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Epoxidation of cyclic-olefins over carbon template mesoporous TS-1 ☆

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ABSTRACT

Mesoporous TS-1 was prepared by varying the amount of carbon particles using as a hard template average size 12 nm under the microwave irradiation. The catalytic activity of carbon templated mesoporous TS-1 (C-meso-TS-1) was ratified by epoxidation of various cyclic olefins and the catalytic activity was compared with TS-1 synthesized by hydrothermal method. The activity of mesoporous TS-1 increased with increasing the carbon content. Mesoporous TS-1 showed higher activity than the microporous TS-1.

1. Introduction

TS-1 zeolite is Ti substituted silicalite-1 which belongs to the MFI structural group. Over the last decades, TS-1 zeolite known to have an excellent catalytic properties for selective oxidation of number of organic substrates, using hydrogen peroxide as an oxidant under mild condition [1,2]. TS-1 has also been used in several types of oxidation reactions including hydroxylation, epoxidation, ammoxidation and aromatic oxidation. Moreover, hydrogen peroxide used as a green oxidant in these reactions due to the fact that by-product is only water [3]. In alkenes epoxidation, many studies have been done to enhance the epoxide selectivity. Epoxides play an important role both in organic synthesis and pharmaceuticals. TS-1 is being used commercially for the production of catechol and hydroquinone from phenol, and also for the synthesis of cyclohexanone oxime from cyclohexanone [4,5].

The successful applications of TS-1 as a catalyst arise due to unique synthetic procedure by which the pore diameter can control topology, and also the nature, concentration of active sites. More than eight types of zeolite have been used in oil refining process. The number will be more if it counted especially in the field of catalysis for production of bulk chemical and fine chemicals. However, main drawback is that the pore blockage by coking, reduced yields and selectivity which cause the slow diffusion rate of reactants and products in microporous channel structures (typically smaller than 1.2 nm) are serious problems that routinely arise in catalytic applications of zeolites [6,7]. The inclusion of broad pores may help to overcome these problems [8]. The increased diffusion limitation of zeolites is responsible for significant decrease of the undesired product selectivity due to the increased interaction time between the active sites and reactants in zeolite pores [9].

This fact has stimulated research of zeolites with larger pores and amorphous mesoporous titanium containing materials [10]. Mesoporous materials such as MCM-41 family and SBA series have uniform pore like zeolites but with a diameter greater than 20 Å. The initial work from Mobil R&D Corp. demonstrated that cationic surfactants, such as cetyltrimethylammonium cation ($CTMA^+$), can act equivalently like the organic structure directing agents of zeolites which can generate aluminosilicate and other metal oxide materials with uniform channels in the mesoporous region [11,12]. Although, improvement of mesoporous materials suggest a new opportunity, the relatively weak activity and poor hydrothermal properties of mesoporous materials have resulted limitations in the practical applications. In view of this, mesoporous zeolites which can provide several benefits which could potentially improve the efficiency of zeolite in catalysis such as the increase the external surface area, low limitations on transport in zeolites channels and a high hydrothermal stability are highly demanded. Moreover, the development of mesopores can favor the production of various unexplored products those may be in demand for numerous applications. To develop mesoporosity in zeolite single crystals increase the accessibility to the internal surface, several methods research such as dealumination, desilication and other chemical treatment for forming defect site, a hard templating method have been introduced [13–16]. Using carbon materials as hard template is one of the most reliable methods to synthesize mesoporous zeolites with fully crystalline walls. This kind of

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mesoporous zeolite have been prepared by crystallizing in the presence of carbon materials such as carbon black [10,13–21], mesoporous carbon [22,23], colloid imprinted carbon [24], and carbon aero gel [25].

It was found that the microwave process is especially useful for the synthesizing of porous crystalline materials. Microwave heating was conceived about 50 years ago and it is a relatively new in the field of synthesis nano materials [26]. A significant increase in microwave processing research began in the late 1980s for ceramics and polymers. Especially, researchers of Mobil Co. studied the application of microwave in the nanoporous materials in 1988. So far, there are numerous research groups worldwide that are applying microwave energy to different types of materials and products.

Here we are reporting the preparation of mesoporous TS-1 with different amount of carbon as a hard template under microwave irradiation. Nanosized carbon materials as a template during the zeolite crystallization were utilized to make a mesoporous TS-1. Here we also described the epoxidation of different size of cyclic-olefins by carbon templated mesoporous TS-1. In this work, we have prepared carbon template mesopoorus TS-1 in order to widen its catalytic application for relatively larger size olefin such as cyclohexene, cyclooctene, and cyclododecene.

