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Catalytic properties of benzene hydroxylation by TS-1 film reactor and Pd–TS-1 composite membrane reactor

Xiaobin Wang[a], Yu Guo[a], Xiongfu Zhang[a,*], Yao Wang[a], Haiou Liu[a], Jinqu Wang[a], Jieshan Qiu[a], King Lun Yeung[b,1]

[a] State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, No. 158 Zhong Shan Road, Dalian, Liao Ning 116012, PR China
[b] Department of Chemical and Biomolecular Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, SAR, PR China

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ABSTRACT

Titanium silicalite-1 (TS-1) and mesoporous TS-1p were incorporated as catalyst for the direct hydroxylation of benzene to phenol in a palladium membrane reactor. The zeolite also served as intermediate support layer and diffusion barrier against contaminants. Pd–TS-1 and Pd–TS-1p were characterized and tested for hydrogen permeation before investigating their performance for the benzene direct hydroxylation reaction. The effects of reactor configuration, reaction conditions and catalysts on conversion, product yield and water production were examined. The phenol yield of Pd–TS-1p was the highest followed by Pd–Sil-1 and Pd–TS-1 with Pd–TS-1p and Pd–TS-1 having phenol selectivity higher than 95%. The optimum reactor configuration and H_2/O_2 molar feed ratio were identified.

1. Introduction

Phenol is mainly produced by the energy-intensive cumene process and this motivates research into cleaner and more energy efficient processes. A single step synthesis routes based on H_2O_2 and N_2O as oxidant are attractive [1–4], but considerable economic advantages could be gained if oxygen could be used. There is growing number of reports on phenol production from H_2/O_2 mixtures over precious metal catalysts [5–7]. However, the operation is restricted by the flammability of the reaction mixture and the need for acid solvent. A new synthetic route was introduced by Niwa et al. [8] using Pd membrane to separate and control the reaction between H_2 and O_2 to generate 'in situ' H_2O_2 for the direct hydroxylation of aromatic compounds. It is a clean and economically-attractive process. Although the benzene conversion in the Pd membrane reactor can be high, the hydrogen efficiency was low and the production rate of water was 500–1000 times that of phenol [9–12]. Therefore, the phenol productivity must be improved.

Zeolites can catalyze many reactions and several works have been published reporting the performance of zeolite films and membranes for reactions and separations [13–17]. The TS-1 zeolite is an active catalyst for the selective oxidation of organics using hydrogen peroxide. The framework titanium atom is identified to be active site for the reaction. It is known to generate Ti peroxo species (Ti-OOH) with H_2O_2 before reacting with neighboring hydroxyls to form a stable complex of five-membered ring structure [18–20]. TS-1 films and membranes were grown on various supports and used to catalyze various reactions [21–25]. Yeung and co-workers [26–28] investigated epoxidation and selective oxidation reactions over TS-1 films and membranes in microreactors and our recent works reported the performance of TS-1 membranes for phenol and styrene hydroxylation reactions [29,30].

This work explores the use of titanium silicalite-1 (TS-1) zeolites as catalyst for the direct hydroxylation of benzene to phenol using oxygen and hydrogen as co-reactants. The zeolite also serves as intermediate support layer and diffusion barrier for the palladium membrane in the Pd–TS-1 composite membrane. Since TS-1 zeolite stabilizes reactive oxygen species, it is expected that it would improve the reaction for the direct hydroxylation of aromatics. The effect of reactor configuration, reaction conditions and catalysts on conversion, product yield and water production are examined. A mechanism is proposed to explain the observed reaction behavior.

2. Experimental

2.1. Materials

The α-Al_2O_3 tubes from Fo Shan (Guangdong, China) with inner and outer diameters of 9 and 13 mm respectively and a length of 75 mm were used for membrane support. The tubes have pores of 3–5 μm and a porosity of 40%. The chemicals for mem-

* Corresponding author. Tel.: +86 411 39893605; fax: +86 411 39893605.
E-mail addresses: xfzhang@dlut.edu.cn (X. Zhang), kekyeung@ust.hk (K.L. Yeung).
[1] Tel.: +852 2358 7123; fax: +852 2358 0054.

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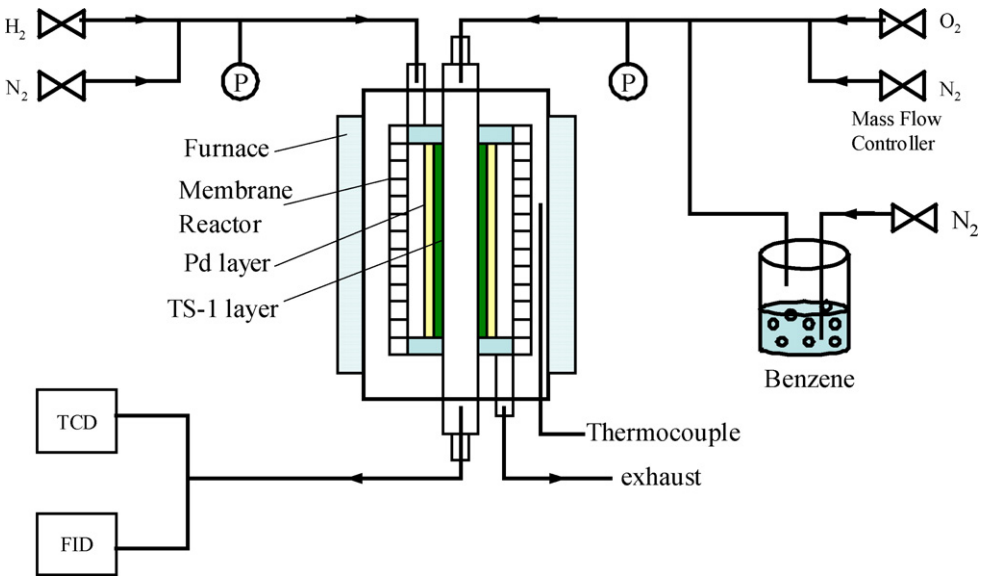

