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Effect of semi-batch reactor configuration on aromatic hydroxylation reactions

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ABSTRACT

Phenol, toluene and ethyl benzene hydroxylation were studied to investigate the potential benefits of semi-batch operation on aromatic hydroxylation reactions. Small crystallites of TS-1 and Al-free Ti-Beta were used as catalysts either in closed batch reactors or in a semi-batch system with the hydrogen peroxide added slowly over time. Water and methanol were used as solvents for all substrates and acetonitrile and solvent free systems were investigated additionally for toluene and ethylbenzene. It was seen that tar formation was higher when more H_2O_2 was present. For phenol hydroxylation, semi-batch operation significantly improved reaction performance with specific catalyst/solvent combinations. The best results were seen with Al-free Ti-Beta using the methanol solvent. This was attributed to increased formation of di(hydro)peroxo species in the pores of Al-free Ti-Beta, particularly in the presence of the methanol. In all cases, the lifetime of the catalyst was observed to increase when using semi-batch operation due to the decreased tar formation. Semi-batch operation also improved the catalyst lifetime for toluene hydroxylation as well as improving the reaction activity and selectivity in select cases.

1. Introduction

1.1. Hydroxylation of aromatic compounds

Direct hydroxylation of aromatic compounds with H_2O_2 over heterogeneous catalysts is an important approach to forming hydroxyaromatic compounds [1]. Various systems exist which take this approach. Possibly the best studied is phenol hydroxylation to hydroquinone and catechol, which was commercialised in the early 1990s by EniChem, Italy [2–4]. Other systems that have employed direct hydroxylation include the hydroxylation of benzene to phenol [1,5], toluene to cresols [1], and anisole to p-hydroxyanisole [1]. The importance of these reactions lies in adding value to the feed stock under comparatively benign environmental conditions [6].

The products of aromatic hydroxylation have wide-ranging uses. Phenol is used to synthesize Bisphenol A, a precursor to engineering thermoplastics; phenolic and epoxy resins; caprolactum; and alkylphenols [7]. Hydroquinone is used as a photographic reducing agent, a dye releaser, a resin stabiliser, in oxidation hair dyes, and in the formation of inclusion compounds [8]. Cresols have many uses including wood preservers, disinfectants in soap, and precursors to synthetic tanning agents. They are also used in ore flotation, fibre treatment, metal degreasing, and as extracting solvents [9].

Control of reaction selectivity is of considerable importance in aromatic hydroxylation reactions. Firstly, hydroxylation of the correct position on the aromatic ring is necessary. E.g., in phenol hydroxylation it is preferable to hydroxylate the para-position to form hydroquinone, rather than the ortho-position to form catechol. Similarly, in toluene hydroxylation, the production of para-cresol is preferred over ortho- or meta-cresol. In addition, over oxidation of the reaction product should be suppressed. Tar (oxygenated polyaromatic) formation, which can be a result of over oxidation of substituted aromatic compounds [2,5,10], is a particular challenge in these types of reactions. Disposal of undesired reaction products can cause constraints on the economic viability of these hydroxylation processes [11].

1.2. Catalysts/systems used

Many different catalyst systems have been used for aromatic hydroxylation reactions. These include substituted zeolitic materials, e.g., TS-1, TS-2 and Ti-Beta [4,12,13]; unsubstituted zeolitic materials, e.g., H-faujasite, Y and beta [14]; mesoporous crystalline and micro-mesoporous titanosilicates [15], e.g., Ti-MCM-41; and supported metal catalysts, e.g., Pt/ZSM-5 [16] and Fe-MCM-41 [17]. More recently supported Cu catalysts, including Cu-containing layered double hydroxides [18] and Cu nano-particles, supported on silica [19], have been investigated. Of the many different catalyst systems, TS-1 is generally agreed to be that the best catalyst for hydroxylation reactions with H_2O_2 as the oxidant. The “best” catalyst is defined in terms of overall performance, evaluated in terms of activity, selectivity and catalyst reusability [10].

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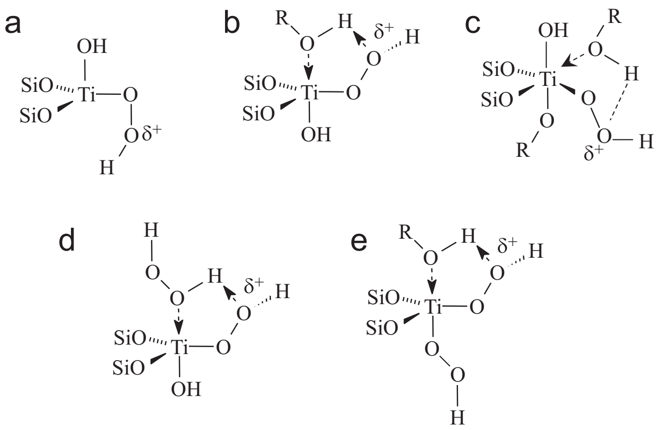

Fig. 1. Proposed configurations of the hydroperoxo-titanium active site of Ti-substituted zeolites [26–29].

TS-1 has two primary advantages for aromatic hydroxylation reactions, the high activity of the catalyst and the overall catalyst stability. The spent catalyst may also be regenerated as either calcination or refluxing with dilute hydrogen peroxide rejuvenates the catalyst to virtually as new performance [20]. The catalyst performance may be manipulated by changing the crystallite size which affects the ratio of internal to external active sites [5]. This is critically important when the size constraints imposed on the inner surface are necessary for obtaining the desired shape selectivity.

