Molecular Catalysis 442 (2017) 27–38

Contents lists available at ScienceDirect

Molecular Catalysis

journal homepage: www.elsevier.com/locate/mcat

Editor's choice paper

Selective hydroalkylation of benzene over palladium supported Y-Zeolite: Effect of metal acid balance

S.A. Kishore Kumar[a,b], Mathew John[a], Shivanand M. Pai[a], Sayanti Ghosh[a], Bharat L. Newalkar[a,**], Kamal K. Pant[b,*]

[a] *Corporate R&D Centre, Bharat Petroleum Corporation Limited, Plot 2A, Udyog Kendra, Greater Noida, 201306, India*
[b] *Department of Chemical Engineering, Indian Institute of Technology Delhi, Hauz Khas, New Delhi, 110016, India*

ARTICLE INFO

Article history:
Received 14 May 2017
Received in revised form 27 August 2017
Accepted 30 August 2017

Keywords:
Bi-functional catalyst
Metal acid balance
Hydroalkylation
Kinetic modeling
Cyclohexylbenzene

ABSTRACT

Bifunctional Palladium (Pd) supported Y-zeolite, with SiO_2/Al_2O_3 ratios 5, 12, 30 and 60, prepared by impregnation method were used for hydroalkylation of benzene. It is found that the reaction condition and catalyst composition influence the hydroalkylation activity and cyclohexylbenzene (CHB) selectivity. CHB selectivity of a hydroalkylation catalyst can be determined by the destiny of the intermediate cyclohexene formed by partial hydrogenation of benzene on the metal site of the catalyst. That is, if the intermediate cyclohexene hydrogenates to cyclohexane on the metal site, the selectivity for CHB decreases whereas, if the intermediate cyclohexene is alkylated with benzene on the acid sites, the selectivity for CHB increases. Thus, there is a requirement of optimum balance of exposed metal and acid sites of the catalyst for enhancing CHB selectivity. At 42.2% of benzene conversion, Pd (0.2 wt%)/HY5 ($SiO_2/Al_2O_3 = 5$) catalyst gave a CHB selectivity of 75% in comparison to 70.3% for the best patented catalyst. Furthermore, a kinetic model has been developed for the hydroalkylation of benzene, assuming dissociative, non-competitive addition of hydrogen. Finally, the developed kinetic model along with experimental data was used to study the effect of mole ratio of acid sites to exposed metal sites of Pd/HY catalyst system for hydroalkylation reaction. Based on these results, the ratio of number of acid sites to exposed metal sites can be tuned to maximize CHB yield.

1. Introduction

Phenol is an important industrial chemical with numerous applications. It is also the starting material for the synthesis of several important products like phenolic resins, bisphenol A, ε-caprolactam and alkylphenols [1]. Currently more than 90% of the world's phenol production technology is based on the Hock process and this process is based on alkylation of benzene with propylene to produce cumene followed by oxidation of cumene to cumene hydroperoxide and its cleavage to phenol and acetone [1,2].To operate this process economically, the demand for both the products must be in proportion to their production rate (i.e 1: 1 molar ratio for phenol and acetone). However, the world demand for phenol is growing more rapidly than that of acetone making the process less economical [1–3]. Oxidation of cyclohexylbenzene (CHB) to benzylic hydroperoxide and the cleavage of this hydroperoxide to produce phenol and cyclohexanone, as shown in Fig. 1 can be more attractive route for the production of phenol. Furthermore this alternate route produces more valuable cyclohexanone as a co-product and does not require costlier propylene as raw material [1–3]. However, this alternate route requires the development of efficient catalyst and economical process for the commercial production of CHB, which also has several direct applications like solvent and plasticizer in plastics, coatings and adhesive fields [4]. It is also used as an over charge protecting agent in lithium ion batteries and a base material for LCD derivatives. Furthermore, the co-produced cyclohexanone is a useful intermediate for the manufacture of adipic acid, caprolactam and nylon [5,6]. Dehydrogenation of CHB also offers a cost effective route for the production of biphenyl, and the produced biphenyl is mainly used as a heat transfer fluid and dye carrier in textile industry [7]. In view of the above, the main objective of the present study is to develop an efficient catalyst for the conversion of benzene to cyclohexylbenzene.

