Available online at www.sciencedirect.com
ScienceDirect
Applied Catalysis A: General 313 (2006) 101–105
APPLIED CATALYSIS A: GENERAL
www.elsevier.com/locate/apcata

Selective synthesis of di-*tert*-butylperoxide catalyzed by highly active microporous H-beta zeolite

Suman K. Jana [1], Masamitsu Nakamura, Tsuyoshi Kugita, Seitaro Namba *

Department of Materials, Teikyo University of Science & Technology, Uenohara-machi, Yamanashi 409-0193, Japan

Received 11 May 2006; received in revised form 11 July 2006; accepted 13 July 2006

Abstract

Liquid phase di-*tert*-butylperoxide synthesis from the condensation reaction between *tert*-butyl alcohol and *tert*-butylhydroperoxide over microporous H-beta zeolites, having Si/Al molar ratios ranging from 11.5 to 120, has been investigated. With increasing Al content or in other words the acidity of H-beta zeolite, the catalytic activity is increased and passes through maxima; however, the selectivity for di-*tert*-butylperoxide is decreased initially to a small extent and then maintain almost the same level. Among the different Al-containing beta zeolites, the catalyst with a Si/Al molar ratio of 40 shows the best performance in the above condensation reaction. Additionally, when compared with other commonly used heterogeneous acidic microporous zeolites (H-ZSM-5, H-mordenite, H-Y, H-MCM-22) and mesoporous solids (Al–MCM-41, Al:SBA-15) having similar Si/Al ratios but different pore structures, the catalytic activity of the H-beta zeolite in the di-*tert*-butylperoxide synthesis process is found to be much higher.

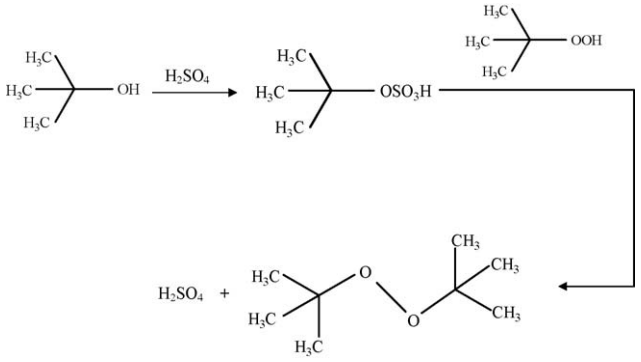
Keywords: Di-*tert*-butylperoxide; *tert*-Butyl alcohol; *tert*-Butylhydroperoxide; H-beta zeolite

1. Introduction

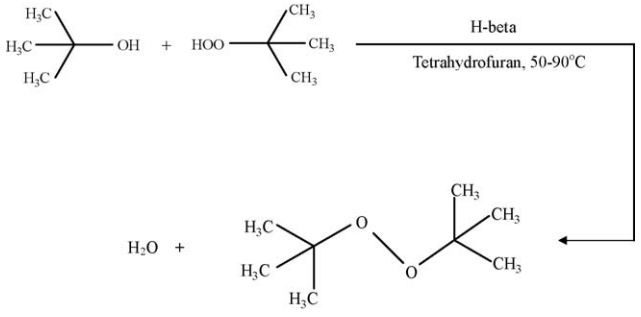
Di-*tert*-butylperoxide is an important chemical having use as an initiator in various radical polymerizations and organic syntheses and having special utility as an additive to diesel fuel formulations in order to improve its characteristics and/or qualities [1,2]. Industrially it is produced by two-step homogeneous reactions using stiochiometric amount of concentrated sulfuric acid catalyst (Scheme 1). The other homogeneous catalysts reported so far for this transformation include inorganic heteropoly acids, methane sulfonic acid, toluene sulfonic acid and various commonly known water soluble protic and Lewis acids [1–5]. However, the use of homogeneous catalysts poses several problems, such as requirement in stoichiometric amounts, difficulty in separation and recovery, disposal of spent catalyst, corrosion, high toxicity, etc. Heterogeneous catalysts, on the other hand, are found to be environmentally friendly; they offer advantages of easier separation, reusability and sometimes higher selectivity of the product(s) over the homogeneous ones [6–9]. Hence, it is important to explore the use of heterogeneous solids having high catalytic activity and/or selectivity for the industrially demanding di-*tert*-butylperoxide synthesis both on environmental and economic grounds. To the best of our knowledge, the literature on the uses of heterogeneous solid to mediate di-*tert*-butylperoxide synthesis is scarce. In this regard, we report here the high activity of H-beta zeolite, the acidic microporous solid having a three-dimensional distorted tetrahedral channel structure with three mutually intersecting 12-ring channels, in the acid-catalyzed synthesis of di-*tert*-butylperoxide (DTBP) from the condensation reaction between *tert*-butylhydroperoxide (TBHP) and *tert*-butanol (TBA) in the presence of tetrahydrofuran (THF) solvent (Scheme 2). The catalytic performance shown by the beta zeolite is superior when compared to the activity obtained with different acidic microporous zeolites (H-ZSM-5, H-mordenite, H-Y, H-MCM-22) and mesoporous solids (Al-MCM-41, Al:SBA-15). Additionally, beta zeolite exhibited excellent reusability, which is of great practical importance.

