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Catalytic cracking of gas-oils in electromagnetic fields: I—dielectric properties of zeolitic catalysts

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Three different zeolitic catalytic systems (13X, 5A and Ammonium Y) were tested for their dielectric properties, surface area and pore-size distribution. The 13X catalyst conductance is higher than other catalysts. The activation energies for 13X, 5A and Ammonium Y are 100, 80, and 50 kJ/mole respectively. The capacitances of 13X catalyst increase with increasing temperature causing a complex behaviour at higher temperatures and frequencies while the capacitances of 5A catalyst are usually less than 10 pF and those of Ammonium Y catalyst are erratic at low temperature. The 13X catalyst is the most suitable catalyst for its dielectric properties and proves to have a good potential to be heated by a RF dielectric reactor. The BET surface area in m^2/g are 524 ± 2, 353 ± 1 and 684 ± 3 while the average pore diameters (in Å) by the BET technique are 33, 22, 26 and the micropore volumes in cm^3/g are 0.187, 0.125 and 0.220 for 13X, 5A and Ammonium Y respectively.

KEY WORDS: dielectric; zeolite catalysts; capacitance; conductance; loss tangent; radio frequency (RF); catalytic cracking; gas oil and dielectric reactor

1. Introduction

The use of radio-frequency power to heat catalysts has been developed to convert heavy oils and residues to useful commercial products without carbon formation [1]. In an electromagnetic field, the heating ability of a material depends on its magnetic and dielectric properties [2]. Catalysts for use at RF fields must have sufficient magnetic and/or dielectric loss to absorb energy from the electromagnetic field and so reach and maintain reaction temperature [3]. In dielectric heating the dielectric properties alone are more important. Such heating depends on materials of high dielectric loss, which increases as frequency increases [4]. In addition to these properties and as a catalyst, the catalytic material must have the desired properties of activity, selectivity and long life.

In this work, three different zeolite catalysts (13X, 5A and Ammonium Y) have been selected and tested for their dielectric properties, surface areas and pore-size distributions, to be used in a radio frequency RF dielectric reactor. Their dielectric effects on the catalytic cracking of gas oil using a three-phase spouted-bed catalytic reactor powered by electromagnetic energy will be analysed and discussed in a separate publication.

Zeolites are commercially important solid acid catalysts for hydrocarbon conversion processes such as cracking, hydrocracking, isomerisation and alkylation. Zeolites used in the manufacture of FCC catalyst are synthetic versions of natural zeolites called faujasite. Faujasite is a naturally occurring mineral, which has a specific crystalline alumina-silicate structure. About 40 natural zeolites are known and more than 150 synthetic zeolites have been reported [5]. Only a few of this large number of zeolites have found commercial applications. Engelhard, Akzo and Grace-Davison are the three major catalyst manufacturers of zeolites.

The FCC zeolites are type X, type Y and ZSM-5. X zeolite has, essentially, the same crystalline structure as Y. The major difference is that the zeolite type X has a lower silica/alumina (SiO_2/Al_2O_3) ratio and lower thermal and hydrothermal stability. Earlier FCC zeolite catalysts contained X zeolite, whilst most of the recent catalysts used contain Y zeolite or modifications. 13X is the sodium form of the type X crystal. It has a much larger pore opening than the type A crystals. It also has the highest theoretical capacity of the common adsorbents and good mass transfer rates. It can remove impurities too large to fit into a type A crystal. In addition, it can adsorb molecules of larger critical diameters, such as aromatics and branched-chain hydrocarbons. Type 13X is used commercially for general gas drying, air plant feed purification (removal of H_2O and CO_2) and liquid hydrocarbon and natural gas sweetening (H_2S and mercaptan removal). The zeolites usually used in the catalysts for octane boosting are modified Y zeolites in which some aluminium has been removed from the structure [6].

