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Mesoporous catalysts for the synthesis of clean diesel fuels by oligomerisation of olefins

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Abstract

Si/Al MCM-41 type mesoporous compounds, as such or containing small amounts of metal (Ni, Rh or Pt), were investigated in the synthesis of clean diesel fuels by oligomerisation of orphan olefin streams. Very good catalytic performances were obtained with C_4 and C_5 olefins, while almost no conversion occurred with ethylene. The activity increased with increasing reaction pressure, temperature and contact time, while high Si/Al ratios had a negative effect on both activity and catalyst stability. The presence of small amount of metal inside the mesoporous structure did not significantly modify the catalytic activity, although specific effects were detected for each element. Since the evaluation of the cetane number by H-NMR gave rise to values about 20% lower than the actual value, a new and more complex algorithm is proposed to calculate the cetane number. Using the proposed algorithm, a good correlation index was found between calculated and motor values for pure compounds. Further study is necessary to move from pure compounds to experimental mixtures.

Keywords: MCM-41; Diesel; Olefins; Oligomerisation; Rh; Ni; Pt; Cetane number

1. Introduction

The world demand for diesel fuels, in particular that in the western Europe, is expected to grow more rapidly than that of gasoline (Fig. 1) [1]. Furthermore, the irreversible trend towards increasing regulation of the emission of pollutants [2–6] calls for better quality of the fuels which, together with innovations in engines, can contribute to fulfil the legislative requirements. The options in diesel reformulation are however limited. Optimum would be a high quality oil which however is just the opposite to the actual general worsening of crude oil. The main route therefore is a hydrogenation step of the cuts to be blended. The severity of treatment (from mild hydrotreating to more severe hydrocracking with the removal of heteroatoms) is still a function of the raw material and specifications to be reached [7–11]. A complementary approach is the synthesis of diesel components like distillates (Fischer–Tropsch reaction, rapeseed oil methyl esters, oxygenated compounds, etc.). Diesel fuel obtained by oligomerisation of light olefins can be considered in this group, since it has two advantages, the absence of sulphur (a key plus factor since there is a general agreement in its reduction) and aromatics, if the conversion is properly carried out. However, since the value attributed by the market to high quality diesel components is not clear, the raw material has to be a “low value” stream. Due to gasoline reformulation and/or local refinery situations, some orphan streams may be available for oligomerisation to the diesel cut (b.p. 180–350 °C, corresponding

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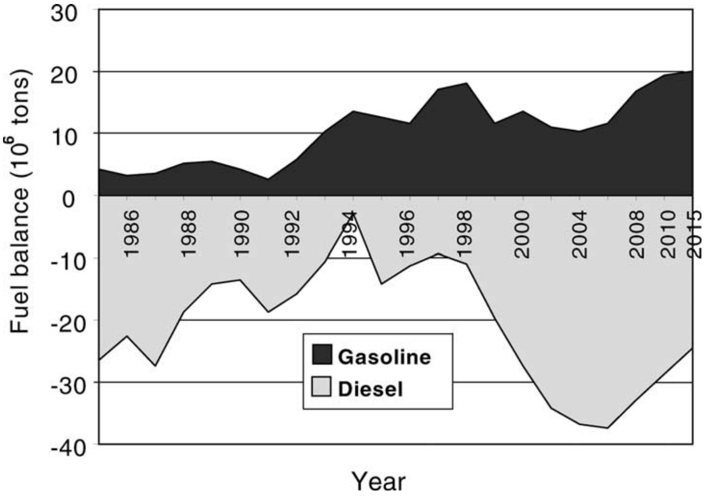

Fig. 1. Evolution of the fuel balance (industrial production – market demand) in Western Europe [1].

approximately to the C_{10}–C_{20} paraffinic range), sulphur and aromatic free, with a good cetane number.

Both homogeneous (Lewis acids, organometallic complexes, etc.) and heterogeneous (mixed oxides, zeolites, clays, etc.) catalysts may be used, although the latter approach seems easier to scale-up and apply industrially. Considering that pore shape and size and acidity affect the product distribution, in this paper we report an investigation on the catalytic behaviour in olefin oligomerisation to diesel fuels of MCM-41 type mesoporous aluminosilicates, with and without small amount of metals inside the structure. In these materials, the acidity and the size of the uniform system of channels may be tailored by selecting the Si/Al ratio and template, respectively, but in all cases they exhibit acid OH groups of lower strength than those in zeolites [12].