Fig. 1. Schematic of experiment apparatus used in this work.

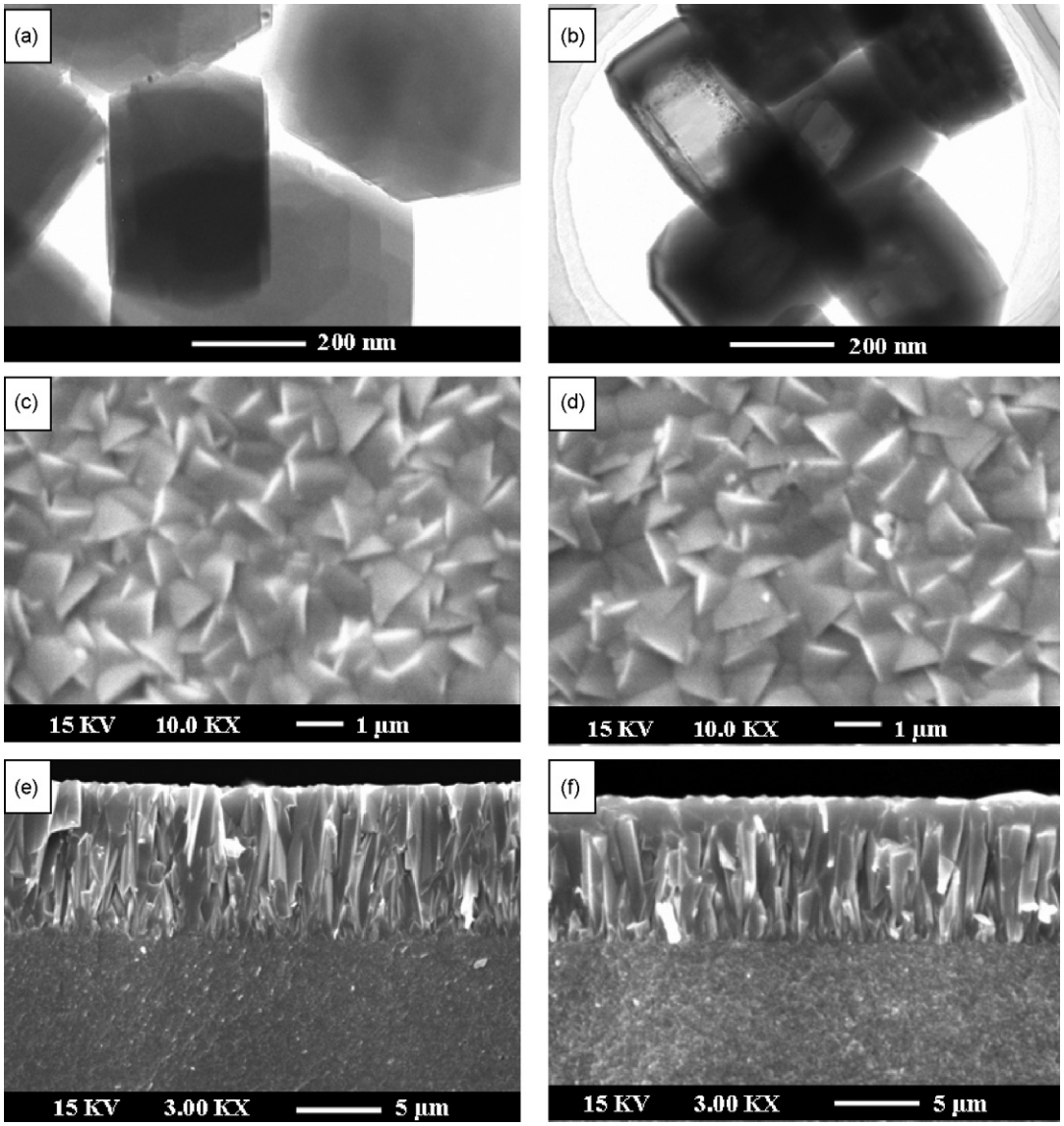

Fig. 2. TEM micrographs of TS-1 zeolite before (a) and after (b) post-treatment; SEM images of TS-1 films before ((c) surface and (e) cross-section) and after ((d) surface and (f) cross-section) post-treatment.