The pore structure varies significantly from one zeolite to another [7]. In zeolites X and Y the diameter of the cavities surrounded by the supercage is of the order of 13 Å, whilst the width of the aperture giving

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access to these cavities is 8 Å. In zeolite A, the average cavity diameter is 11 Å, whilst the access aperture widths are 4 Å (Type 4A) and 3 Å (Type 3A) for sodium and potassium form, respectively [8]. Type 5A (pore size of 5 Å) is the calcium exchanged form of the Type A crystal. The strong ionic forces of the divalent calcium ion make it an excellent adsorbent for removing CO_2, H_2S and other weakly polar molecules. Generally, as a result of small pore sizes, type A zeolites will allow the entry of small molecules only, such as H_2O, H_2S and light normal paraffins (up to C_3). So, they are employed for finishing treatments, such as drying and elimination of sulphur compounds, or in separation of normal from branched paraffin hydrocarbons. In contrast, zeolites X and Y and faujasite, whose access apertures are much larger, will absorb a large number of hydrocarbon molecules. Therefore, they are of importance as catalysts in cracking and related reactions as all of their surface area can be used.

ZSM-5 is a shape-selective zeolite, with a pore size of 5.1–5.6 Å, that was introduced by the Mobil Oil Company. It is used as an octane-boosting additive and to increase the light olefin yields of the FCC gasoline in gas-oil cracking. ZSM-5 is widely used as an additive because it is easy for refiners to add when light paraffins are needed [9]. In addition to the zeolites described above, other zeolites have been reported. Chester *et al.* [10] reported that besides ZSM-5, different members of the ZSM-5 family of zeolites, namely ZSM-11, ZSM-12, ZSM-23, ZSM-35 and ZSM-38, have octane-boosting capability.

2. Measurements of dielectric properties

13X, 5A, and Ammonium Y zeolite catalysts of 1.6 mm pellets, supplied by the Sigma–Aldrich Company, were the three catalysts tested in this work. These will be referred to as Z1, Z2 and Z3, respectively. Before doing the AC (alternating current) measurements, as a simple test, the three catalysts were tested for their heating ability by heating them directly in the RF reactor. 13X appeared to heat much more quickly and reached the desired temperature of 800 K.

To carry out the AC measurements, samples of the three catalysts, pressed in tablet form about 2–6 mm thick and 14 mm in diameter, with Pt enamel contacts, were used in an atmosphere of argon. A Hewlett Packard 4194A Impedance Analyser was used in conjunction with a programmable Eurotherm split tube furnace working up to 1473 K. Properties were measured at frequencies of between 100 Hz and 1 MHz and over the temperature range 294–1073 K, with a temperature ramp $dT/dt = 5\,K/min$. Since at high temperatures the current–voltage characteristics are linear the AC conductivity is taken to be proportional to the AC conductance.

3. Results and discussion

Typical conductance (*G*), temperature (*T*) and frequency (*f*) characteristics are shown in figure1 (a), (b) and (c), whilst typical capacitance (*C*), temperature (*T*) and frequency (*f*) characteristics are shown in figure 2 (a), (b) and (c) and typical loss tangent ($\tan\delta$), temperature (*T*) and frequency (*f*) characteristics are shown in figure 3 (a), (b) and (c) for Z1, Z2 and Z3, respectively. The interpretations of these figures are as follows.

3.1. Conductance (G)

The ability of a material to absorb energy from an electromagnetic field is proportional to AC conductivity. AC conductance reflects the transport of all charge carriers and also incorporates losses due to dipole relaxation processes at RF. Changes in the AC conductance reflect changes undergone by the catalyst such as phase changes, chemical changes arising from chemisorption and structural changes due to sintering. Thus the electrical properties under reaction conditions can be used to determine the stability of a material and its potential as a suitable catalyst. The conductivity (σ) in ($\Omega^{-1}\,m^{-1}$) is a function of temperature according to the following expression:

$$\sigma \propto e^{(-E_A/kT)} \tag{1}$$

where E_A (eV) is the activation energy, k is the Boltzmann constant (eV/K) and T is the temperature (K). The activation energy can be obtained from equation (1) by plotting $\log\sigma$ *versus* $1/T$.