2. Experimental

MCM-41 type catalysts with different Si/Al ratios and with and without small amounts of transition metal ions (Ni^{2+}, Pt^{2+} or Rh^{3+}) were prepared following procedures in the patent literature [13], starting from cethyltrimethylammonium chloride (as the templating agent), sodium aluminate, fumed silica and tetramethylammonium silicate (TMAS) (Aldrich). Where required, the metal salt ($RhCl_3 \cdot xH_2O$, Pt acetylacetonate or $NiCl_2 \cdot 6H_2O$) was added to the reagent solution before introducing the TMAS. The gel obtained after 4–5 h under agitation was placed in a static autoclave for 48 h at 150 °C and then filtered, washed, dried in air and calcined at 540 °C for 7 h. The XRD powder analysis were carried out with a Philips PW 1050/81 diffractometer equipped with a graphite monochromator in the diffracted beam and controlled by a PW1710 unit ($\lambda = 0.15418$ nm, 40 kV, 40 mA). The surface area was determined by N_2 adsorption using a Carlo Erba Sorptomatic model 1900. The total acidity of the catalysts dried at 120 °C was determined, after exchange for 0.5 h with a 5 wt.% solution of NaCl, by titration with 0.1 N NaOH using phenolphthalein as indicator.

The catalytic tests were carried out in a steel fixed-bed microreactor (i.d. 12 mm ca.), with an isothermal zone assured by a oven of about 5 cm in the middle. The reaction temperature and the absence of any axial-thermal gradients were checked by a J-thermocouple sliding in a sheath inside the catalytic bed. The tests were carried out using 1–2 ml of catalyst (0.71–0.85 mm size), operating in the $T = 413$–523 K, $P = 1.5$–5.0 MPa and WHSV $= 2$–$11\,h^{-1}$ (referred to olefin) ranges. The following mixtures were fed: (1) 1-pentene:*iso*-pentane (30:70 (w/w)); (2) 1-butene: *n*-butane (88:12 (w/w)); (3) 1-butene and 2-butene:*iso*-butane (80:20 (w/w)); (4) ethylene:N_2 (30:70 (v/v)). In each test, the time-on-stream was generally 200 min, after which regeneration was carried out by heating the catalyst at 550 °C ca. for 5 h in air, and purging the lines before and after this step with N_2. Finally, the catalytic test was repeated at least one time to check the performance after the oxidative regeneration. This sequence was repeated two or three times to determine whether or not the catalyst could tolerate the high temperature regeneration.

The out-stream was generally fully condensed in a cold flask and analysed off-line, while when its volatility was too high to allow complete condensation, the analysis was carried out on-line. In both cases, a gas chromatograph HP 5890II, equipped with a cryogenic valve, a HP-PONA column and FID detector was employed. The products were divided in C_n fractions on the basis of their retention time intervals, referring to some calibration mixtures of pure C_5–C_{20} *n*-paraffins. The performances of each catalyst were reported in terms of:

- Conversion (%): conversion of the olefin to products other than those due to isomerisation reactions (for example, the conversion of 1-pentene to 2-pentene or isoamyleens was not taken into account).
- Dimer selectivity (%): selectivity to dimers, since they were outside (C_8) or just at the lower limit (C_{10}) of the diesel fraction
- Diesel selectivity (%): selectivity to diesel range products, corresponding approximately to the C_{10}–C_{20} *n*-paraffinic range.

The cetane number of the mixtures obtained was calculated according to O'Connor et al. [14] on the basis of the H-NMR analysis, performed after separation of the light products and hydrogenation of unsaturated products.

3. Results and discussion

The Si/Al catalysts synthesised exhibited, both before and after the catalytic tests, XRD patterns (Fig. 2) and surface area values (Table 1) typical of mesoporous MCM-41 type samples with a hexagonal structure [13,15,16]. Analogous results have been also obtained for the catalysts containing small amounts of Ni^{2+}, Pt^{2+} and Rh^{3+} ions inside the Si/Al framework. The increase of the Si/Al ratio gave rise to a slight shift of the XRD pattern towards low 2θ values and a decrease of the total acidity value.