TS-1 has one main limitation for aromatic hydroxylation reactions. As it is a medium-pore (10 member-ring or 10-MR) catalyst there may be size constraints on the reactants, products and/or transition states formed during the reactions. The pore size limitations can lead to diffusion limitations in the pores, particularly for larger molecules, e.g., styrene [21,22]. As a result, the compounds found in the catalyst pores are limited to relatively small kinetic diameters (<6 Å). The zeolite channels will not accept o- or m-disubstituted aromatics or tertiary aliphatic compounds, limiting the catalytic potential of TS-1 to linear hydrocarbons or monofunctionalised benzene derivatives only [23]. Where larger molecules are to be hydroxylated, a mesoporous catalyst, e.g., Ti-MCM-41 may provide a better solution than the small pore TS-1.

Aluminium free Titanium Beta (Al-free Ti-Beta) is a large-pore (12-MR) titanium-containing zeolite, which has frequently been used as a catalyst for hydroxylation reactions. An example is epoxidation where similar performance to TS-1 was observed, although the selectivity is never quite as good [12,24,25]. This has been attributed to the occurrence of side reactions due to the Ti site of Ti-Beta having fairly strong acidic properties, especially in the presence of protic solvents [24]. In summary, Al-free Ti-Beta is a catalyst that may be suitable for hydroxylation of larger substrates but at the possible expense of reaction selectivity.

1.3. Mechanism

The reaction mechanism is traditionally viewed as being relatively simple. The Ti atom in the catalyst structure forms the active species when it complexes with a peroxide molecule (species a in Fig. 1). This species then reacts with the organic substrate to form the selective oxidation product. It has been proposed, however, that the reaction mechanism of aromatic hydroxylation over titanium substituted catalysts is different to the mechanism of epoxidation. Wilkenhöner et al. [26] proposed an electrophilic attack by the terminal OH of the titanium hydroperoxide group on the aromatic ring. The most noticeable difference is that various configurations for the hydroperoxo-titanium sites were proposed. With the presence of protic molecules, the coordination sphere of the Ti can expand from 4 to 5 or even 6 (species a–c, respectively in Fig. 1) [26–28]. It has also been proposed that in the presence of higher concentrations of H_2O_2, the H_2O_2 molecules may compete with the solvent molecules for coordination at the Ti site, forming di(hydro)peroxo species (species d and e) [26,29].

1.4. Reaction conditions

The yield and selectivity observed for a particular reaction may be manipulated by controlling a number of the reaction parameters, in addition to the catalyst type and crystallite size. These parameters include reactant concentration; solvent type; temperature; catalyst synthesis, pore geometry, and crystal size; and reactor configuration. Higher substrate concentration favours para-selectivity in the hydroxylation of phenol to hydroquinone and catechol over TS-1 [30]. There is some evidence that lower H_2O_2 concentrations may favour the reaction activity and selectivity. It has been seen that over TS-1 lower temperature favour para-selectivity [30]. This means that the temperature should be kept as low as possible but still high enough to obtain sufficient conversion.

The solvent, or solvent mixture, employed influences both the reaction activity and product selectivity [4,5,31,32]. The solvent type can also influence tar formation [5,26]. In previous work [26], with a TS-1 catalyst, using water as the solvent for phenol hydroxylation gave a higher reaction rate, but lower hydroquinone selectivity, than using methanol as the solvent. Similarly, in work on phenol hydroxylation over Al-free Ti-Beta it was found that performing the reaction in pure water solvent gave high activity, while low water concentrations water in the water/methanol solvent mixture (7–26 vol%) gave high para-selectivity [23]. The effect on activity was attributed to the dominating effect of methanol in the adsorption dynamics. The effect on selectivity was attributed to the competition between methanol and phenol to coordinate with the titanium hydroperoxo group. It was argued [23] that this is due the fact the protic methanol molecule co-ordinates with the Ti site of the catalyst, forming a larger, penta-coordinated, active site. This causes steric constraints, which forces hydrogen bonded phenol molecule to approach the titanium hydroperoxo group with its OH group pointing away, resulting in hydroxylation of the para position.

The influence of the solvent(s) is predominantly associated with their significant influence on the local environment of the active titanium cation sites [33]. Aprotic solvents (such as acetone and acetonitrile) cannot form stable complexes with the titanium metal sites, thus limiting formation of the peroxo intermediates at the active sites in the pores [3]. As mentioned above, when protic solvent molecules (such as alcohols and water) are present, a larger penta-coordinated active intermediate complex, stabilised by hydrogen bonding, can be formed [27,28]. This complex significantly increases the size of the Ti site, which could substantially narrow the TS-1 or Ti-Beta micropore channels and lead to a geometric constraint for an approaching phenol molecule. With the OH group pointing away from the bulky active titanium centre, the para-position is closer to the active site and para-hydroxylation occurs. In summary, there is a multi-way interaction between the solvent, substrate, product and catalyst. Competitive adsorption between the substrate and solvent can significantly influence the product distribution obtained.

The addition of H_2O_2 in discrete amounts, rather than a single aliquot, has been shown to be advantageous for similar reactions. For example, Fraile et al. [34] showed that in the epoxidation of cyclohexene, the slow addition of dilute H_2O_2 gave improved selectivity to the epoxide, while suppressing side reactions and radical mechanism pathways, which resulted in a reduced carbon content on the recovered catalyst. Wilkenhöner et al. [26] and Thangaraj