From figure 1 the conductance is low for Z2 and Z3, whilst much higher for Z1 at high temperatures. At 1 MHz (closest to the RF operating frequency), activated conductance is above about 573 K for Z1 and 773 K for both Z2 and Z3, with activation energies about 100, 80 and 50 kJ/mole (1, 0.8 and 0.5 eV) for Z1, Z2 and Z3, respectively (1 eV is equivalent to 100 kJ/mole). Similar behaviour is likely at 27 MHz, the operating frequency of the reactor, with the same activation energies at high temperature but with highly activated behaviour starting at slightly higher temperatures than at 1 MHz. Thus Z1 is expected to heat well once above 573 K or so. Z2 and Z3 are likely to heat much more slowly and may not reach the desired temperatures, which agrees with the scouting experiment carried out earlier. If temperatures above about 773 K are achieved then thermal runaway may occur. It is important that the high temperature conductivity and the activation energy are not too high or the heat absorbed will always exceed the heat losses and thermal runway will occur if the control of the input power to the reactor is insufficiently fast. This phenomenon has been observed with other high conductivity materials but may be controlled by the addition of suitable proportions of an insulator [4]. The dependence of AC conductivity on frequency, temperature and

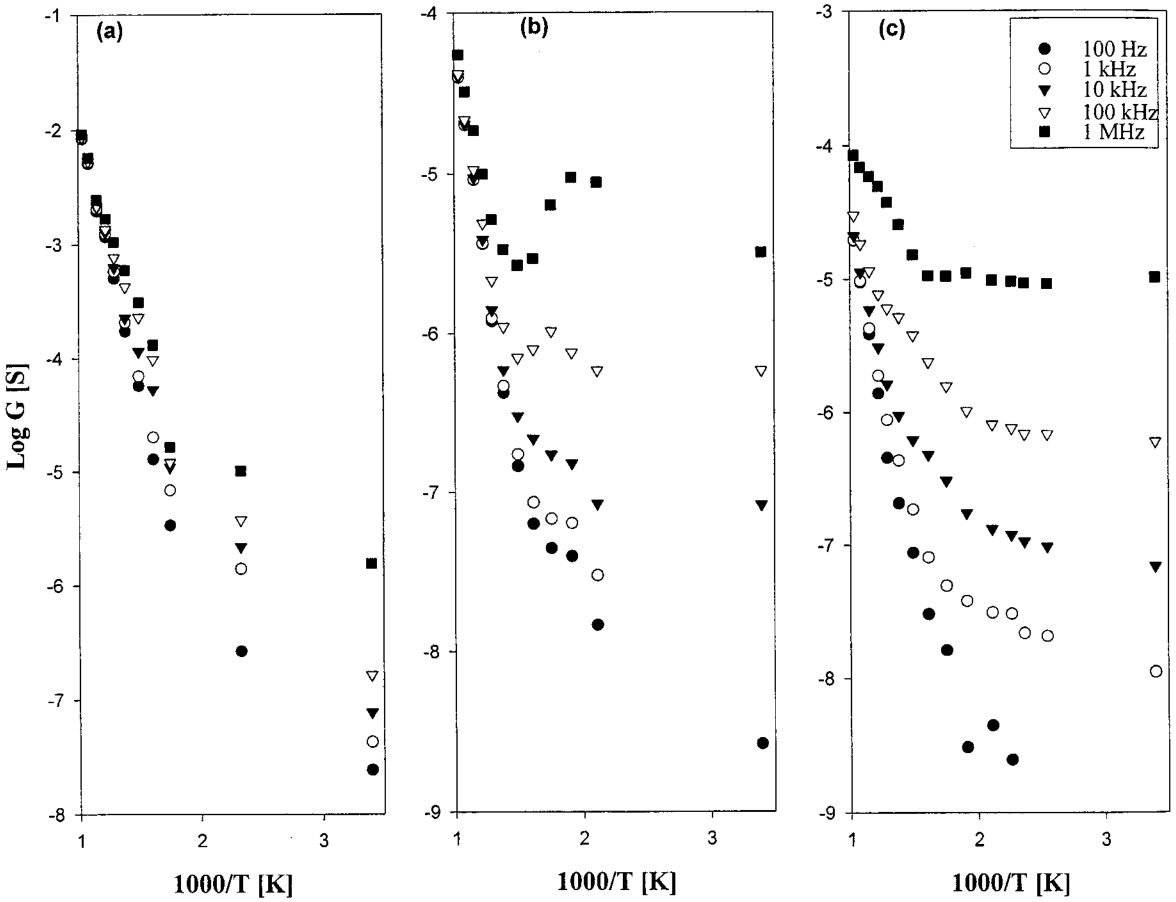

Figure 1. Conductance for Z1 Sample (a), Z2 Sample (b) and Z3 Sample (c) as a function of temperature and frequency.