Table 1
Surface area and total acidity values for the Si/Al MCM-41 type catalysts investigated

Sample	Surface area ($m^2\,g^{-1}$)		Acidity ($mmol\,g^{-1}$) (before)
	Before	After	
Si/Al = 10	700	691	0.25
Si/Al = 20	818	781	0.18
Si/Al = 70	820	805	ND

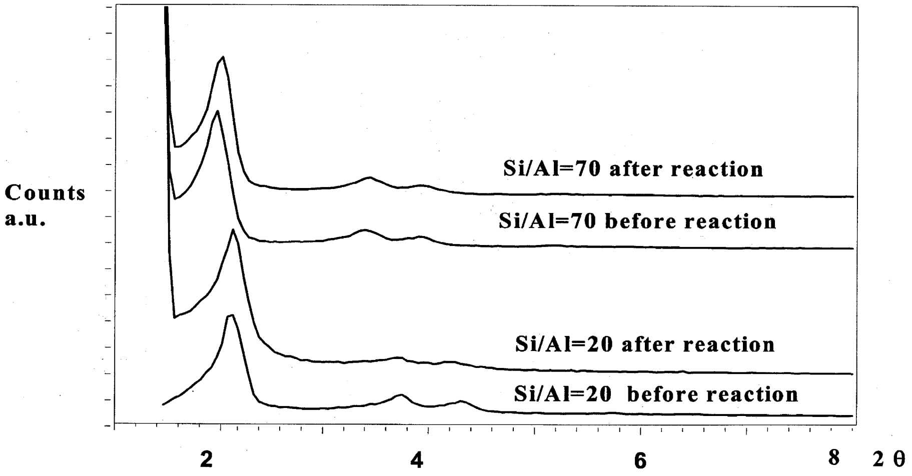

Fig. 2. XRD patterns of two Si/Al MCM-41 type catalysts, before and after reaction.

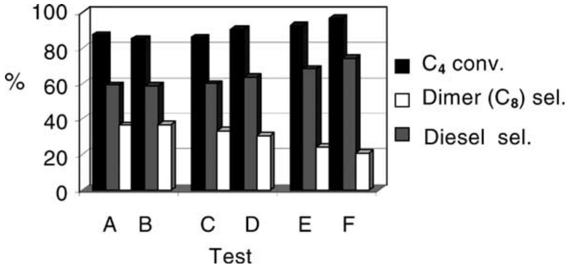

Fig. 3. Catalytic performance for a MCM-41 type (Si/Al = 10) catalyst as a function of the reaction parameters (pressure = 5.0 MPa; reaction temperature = 140 °C (tests A–D) or 160 °C (tests E and F); WHSV = 10.6 h^{-1} (tests A and B) or 5.6 h^{-1} (tests C–F); time-on-stream = 3 h (tests A, C and E) or 6 h (tests B, D and F, after the oxidative regeneration at 550 °C ca.)).

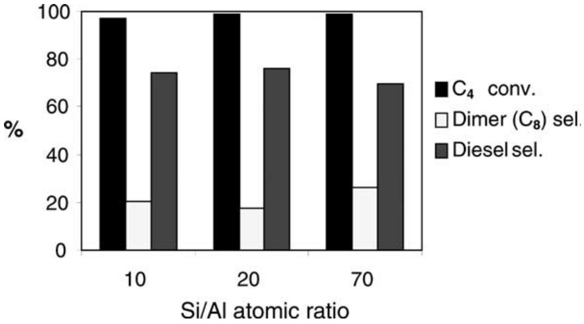

Fig. 4. Catalytic performance for the MCM-41 type catalysts as a function of the Si/Al atomic ratio (pressure = 5.0 MPa; WHSV = 5.3 h^{-1}; time-on-stream = 3 h; reaction temperature = 160 °C (180 °C for the Si/Al = 70 sample)).

Preliminary tests performed feeding the 1-pentene-*iso*-pentane mixture and using a zeolite-based catalyst showed a significant decrease in the selectivity to dimers with a corresponding increase in that to the diesel fuel range with increasing the pressure from 1.0 to 5.0 MPa; thus all following tests were carried out at the latter pressure. The Si/Al MCM-41 type catalysts showed very interesting catalytic performances, in terms of both activity and selectivity to diesel range products with both C_5 and C_4 feeds, in the latter case without any significant difference due to the presence of 2-butene and to the nature and/or amount of the paraffin present (*n*-butane or *iso*-butane).

