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Evidence for a participation of zeolite acid sites in the coke removal through oxidative treatment

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Coke removal by oxidative treatment was investigated for a number of HY zeolites with framework Si/Al ratios of 4–100, coked at different levels (from 2 to 20 wt%) during propene transformation at 450°C. A strong influence of the density of framework aluminium atoms hence of the density of the acid sites was found. On the other hand the content of the zeolite in extraframework aluminium species as well as the composition of coke were of minor importance for coke removal. A mechanism involving radical carbocations as intermediates is proposed.

Keywords: Coke oxidation; HY zeolites; mechanism active sites; acidity

1. Introduction

The formation of carbonaceous compounds ("coke") inside the pores or on the outer surface of zeolites is the principal cause of their deactivation during the transformation of organic reactants [1–3]. This deactivation increases considerably the cost of the processes and great efforts are being made to find methods (i) to limit the formation of coke and its deactivating effect and (ii) to regenerate the activity. Thanks to a large number of fundamental investigations the modes of coking and of deactivation of zeolites are now well understood. On the other hand most of the investigations of the zeolite regeneration were carried out by industrial researchers so that the results are generally inaccessible.

The regeneration of zeolites is generally carried out through a simple combustion of coke under air flow, sometimes with oxygen added. The choice of the operating conditions is important for limiting the detrimental effects the water produced has, at high temperature, on the zeolite pore structure [4,5]. This is why, in particular, a two-stage regeneration is often carried out in fcc units. In the first stage operating at low temperature 40–60% of the carbon and practically all the hydrogen of the coke are burned off; in the second stage operating at high temperature practically no water is formed, hence the degradation of the zeolite is limited [4].

The mode of oxidation of zeolite coke has been investigated by various authors [6–16]. It has been shown that the oxidation of coke molecules begins by their hydrogen atoms with formation of oxygenated intermediates which are subsequently decomposed into CO and CO_2. Ketonic, aldehydic, anhydride, phenolic compounds have been identified in partially oxidized samples of coked HY [6] and HZSM5 [16] zeolites. Carboxylate and carbonate like intermediates as well as quinones of polyaromatics have also been identified [8,15].

Furthermore the zeolite pore structure could play a significant role in the oxidation of coke [6,7]. As oxidation of coke was more rapid for HY and H mordenite than for HZSM5, it has been concluded that coke oxidation was, like coking and ageing, a shape selective process [6]. However, the possible role of the zeolite composition (framework Si/Al ratio, amount of extraframework species etc.) was not examined.

The objective of this work was to investigate the effect of the composition of zeolites on the rate of coke oxidation. The study was carried out on a series of HY zeolites with framework Si/Al ratios ranging from 4 to 100 and with different contents of extraframework aluminium species, these zeolites being coked during propene transformation at 450°C.

2. Experimental

Five different HY zeolites, supplied by Conteka (CBV 500, CBV 720 and CBV 760) and by PQ zeolites (CBV 740 and CBV 780), were coked to different extents by propene in a fixed bed reactor at 450°C. The partial pressures of propene and of N_2 were 0.3×10^5 Pa and 0.7×10^5 Pa; 0.718 g propene was introduced per gram catalyst per hour. The zeolite properties are given in table 1.

The oxidation of coked catalysts was carried out in pure O_2 in a fixed-bed

Table 1
Characteristics of the HY zeolite samples

Name	Unit cell formula	N_{EFAL} [a]	Si/Al	
			global	framework [b]
CBV 500	$Na_{0.4}H_{38.8}Al_{39.2}Si_{152.8}O_{384}$	9.6	2.9	3.9
CBV 720	$Na_{0.3}H_{11.0}Al_{11.3}Si_{180.7}O_{384}$	2.4	13.0	16.0
CBV 740	$Na_{0.05}H_{9.45}Al_{9.5}Si_{182.5}O_{384}$	0.1	19.0	19.2
CBV 780	$Na_{0.15}H_{6.05}Al_{6.2}Si_{185.8}O_{384}$	0.0	30.2	30.2
CBV 760	$Na_{0.5}H_{1.4}Al_{1.9}Si_{190.1}O_{384}$	10.0	15.1	≈ 100

[a] N_{EFAL}: number of extraframework aluminium per unit cell.
[b] Determined from the unit cell parameter according to ref. [17].