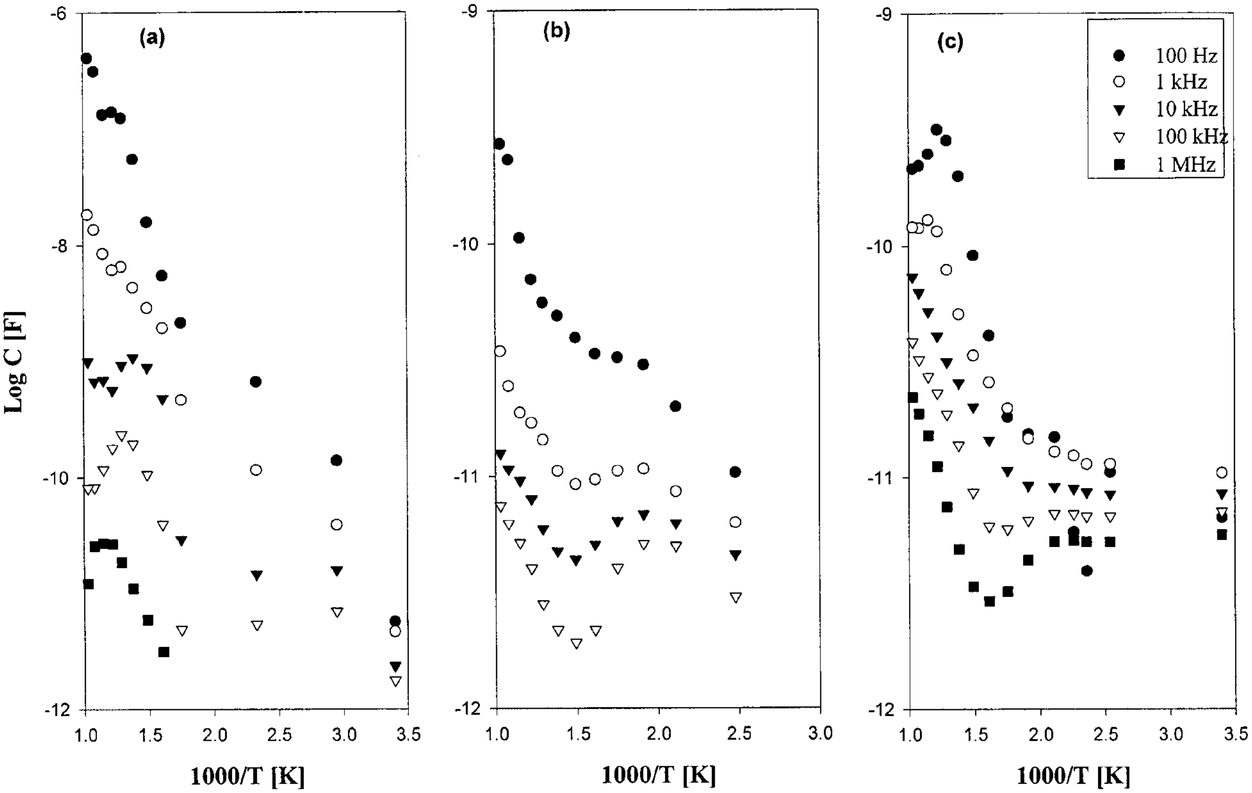

Figure 2. Capacitance for Z1 Sample (a), Z2 Sample (b) and Z3 Sample (c) as a function of temperature and frequency.