---

* Corresponding author.
** Corresponding author.
E-mail addresses: newalkarbl@bharatpetroleum.in (B.L. Newalkar), kkpant@chemical.iitd.ac.in, dr.kkpant@gmail.com (K.K. Pant).

http://dx.doi.org/10.1016/j.mcat.2017.08.021
2468-8231/© 2017 Published by Elsevier B.V.

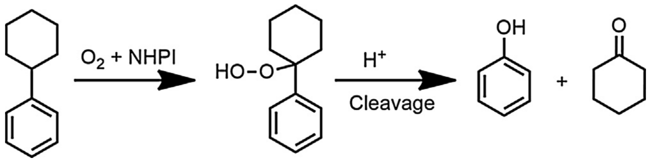

Fig. 1. Cyclohexylbenzene oxidation and decomposition to phenol and cyclohexanone.

Owing to CHB applicative potential, numerous attempts have been reported to convert benzene to CHB. In this context, hydroalkylation/alkylation of benzene has been investigated. Typically, CHB is produced by the direct alkylation of benzene and cyclohexene using aluminium chloride or sulphuric acid as catalysts. This direct alkylation route not only uses hazardous acid catalysts such as sulfuric acid and aluminium chloride but also offer low selectivity (around 44%) for CHB [8,9].Considering the environmental hazard associated with the direct alkylation route it is imperative to look for alternative environmental friendly routes. Hydroalkylation of benzene using heterogeneous bifunctional catalyst provides such an alternative route for CHB synthesis [5,10]. Based on literature, hydroalkylation reaction pathway (Fig. 2) involves partial hydrogenation of benzene at the metal site to produce cyclohexene which then alkylates with benzene at the acid site to produce CHB. However, formation of by-products like dicyclohexylbenzene (DCHB) and cyclohexane are reported to form during the course of the reaction. Furthermore, under severe conditions, formation of bicyclohexyl by hydrogenation of CHB at the metal site of the catalyst is also reported [5,10]. Thus, several bifunctional catalyst recipes comprising of Pd, Ru, Ni, Co, Pt, Rh, Re, Sn, Zn metal supported on SiO_2, Al_2O_3 and zeolites like MOR, Beta, 13X, MCM-22 have been investigated for hydroalkylation of benzene [5–14].

Fahy et al., studied the hydroalkylation of benzene on four component catalyst system consisting of Nickel, Platinum, Rare earth ions over zeolite 13X and suggested that the addition of rare earth alters the electron transfer to the metal thereby reducing adsorption strength of benzene which in turn helps in hydroalkylation rather than hydrogenation thus improving CHB selectivity [10]. This study also suggested that, addition of small amount of platinum on the catalyst will facilitate the reduction of nickel which in turn favors hydroalkylation at lower temperatures. The best catalyst, 5 wt.%Ni/10 wt.%Re/0.1 wt.%Pt loaded on 13X zeolite showed a selectivity of 70% for CHB at 20% benzene conversion [10] (refer Table 1, entry 1).

Jun et al., studied the hydroalkylation activity in a batch process over palladium supported on Beta zeolite with different Si/Al ratio [5]. Beta zeolite with a low SiO_2/Al_2O_3 ratio showed better activity for hydroalkylation due to higher Brønsted acidity (refer Table 1, entry 2). This concluded that 0.2%Pd/Hβ25 is a promising catalyst for hydroalkylation of benzene and having optimum balance between metal active sites and acidic sites in the catalyst is the key to better selectivity for CHB formation during benzene hydroalkylation. Kralik et al., studied the hydroalkylation activity in a batch reactor over 0.2 wt.% of ruthenium loaded on mordenite and beta zeolites [11]. The obtained results demonstrated higher activity of 0.2 wt.% Ru/Beta zeolite vis-à-vis 0.2 wt.% Ru/Mordenite owing to ease of accessibility of acid sites for hydroalkylation leading to the best catalyst selectivity with the sum of CHB and DCHB which varied from 60 to 40% at benzene conversion of 30 and 80%, respectively (refer Table 1, entry 3).