reactor (i.d. 16 mm) with stepwise programmed temperature in the range of 25–550°C. 0.5–0.7 g coked catalyst was used, and the oxidation was monitored by trapping the oxidation products and weighing. The water and the carbon dioxide liberated were trapped by anhydrone and ascarite respectively. Subsequently, the reactor effluent was passed over a Pt-containing catalyst at 400°C for combustion of CO. The total amount of carbon measured as CO_2 and CO (oxidized into CO_2) agreed within ±10% to the amount of carbon determined by CNRS. Blank tests (empty reactor) showed that gas phase oxidation of CO as well as CO oxidation catalyzed by possible impurities present in the system, was negligible at the oxidation temperatures employed.

3. Results

CO was formed in considerable amounts together with CO_2 during coke oxidation. A typical example of oxidation of a coked HY zeolite (CBV 720) is given in fig. 1. The formation of CO_2 and CO which started at temperatures above 250°C, passed through a maximum at temperatures comprised between 425 and 500°C depending on the zeolite.

The oxidation of coke was not much influenced by the coke content. Only a slight tendency towards higher oxidation temperatures with increasing coke contents can be observed. This is shown in fig. 2, representing the removal of carbon from the coked CBV 720 zeolite expressed as the sum of CO_2 and CO evolved.

The coke removal depended very much on the zeolite. Fig. 3 shows that for coke contents of 5 wt% for CBV 760 and 7–9 wt% for the others, the whole oxidation curve was shifted towards higher oxidation temperatures with increasing zeolite framework Si/Al ratios. Furthermore, identical curves were found for a CBV 500 sample in which part of the extraframework aluminium species (EFAL) were eliminated through washing with a hydrochloric acid solution (6.1 EFAL/u.c.) and

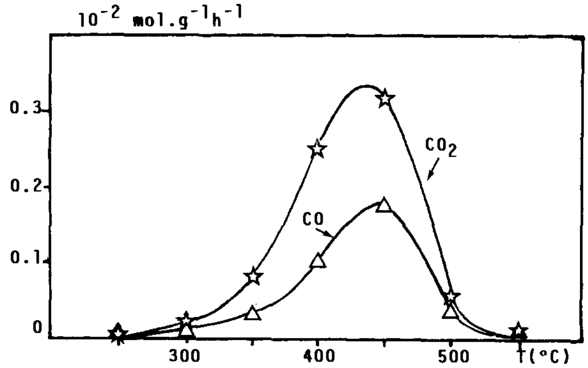

Fig. 1. Oxidation of coke on CBV 720 (13.2 wt% C). Evolution of CO_2 and CO as function of the oxidation temperature.

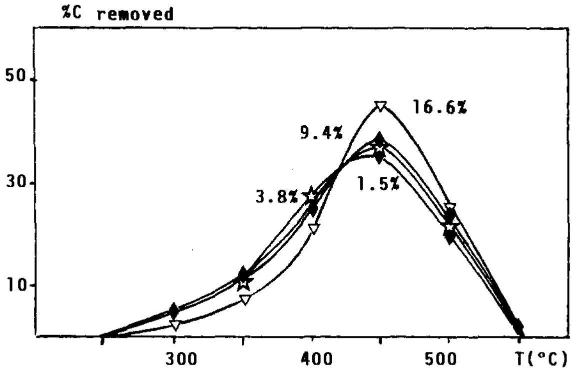

Fig. 2. Oxidation of coke on CBV 720. Effect of coke content.

for the non treated CBV sample (9.6 EFAL/u.c.). It must be noted that this treatment also removed 3 framework aluminium/u.c., but did not cause any change in crystallinity.

The relative amounts of coke which required the highest temperature (>450°C) for oxidation (refractory coke) are plotted in fig. 4 as function of the number of framework aluminium atoms per unit cell (N_{Al}). The greater N_{Al}, the lower the amount of this refractory coke.

