Pyrene oxidation as a model reaction for characterizing the mechanism of coke oxidation on Y zeolites

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The same effect of temperature on the production of CO, CO_2 and H_2O was found during oxidative treatment of HY zeolites either impregnated with pyrene or coked. Therefore, pyrene oxidation can be used to specify the mechanism of coke oxidation. Three types of reactions can be distinguished: (a) condensation of polyaromatic molecules, (b) oxidation of polyaromatics into aldehydes, ketones, acids and anhydrides and (c) decarbonylation or decarboxylation of oxygenated compounds, all these reactions involving protonic sites.

Keywords: coke; zeolites; catalyst regeneration; oxidation

1. Introduction

Carbonaceous compounds ("coke") blocked inside the pores or on the outer surface of zeolites are mainly responsible for their deactivation during the various processes of refining and of petrochemicals [1–3]. This coke is generally removed through an oxidative treatment under air flow, sometimes with oxygen added. As most of the information concerning the regeneration of zeolite catalysts has been obtained by industrial researchers the results are not available.

However, various terms have investigated the mode of coke oxidation as well as the effect of coke removal on the characteristics of zeolite catalysts. In particular it has been shown that coke oxidation begins with hydrogen yielding oxygenated intermediates, which are decomposed subsequently into CO and CO_2 [4]. Oxygenated compounds have been identified in partially oxidized samples of coked zeolites. However, the exact composition of partially oxidized coke was difficult to obtain because of the large variety of the components and of their high molecular weights [5]. That is why we have tried to find a model reaction of coke oxidation. We show here that oxidation of pyrene molecules located inside the pores of Y zeolites occurs in the same way as that of Y zeolite coke. The products of partial oxidation of pyrene were recovered from the zeolite and analyzed through GC and GC-MS, which allowed to specify the mechanism of coke oxidation.

2. Experimental

The study of coke and pyrene oxidation was carried out on four HY zeolites with framework Si/Al ratios between 4 and 30: CBV 500 and CBV 720 samples from Conteka (Si/Al = 4 and 16), CBV 740 and CBV 780 from PQ zeolites (Si/Al = 19 and 30). These zeolites were coked at about 14 wt% with propene (0.3 bar) in a flow reactor at 450°C, or impregnated at 14 wt% with pure pyrene. The impregnation was carried out by heating pure pyrene deposited on top of the catalyst layer. At 160°C pyrene had "wetted" the catalyst layer homogeneously. 0.7 g of the samples obtained were treated in a flow reactor in pure oxygen (flow rate = 10 cm^3/min) with stepwise programmed temperature in the range of 250–550°C. The amounts of CO, CO_2 and H_2O liberated were determined as previously described [6].

The composition of the products remaining on the pyrene impregnated samples after oxidative treatment during half an hour at 160, 250, 350 and 400°C was determined in this way: soxhlet extraction with CH_2Cl_2 before and after dissolution of the zeolite in a 40% hydrofluoric acid solution, weighing of the soluble compounds and analysis through GC and GC-MS coupling.

3. Results and discussion

3.1. COMPARATIVE STUDY OF THE REMOVAL OF COKE AND OF PYRENE FROM Y ZEOLITES

The same temperature program was applied for the treatment under oxygen flow of four samples of HY zeolites (differing by their Si/Al, hence by the number of acid sites) either about 14% coked during propene transformation or about 14% impregnated with pyrene. This amount of pyrene corresponded roughly to one molecule of pyrene per supercage. Through this treatment 90–95% of pyrene was recovered as CO and CO_2, which shows that pyrene was firmly retained on the zeolite. Furthermore it was shown that after treatment under nitrogen at 250°C of the CBV 500 sample impregnated with pyrene, only 15% of the pyrene could be extracted by soxhlet treatment. The remaining 85% could only be recovered after dissolution of the zeolite in a hydrofluoric solution. This shows that most of the pyrene molecules were located in the pores of the zeolite during the oxidation treatment.