More recently, several researchers have studied the hydroalkylation of phenolic compounds on Pt, Pd doped HY, HBEA and H-Mordenite zeolites [15–17]. In their study, the authors suggested that an optimum metal acid balance is required to achieve highest hydroalkylation activity and selectivity. Their study also suggested that, Pd doped zeolite is more effective catalyst than Pt doped zeolite for the hydroalkylation reaction and among zeolites, 3D pore zeolites like HY are more active and selective for hydroalkylation reaction. However, its utility for benzene hydroalkylation reaction remains unexplored.

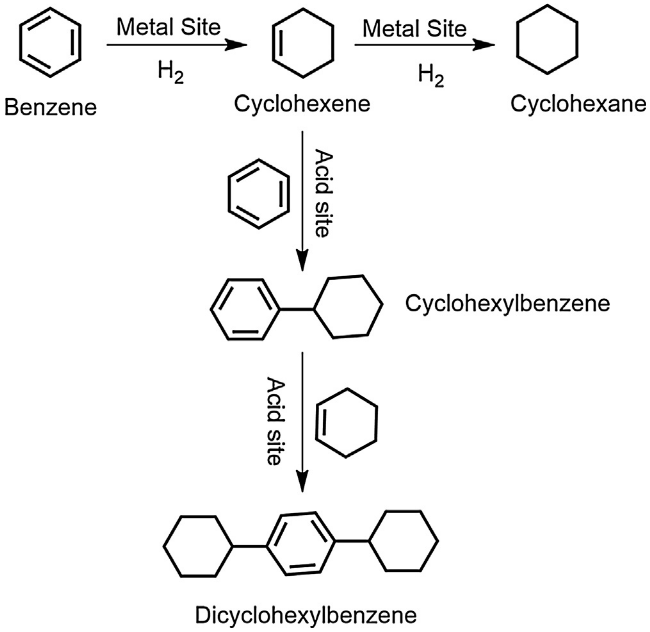

Fig. 2. Reaction network for hydroalkylation of benzene on dual function catalyst.

A summary of benzene hydroalkylation performance for different literature reported catalyst recipes is listed in Table 1. Amongst several catalyst formulation described in Table 1, catalyst 4 (0.3%Ru/0.3%Sn/MCM-22), catalyst 5 (0.3%Pd/MCM-22), and catalyst 7 (0.3%Pd/MCM-49) exhibited superior catalytic performance for benzene hydroalkylation with good selectivity for CHB at reasonably higher benzene conversions. Out of these three, catalyst 5 (0.3%Pd/MCM-22) displayed the best selectivity for CHB (70.3%) at highest benzene conversion of ~48%.

From Table 1, it is evident that most of the catalysts reported in literature suffer from the problems pertaining to low selectivity for CHB, low benzene conversion, use of proprietary zeolite supports, formation of large amounts of impurities and high metal loading (over 0.6 wt%) which in turn restricted the commercial application of these catalysts, till date, for benzene hydroalkylation process. Furthermore, several researchers have discussed the importance of metal acid balance of the catalyst for the hydroalkylation reaction however none of the researchers have presented a detailed kinetic study of the effect of relative amounts of acid sites and exposed metal sites of the catalyst on the hydroalkylation reaction [3,5,6,10–12,19].

In view of the above, the present research work focuses on the development of a highly selective, and stable catalyst for converting benzene to CHB. The influence of catalyst properties and the reaction operating conditions were studied on the hydroalkylation activity of the catalyst. In this context, palladium loaded HY zeolite with varied Si/Al ratio were prepared and evaluated for the hydroalkylation activity. Furthermore, a kinetic model has been developed for the hydroalkylation of benzene. The developed kinetic model along with experimental data was used to study the effect acid sites to exposed metal mole ratio of the Pd (0.2 wt.%)/HY5 catalyst system. Finally, the obtained experimental and kinetic modelling results are discussed in terms of the support and metal characteristics for maximization of CHB yield.