Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Molecular Catalysis A: Chemical 237 (2005) 137–145

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

www.elsevier.com/locate/molcata

Alkylation of benzene with α-olefins over zirconia supported 12-silicotungstic acid

Dhanashri P. Sawant, S.B. Halligudi [*]

Inorganic Chemistry and Catalysis Division, National Chemical Laboratory, Pune 411 008, India

Received 29 March 2005; received in revised form 16 April 2005; accepted 17 April 2005
Available online 9 June 2005

Abstract

Liquid phase alkylation of benzene to linear alkyl benzene (LAB) with α-olefins has been investigated with 12-silicotungstic acid supported on zirconia (STA/ZrO_2) as the catalyst. Among the catalysts, 15 wt.% STA/ZrO_2 calcined at 750 °C was found to be most active than others in the alkylation reaction. The total amount of acid sites of different STA loaded catalysts were estimated by TPD of NH_3 and 15 wt.% STA/ZrO_2 calcined at 750 °C was found to have the highest acidity and more active in the reaction. The optimization of reaction conditions of alkylation of benzene with 1-dodecene was performed with 15 wt.% STA/ZrO_2 calcined at 750 °C by varying catalyst concentration (1–5 wt.% of reaction mixture); temperature, 373–423 K and benzene:1-dodecene (1-dd) molar ratio, 5–15 in a Parr autoclave under N_2 pressure. Under the optimized reaction conditions, conversion of 1-dodecene (50.8%) gave high selectivity to 2-phenyl dodecane (47.1%) and the remaining 3-, 4-, 5- and 6-phenyldodecanes in 4 h. The reaction was found to be heterogeneously catalyzed and no contribution from homogeneous (leached) STA into the reaction medium.

Keywords: Alkylation; Benzene; 12-Silicotungstic acid; LAB; Zirconia; 1-Dodecene

1. Introduction

Linear alkyl benzenes (LABs) are important intermediates for synthetic detergents and these are traditionally manufactured in presence of aluminum trichloride or hydrofluoric acid catalysts. Because of the hazardous nature of conventional systems, there is a need to develop solid acid catalysts to replace the existing production methods. Solid acid catalysts such as zeolites [1–7], clays [8,9], heteropoly acids [10–14], fluorided silica-alumina [15], ionic liquids [16–18], H-ZSM-5, H-ZSM-12, H-Y [19–21], La-doped Y zeolite [22] and high silica mordenite (HSM) [23] have been widely investigated for the above transformations. Immobilized $AlCl_3$ over MCM-41 has been used for benzene alkylation with 1-olefins [24]. Already UOP/Petresa has industrialized a process with aluminum–magnesium silicate catalyst for alkylation of benzene with α-olefins [25,26]. A new catalytic distillation technology for benzene alkylation with α-olefins with suspended catalytic distillation (SCD) column has been developed [27]. Recently, supported tungstophosphoric acid catalyst was used for synthesizing LAB with high activities and with high selectivities to 2-LAB [28,29].

The present work deals with the alkylation of benzene with 1-dodecene using zirconia supported silicotungstic acid as the catalyst. The reaction was carried out with an aim to maximize 1-dodecene conversion together with the selectivity to 2-phenyldodecane as compared to other isomers like 3-, 4-, (5 + 6)-linear alkyl benzene. The influence of STA loading and catalyst calcination temperature on 1-dodecene conversion was studied. The catalyst with highest activity was used to study various reaction parameters such as temperature, molar ratio and catalyst weight. The catalyst regeneration and heterogeneity of reaction were also examined in the above reaction.

---

[*] Corresponding author. Tel.: +91 205893300; fax: +91 205893761.
E-mail address: sb.halligudi@ncl.res.in (S.B. Halligudi).

1381-1169/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.molcata.2005.04.042

2. Experimental

2.1. Materials

Zirconium oxychloride ($ZrOCl_2·8H_2O$) and ammonia (25%) were procured from S.D. Fine Chemicals Ltd., Mumbai. Benzene and 1-dodecene were obtained from Merck (India) Ltd. and Aldrich, respectively. Silicotungstic acid ($H_4SiW_{12}O_{40}·xH_2O$) was purchased from Aldrich. All the chemicals were research grade and used as received without further purification in the catalyst preparation and alkylation experiments. Zeolites with (SiO_2/Al_2O_3 ratio), H-beta (30), H-ZSM-5 (60) and H-Y (13.5) recovered by calcining NH_4-Y were obtained from Catalysis Pilot Plant (CPP-NCL, Pune). H-Mordenite (20) was obtained from PQ Zeolites BV, Netherlands. All catalysts used in the reactions were in the powder form and were activated prior to their use in the reaction.

