



Understanding the spatial distribution of coke deposition within bimodal micro-/mesoporous catalysts using a novel sorption method in combination with pulsed-gradient spin-echo NMR

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ABSTRACT

A new method for the determination of the spatial distribution of metal surface area within bimodal micro-/mesoporous solids has been developed. This novel technique involves incorporating a nonane pre-adsorption stage between two successive chemisorption experiments. This method has been used to probe the distribution of platinum amongst the micropores and mesopores of a range of bi-functional PtH-MFI catalysts, each possessing differing surface acidities, which have been used for benzene alkylation with ethane. It has been found that the catalyst with the lowest Si/Al ratio, and thus highest number of acid sites, also possessed the largest metal surface area within its microporosity. This catalyst was also the one that deactivated most rapidly, with coke being deposited predominantly within the micropore network. This was attributed to the bi-functional mechanism for coke formation at higher temperatures. Pulsed-gradient spin-echo NMR has also been used to show that a combination of higher mesopore platinum concentration and higher mass transport rates facilitated greater coke deposition within the mesoporosity.

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1. Introduction

Alkylation of benzene with ethene is currently used to synthesise ethylbenzene, a vital intermediate in the manufacture of polystyrene. However, the process is very energy intensive, involving naphtha reforming. A potential alternative is the direct alkylation of benzene with ethane using a bi-functional catalyst that performs both the dehydrogenation and alkylation steps. Platinum on MFI zeolite has been proposed as a potential catalyst, and the reaction studied in detail [1]. However, under certain conditions, the catalyst deactivates rapidly by coking. In order to better design the process, a detailed understanding of the coking mechanisms is essential. In previous work [1], it was shown that zeolites with differing Si/Al ratios gave rise to differing coking behaviour. In particular, it was found that coke was predominantly deposited in different locations, depending on the Si/Al ratio, with more losses of surface area due to coke arising within the microporosity at lower values of the ratio, and in the mesopore network at higher values. In this work, the reasons for the particular coke distribution in different catalysts will be

explored. In particular, it will be shown that the spatial distribution of platinum and the mass transfer rates contribute to the coke location. To facilitate this study, a novel method for determining the spatial distribution of platinum within the catalyst has been developed based upon the nonane pre-adsorption method, previously used to assess microporosity [2].

Methods for studying the spatial distribution of platinum nanoparticles within heterogeneous catalysts have been developed but have their limitations. The spatial arrangement of platinum nanoparticles has been observed directly using electron tomography [3]. However, the characteristic overall dimension of the sample volume that can be studied is only ~500 nm, and thus these data may be statistically unrepresentative of a real macroscopic catalyst pellet. Pressure-jump IR spectroscopy of adsorbed CO has been used to study spatial locations of platinum particles but can only distinguish internal from external particles [4]. Hence, there is a lack of a technique that can provide more representative information on the location of platinum nanoparticles within a bimodal micro-/mesoporous system.

The balance between mass transport and reaction rates is known to influence the pattern of coke lay-down in catalysts, and thus has been the subject of extensive modelling work [5].

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Coke distribution and mass transport in catalyst pellets deactivated by coke deposition have been studied previously using a range of NMR methods. Cheah et al. [6] used MRI methods to study the spatial distribution of coke within catalyst pellets over macroscopic dimensions. While these studies revealed the heterogeneous spatial distribution of coke deposits, due to the variation in relaxation time of the static imbibed fluid over fresh and coked surfaces, only qualitative information could be obtained. Stapf et al. [7] probed the spatial distribution of coke residues in porous catalyst pellets using field-cycling relaxometry. Pulsed-gradient spin-echo (PGSE) (also known as pulsed-field gradient (PFG)) NMR has been used [8,9] to determine how the tortuosity of a porous catalyst pellet varies with coking levels. In this work, PGSE NMR will be used to measure mass transport rates in the mesopore network of the bimodal PtH-MFI catalysts.

This paper is constructed as follow. First, a theory, concerning how both the spatial arrangement of platinum metal and mass transport rates can effect coking, will be outlined. Then, the new method to obtain an experimental measurement of the spatial distribution of platinum metal will be described. It will then be seen how data obtained from this new method can shed light on the reasons for the different distributions of coke deposition for different catalysts observed in earlier work.