Fig. 1 compares for each plateau of temperature the percentages of coke and of pyrene removed in the form of CO and CO_2. Whatever the zeolite, the formation of

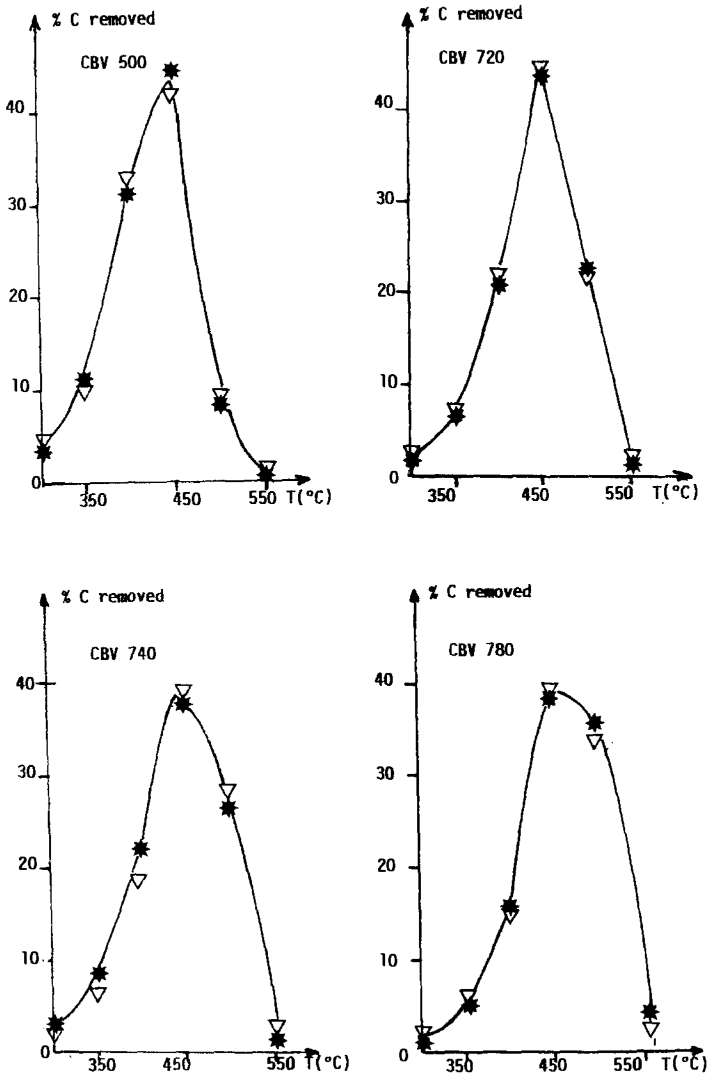

Fig. 1. Oxidation of pyrene on various zeolites (▽). Comparison with coke oxidation (★).

CO and CO_2 began at 300°C and ceased at 550°C; identical curves were obtained for the removal of coke and of pyrene. As has been shown, the greater the density of the acid sites of the zeolite, the easier the removal of coke [6] and of pyrene. Thus for CBV 500 ($\mathrm{Si/Al} = 4, n_{\mathrm{H}^+} = 20 \times 10^{20}\ \mathrm{g}^{-1}$) 90% of the coke or of the pyrene was oxidized at temperatures $\leqslant 450°\mathrm{C}$ while this was the case for only 60% of the coke and 65% of the pyrene of CBV 780 ($\mathrm{Si/Al} = 30, n_{\mathrm{H}^+} = 3.1 \times 10^{20}\ \mathrm{g}^{-1}$). Similar curves were also found for the formation of water from coke and from pyrene. Thus the atomic H/C ratio of the oxidation products dropped from about 2 at 300°C to 0.1 at 500°C during the removal of both coke and pyrene. This confirms that polyaromatic oxidation begins with the hydrogen atoms [5]. The similarities between the removal of coke and of pyrene from the Y zeolites lead us to conclude that pyrene oxidation can be used as a model reaction for coke oxidation.