2.2. Preparation of STA/ZrO_2 catalysts

The catalysts were prepared by impregnation method using zirconium oxyhydroxide as the support by following our earlier reported procedure [30]. After impregnation, catalysts were dried and calcined in air at 750 °C. Catalysts with different STA loading 5–25 wt.% were prepared and calcined at 750 °C. STA/ZrO_2 (15 wt.%) was prepared and calcined at different calcination temperatures. Similarly, 15 wt.% STA/SiO_2 was prepared as above using silica gel and calcined at 750 °C. Silica gel support was prepared by known procedure [31].

2.3. Characterization

X-ray powder diffraction of the samples were carried out with Cu Kα radiation (Rigaku model D/MAXIII VC, Japan, $\lambda = 1.5418$ Å). The total amount of acid sites present on the catalysts with different TPA loadings were measured by TPD of ammonia. The acidity of the catalysts were measured by temperature programmed desorption of NH_3 (NH_3-TPD) using micromeritics AutoChem-2910 instrument. It was carried out after ~0.5 g of the catalyst sample was dehydrated at 600 °C in He (30 cm^3 min^{-1}) for 1 h. The temperature was decreased to 100 °C and NH_3 was adsorbed by exposing samples treated in this manner to a stream containing 10% NH_3 in He for 1 h at 100 °C. It was then flushed with He for another 1 h to remove physisorbed NH_3. The desorption of NH_3 was carried out in He flow (30 cm^3 min^{-1}) by increasing the temperature to 600 °C at 10 °C min^{-1} measuring NH_3 desorption using TCD detector.

2.4. Aromatic alkylation

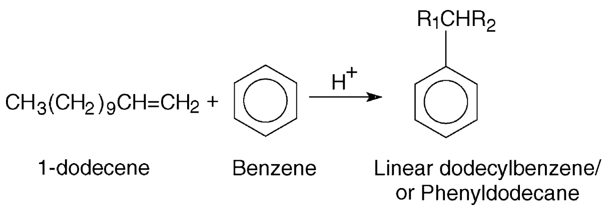
Experiments on alkylation of benzene were conducted in a 50 ml Parr autoclave under nitrogen pressure. The catalysts were activated at 500 °C for 4 h and cooled to room temperature prior to their use in the reaction. In a typical run, a weighted amount of 15 wt.% STA/ZrO_2 mixed with known amount of benzene and 1-dodecene was placed in the reactor. The reactor was pressurized with nitrogen (6–7 bar) and heated to the desired temperature with stirring at 500 rpm. After a fixed interval of time, the reactor was cooled to room temperature and a sample of the reaction mixture was withdrawn and centrifuged to get a clear solution and analyzed for products. The products of alkylation of benzene were analyzed by Shimadzu 14B gas chromatograph fitted with a SE-52 capillary column coupled with FID. Since, benzene was in excess, conversions were estimated based on the limiting alkylating reagent. The products were also identified by GC–MS analysis.

3. Results and discussion

Alkylation of benzene with 1-dodecene catalyzed by 15 wt.% STA/ZrO_2 calcined at 750 °C under optimized reaction conditions gave 2-, 3-, 4- and (5 + 6)-phenyldodecane as shown in the Scheme 1. The formation of these isomers of phenyl dodecane are likely by the electrophilic substitution of cabenium ion, which is formed upon chemisorption of 1-dodecene on the catalyst surface as shown in Scheme 2.

3.1. Catalysts characterization

Wide angle XRD pattern for different STA (%) loadings over zirconia and calcined at 750 °C is shown in Fig. 1(A). Zirconia calcined at 750 °C mainly shows monoclinic form with small amount of tetragonal form. As (%) loading of STA increases, it shows increase in tetragonal phase, while 15 wt.% STA is showing fully tetragonal form of zirconia. This is due to monolayer coverage of STA over zirconia. But on further increase in STA loading, it shows monoclinic along with tetragonal phase and WO_3 crystallites due to the decomposition of STA (Keggin unit). Fig. 1(B) XRD pattern shows the effect of different calcination temperatures over 15 wt.% STA/ZrO_2. At calcination temperature of 750 °C, it shows fully tetragonal form of zirconia and on further increase in temperature WO_3 crystallites are observed. Acidity measurement by TPD of ammonia is shown in Figs. 2 and 3 along with catalytic activity. From Fig. 2, it is seen that with increase in STA loading up to 15 wt.%, it shows increase in acidity and so catalytic activity. But on further increase in STA loading,



Scheme 1. Alkylation of benzene with 1-dodecene.