* Corresponding author. Tel.: +81 554 63 6856; fax: +81 554 63 6856.
E-mail addresses: suman_kj@hotmail.com (S.K. Jana), namba@ntu.ac.jp (S. Namba).
[1] Present address: Chemical Resources Laboratory, Tokyo Institute of Technology, Nagatsuta 4259, Yokohama 226-0583, Japan.

0926-860X/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.apcata.2006.07.012



Scheme 1.



Scheme 2.

2. Experimental

Microporous H-beta zeolites having Si/Al molar ratios of 11.5, 40, 90 and 120 were obtained from Zeolyst International and were calcined at 500 °C for 2 h before use. The zeolite samples were characterized for their acidity by NH_3–TPD in a flow-type fixed bed reactor using a Japan BEL TPD-77 instrument under the following conditions. Before ammonia adsorption, the sample was evacuated at 500 °C for 1 h. The ammonia was then adsorbed at 150 °C for 30 min followed by evacuation at the same temperature for 1 h, cooled to room temperature and then finally the temperature was gradually raised to 650 °C at a rate of 10 °C per minute. A number of various other Al-containing microporous zeolites: H-ZSM-5 (synthesized by hydrothermal method), H-mordenite (SŰD-CHEMIE), H-Y (N.E. CHEMCAT, Japan), H-MCM-22 (obtained as a gift from Professor T. Tatsumi of Tokyo Institute of Technology, Japan), and mesoporous solids: Al-MCM-41 (prepared by hydrothermal method), Al:SBA-15 (prepared by reacting silica SBA-15 with aluminum isopropoxide, whereas, silica SBA-15 was prepared by hydrothermal method), were used for comparison.

Liquid phase *tert*-butyl alcohol and *tert*-butylhydroperoxide condensation reaction over various acidic solid catalysts were carried out in a magnetically stirred round-bottomed glass reactor (capacity: 50 cm^3) fitted with a reflux condenser and a digital temperature controller at the following reaction conditions: reaction mixture = 55.5 mmol *tert*-butyl alcohol (Kanto Chemical Co., Japan), 55.5 mmol *tert*-butylhydroperoxide (NOF Co., Japan) and 12 mmol dehydrated tetrahydrofuran, amount of catalyst = 0.5 g, temperature = 50–90 °C and reaction time = up to 12 h. The reaction was started by adding powder catalyst into the reaction mixture containing both the reactants and solvent, after attaining the desired reaction temperature. The course of the reaction was followed by measuring quantitatively the product(s) formed during the condensation reaction by GC equipped with FID detector and a capillary column as a function of time. Di-*tert*-butylperoxide yield and selectivity were calculated on a percentage basis based on *tert*-butylhydroperoxide using internal standard method.

3. Results and discussion

3.1. Catalyst characterization

The phase purity of H-beta zeolites used in the present study has been re-confirmed by X-ray powder diffraction measurement and is found to be similar to that reported in the literature for pure and highly crystalline zeolite beta (not shown). H-beta zeolites having different aluminum contents [expressed in terms of Al/(Si + Al)mol mol^{-1}] exhibit different acidity and the acid amount (i.e. total acidity) is gradually increased with the increase in aluminum concentration in the catalyst as observed from the results of NH_3–TPD (Fig. 1).

3.2. Catalytic reaction

In order to identify highly active zeolite based heterogeneous catalyst for the synthesis of di-*tert*-butylperoxide from *tert*-butanol and *tert*-butylhydroperoxide condensation reaction, a study on various heterogeneous acidic microporous zeolites (H-beta, H-ZSM-5, H-mordenite, H-Y, H-MCM-22) and mesoporous solids (Al-MCM-41, Al:SBA-15) having different structural features (i.e. pore type and dimension) but

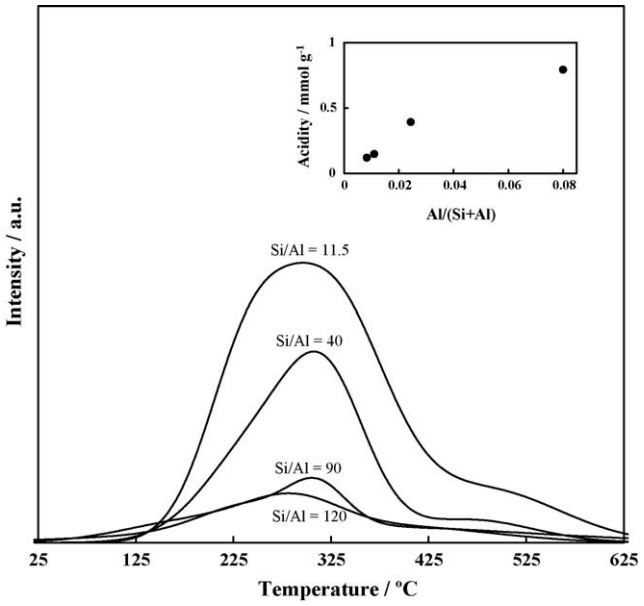


Fig. 1. Ammonia TPD spectra of H-beta zeolites having different Si/Al molar ratios (inset: dependence of acidity on the Al content of H-beta zeolite).