

TITRATION OF ACTIVE ACID SITES ON H-ZSM-5 BY SELECTIVE POISONING WITH PYRIDINE

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ABSTRACT

The number and strength of active acid sites on H-ZSM-5 (with different Si/Al ratios) for cumene cracking and o-xylene isomerisation reactions have been determined using the pulse poisoning technique based on selective poisoning of stronger acid sites with pyridine. Only those acid sites which can absorb pyridine irreversibly at $\geq 570\text{K}$ are involved in both the reactions. The number of active acid sites on the zeolite was found to decrease almost linearly with the Si/Al ratio. On the other hand, the number of active acid sites per Al-atom of the zeolite increases with the Si/Al ratio upto the Si/Al ratio of 31.1 and levels-off thereafter.

INTRODUCTION

H-ZSM-5 zeolite has shown considerable promise as a catalyst in the conversion of alcohols to hydrocarbons [1-6], alkylation of aromatics [7,8] and also in a number of hydrocarbon conversions [9-13], and syngas conversion [14]. The acid strength distribution on this zeolite has been found to be broad [15-19]. It is therefore important to know the number of active acid sites which are actually involved in a particular catalytic reaction and also the minimum strength possessed by them. The present investigation was undertaken with the objective of determining the active acid sites on H-ZSM-5 zeolites (with different Si/Al ratios) for the model reactions viz. cumene cracking and o-xylene isomerisation, which are normally employed for studying protonic acid sites on solid catalysts [20]. The poisoning technique [9,21] in which the stronger acid sites are selectively poisoned in the order of their strength has been employed for this purpose.

EXPERIMENTAL

The preparation and characterisation of the H-ZSM-5 zeolites with different Si/Al ratios (varying from 13.6 to 39.7) have been described elsewhere [9].

The catalyst poisoning experiments for measuring the active acid sites

for the cracking and isomerization reactions were carried out in a pulse micro-reactor connected to a gas chromatograph (Perkin Elmer Sigma 3B, with flame ionisation detector) using nitrogen (99.99%) as the carrier gas. The micro reactor consisted of a stainless steel tube (o.d. 6 mm; i.d. 4 mm and length 22 cm) with the zeolite particles (0.2 mm size) packed between the quartz wool plugs. The temperature of the zeolite bed and the injection part of the micro-reactor could be varied independently. The reaction conditions were as follows: amount of catalyst, 0.05 g; N_2 -flow rate, 800 min^{-1} ; reaction temperature, 573K; pulse size, 0.07 mmol; and pressure, 370 kPa. A part of the reactor effluent was bypassed before it entered the gas chromatograph. The reaction products were analysed in a carbowax 20M (10%) on chromosorb - W column at 343K (carrier gas flow rate: $40 \text{ cm}^3 \cdot \text{min}^{-1}$).

The catalytic titration of the active sites on the zeolite was performed by making the sites with increasing acid strength available for the catalytic reaction by saturating them with pyridine irreversibly adsorbed at 598, 673, 723 and 773K and also by using the zeolite without poisoning. Thus only the acid sites which were weaker than those blocked by the base at the saturation (or poisoning) temperature (T_s) were available for the reaction on the poisoned zeolite. The desorption of the adsorbed pyridine from the poisoned zeolite during the activity test was prevented by carrying out the reaction at a temperature (which was 573K) lower than the lowest temperature at which the acid sites were blocked with irreversibly adsorbed pyridine. A detailed procedure for poisoning the zeolite and measuring its catalytic activity has been described earlier [9].

RESULTS AND DISCUSSION

The results of the catalytic titrations are presented in Fig. 1. For both the cracking and isomerization reactions, the catalytic activity of the zeolite (with the different Si/Al ratios) decreases with the decrease in T_s (i.e. the temperature at which the zeolites are saturated with irreversibly adsorbed pyridine). It can also be noted that the activity vs. T_s curves for both the reactions on zeolites when extrapolated to zero activity meet almost at the same point. This point which corresponds to the temperature T_s required for blocking nearly all the active sites involved in the reactions. These results reveal that the sites having an acid strength of $T_d > 570\text{K}$ (where T_d is the temperature at which the irreversibly adsorbed pyridine desorbs) are responsible for both the reactions on the zeolite, or in other words only those acid sites, which can adsorb pyridine irreversibly at or above 570K, catalyse the reactions.