4. Discussion

The oxidation of coke depends slightly on the coke content: the higher the coke content, the more difficult the removal through oxidative treatment. This can be related to a change in the composition and/or in the location of coke with the coke content. Indeed at low coke contents coke is mainly constituted of pyrene derivatives molecules relatively rich in hydrogen (atomic H/C ratio of 0.8–1.0) located in

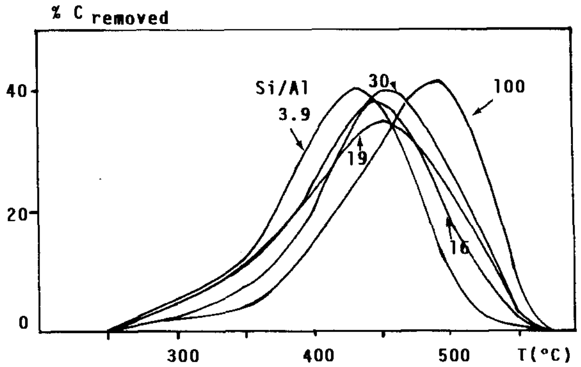

Fig. 3. Oxidation of coke on various zeolites (coke content of about 5–9 wt%).

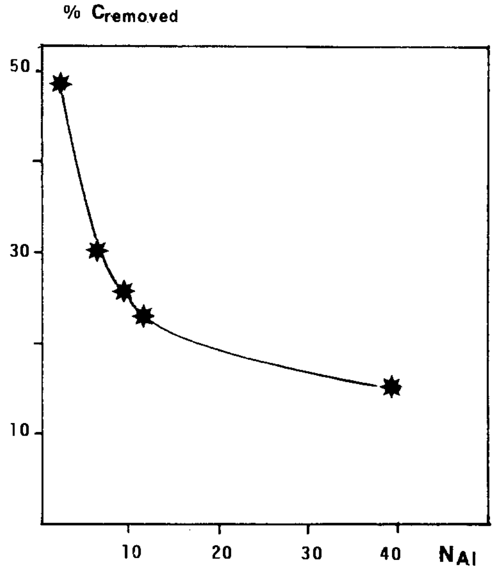

Fig. 4. Amount of coke oxidized above 450°C as function of the number of framework aluminium atoms per unit cell (N_{Al}) of the zeolites.

the zeolite supercages. At high coke contents the growth of these molecules leads to highly polyaromatic compounds (H/C @ 0.4) that overflow onto the surface of the zeolite crystallites [3]. The slight increase in the difficulty of coke removal can be related to the decrease in the H/C ratio and/or to a limitation or a blockage of the access of oxygen molecules to the internal coke.

An effect of the Y zeolite pore structure is very unlikely. Indeed mesopores exist with all the samples except CBV 500 [18]. Moreover limitations in oxygen diffusion in the tridimensional large pore system of Y zeolites are not expected.

It has been shown that Na ions catalyzed hydrocarbon oxidation [19]. However CBV 500 and CBV 760 being the zeolites having the larger sodium content (0.1 wt%) it can be concluded that the sodium content is not the determining factor in coke oxidation.

Likewise extraframework aluminium (EFAL) species have practically no effect: (i) the partial elimination of EFAL species from CBV 500 does not affect the oxidation curve, (ii) the two zeolites containing the largest amounts of EFAL species are those for which the coke removal is the easiest (CBV 500) and the most difficult (CBV 760).

The main parameter determining the coke oxidation is the composition of the zeolite framework. The greater the density of framework Al atoms the easier the coke removal (fig. 4). This seems to indicate that acid sites participate in coke oxidation.

There is practically no information about such oxidation reactions over purely acidic zeolites. However Dong et al., have recently shown that oxygenated products could be formed by transformation of benzene or toluene in the presence of oxygen over HZSM5 at 300–500°C [20]. A mechanism involving adsorbed radical carbocations formed through reactions between benzenium ions and molecular oxygen has been proposed to explain this oxidation. Activation of oxygen which occurs on transition metal oxide would not take place in acid zeolites as shown by studies of isotopic exchange of $^{18}O_2$ and $^{16}O_2$ [7]. This mechanism allows to explain the positive role the density of aluminium atoms (hence of protonic acid sites) has on the removal of coke from Y zeolites.

5. Conclusion

The removal of coke from HY zeolites by oxidative treatment depends very much on the zeolite composition and slightly on the composition of coke. Coke is more easily oxidized with the zeolites having a high density of framework aluminium atoms (hence of protonic acid sites). Extraframework aluminium species have no determining effect on the rate of coke oxidation. A mechanism involving the adsorption of coke molecules on the protonic acid sites and the formation of radical cations through reaction of molecular oxygen on the protonated coke molecules is proposed.

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