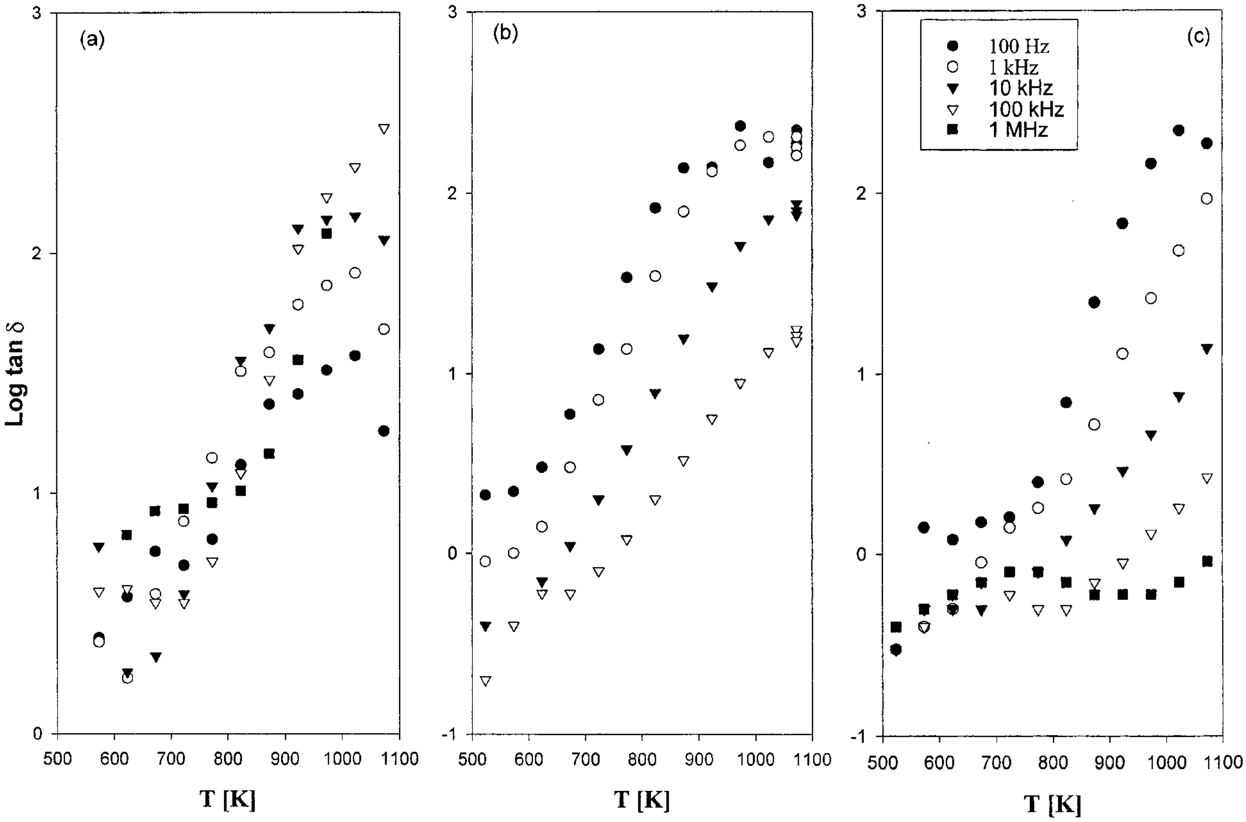

Figure 3. Loss tangent for Z1 sample (a), Z2 sample (b) and Z3 sample (c) as a function of temperature and frequency.

atmosphere determine the heating characteristics and hence the suitability of a material in a reactor of electromagnetic type.

The approximate dielectric loss factor (ε''), which is a parameter determining the energy dissipated in the dielectric and equals the product of the dielectric constant (ε_r) and the loss tangent ($\tan\delta$) [11], have been calculated at 1 MHz as a function of temperature and are presented in figure 4.

3.2. Capacitance (C)

Figure 2 shows the typical capacitance (C), temperature (T) and frequency (f) characteristics for Z1 (a), Z2

