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Deactivation of PtH-MFI bifunctional catalysts by coke formation during benzene alkylation with ethane

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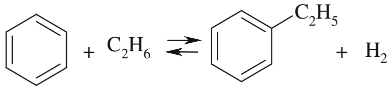
ABSTRACT

The alkylation reaction of benzene with ethane was studied at 370 °C over two Pt-containing MFI catalysts with Si/Al ratios of 15 and 40. The deactivation of the PtH-MFI-15 catalyst was found to be more significant, when compared with the PtH-MFI-40 catalyst, as a result of differences between the two catalysts in the formation of coke. The differing locations of the coke deposition were found to profoundly affect the product selectivity and deactivation behaviour of the two PtH-MFI catalysts. Results from gas sorption and X-ray diffraction experiments showed that coke is preferentially formed towards the centre of crystallites of the PtH-MFI-15 catalyst, as opposed to coke deposition on the outside surface of the PtH-MFI-40 crystallites, subsequently blocking entrance to the zeolite channels. Partial blockage of the internal pore structure of the PtH-MFI-15 catalyst with coke decreased the diffusion length within the PtH-MFI-15 crystallites. The effect of this reduction in the diffusion length within the PtH-MFI-15 crystallites is consistent with the observed decreasing *para*-selectivity of the diethylbenzene (DEB) isomers with time-on-stream. These findings are in contrast to the typical effect of coking, where, generally, the selectivity of *para*- isomers would be enhanced with coke deposition.

1. Introduction

Ethylbenzene is an important intermediate in the production of polystyrene. The worldwide capacity for ethylbenzene production was estimated to be 23 million tonnes per year in 2001, with a projected annual growth rate of approximately 4% [1]. Benzene alkylation with ethene is a vital step in the synthesis of ethylbenzene. However, the use of ethene is not favourable as it is the product of highly energy intensive processes, such as ethane and naphtha reforming [2]. Due to environmental and economical concerns, ethane can be used as an alternative alkylating agent.

Recently, a new bifunctional PtH-ZSM-5 zeolite catalyst has been studied for benzene alkylation with ethane:



(1)

where the optimum reaction temperature (370 °C) [3] and the analysis of the kinetics of the alkylation reaction have been discussed previously [4]. The ZSM-5 type zeolite was chosen because it has become a well-known solid catalyst for acid-catalysed reactions due to its shape-selectivity property [5] and its high resistance to deactivation in comparison with other commercial zeolite catalysts [6]. Despite the promising results demonstrated by the PtH-ZSM-5 catalysts for the benzene alkylation reaction [3,4], the deactivation of the catalyst, caused by deposition of carbonaceous compounds, potentially could limit the development of this process. However, the details of the mechanism of coke formation during the ethylbenzene production process have remained unknown until now.

Catalyst deactivation, as a result of coke formation, has been a challenge in the catalyst industry for many hydrocarbon processes. Extensive studies on the subject of coke and catalyst deactivation have been previously carried out on other hydrocarbon-processing reactions [5–8], though not for the reaction of benzene alkylation with ethane. Two mechanisms of coking have been identified: pore blocking where coke blocks the access of reactants to active sites and active site coverage where coke poisons the active sites responsible for the reaction [6,7]. Depending on the loss of adsorption capacity of the coked catalyst and the amount of coke formed, Bibby et al. [5] and Guisnet and Magnoux [8] were able to identify the different modes of deactivation and the broad location of the coke deposition. This method was then employed by other researchers [6,7,9] to further understand the effect of coke formation in different catalytic reactions.

Modification of the ZSM-5 catalysts, by chemical treatment with different agents, or by varying the crystallite size of the catalyst, or by coking, have been reported to influence the product distribution of shape-selective reactions [6,10,11]. The effect of coke

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deposition on *para*-selectivity was found to be dependent on the location of coke, specifically whether it was located either within the internal pore structure or on the external surface of the zeolite catalyst [6,11]. For example, some partially deactivated catalysts have been shown to become less *para*-selective because of coke deposition by pore filling, as demonstrated by Soleto et al. [6], who studied the deactivation of the toluene alkylation with methanol reaction on ZSM-5 catalysts. Conversely, Chen et al. [11] showed that, with increasing coke content, *para*-diethylbenzene (DEB) selectivity increased during the disproportionation of ethylbenzene (EB). Similarly, Lin et al. [12] showed that pore blockage, as a result of coke formation, caused an increase in the *para*-xylene selectivity with prolonged time-on-stream (TOS). However, this previous work on the influence of coking on selectivity has only considered gross features of the spatial distribution of coke laydown on selectivity, such as the balance between external (pore mouth blocking) and internal laydown. Internal coke laydown can affect intrinsic diffusivity (through impact on pore connectivity) and/or diffusional path length. Hence, gross characteristics are insufficient to fully understand the impact of coking on mass transfer, and subsequently selectivity.

