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FLUORANTHENE FORMATION OVER ZEOLITES

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ABSTRACT

Gaseous 1-phenylnaphthalene was allowed to react with two H^{+}ZSM-5 zeolites distinguished by a different acidity. The isomerisation to 2-phenylnaphthalene was the principal reaction observed, but also fragmentation to benzene plus naphthalene and self-condensation to fluoranthene occurred. The yields of all the products were higher when the more acidic zeolite was used. A temperature dependence study showed that, varying the temperature from 390 to 450°C, the yield of fluoranthene increased. By the Arrhenius plots for fluoranthene formation it was concluded that the activation energy of this reaction is independent on the acidity of zeolites.

INTRODUCTION

The family of polycyclic aromatic hydrocarbons is ubiquitously present in the environment. Their formation is generally ascribed to incomplete combustion processes. As suggested by Badger[1] many years ago, C-H bonds are cleaved and the intermediates formed undergo cyclisation processes through a radicalic mechanism. However, some years later report[2] concerning the chemistry of flames showed that also ionic species are formed. As a consequence, it was very tempting to demonstrate the existence of an ionic pathway to polycyclic aromatic hydrocarbon. Therefore, we investigated the reactions between phenylium ions and biphenyl[3] and between naphthyl ions and benzene[4] which led to the formation of triphenylene and fluoranthene, respectively, using β-decay techniques. Furthermore, by the radiolytic technique introduced by Ausloos[5], the gas phase protonations of o-terphenyl[6], 1-phenylnaphthalene[7], and 9-phenylanthracene[8] were studied and self-condensation reactions, leading to the formation of the correspondent self-condensation products were observed.

The protonating agents, used in the cited investigations, were strong Brønsted acids, which led to the formation of excited protonated intermediates, which, if not stabilised by collision, could underwent either fragmentation, isomerisation, or self-condensation reactions.

In the present paper we extend the study on the self-condensation of 1-phenylnaphthalene to the investigation of the reactions promoted by zeolites, which show some advantages with respect to the gas phase protonation. The zeolites can operate over a large range of temperatures and their acidity can be modulated by changing the ratio between SiO_2 and Al_2O_3; structural models have been developed to correlate such acidity to the thermodynamic data of proton transfer in the gas phase[9]. The energy of the intermediate should be not influenced by the exothermicity of the protonation, which with the radiolytic reagents depends on their enthalpy of formation[10]. Among the wide family of zeolites we selected the ZSM-5 group for their well-known catalytic activity[11-12] and their suitable porosity toward 1-phenylnaphthalene[13].

Apart of the intrinsic interest concerning the knowledge of the product distribution in the presence of these solid acids, the present study could confirm the ionic pathway to polycyclic aromatic hydrocarbon, in relatively mild condition as employed in industrial petroleum chemistry, when heavy petroleum feedstocks are pyrolysed in the presence of rocks. We start from one of the simplest reaction: the self-condensation of 1-phenylnaphthalene to fluoranthene, which is one of the major component of the polyaromatic family in the environment[14].

EXPERIMENTAL

Materials. 1-phenylnaphthalene was a Ega-Chemie (Germany) product, whose content of 2-phenylnaphthalene was < 0.3%, as measured by gas-chromatography. NH_4^+ forms ZSM-5 zeolites, with SiO_2/Al_2O_3 ratios 35 and 235, were provided by BP Chemicals.