3.2. REACTIONS INVOLVED IN PYRENE AND COKE OXIDATION

We have investigated the transformation undergone by pyrene molecules blocked in the pores of Y zeolites so as to specify the reactions involved in coke removal through oxidative treatment. The study was carried out on the CBV 500 sample; the products remaining on this zeolite after treatment under oxygen flow at various temperatures θ_{ox} (160, 250, 350 and 400°C) were recovered in the solvent methylene chloride. The products located on the outer surface of the crystallites were recovered by direct soxhlet extraction, those located in the pores after dissolution of the zeolite in a hydrofluoric acid solution. Only the pyrene molecules were recovered through the direct soxhlet extraction. The compounds recovered after zeolite dissolution consisted of two parts: one soluble in methylene chloride mainly constituted of oxygenated molecules (and of about 10% of pyrene for $\theta_{ox} = 160°C$), the other one insoluble constituted of black particles, probably high polyaromatic. The insoluble compounds could not be recovered for analysis. It must be underlined that insoluble coke compounds were also formed during the oxidation of coked Y samples [7].

Fig. 2 gives as function of θ_{ox} the total amount of compounds retained on the zeolite and the amounts of unreacted pyrene, of oxygenated and of insoluble compounds. Insoluble compounds appeared only for $\theta_{ox} \geqslant 250°C$ and the amount passed through a maximum for $\theta_{ox} = 350°C$. On the other hand, the amount of pyrene and of oxygenated molecules decreased when θ_{ox} increased.

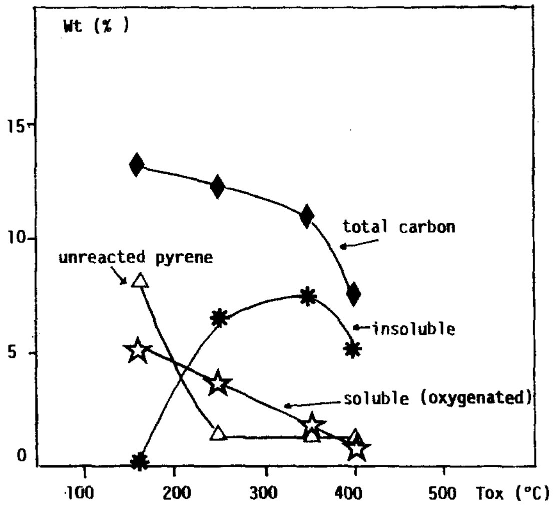

Fig. 2. Amount of compounds retained on the zeolite (wt% C) as function of the oxidation temperature.

The composition of the oxygenated compounds was determined through GC-MS coupling. For $\theta_{ox} = 160$ and 250°C, there was formation of ketones with a pyrenic skeleton and of aldehydes, acids and anhydrides with a phenanthrenic skeleton. The main compounds were dialdehyde, acid aldehyde and anhydride with the phenanthrenic skeleton. For $\theta_{ox} = 350$ and 400°C less bulkier oxygenated compounds with the same functional groups appeared.

Therefore the reactions involved in the oxidation of pyrene are:

(1) Functionalization of polyaromatics, without or with elimination of water, which occurs even at low temperature (160°C).

(2) Condensation of pyrene or/and of its oxidation products with formation of highly polyaromatic compounds insoluble in methylene chloride. This reaction occurs from 250°C in the presence of oxygen but not in the presence of nitrogen.

(3) Decarbonylation and decarboxylation of oxygenated compounds. These reactions occur only for $\theta_{ox} \geqslant 300$°C (fig. 1).

A mechanism involving carbocation radicals as intermediates has been recently proposed to explain the increase in the rate of coke oxidation when the density of acid sites of Y zeolites increases [6]. Fig. 3 shows how pyrene can be transformed