All the catalysts showed an improvement in the catalytic performance with increasing temperature and decreasing WHSV value (Fig. 3), together with general good stability in the oxidative regeneration, easily predictable as necessary to remove the heavy by-products fouling the surface. However, an optimum value of 20 ca. was identified for the Si/Al atomic ratio (Fig. 4), notwithstanding the decrease of the total acidity with increasing Si/Al ratio (Table 1), showing the necessity of a proper equilibrium between number and strength of acid sites. It is noteworthy that the acidity data do not support the hypothesis suggested by one of the referees of a lower acidity for the Si/Al = 10 sample, due to extensive dealumination during the calcination step to remove the organic template. While slight differences were observed with decreasing Si/Al ratio down to 10, the catalyst with Si/Al = 70 achieved the same good catalytic performance at higher temperature (180 °C), whereas at lower temperature, the selectivity in the diesel fraction decreased significantly and the dimers became the main products. Furthermore, a drop in conversion and diesel selectivity was observed for this catalyst when the tests were repeated after the oxidative regeneration. Considering the XRD pattern (Fig. 2) as well as the value of surface area value (Table 1) of this sample after the catalytic tests, the loss of activity has to be attributed to an irreversible deactivation of the few acid sites present for high Si/Al ratios.

Although Ni, Pt or Rh were introduced as ions inside the Si/Al framework and no preliminary reduction was carried out, considering the reaction atmosphere, it may be reasonable to assume that in steady-state conditions these elements were present mainly as metal particles. Regardless of the amount (0.3–2.0 wt.%), Rh and Pt had a negligible effect on the catalytic performance, while Ni worsened the performance, as evidenced by the higher temperature required to achieve similar results (Fig. 5). The negative trend of Ni was more evident at the higher Ni content, 3.0 wt.%; notwithstanding the increase in temperature to 200 °C, this latter catalyst showed a decrease in conversion to 20% ca., with preferential formation of dimers (selectivity 80% ca.). However, in no case did the presence of small amounts of metals decrease the stability of the catalyst structure in the oxidative regeneration. Again, no significant difference was observed with the C_5 and the two C_4 feeds. However, unlike that recently claimed for Ni-containing catalysts [17], both the Rh- and Ni-containing MCM-41 type catalysts were not able to convert ethylene,

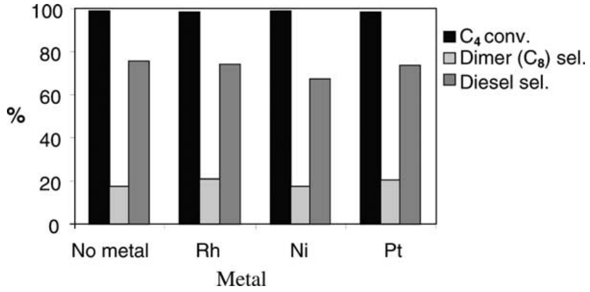

Fig. 5. Catalytic performance for the MCM-41 type catalysts as a function of the nature of the metal present (Si/Al atomic ratio = 20; metal amount = 1.0 wt.%; pressure = 5.0 MPa; WHSV = 5.3 h^{-1}; time-on-stream = 3 h; reaction temperature = 160 °C (180 °C for the Ni-containing sample)).

showing very low conversion values (≤6% ca.) and formation mainly of the dimers, with large amounts of trimers and light cracking products.

The cetane number is a key parameter for diesel fuels, unfortunately the determination of the motor value using the ASTM standard method [18] is not useful in the screening step of the catalysts since it requires a large amount of product (800–1000 ml). Thus, the cetane number values were calculated using the correlation proposed by O'Connor et al. [14] and the H-NMR determination of the CH_2/CH_3 ratio. Although no definitive conclusion may be derived on the basis of the values reported in Table 2, since the small differences, it is possible to hypothesize a positive effect of a slight amount of metal, in particular Rh. However, the low values determined for all the samples stimulated investigation of the reliability of the equation proposed by O'Connor et al. [14]. First of all, for a synthetic diesel fraction obtained using a commercial zeolite-based catalyst, the cetane number determined using the ASTM method [18] was compared with that calculated on the basis of the H-NMR analysis [14]. In the latter case, a value about 20% lower was obtained. Furthermore, when the values for some pure C_{10}–C_{20} paraffins calculated according to O'Connor et al. [14] were plotted versus their actual value [19], a very poor correlation index ($R^2 = 0.80$) was obtained (Fig. 6) with, for some compounds, differences exceeding 100%. A more detailed analysis of the data indicated that the deviations were higher for highly branched paraffins, while the linear paraffins seemed to be very well predicted.