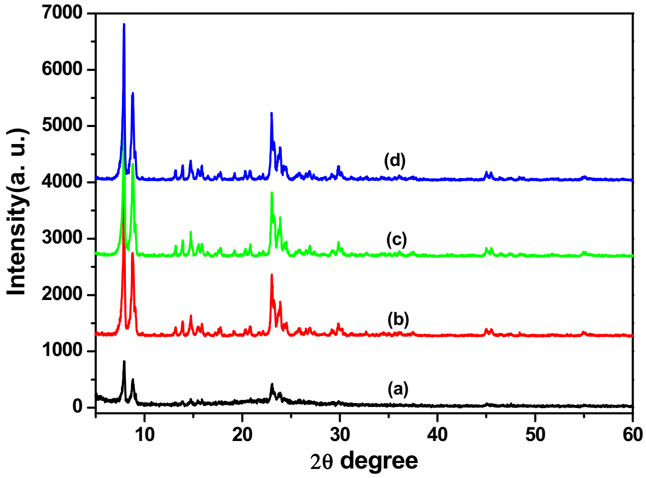

Fig. 1. High angle XRD patterns of C (a) 10 wt%, (b) 20 wt%, (c) 30 wt%, and (d) 40 wt% of mesoporous TS-1 prepared by microwave synthesis.

2. Experimental

2.1. Preparation of carbon template mesoporous TS-1

TS-1 zeolite (Si/Ti = 100) was synthesized using tetraethylortho silicate (TEOS, 95%, Aldrich) as the silica source and titanium tetra isopropoxide ($Ti(OPr)_4$, 97%, Aldrich) as the Ti source. Moreover, tetrapropyl ammonium hydroxide (TPAOH, TCI, 25%) was used as the structure-directing agent. The composition of the final gel with Si/Ti was: SiO_2:TiO_2:TPA-OH:H_2O:IPA = 1:0.01:0.5:23.33:1.13

In typical synthesis, 48 g TPA-OH was mixed in 48 g of distilled water and appropriate amount of carbon (Carbon Black Pearl 2000 – ranging from 10 to 40 wt% of C/Si source) was added and allowed to stir for 12 h. TIP (0.328 g) was dissolved in 8 g of isopropyl alcohol (IPA, 99%, DC chemical) and 24 g TEOS was added and allowed to stir for 12 h then added to the above mixture. Finally, the whole mixture was vigorously stirred for 4 h.

After stirring it was put into a microwave oven equipped with a Teflon autoclave, and was irradiated at 80 °C for 30 min under 1200 W microwave power after that increasing temperature at 165 °C under 1200 W holding 5 min and was maintained at 165 °C under 1200 W microwave power during 60 min. The resulting solid product was filtered, washed with deionized water; and dried in air at 60 °C for 12 h. To remove the organic template, the as-synthesized samples were calcined at 550 °C for 10 h in air.

2.2. Characterization of carbon templated mesoporous TS-1

Crystallinity and phase purity of this materials was determined by powder X-ray diffraction using a Rigaku diffractometer

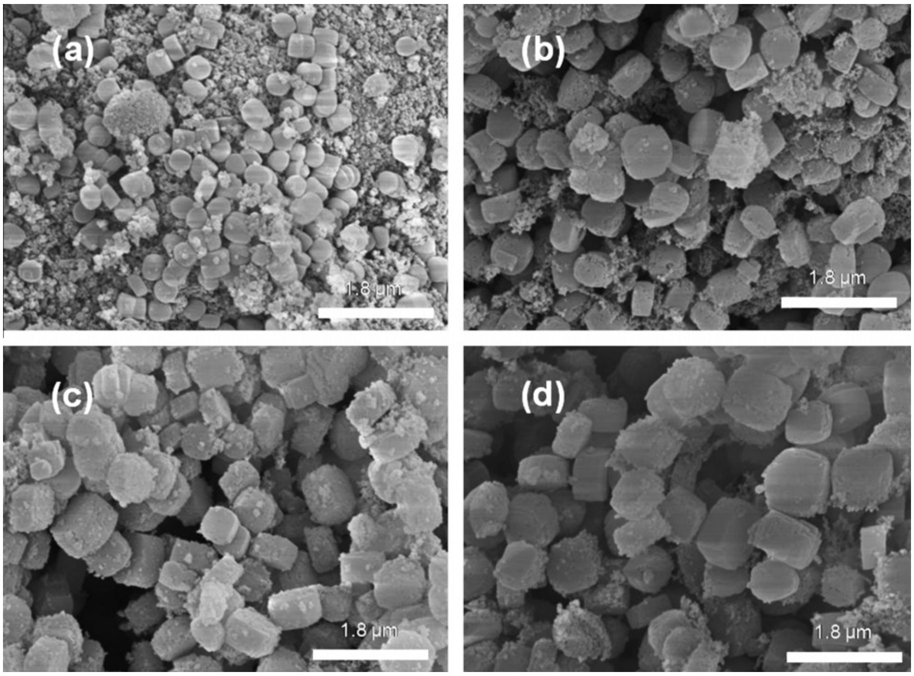

Fig. 2. SEM images of (a) C 10 wt%, (b) C 20 wt%, (c) C 30 wt%, and (d) 40 wt% of mesoporous TS-1 prepared by microwave synthesis.