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TS-1 coated microreactor for selective oxidations

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ABSTRACT

A TS-1 catalyst layer has been coated inside a capillary microreactor by the transformation of a porous silica precoating using an in-situ hydrothermal synthesis method. The use of the silica precoating to favour TS-1 nucleation and growth on the microchannel surface has shown to provide a final TS-1 coating of high surface area and titanium loading with good stability. The ability to transform the silica precoating to a TS-1 coating was achieved by correctly balancing the silica precoating dissolution, zeolite nucleation and growth rates, and insertion of titanium into the zeolite framework. The 4 μm TS-1 coating, consisting of TS-1 crystals of approximately 800 nm in size, was applied in the epoxidation of propene as a model reaction to demonstrate its catalytic activity. The TS-1 microreactor obtained a propylene oxide productivity of 2 g_{PO}/g_{cat} h with a propylene oxide selectivity above 90%. Long-term stability tests of the TS-1 microreactor showed that the TS-1 coating is very stable with only a small deactivation noted over a 500 h time-on-stream period.

1. Introduction

Titanium silicate-1 (TS-1) is an efficient catalyst for the oxidation of organics with exceptional activity and selectivity when used in the presence of hydrogen peroxide. Such reactions include the epoxidation of olefins [1–4], ammoxidation of ketones [5–7], hydroxylation of phenol and benzene [8–10], and oxidation of saturated hydrocarbons [11,12], alcohols [13,14], and amines [15]. These reactions have a high reaction rate and are typically used in the synthesis of fine chemicals. Since microreactors are becoming an attractive alternative to replace the commonly used batch processes in fine chemical and pharmaceuticals production by a continuous process, the incorporation of TS-1 in microreactors is of significant interest [16–18].

One of the advantages for the incorporation of zeolite coatings in microreactors is that the zeolite can be grown onto the microchannel surface, which can result in improved uniformity and adherence in comparison to other coating techniques [19]. While the zeolite can be directly grown onto the substrate surface [20–23], it is necessary to favour the formation of a coating on the surface over bulk crystallization, as well as to increase the surface coverage of the coating. Typically, this is done by an initial seeding step whereby a layer of zeolite seeds are initially coated onto the surface followed by hydrothermal synthesis thus allowing the zeolite nucleation and growth steps to be decoupled [24]. However, this often results in the final zeolite coating to consist of relatively large zeolite crystals (>1 μm) and the formation of a highly inter-grown coating, which can lead to transport limitations.

An alternative method to favour the growth of a zeolite layer is to use a mesoporous precoating containing nutrients (e.g. silica) [25]. The higher concentration of nutrients on the surface favours zeolite nucleation and growth whereby the precoating is transformed to a zeolite layer. Dissolution of the silica precoating increases the local supersaturation level which enables a higher nucleation rate resulting in the formation of a zeolite coating to be favoured over bulk crystallization. This approach was demonstrated to work well for membrane application where a mesoporous silica precoating on an alumina tube was transformed to a continuous MFI membrane which contained a unique pore size distribution and good stability [26]. Similarly, for microreactor application, a silica precoating in a capillary microreactor was transformed to a ZSM-5 coating whereby the crystal size could be controlled by changing the hydrothermal synthesis conditions to obtain a high surface area zeolite coating [27]. However, the transformation of a mesoporous silica coating to other zeolites such as TS-1 has not been reported. The preparation of a TS-1 layer is significantly more complex due to the incorporation of titanium into the framework being more difficult than the aluminium-containing, ZSM-5, zeolite counterpart. The larger ionic radius of titanium in comparison to silicon makes its inclusion into

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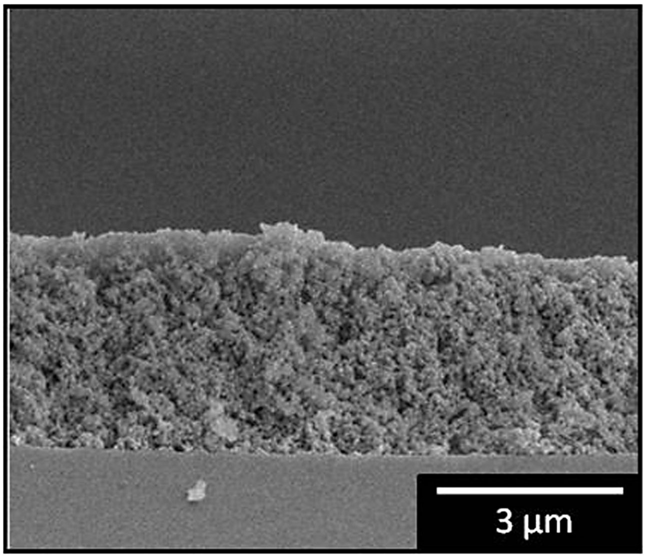

Fig. 1. Silica precoated capillary of ~4 μm thickness.

the framework limited and slows down the crystallization rate [28,29]. In addition, the correct balance between the silicon and titanium alkoxide hydrolysis, zeolite nucleation and growth rates is important in minimizing extra-framework titanium [30–32]. The susceptibility of titanium leaching from the TS-1 coating has also shown to be a main factor affecting the life-time of TS-1 microreactors. The 1-pentene epoxidation in a TS-1 microreactor (grown out of TS-1 seeds) showed the catalytic activity to decrease substantially over the first 30 h time-on-stream due to an irreversible deactivation of Ti leaching from the TS-1 coating and a reversible form of deactivation caused by the deposition of carbonaceous products [18].