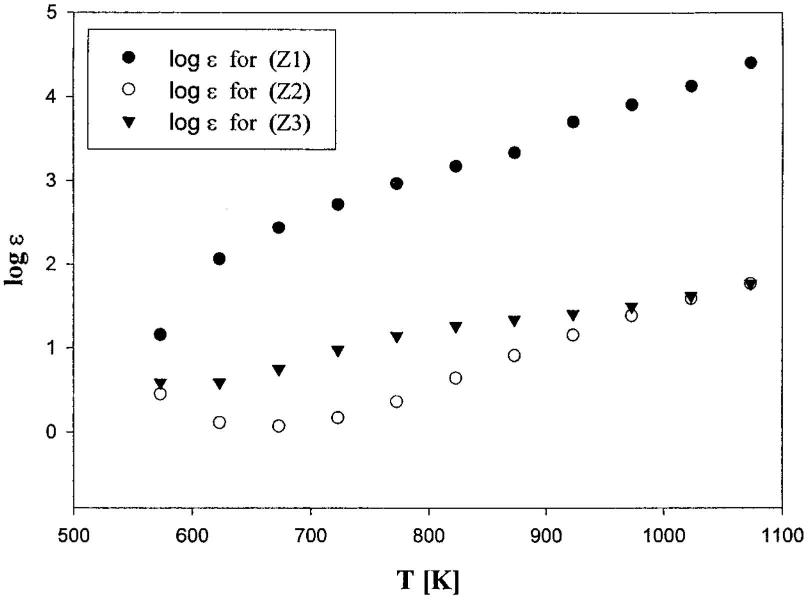

Figure 4. Dielectric loss factor (ε'') of samples of materials Z1, Z2 and Z3 as a function of temperature at 1 MHz frequency.

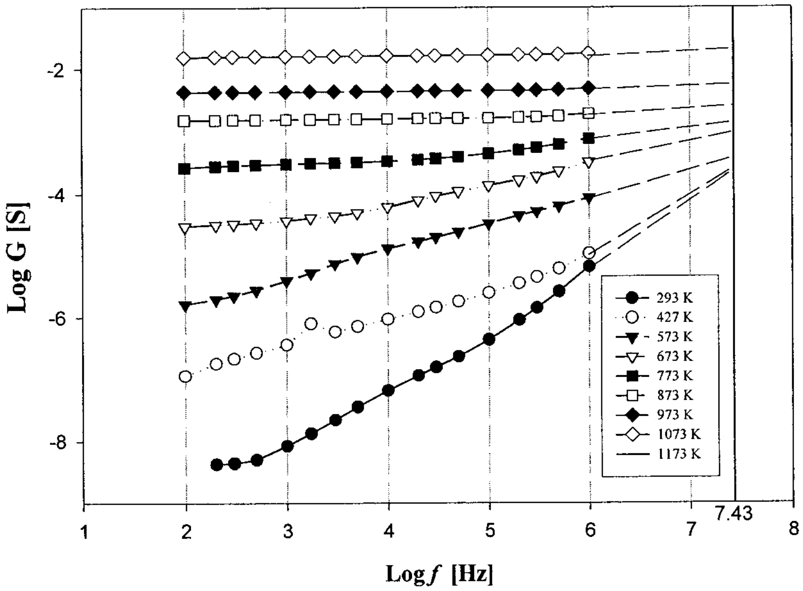

Figure 5. Conductance *versus* frequency of material Z1 (13X) at different temperatures (extrapolation purpose).

(b) and Z3 (c) respectively. As shown in figure 2, Z1 capacitances reach high values as temperature increases, with complex behaviour above about 673 K over 10 kHz. At 1 MHz, capacitances are less dependent on temperature and are of the order 10 pF, typical of bulk dielectric behaviour.

Z2 capacitances at 1 MHz could not be measured but were likely to be below 10 pF. Above 1 kHz, capacitances go through a minimum at about 723 K. Z3 capacitances at 100 Hz are erratic at low temperature. At 1 MHz, minimum capacitance is at 623 K. Values at 1 MHz are typical of bulk dielectric behaviour.

3.3. *Loss tangent (tan δ)*

The loss tangent (tan δ) is the ratio of the effective loss factor ($\varepsilon''_{\mathrm{eff}}$) to the dielectric constant (ε_r) [11]. Both $\varepsilon''_{\mathrm{eff}}$ and ε_r are frequency- and temperature-dependent. The loss tangent (tan δ) is a useful indicator of the potential of a material to extract energy from an electromagnetic field [12]. The higher the value and the lower the rate of change with temperature, the better will be the rate of heating and stability at the required operating temperature.

Figure 3 (a), (b) and (c) shows the typical loss tangent (tan δ), temperature (T) and frequency (f) characteristics for Z1, Z2 and Z3, respectively. At 1 MHz, there are no tan δ values for Z2, whilst they are low and almost independent of temperature for Z3 but thermally activated above about 823 K for Z1, reaching values between about 10 and 100 for a temperature range between 823 K and 1073 K.