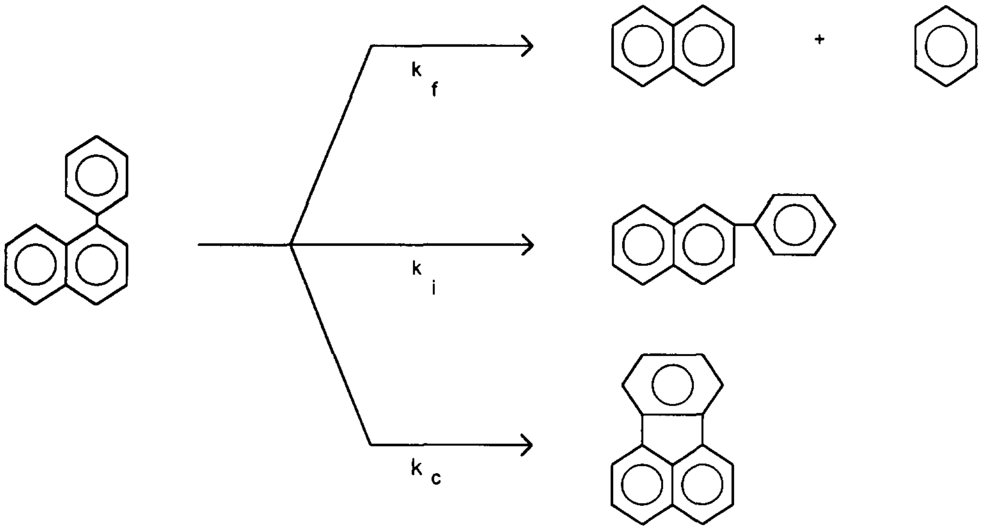
Procedure. 20 μL of 1-phenylnaphthalene were introduced into 10 mL Pyrex vials, containing 4 mg of zeolite, previously activated to the H^+ form at 450°C for 24 h. Blanks were carried out in the absence of catalyst. The vials were then outgassed, sealed, and heated at the selected temperatures for 17 h. The vials were then opened and n-hexane was added to dissolve the organic compounds. Fractions of these solutions were then injected into a HP 5890 gas chromatograph equipped with a 25 m (0.32 mm I.D) HP-1 column operating from 50 to 220°C.

The amount of each product was measured from the area of the correspondent peak, as measured by a HP 3395 Integrator connected with a flame ionization detector.

RESULTS AND DISCUSSION

ZSM-5's are conventionally defined as medium pore zeolites. When SiO_2 tetrahedra of silicalite are isomorphically substituted by Al_2O_3, a negative charge is created in the lattice, which is compensated by a proton bonded to the oxygen atom neighbouring silicon and aluminium atoms. The results is the formation of a bridged hydroxyl group which is the site responsible for the acidic activity of the zeolites. Therefore, more are the SiO_2 substituted, higher is the acidity.

As it was underlined previously, the protonation of 1-phenylnaphthalene (1-PN) can lead to the formation of four products: benzene and naphthalene (N) by C-C cleavage, 2-phenylnaphthalene (2-PN) by 1,2-phenyl shift, and fluoranthene (F) by self-condensation reaction, as reported in the reaction Scheme, where k_f, k_i, and k_c refer to the kinetic constants of fragmentation, isomerisation, and self-condensation reactions respectively.



The same products are obtained by a thermal process as shown by the results listed in Table 1, where, owing to the relatively high volatility of benzene, we reported only the value of naphthalene for fragmentation.

Table 1. Pyrolysis of 1-phenylnaphthalene: relative concentrations of products (as %).

	390°C	410°C	430°C	450°C
1-PN	99.37	99.21	99.09	98.79
N	0.02	0.07	0.16	0.44
F	0.44	0.51	0.55	0.77

The concentration of 2-PN among the products was not reported since it (0.17-0.19%) did not differ from the content of this impurity in the starting material within the experimental uncertainty at all the temperatures investigated. As it can observed an increase of the temperature acts essentially on the yields of naphthalene and fluoranthene, suggesting that the radicalic mechanism, inherent to the pyrolytic process, does not lead to isomerisation but only to C-H and C-C bonds cleavages . The amount of these products, reported in Table 1, has been considered as the contribution of a radicalic reaction and, therefore, as a blank, it has been subtracted from the yields reported in Tables 2 and 3.

Table 2. Reaction between 1-PN and H^+ZSM-5/235: product distribution (%).

	390	410	430	450
1-PN	80.29	72.98	62.22	52.76
N	0.28	0.26	0.27	0.25
2-PN	18.79	25.89	36.56	43.39
F	0.18	0.21	0.28	0.39

From the reported results it can be observed that an increase of the acidity of the zeolite leads to the formation of larger amounts of products, as a consequence of a major conversion of 1-PN to 2-PN, the more stable isomeric form[15]. Furthermore, while the yield of naphthalene appears to be independent on the temperature, the amount of fluoranthene increases when the temperature rises from 390°c up to 450°C.

