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# Highly efficient synthesis of cumene via benzene isopropylation over nano-sized beta zeolite in a submerged ceramic membrane reactor

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ABSTRACT

A submerged ceramic membrane reactor was developed for the cumene production via liquid-phase isopropylation of benzene with isopropanol over beta zeolite catalyst, which realized the in-situ separation and reuse of nano-sized beta zeolite catalyst. Evaluation of the introduction of ceramic membranes with different pore sizes on the catalytic performance and filtration process was investigated. No considerable influence was observed in the catalytic performance as far as the benzene conversion and cumene selectivity are concerned, but the filtration rate was significantly affected by the membrane pore size. The reaction and filtration performance depended strongly on the operation conditions. Semi-continuous benzene isopropylation to cumene showed that the beta zeolite catalyst could maintain a benzene conversion at ~2.8% and a cumene selectivity above 98.1%, and the ceramic membrane exhibited better filtration performance and excellent stability during the entire isopropylation process. The study provides new insights for the benzene isopropylation reaction.

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## 1. Introduction

The worldwide production of phenol and acetone is mainly based on the cumene process. Conventionally, cumene is prepared by isopropylation of benzene with propylene or isopropanol by using Friedel-Crafts catalysts [1] or solid phosphoric acid catalysts [2]. However, these catalysts are corrosive in nature and not environmentally friendly. To develop a novel and green catalyst, numerous efforts have been made in the last decades, and the beta zeolite catalyst attracts great attention because of its unique structure, thermal stability, acidity and shape-selective property [3–6]. With regard to the alkylating agent, the use of propylene for producing cumene results in coke formation and catalyst deactivation [7–9]. Alternatively, the isopropanol-based method with low coke formation is cost-effective and easy to operate [9]. Recently, the isopropylation of benzene over beta zeolite using isopropanol as an alkylating agent is becoming preferable to producing cumene [5].

Many efforts are devoted to (i) the development of beta zeolite with various modifications [3,4], (ii) the study on the effects of process parameters in benzene isopropylation [6] and (iii) the alkylation kinetics of benzene [10]. At present, most of the zeolite catalysts are prepared by embedding zeolitic phase in a suitable binder to provide enough mechanical strength. The activity and selectivity of the zeolite catalyst are determined by the binder property and the catalyst shape [11,12]. The catalyst in suspension often has a better catalytic activity than the immobilized counterpart, but the suspended catalysts bring the difficulty in separating catalyst particles from the reaction slurry due to the small particle size [13,14].

The membrane reactor has emerged as a promising approach to achieve the separation of ultrafine catalysts from the reaction mixture [15]. The catalytic membrane reactor (CMR) was used for the selective synthesis of cumene by isopropylation of benzene [5]. In the case of CMR, the catalyst particles were deposited on the polymeric membrane, which allowed the catalysts to be easily separated from the reaction medium. Meanwhile, cumene was selectively removed due to the presence of zeolite membrane which shifted the reaction equilibrium in the forward direction. However, the amount and quality of deposited catalyst particles on the membrane remain significant challenges and the intrinsic characters of polymeric membrane make it unsuitable for tough reaction conditions [16,17]. The porous ceramic membrane reactor, a process coupling the heterogeneous catalytic reaction in slurry with the membrane separation, has been considered as a promising approach to solve the problems described above [18]. It is based on the sieving effect of ceramic membranes to retain the

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catalysts, while the reactants or products permeate through the membranes [18]. The configuration of the ceramic membrane reactors for heterogeneous catalysis in suspension can be classified as the side-stream reactor and submerged reactor. Much attention has been paid to the submerged ceramic membrane reactors, since the catalyst loss and the energy consumption are low in the submerged reactor configuration [19–21]. To the best of our knowledge, no reports on the application of submerged ceramic membrane reactors in the isopropylation of benzene with isopropanol to produce cumene have been put forward.

In the present work, the liquid-phase isopropylation of benzene to cumene over nano-sized beta zeolite catalyst was carried out in a submerged ceramic membrane reactor. To investigate the feasibility of the process, the effects of membrane pore size and the operation conditions such as stirring rate, catalyst concentration, transmembrane pressure and temperature on the reaction and filtration performance were investigated systematically. And the semi-continuous operation under the optimal conditions was carried out to evaluate the stabilities of the nano-sized beta zeolite catalyst and ceramic membrane.

## 2. Experimental

### 2.1. Materials

The beta zeolite catalyst (average particle size 570 nm, measured by MasterSizer 2000) was supplied by SINOPEC Shanghai Research Institute of Petrochemical Technology, China. Benzene was provided by Shanghai Lingfeng Chemical Reagent Co., Ltd., China. Isopropanol was acquired from Shanghai Shenbo Chemical Co., Ltd., China. Methanol (greater than 99.9% chromatography grade) was supplied by Yuwang Group. *n*-Hexane was purchased from Shanghai Shisihewei Chemical Co., Ltd., China. All materials were of analytical grade and used without further treatment.