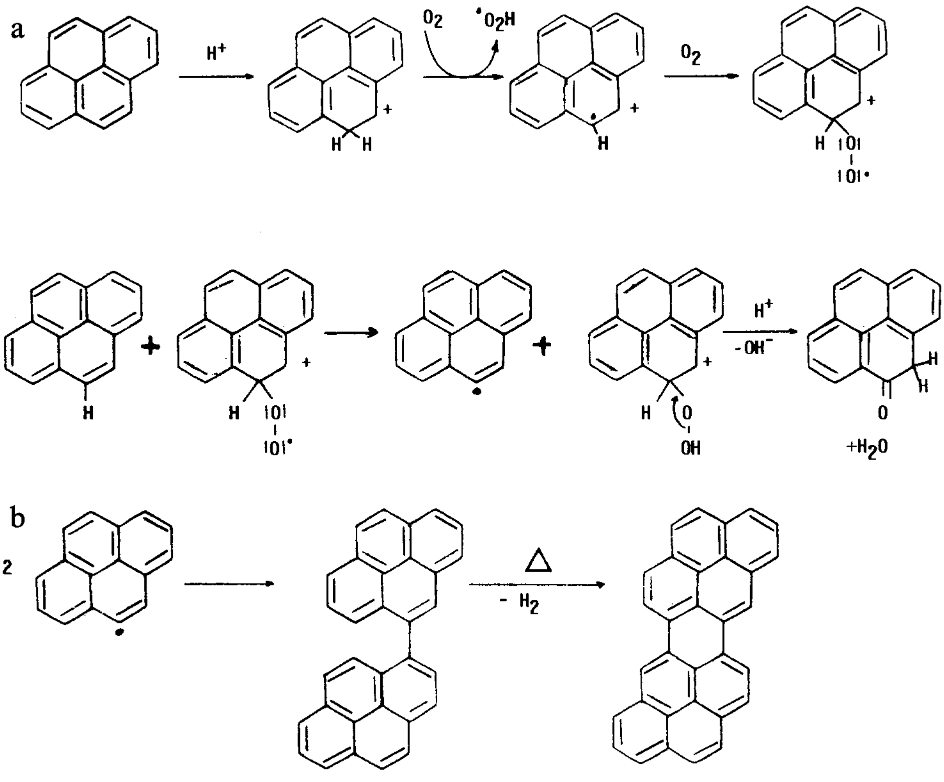

Fig. 3. Mechanisms of pyrene oxidation into oxygenated compounds (a) and of pyrene condensation (b) via carbocation radicals.

into oxygenated compounds and into highly polyaromatic molecules through this type of intermediates.

The decomposition into CO and CO_2 of oxygenated compounds formed by oxidation of zeolite coke has been demonstrated by Novakova and Dolejsek [4]. The decarbonylation of carboxylic acids can be catalyzed by sulfuric acid solutions [8,9] or by protonic acid solids such as heteropolyacids and silica alumina [10,11]. This reaction would occur through the following scheme in which the limiting step would be the elimination of CO (step 3) [8,9]:

$$\mathrm{R{-}COOH} + \mathrm{H}^+ \rightleftarrows \mathrm{RCOOH}_2^+ \qquad (1)$$

$$\mathrm{RCOOH}_2^+ \rightleftarrows \mathrm{RCO}^+ + \mathrm{H_2O} \qquad (2)$$

$$\mathrm{RCO}^+ \rightleftarrows \mathrm{R}^+ + \mathrm{CO} \qquad (3)$$

$$\mathrm{R}^+ \rightleftarrows \text{alkene} + \mathrm{H}^+ . \qquad (4)$$

Formation of ketones and CO_2 from carboxylic acids was shown to be catalyzed by acid zeolites. According to Servotte et al. [12] this bimolecular reaction occurs through nucleophilic attack of RCO^+ (formed by steps 1 and 2) by a carboxylate anion (whose formation causes the dehydroxylation of the zeolite: step 6):

$$\mathrm{RCO}^+ + \mathrm{R{-}COO}^- \rightleftarrows \mathrm{R_2CO} + \mathrm{CO_2} \qquad (5)$$

$$\mathrm{RCOOH} + \mathrm{HO{-}Z} \rightleftarrows \mathrm{RCOO^-Z^+} + \mathrm{H_2O} . \qquad (6)$$

These acid catalyzed reactions are most likely responsible for the production of CO and CO_2 from the partially oxidized pyrene and coke molecules.

4. Conclusion

We have shown that pyrene oxidation in Y zeolites can be considered as a model reaction for coke oxidation. Three types of reactions are involved in pyrene (hence in coke) oxidation: (i) condensation of polyaromatic molecules to form highly polyaromatic molecules, (ii) oxidation of polyaromatics into oxygenated compounds, (iii) decarbonylation and decarboxylation of these oxygenated compounds. Mechanisms are proposed to explain these acid catalyzed reactions.

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