Table 3. Reaction between 1-PN and H^+ZSM-5/35: product distribution (%).

	390	410	430	450
1-PN	19.45	20.83	21.50	23.18
N	0.50	0.44	0.46	0.45
2-PN	79.55	77.17	76.07	73.30
F	0.77	0.98	1.46	1.87

Also with the more acidic H^+ZSM-5/35 the yield of naphthalene is independent on the temperature while that one of fluoranthene increases with the temperature. With respect H^+ZSM-5/235 a particular trend is shown by the concentrations of the isomeric phenylnaphthalenes. The appearance is that the conversion of 1-PN decreases when the temperature increases. Owing to the constant value of naphthalene formation and the increase of fluoranthene in the same range of temperature we can ascribe this apparent ambiguous result to the fact that the thermodynamic equilibrium between the two isomers is reached.

The more interesting result is the formation of fluoranthene. It can be observed that at the same temperature its yield depends on the zeolite acidity and increases from 390°c to 450°C. Since in this range of temperatures fluoranthene shows high stability[16], we can consider that its rate of formation is proportional to its concentration, and, therefore, we can obtain the Arrhenius plots reported in Figure 1.

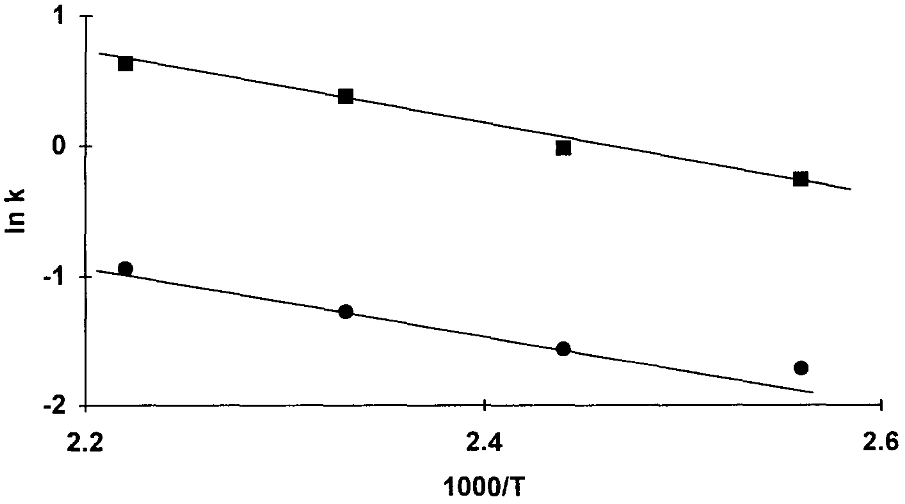


Figure 1. Arrhenius plots for the reaction 1-PN → F over H^+ZSM-5/35 (■) and H^+ZSM-5/235 (●).

As it can be observed two straight lines are obtained with the same slope. This indicates that the same reaction occurs in both zeolites and that the reaction rate depends only on the acidity of the zeolite.

By comparison of the results reported in the present work with those obtained in the gas phase protonation of 1-PN, some difference can be underlined.

In the gas phase protonation the ratio between the fragmentation and the self-condensation rate constants showed that the second process is favoured. In the present experiments the same result is obtained only when the more acidic zeolite is used as a catalyst. Taking into account that, from the present data, it results that a higher activation energy is required for self-condensation reaction with respect to fragmentation, the previous results can be explained by the high excitation energy of the protonated intermediate formed. Furthermore, the present results indicate that isomerization is the most favoured process. It requires a low activation energy, which we could not measure owing to the occurrence of the reverse reaction. However, the obtained results show the existence of an ionic pathway to fluoranthene over acidic solids. Such a result should be taken into account when heavy petrol fraction are converted in lighter fuels by catalytic cracking. It was shown[17] that the presence of clays or rocks favours the formation of fuels. This is certainly true, but also the formation of polycyclic aromatic hydrocarbons increases in the same conditions. As a matter of fact, Tables 2 and 3 show the contribution of acidic sites to the formation of products. Therefore, in such kind of processes the acidity of the mineral plays an important role.

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