### 2.2. Submerged ceramic membrane reactor system

A submerged ceramic membrane reactor system, as shown in Fig. 1, was developed for the cumene production by liquid-phase isopropylation of benzene with isopropanol. The system mainly consisted of an autoclave, a ceramic membrane module and nitrogen resource. The autoclave was made of stainless steel with a working volume of 1 L, which was equipped with an internal thermocouple and an external heater for temperature control and a pressure gauge for pressure monitoring. The ceramic membrane was made up of a fine layer of $ZrO_2$ (nominal pore size of 50 or 200 nm) or $\alpha$-$Al_2O_3$ (nominal pore size of 500 nm) on the outer wall of a tubular $\alpha$-$Al_2O_3$ porous support, and was provided by Nanjing Jiusi High-Tech, China. The membrane with an outer diameter of 12 mm, an inner diameter of 8 mm and a length of 8 cm, was connected with the liquid outlet valve at one end and the other end was sealed with glaze.

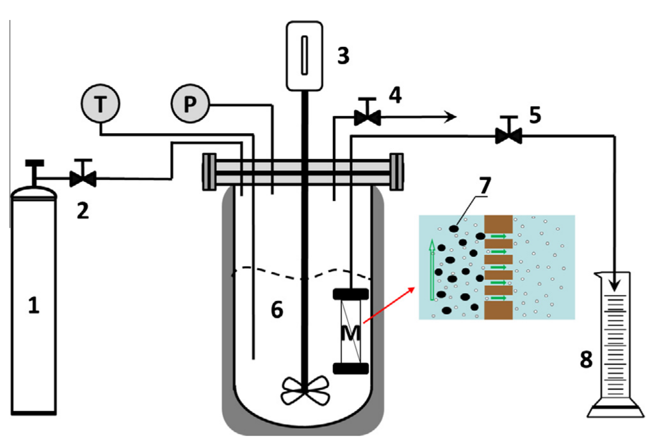


**Fig. 1.** Schematic diagram of the submerged ceramic membrane reactor system: (1) nitrogen source, (2) gas inlet valve, (3) stirrer, (4) exhaust valve, (5) liquid outlet valve, (6) autoclave, (7) solid catalyst, (8) liquid storage tank, (M) membrane module, (T) thermocouple, (P) manometer.

### 2.3. Benzene isopropylation reaction

In the preliminary works, the effects of reaction conditions such as selection of solvent, benzene concentration, benzene/isopropanol molar ratio, reaction temperature, reaction pressure, stirring rate, catalyst concentration and reaction time on the catalytic performance of benzene isopropylation with isopropanol over beta zeolite were investigated in an autoclave without the ceramic membrane module. Taking into account the benzene conversion and cumene selectivity (Fig. S1), *n*-hexane was chosen as the solvent and the optimal reaction conditions were determined as follows: stirring rate of 800 rpm, benzene/isopropanol molar ratio of 3, catalyst concentration of 7.5 g $L^{-1}$, pressure of 3.0 MPa, reaction temperature of 180 °C, reaction time of 3 h and benzene concentration of 1.6 mol $L^{-1}$. When the ceramic membrane module was installed into the reactor system, the adsorption of beta zeolite catalyst onto the membrane as well as the fluid field of reaction slurry interrupted by the membrane module should be taken into account for further research. Therefore, based on the results of preliminary works, some catalytic reaction conditions including stirring rate and catalyst concentration were further investigated for the submerged ceramic membrane reactor system. After reactions under the optimal reaction conditions in the submerged membrane reactor, the membrane filtration experiments were performed, in which the effects of filtration conditions such as stirring rate, transmembrane pressure and filtration temperature on the membrane filtration were examined. The variation of these conditions may have a great impact on the fluidity of reaction mixture and formation of cake layer on the membrane surface, resulting in different extent of membrane fouling that affects the membrane permeation performance.

The liquid-phase isopropylation of benzene to cumene over beta zeolite catalyst was conducted in the submerged ceramic membrane reactor system as shown in Fig. 1. Typically, a desired amount of beta zeolite catalyst, 67 mL of benzene and 19.5 mL of isopropanol dissolved in 385 mL of *n*-hexane were first introduced into the autoclave reactor, then the autoclave was sealed and purged with $N_2$ for five times for air removal and subsequently heated to a desired reaction temperature of 180 °C under a set stirring rate. Then, $N_2$ was fed into the reactor to adjust the pressure to 3.0 MPa, and the benzene isopropylation reaction started. Each reaction ran for 3 h to investigate the effects of operation conditions. After reaction, the reactor was cooled to a set temperature, and the nitrogen was discharged. Subsequently, the membrane filtration was performed at the set temperature, $N_2$ pressure and stirring rate. The fine beta zeolite catalyst powders were separated from the liquid phase mixture and retained in the reactor via the membrane filtration process for the next benzene isopropylation. The permeate was collected in a measuring cylinder, and the membrane filtration rate was calculated by the filtration volume per time. To estimate the feasibility of the submerged ceramic membrane reactor for the cumene production, after the membrane filtration, the fresh *n*-hexane solution of benzene and isopropanol was added up to the original volume of ~470 mL into the reactor, and the processes of isopropylation and membrane filtration were repeated. The products in the permeate were analyzed by an HPLC system (Agilent 1200 Series, USA) equipped with a diode array

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