From these investigations, it became clear that Z1 (13X) is the most suitable catalyst among the others. Thus most investigations have been carried out for Z1. It was necessary to extrapolate the data to 27 MHz, the reactor operating frequency. This can be done by plotting log conductance (G) against log frequency (f) for various temperatures and then roughly extrapolating, as shown in figure 5. In contrast, figure 6 shows the typical conductance (G), temperature (T) and frequency (f) characteristic, based on this extrapolation. At 27 MHz conductance is thermally activated at 973–1073 K with an activation energy about 110 kJ/mole (1.1 eV) and at 873–973 K about 34 kJ/mole (0.34 eV). As a result, providing the temperature is kept below about 973 K, there should not be too much of a problem with thermal runaway. However, TGA (Thermo-Gravimetric Analysis) for Z1 (13X) shows that it melts at about 1023 K, which means it is not suitable for RF at temperatures higher than 1023 K.

The dielectric constant (ε_r) is difficult to extrapolate at this frequency, due to low values of capacitance (difficult to measure accurately) and odd behaviour of the capacitances above about 773 K. Figure 7 shows the dielectric constant (ε_r) at frequencies of 100 Hz and 1 MHz for various temperatures.

The energy transferred from the RF field to the reaction media is expected to depend heavily on the dielectric properties of the catalysts. Therefore, these dielectric measurements lead us to focus on the utilization of a RF dielectric catalytic reactor for catalytic cracking of gas oil in electromagnetic fields. Mirza *et al.* [13] have shown that the selectivity towards olefins production in the RF reactor is enhanced for composite catalysts, which have higher electronic and ionic conductivities than found in conventional supported metal catalysts. The analysis for such investigations will be illustrated and discussed for the catalysts reported in this work in the next publications.

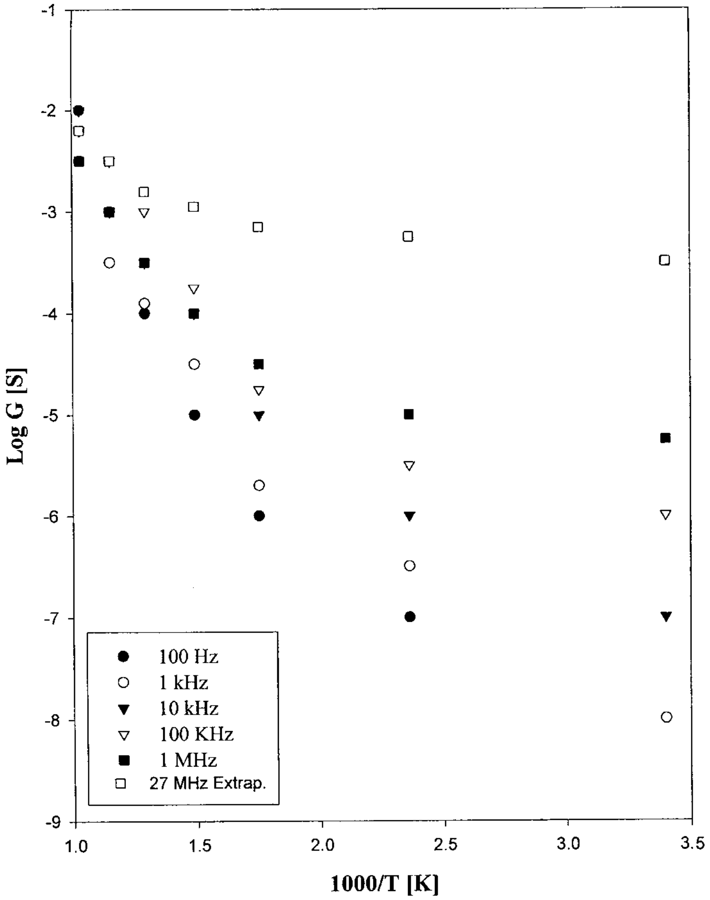

Figure 6. Extrapolated conductance of Z1 as a function of temperature and frequency.