This study provides a method for the preparation of stable TS-1 coatings in capillary microreactors by the in-situ transformation of a mesoporous silica precoating. The synthesis parameters necessary for the zeolite crystallization and titanium incorporation are discussed. The catalytic activity and stability of the coated TS-1 capillary microreactor are tested in the epoxidation of propene and compared to bulk synthesized TS-1 powder in a fixed-bed reactor configuration.

2. Experimental

2.1. Synthesis of TS-1 coated capillary and TS-1 powder

The method used to prepare the TS-1 coated capillaries was adapted from a similar method used to prepare ZSM-5 coatings in capillary microreactors [27]. A precursor suspension was prepared by mixing titanium butoxide (TBOT, 97%, Aldrich) with anhydrous isopropyl alcohol (2-propanol, anhydrous, 99.5+%, Alfa Aesar). Afterwards, deionized water and aqueous tetrapropylammonium hydroxide (TPAOH, 40% aq. sol., Merck) was mixed together and added dropwise to the TBOT mixture, followed by the addition of tetraethylorthosilicate (TEOS, 98%, Aldrich). The synthesis mixture was stirred for 24 h at room temperature. The TS-1 precursor suspension was injected into a 1 m capillary commercially precoated with a 4 μm silica layer (CP-silicaPLOT, 0.32 mm i.d., ±4 μm silica, fused silica, Agilent) (Fig. 1) and the capillary ends were sealed with glass end caps (Atas GL International). Thereafter, the sealed capillary was inserted into a ¼" steel tube and sealed. Hydrothermal synthesis was carried out at 150 °C for 24 h in a convectional oven (a uniform temperature in the oven was important in the realization of uniform coatings along the capillary length). After the hydrothermal synthesis was completed, the capillary seals were detached and the excess solution contained in the capillaries was removed. Thereafter, distilled water was flowed through the capillary followed by drying overnight at 120 °C. The capillary was calcined at 350 °C (limited due to a 370 °C temperature limitation of the capillary material) in an oxygen flow to remove the template. Synthesis of the powder catalyst used for the fixed-bed microreactor was prepared using the same TS-1 precursor suspension and inserted into a PEEK-lined autoclave where hydrothermal synthesis was conducted at 150 °C for 24 h. Thereafter, the synthesized powder was washed thoroughly with distilled water, dried, and calcined at 350 °C under oxygen flow. Finally the catalyst was pelletized between 150 and 250 μm.

2.2. Characterization

The titanium coordination state of the TS-1 was evaluated with X-ray photoelectron spectroscopy (XPS) using a Thermo Scientific K-Alpha equipped with a monochromatic small-spot X-ray source and a 180° double focusing hemispherical analyser with a 128-channel detector. Carbon C(1s) with a binding energy of 284.8 eV was used as an internal charge correction. The peaks were fitted

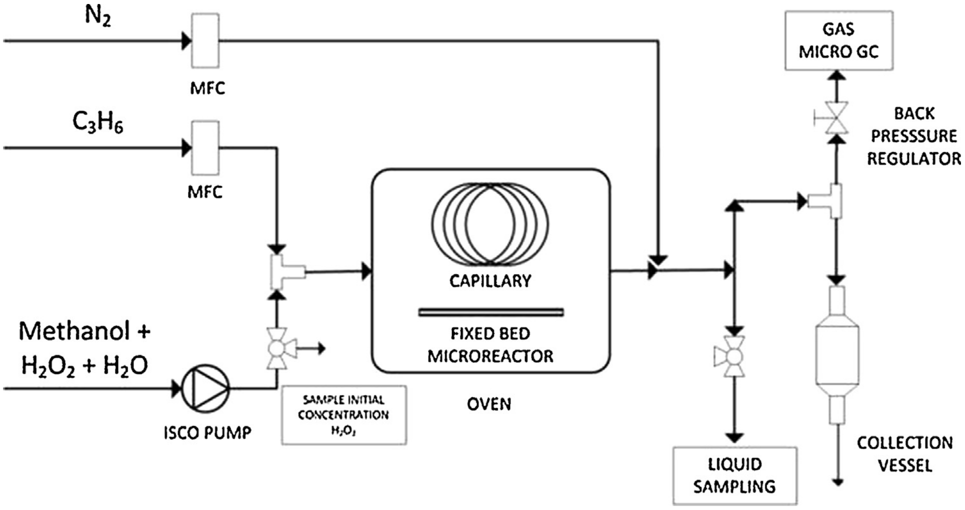

Fig. 2. Experimental setup for the epoxidation of propene with hydrogen peroxide in a microreactor.