Catalysis Today 141 (2009) 130–137

Contents lists available at ScienceDirect

Catalysis Today

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

Monoalkylation of biphenyl over modified heteropoly acids: Novelty of cesium substituted dodecatungstophosphoric acid supported on hexagonal mesoporous silica[☆]

Ganapati D. Yadav [*], Ginish George

Department of Chemical Engineering, University Institute of Chemical Technology, University of Mumbai, Matunga, Mumbai 400019, India

ARTICLE INFO

Keywords:
Friedel–Crafts alkylation
Heteropolyacids
Hexagonal mesoporous silica
Kinetics
Dodecaungstophosphoric acid

ABSTRACT

The current study reports the development of environmentally benign route for the alkylation of biphenyl with benzyl chloride for benzylbiphenyl synthesis. Cesium substituted dodecatungstophosphoric acid supported on hexagonal mesoporous silica (20% w/w $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/HMS) was synthesized. This novel nanocatalyst was very active and stable without any deactivation. The catalyst is fully characterized. A systematic investigation of the effect of various operating parameters is done. Furthermore, a second order rate equation is developed to describe the reaction kinetics, which is validated with experimental results.

1. Introduction

Electrophilic aromatic substitution and in particular, Friedel–Crafts reactions require Lewis and Bronsted acid catalysts such as $AlCl_3$, $ZnCl_2$, HF, H_2SO_4, BF_3 and *p*-toluenesulfonic acid. Most of the batch processes use $AlCl_3$ as a homogeneous catalyst which is inexpensive, very reactive and is one of the most powerful Lewis acids. Unfortunately, it is difficult to handle $AlCl_3$ and similar metal halides as catalysts since they get readily hydrolyzed. Very often such catalysts are required in stoichiometric quantities. A large inventory of these materials poses health, safety and storage problems. Furthermore, the traditional route of liquid phase alkylation using mineral acids and $AlCl_3$ as catalysts suffers from the disadvantages of high capital cost, reactor corrosion, formation of by-products and the difficulty in catalyst regeneration [1]. For the development of cleaner and sustainable techniques in the chemical industry, such polluting catalytic processes need to be replaced.

In recent years, a great deal of effort has been directed towards the promotion of solid acid catalysts and several synthetic procedures have been reported. They are non-corrosive; presenting fewer disposal problems, their separation from liquid phase is much easier, which allows their repeated use. They permit the use of cheaper and non-polluting reagents, and offer several different reactor configurations [2]. In addition, physical and chemical properties of solid acids can be tailored and tuned to promote reactivity and selectivity and prolonged catalyst life.

Our laboratory has been investigating different aspects of green processes with benign solid acid catalysts, which have direct industrial relevance in refineries, petrochemicals, pharmaceuticals, rubber chemicals, dyestuff, agrochemicals, perfumery and flavour chemicals. Synergetic combinations of various heteropoly acids with inorganic supports as nanocatalysts have been successfully developed and evaluated in a number of industrially important reactions [3–17].

Heteropoly compounds are condensates of different oxyacids. Among many solid acid systems, heteropoly acids (HPAs) with Keggin anion structures have received the most attention due to their facile preparation and strong acidity. Extremely low surface area, poor stability and rapid deactivation are the major problems associated with heteropoly acids. Dodecatungstophosphoric acid (DTP) is the most stable among all HPAs and is commonly used for acid catalysis since it possesses the highest Bronsted acidity. The structure has a net (−3) charge, which requires three cations to satisfy the electro neutrality. If these cations are proton, the material functions as a Bronsted acid catalyst [3,18–20]. Attempts have been made to improve the efficiency of the HPAs by supporting on various high surface area inorganic supports and the replacement of protons with alkali metal salts.

Cesium salts of dodecatungstophosphoric acid (DTP) have been reported as superior catalysts than DTP itself, but the resulting $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (Cs-DTP) is very fine and separation of these

---

[☆] This forms part of the Catalysis Society of India Eminent Scientist Award Lecture.

[*] Corresponding author. Tel.: +91 22 24102121; fax: +91 22 2414 5614.
E-mail addresses: gdyadav@yahoo.com, gdyadav@udct.org (G.D. Yadav).