2. Theory

2.1. Pulsed-gradient spin-echo (PGSE) NMR

For more details on the PGSE (or PFG) NMR method, the reader is referred to earlier work by Hollewand and Gladden [10]. In PFG-NMR, the echo attenuation, R , is defined as the ratio of the echo intensity in the presence of a gradient ($M(g)$) to the echo intensity in the absence of a gradient ($M(0)$). For the NMR pulse sequence (detailed below) used in this work, the echo intensity variation for a single component diffusion is given by:

$$R = \frac{M(g)}{M(0)} = \exp \left[-D\gamma^2 g^2 \delta^2 \left(\Delta - \frac{\delta}{3} - \frac{\tau}{2} \right) \right], \quad (1)$$

where D is the diffusion coefficient, γ is the gyromagnetic ratio, g is the pulsed-field gradient strength, δ is the duration of the pulsed gradient, Δ is the diffusion time and τ is the correction time between bipolar gradients. A range of echo attenuations are obtained by varying g , and a plot of $\ln R$ against $\gamma^2 \delta^2 g^2 (\Delta - \delta/3 - \tau/2)$ yields the diffusion coefficient from the slope of the straight line fit to the data. Since the observed signal contains a contribution from the spin density, which is directly related to voidage, the diffusion coefficient measured by PFG-NMR, D_{PFG} is given by [10]:

$$D_{PFG} = \frac{D_w}{\tau_p}, \quad (2)$$

where D_w is the free diffusion coefficient for bulk liquid at the temperature that the PFG-NMR experiment is conducted at, and τ_p is the tortuosity of the pore space occupied by the fluid. However, given that differences in chemistry and molecular size/shape may mean different liquids have varying levels of interaction with a given type of pore wall surface, which may affect transport along the pore to differing extents, the tortuosities obtained are particular to a specific liquid-adsorbent combination. For more complex systems, the expression for the PFG-NMR log-attenuation will be different to that shown in Eq. (1). In heterogeneous systems, where different regions of the sample do not (significantly) exchange molecules during the course of the PFG-NMR experiment, but have different diffusivities, the NMR signal would be a composite of a set of expressions similar to Eq. (1), weighted by the volume fraction of each region.

2.2. Coking model

Guisnet and Magnoux [11] suggested that, for bifunctional metal/acid catalysis at high reaction temperatures, the coking process occurs by a bi-functional mechanism involving various steps that occur over acid and metallic sites, and that the coke deposits formed are polyaromatic. In our earlier work concerning benzene alkylation with ethane over a PtH-MFI catalyst at 370 °C [1], IR spectra of the coke deposits indicated the presence of polyaromatic species, which suggested that hydrogen transfer (acid catalysts) and dehydrogenation steps (bifunctional catalysts) took place during the coking reaction. A bifunctional mechanism would necessitate coke precursor molecules moving between acid and metal sites. Hence, in a mesoporous environment, where molecules could potentially escape the catalyst surface for the bulk void space of the pore, it might be anticipated that the overall rate of the coking reaction would be proportional to the rate at which coke precursor molecules could move from one type of site to another, and also the spatial concentration of each type of site. Hence, if the diffusivity of molecules and the concentration of metallic sites could be measured, then it would be expected that the overall rate of coking, and hence some measure of amount of coke build up over a given period of time, would be proportional to the product of the diffusivity and metal site concentration. However, within the confinement of micropores, the metal and acid sites would be in very close proximity, and there would be no opportunity for the adsorbed molecules to escape directly into the gas phase and bypass surface sites. Hence, the reaction rate might then be expected to be proportional to the capacity of available sites. Since it is expected that the acid sites would be pervasive across the zeolite surface, then, overall, the metal sites might then be expected to be the rarer, and thus rate-controlling.

3. Experimental

3.1. Materials

The materials studied in this work were two 1 wt.% Platinum-MFI (ZSM-5) catalysts prepared from parent zeolites with Si:Al ratios of 15 and 40 (denoted Pt H-MFI-15 and Pt H-MFI-40, respectively), as described in earlier work [1]. The coked samples were obtained following catalyst use for benzene alkylation with ethane carried out at atmospheric pressure in a continuous flow reactor at 370 °C, as described in earlier work [1]. The amount of coke formed on the used catalysts at different TOS is summarised in Table 1. In spite of an increase in the coke content, the rate of coke deposition declined with time after a rapid increase in the amount of carbonaceous deposits at 4 h TOS.

In earlier work [1], the BET surface areas for the fresh and coked Pt H-MFI-15 and Pt H-MFI-40 catalysts were obtained using both nitrogen and argon, adsorption, and are shown in Table 2. The surface area decreased with TOS, indicating that parts of the zeolite pore network were blocked or isolated by coke molecules formed. Further, in previous work [1], the pore size distributions (PSD) of the PtH-MFI catalysts were obtained, using the Horvath–Kawazoe

Table 1

Values of coke content on coked PtH-MFI catalysts after different time-on-stream (TOS). The coke content measured has a standard error of $\pm 0.03\%$.

Time-on-stream (h)	Total coke (mass%)	
	PtH-ZSM-5(30)	PtH-ZSM-5(80)
4	1.83	0.76
24	3.39	–
48	5.61	2.00

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