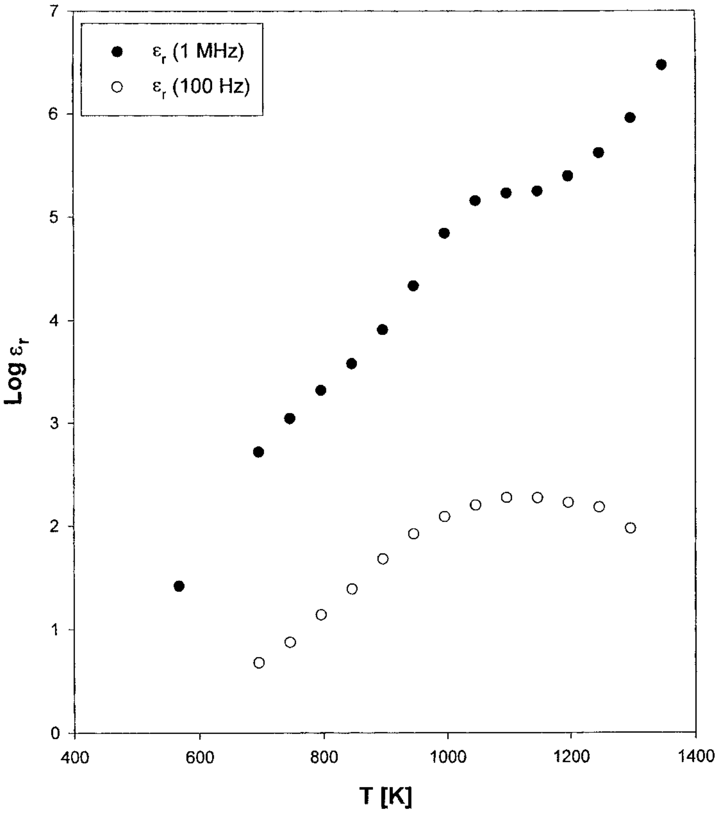

Figure 7. Dielectric constant (ε_r) of material Z1 as a function of temperature at two different frequencies.

4. Surface area and pore-size distribution

Physical properties of a catalyst particle are important in determining its effectiveness, which is determined by the interplay of chemical reaction and transport processes. One of the most important properties of the catalyst is the surface area, which correlates well with its activity. It is commonly determined by the measurement of the amount of nitrogen adsorbed by the catalyst.

Pore-size distribution is another important property of the catalyst. It is measured by mercury penetration, which is used in conjunction with other techniques such as those characterising N_2 adsorption. Pores with diameters less than 20 Å are called micropores, the surface area of which can be calculated using the Langmuir equation, which assumes pure monolayer adsorption. Those with diameters greater than 500 Å are called macropores, whilst pores of intermediate size are called mesopores. The surface area of both should be calculated using the BET (Brunauer, Emmett and Teller) equation, which assumes a multilayer physical adsorption. The Micromeritics ASAP 2010 system (Accelerated Surface Area and Porosimetry Systems), supported with ASAP software, has been used to determine the surface area and pore-size distribution measurements for the selected catalysts. Table 1 shows the results of these measurements. The measurements have shown that the majority of the pores are micropores, and this recommended using Langmuir method of calculations.

Table 1
Surface area and pore size distribution of the selected zeolitic catalysts

Catalyst	BET surface area (m^2/g)	Micropore area (m^2/g)	Average pore diameter (by BET) (Å)	Micropore volume cm^3/g
13X	524 ± 2	463.31	33	0.1865
5A	353 ± 1	307.27	22	0.1254
Ammonium Y zeolite	684 ± 3	544.7	26	0.2199

Conclusions

Zeolitic catalytic systems (13X, 5A and Ammonium Y) were tested for their dielectric properties, surface area and pore-size distribution. These catalytic systems prove to have a potential to be heated by a RF dielectric reactor, especially those that are currently under use by different commercial cracking processes. The measurements of the dielectric properties for these catalytic systems indicated that the 13X catalyst has the largest conductance and activation energy. From these investigations, it became clear that the 13X catalyst is the most suitable catalyst among the others for its excellent dielectric performance; however, this catalyst cannot be used for RF at temperature higher than 1023 K due to its melting conditions. Ammonium Y zeolite has the largest surface area whilst the 5A catalyst has the smallest surface area among these catalytic systems.

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