0920-5861/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2008.04.013

Nomenclature

a_P	solid–liquid interfacial area (cm^2/cm^3 of liquid phase)
A	reactant species A, benzyl chloride
AS	chemisorbed A
B	reactant species B, biphenyl
BS	chemisorbed B
C_A, C_B	concentration of A and B (mol/cm^3)
C_{A0}, C_{B0}	initial concentration of A and B (mol/cm^3)
C_{AS}, C_{BS}	concentration of A and B at solid (catalyst) surface (mol/g cat)
C_E, C_W	concentration of E and W (mol/cm^3)
C_S	concentration of vacant sites (mol/g cat)
C_t	total concentration of the sites (mol/g cat)
C_{WP}	Weisz–Prater constant
C_{WS}, C_{ES}	concentration of W and E at solid (catalyst) surface (mol/g cat)
d_P	diameter of catalyst particle (cm)
D_{AB}	diffusion coefficient of A in B (cm^2/s)
D_{BA}	diffusion coefficient of B in A (cm^2/s)
D_e	effective diffusivity (cm^2/s)
E	benzylbiphenyl
ES, WS	chemisorbed E and W
k_{R2}	reaction rate constant (cm^6/g cat/mol/s)
$k_{SL\text{-}A}$, $k_{SL\text{-}B}$	solid–liquid mass transfer coefficients (cm/s)
k_2	dual site surface reaction rate constant (g cat/mol/s)
K_A, K_B	chemisorption equilibrium constant for A and B on catalyst surface (cm^3/mol)
K_E, K_W	chemisorption equilibrium constant for E and W on catalyst surface (cm^3/mol)
M	C_{B0}/C_{A0}
r_{obs}	observed rate of reaction (mol/g cat/s)
S	vacant site
Sh	Sherwood number
t	time (s)
w	catalyst loading (g/cm^3 of liquid phase)
W	hydrogen chloride
X_A	fractional conversion of A

Greek letters

ε	porosity
ρ_p	density of catalyst particle (g/cm^3)
τ	tortuosity

particles from reaction mixture still remains a problem [21]. Recently our group has successfully incorporated $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ on to K-10 clay by in situ generation of this salt in K-10 clay [11–15]. The catalyst was found to be highly active to many industrially important reactions. As an extension to our earlier research work and to increase the surface area of the catalyst, it was thought to incorporate salt of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ in to highly ordered hexagonal mesoporous silica (HMS).

Benzylbiphenyls, particularly 4-benzylbiphenyl, are mainly used as the components of thermal recording materials and also in the field of electrophotographic photoreceptors [22,23]. Thus it was thought worthwhile to investigate the synthesis of benzylbiphenyl using cesium substituted dodecatungstophosphoric acid supported on hexagonal mesoporous silica (20% w/w $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/HMS) as a catalyst, including the characterization and kinetic modeling and the findings are reported in this paper.

2. Experimental

2.1. Chemicals

The following chemicals were procured from firms of repute and used without further purification: biphenyl, benzyl chloride, cyclohexane, cesium chloride, dodecatungstophosphoric acid, ethanol (S.D. Fine Chem. Ltd., Mumbai, India), hexadecyl amine (Spectrochem. Ltd., Mumbai, India), tetraethyl orthosilicate (Fluka, Germany).

2.2. Catalyst synthesis

Hexagonal mesoporous silica was prepared as follows. 5 g hexadecyl amine was dissolved in 41.8 g of ethanol and 29.6 g of distilled water to which 20.8 g of tetraethyl orthosilicate was added under vigorous stirring. The addition of ethanol improved the solubility of the template. The mixture was aged for 18 h at 30 °C. The clear liquid above the white colored precipitate was decanted and the precipitate HMS was dried on a glass plate. The template was removed by calcining the resulting material at 550 °C in air for 3 h [24].

The catalyst was prepared by incipient wetness technique. 10 g of precalcined HMS was dried in oven at 120 °C for 3 h of which 8 g were weighed accurately. 0.2808 g (1.671×10^{-3} mol) of CsCl was weighed accurately and dissolved in 10 ml of methanol. This volume of solvent used was approximately equal to the pore volume of the catalyst. The solution was added in small aliquots of 1 ml each time to the silica molecular sieve with constant stirring with a glass rod or kneading it properly. The solution was added at time intervals of 2 min. Initially on addition of the CsCl solution to HMS was in powdery form but on complete addition it formed a paste. The paste on further kneading for 10 min resulted in a free flowing powder. The resulted material was dried at 120 °C for 3 h for the removal of solvents. This then was further subjected to impregnation by an alcoholic solution of 2 g (6.688×10^{-4} mol) of dodecatungstophosphoric acid (DTP) in 10 ml of methanol. The solution was added to the treated HMS by following the above procedure. The preformed material was dried in an oven at 120 °C for 3 h and then calcined at 300 °C for 3 h. The catalyst was found to possess highest activity when calcined at above-mentioned temperature.

2.3. Catalyst characterization

Infrared spectra of the samples pressed in KBr pellets were obtained at a resolution of 2 cm^{-1} between 4000 and 400 cm^{-1}. Spectra were collected with a Perkin-Elmer instrument and in each case the sample was referenced against a blank KBr pellet. Surface area measurements and pore size distributions analysis were done by nitrogen adsorption on Micromeritics ASAP 2010 instrument at an adsorption temperature 77 K, after pretreating the sample under high vacuum at 300 °C for 4 h. Powder X-ray diffraction (XRD) patterns were obtained using Cu Kα radiation ($\lambda = 1.540562$). Samples were step scanned from 5 to 45 in 0.045 steps with a stepping time of 0.5 s. The elemental composition of HMS and 20% (w/w) $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/HMS were obtained by Energy Dispersive X-ray Spectroscopy (EDXS) on KEVEX X-ray spectrometer. Scanning electron micrographs of HMS