The number of active acid sites taking part in the reaction was obtained

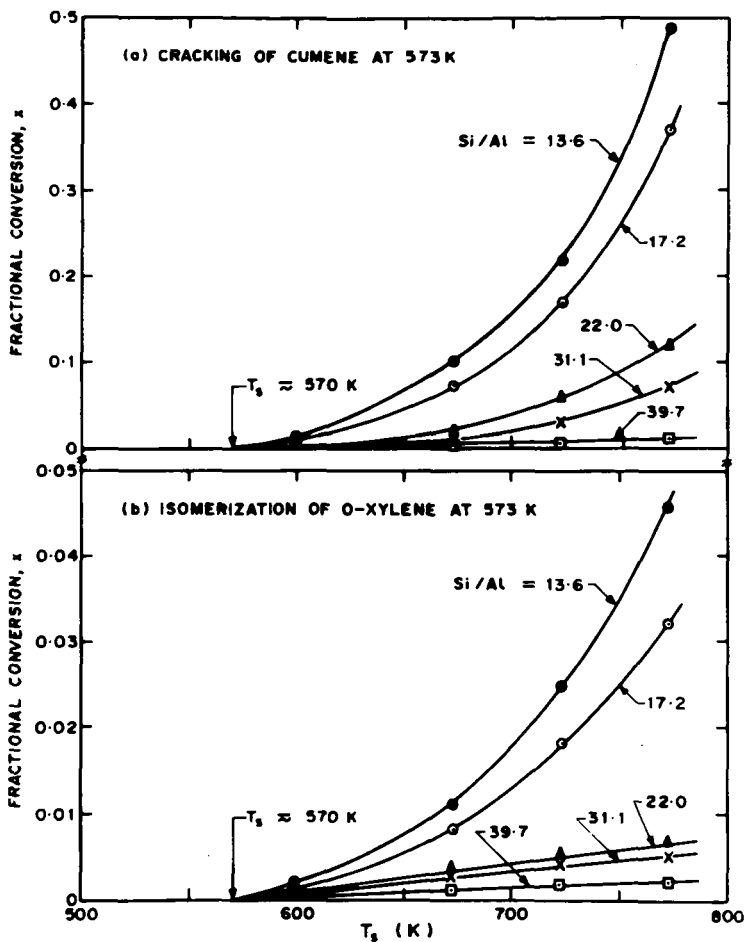


Fig. 1. Dependence of the catalytic activity of H-ZSM-5 (with different Si/Al ratio) on T_s for the cracking and isomerization reactions

in terms of the number of pyridine molecules adsorbed irreversibly at the maximum T_s (570K) required for completely deactivating the zeolite. Figure 2 shows that the number of active acid sites in the zeolite decreases almost linearly with the increase in the Si/Al ratio.

The dependence of the ratio of the active acid sites per unit cell to the Al-atoms per unit cell of the zeolite on the Si/Al ratio is shown in Fig. 2; the active acid sites per Al-atom increases with Si/Al ratio up to the value of 31.1 and levels-off thereafter. This trend in the variation of the active acid sites per Al-atom with the Al-content of the zeolite is expected to be mainly due to the interaction between the structural Al^- anions (which are

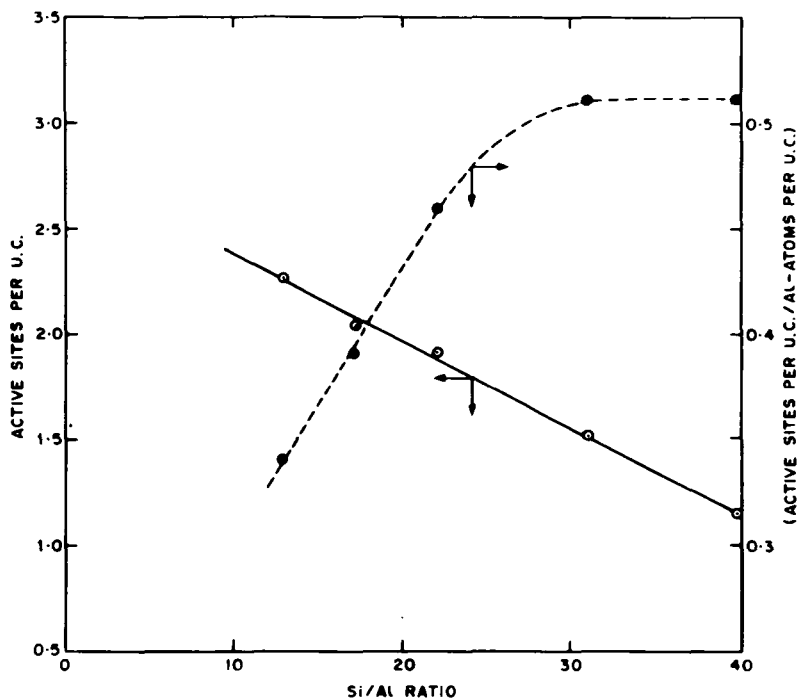


Fig. 2. Dependence of the active sites and the ratio of active sites to Al-atoms on the Si/Al ratio for the cracking and isomerization reactions on H-ZSM-5

responsible for the acid sites). In ZSM-5 zeolite, the structural Al anions are expected to be situated at the channel intersections. Since there are four channel intersections per unit cell of the zeolite [22]; more than one Al^- are present at some of the intersections when the Al-content of the zeolite is more than 4 Al-atoms per unit cell. This situation can also be present in the case of the zeolite containing 4 (or even less than 4) Al-atoms per unit cell when the distribution of the Al-atoms is not uniform. The results (Fig. 2) points to the fact that the number of active acid sites per structural Al-atom on H-ZSM-5 decreases with the increase in the Al-content, the decrease being very pronounced above the Al-content of about 4 Al-atoms per unit cell. The interaction between structural Al^- anions present at the same channel intersection causes a decrease in the strength of the acid sites originating from the Al^- anions, which results in the decrease in the active (or strong) acid sites per structural Al.

The poisoning technique employed in the present study differs from the conventional pulse poisoning technique [23,24] in that the active sites of varying acid strengths are blocked by irreversibly adsorbed pyridine at different temperatures instead of introducing the poison in small doses at the reaction temperature (which does not ensure preferential blockage of active or stronger acid sites), and finding the activity of the catalyst after the introduction of each poison pulse.

The catalyst activity is measured at a temperature lower than the lowest temperature at which the acid sites are blocked by the irreversibly adsorbed poison. The present pulse poisoning technique, therefore, ensures uniform and also preferential blockage of the active acid sites in the order of their strength and eliminates the possibility of the desorption of poison during the activity test. It gives both the number and the minimum strength of the active sites taking part in the catalytic reaction. It can also be employed [9,21,25] for obtaining correlation between the selectivity for the different products and the strength of acid sites involved in the catalytic reactions.

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