In this work, a more detailed study will be made of the particular spatial distribution of coke laydown. A detailed analysis of structural characterisation data using percolation concepts, combined with reaction and transport experimental data, allows a more definitive description of the coking behaviour to be obtained than previously. It will be shown that these studies allow greater insight into the deactivation mechanism during the benzene alkylation reaction with ethane over PtH-MFI catalysts.

A series of bifunctional Pt-H-MFI catalysts, with Si/Al ratios of 15 and 40, coked to different extents were studied to investigate relationships between the evolution of the pore structure of the zeolite catalysts and its effect on adsorption kinetics, transport properties, and changes to the product distribution from the benzene alkylation reaction. A diverse combination of analytical techniques, including thermogravimetric analysis (TGA), X-ray diffraction (XRD), scanning electron microscopy (SEM) and gas sorption measurements were employed in this work to understand the phenomena related to coking.

2. Experimental section

2.1. Catalyst preparation

Two H-MFI (ZSM-5) zeolites with a Si/Al ratio of 15 and 40 (ZEOLYST) were used as the parent catalysts for the benzene alkylation reaction. The Pt-containing zeolite catalysts, defined as PtH-MFI-15 and PtH-MFI-40, were prepared by incipient wetness impregnation of parent H-MFI (Si/Al of 15 and 40), using an aqueous solution of tetraamine–platinum (II) nitrate, $Pt(NH_3)_4(NO_3)_2$. The catalysts were prepared such that the ultimate platinum content for both was 1 wt%. After impregnation, the catalysts were dried at room temperature and then calcined in a muffle furnace at 530 °C for 4 h at a heating rate of 1 °C min^{-1}. For the reaction studies, the prepared bifunctional catalysts were pressed into discs and then crushed and sieved to obtain particle sizes in the range of 250–710 μm.

2.2. Kinetic studies

Benzene alkylation with ethane was carried out at atmospheric pressure in a continuous flow reactor at 370 °C with 9:1 molar feed ratio of ethane to benzene. The catalyst loading of 500 mg was activated by heating in air at 530 °C for 4 h, and then reduced in hydrogen at 500 °C for 1 h. After being run for different times-on-stream (TOS), the reactor was purged with nitrogen (30 ml min^{-1}) for 0.5 h at the reaction temperature and then cooled down to room temperature in a nitrogen atmosphere. The catalysts were then unloaded from the reactor for further analyses.

The conversion of benzene and ethane and the selectivity of products produced from benzene at a certain TOS were defined as follows. The conversion X_i of reactant i was defined as:

$$Conversion,\ X_i = \frac{C_{i0} - C_i}{C_{i0}} \times 100\%, \tag{2}$$

whereas the selectivity, S_i, of product i formed from benzene was defined as:

$$Selectivity,\ S_i = \frac{C_i}{C_{B0} - C_B} \times 100\%, \tag{3}$$

where C_{i0} is the initial concentration of species i, C_i is the concentration of species i in the reaction mixture, C_{B0} is the initial concentration of benzene, and C_B is the concentration of benzene in the reaction mixture.

2.3. Catalyst characterisation

2.3.1. Themogravimetric analysis (TGA)

Thermogravimetric analysis of the coke content of the discharged PtH-MFI catalysts was performed in a Setaram TGA92 thermogravimetric analyzer. Coked samples were heated from room temperature to 1000 °C at a rate of 10 °C min^{-1} in flowing, dry air.

2.3.2. Gas sorption

The structural characteristics of the PtH-MFI samples were determined by gas sorption. Nitrogen and argon sorption experiments were each carried out using a Micromeritics ASAP 2020 volumetric apparatus at 77 K. Ethane sorption experiments were performed on a Hiden IGA at a range of temperatures between 10 and 30 °C. Prior to adsorption analysis, the samples were heated under vacuum at 250 °C, until no further mass loss is observed, to remove any physisorbed water. The temperature of the thermal pre-treatment was chosen to avoid the removal of coke deposited during the preparation process.

2.3.3. X-ray diffraction (XRD)

Powder X-ray diffraction experiments were carried out using a D8 Advance Bruker X-ray diffractometer. Diffraction patterns were recorded using Cu Kα radiation at 40 kV, 30 mA, and a scan rate of 1° min^{-1}.

2.3.4. Scanning electron microscopy (SEM)

Scanning electron microscopy experiments were conducted on a JEOL JSM6480LV system operating at 15 kV. The samples were coated with a thin carbon layer before imaging analyses were carried out. The effect of coke deposition on the platinum particles impregnated onto the H-MFI catalysts was studied by backscattered electron imaging.

3. Percolation modelling

The model of the ZSM-5 lattice used is adapted from previous work by Trout et al. [13] and is presented in Fig. 1. The black dots represent the adsorption sites in the intersections (sites) while the grey dots represent the straight/zig-zag channels (bonds). There are 12 lattice points per unit cell; four in the intersections (there being four intersections in the unit cell) and eight in the straight and zig-zag channels. A large lattice size was used to represent a large zeolite crystallite to avoid finite size effects on the percola-