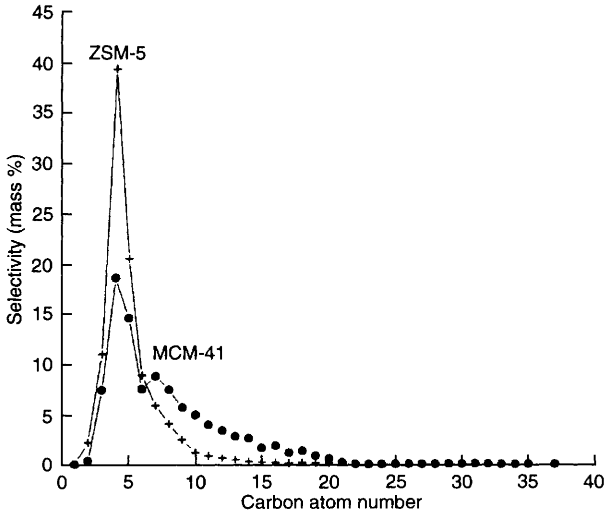

Fig. 2 C_n product distribution obtained with MCM-41 and ZSM-5 (plastic/catalyst mass ratio = 18)

The selectivities towards C_n corresponding to the overall cracking products obtained using ZSM-5 and MCM-41 as catalysts are shown in Fig. 2. The ZSM-5 product shows a sharp maximum for C_4, whereas for MCM-41 a second maximum is observed for C_7 hydrocarbons, which suggests the presence of different cracking pathways for these two catalysts.

The extent of MCM-41 deactivation has been investigated by analysing the reaction products accumulated during time intervals of 0.5 h, in experiments carried out with a high plastic/catalyst ratio (P/C = 50). Although the conversion rapidly decreased over short times (from 26 to 6.75% after 1.5 h), it stabilizes at *ca.* 6% over extended periods of time. The spent catalyst can be regenerated at 500 °C in air, with recovery of 85% of its initial activity. The study of the different phenomena which may be responsible for this slight loss of activity (partial collapse of the structure, decrease of the pore size, partial dealumination, *etc.*) will be the subject of future work.

To summarize, the method used here for the preparation of MCM-41 is simple (under ambient conditions) and leads to a material having tetrahedral Al species and medium-strength acid sites after calcination of the as-synthesized sample. This material presents interesting catalytic properties for the conversion of polyethylene wastes into feedstocks, mainly gasolines and middle distillate fractions with low aromatic content, with potential applications as automotive synthetic fuels.

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