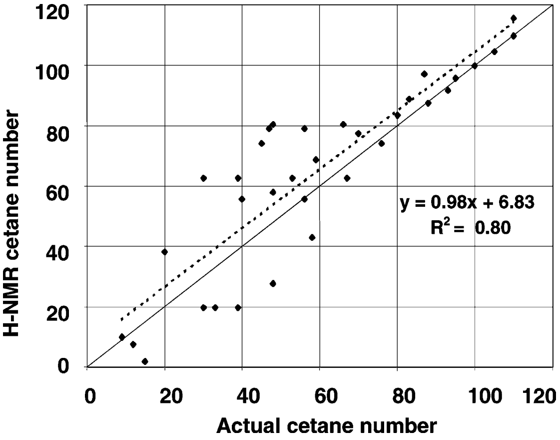

Fig. 6. Cetane number calculated on the basis of the H-NMR CH_2/CH_3 ratio [14] versus actual cetane number for some C_{10}–C_{20} paraffins.

For this reason, a new correlation was developed based on both structural properties (percentage of branching, amount of vicinal $-CH_2$ and terminal *iso*-propilic groups in the hydrocarbon chains) and physical properties [boiling point, b.p.] of the compound:

$$\text{cetane number} = 31.7 + 0.05\,(\text{b.p.}) - 0.99\,(\%\text{branching}) + 3.78\,(\text{vicinal}\ {-CH_2}) + 7.91\,(\textit{iso}\text{-propilic})$$

With this equation, a better correlation ($R^2 = 0.91$) was obtained between the calculated and actual cetane numbers for the C_{10}–C_{20} paraffins with the deviations better distributed between linear and branched

Table 2
Cetane numbers calculated on the basis of the H-NMR analysis [14] for the diesel fuels obtained with some of the MCM-41 type catalysts[a]

No metal	0.3 wt.% Rh	1.0 wt.% Rh	2.0 wt.% Rh	1.0 wt.% Pt	1.0 wt.% Ni
25	30	21	22	27	27

[a] Si/Al atomic ratio = 20; pressure = 5.0 MPa; WHSV = 5.3 h^{-1}; time-on-stream = 3 h; reaction temperature = 160 °C (180 °C for the Ni-containing sample).

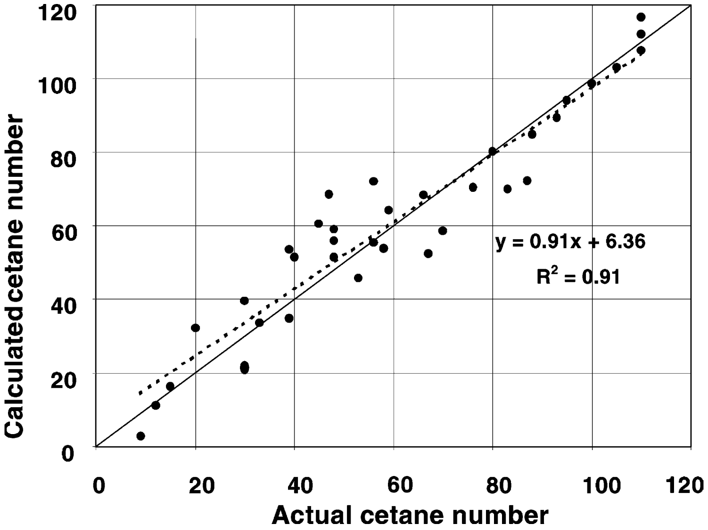

Fig. 7. Cetane number calculated using the proposed algorithm versus actual cetane number for some C_{10}–C_{20} paraffins.

paraffins (Fig. 7). However, in spite of these better results, the deviations for some compounds remain noticeable, indicating the need for further investigation.

4. Conclusions

The main conclusions that may be drawn by the present study are:

- Silico-aluminate MCM-41 type catalysts show promising results in the oligomerisation of C_4 and C_5 olefins, without evidence for deactivation phenomena up to a Si/Al atomic ratio equal to 20. This latter ratio was also identified as optimum for catalytic performances, that are favoured by increasing pressure, temperature and contact time values.
- The presence of small amounts of transition or noble metals has no effect or negative effects on conversion and selectivity, although in the case of Rh, the cetane number slightly increases. It is noteworthy that regardless of the composition, all the MCM-41 type catalysts show negligible activity and selectivity towards ethylene.
- The evaluation of the diesel quality carried out on the basis of H-NMR analysis using the equation proposed by O'Connor et al. [14] significantly underestimates the cetane number, with very poor reliability mainly for the branched paraffins.
- A new algorithm was proposed, based on both structural and physical properties, which gives better correlation between the calculated and actual cetane data for a wide number of C_{10}–C_{20} paraffins. However, further investigations are necessary to clarify the reasons for the deviations observed for some compounds and, mainly, to verify the possible application of the above correlation to a diesel fuel composed of a mixture of hundreds of compounds.

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