Applied Catalysis A: General 452 (2013) 57–63

Contents lists available at SciVerse ScienceDirect

Applied Catalysis A: General

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

Modified polystyrene anion exchange resins with long chain alkyl groups to enhance the aldolization reaction selectivity

Jiexiang Wang[a], Qiang Wang[a], Yu Deng[a], Yunhua Li[a], Bing H. Chen[a,*], Ruyun Zhang[b]

[a] *Department of Chemical and Biochemical Engineering, College of Chemistry and Chemical Engineering, National Engineering Laboratory for Green Chemical productions of Alcohols-Ethers-Esters, Xiamen University, Xiamen 361005, China*

[b] *Department of Environmental and Biochemical Engineering, Wuhan Vocational College of Software and Engineering, 177 Guang-Gu Avenue, Wuhan 430205, China*

ARTICLE INFO

Article history:
Received 11 August 2012
Received in revised form
19 November 2012
Accepted 23 November 2012
Available online 6 December 2012

Keywords:
Solid base
Aldol condensation
Anion exchange resin
4-Hydroxy-2-butanone

ABSTRACT

The aldolization of formaldehyde and acetone to form 4-hydroxy-2-butanone over anion exchange resins with and without modifications is investigated in this work. Attempts such as surfactants addition and Soxhlet extraction are taken aiming to improve the aldolization selectivity thus the product yield. Subsequently, resins grafted long alkyl chains intrigue us for its steric hindrance effect and the synergic effect of weak and strong basic sites. Two types of modifications are carried out (1) one long alkyl chain on the copolymer tertiary amine via Menshutkin N-alkylation reaction; (2) two long alkyl chains: one on polystyrene aromatic ring through Friedel–Crafts alkylation under the circumstances of tertiary amine and the other on the copolymer tertiary amine using the Menshutkin N-alkylation reaction. The reaction results indicate that the yield for 4-hydroxy-2-butanone can be increased from 44.3% to around 50% for the resin with one long alkyl chain (the first case), while this can achieve up to 71.3% for the resin with two long alkyl chains.

1. Introduction

Aldol carbon–carbon addition together with Friedel–Crafts acylations and the Beckmann rearrangements under mild conditions were considered as the most important but challenges green chemical reactions [1,2]. The simplest aldol reaction could be the condensation of acetone and formaldehyde to produce 4-hydroxy-2-butanone, from which often then follows a subsequent dehydration to get methyl vinyl ketone, with a yield of less 60% in liquid phase homogenous catalytic reactions [3–5], actually using NaOH as catalyst in commercial process. This reaction seems to be more difficult to have higher yield than other analogous reactions, such as the aldolization of acetone and benzaldehyde [6–8], mainly due to self-polymerization of acetone and other side reaction under the presence of liquid alkali.

Similar to other catalytic reactions, using heterogeneous catalysts are the tendency for aldol condensation under the consideration of environmental issues and taking the advantages of simplicity of separation and better product quality. Several solid catalysts for this reaction were developed in the literatures, for instance, modified hydrotalcites [9], KF/Al_2O_3 [10], SnO_2 [11], fluoro tetrasilicic mica [12], $Mg_3(OH)_4Si_4O_5$ [4], MgO [13], vanadium phosphate [5], and anion-exchange resins [14]. Among these progresses, simple amines and diamines, especially proline [3,15] and weak basic anion ion exchange resins [10,16] have been widely recognized as effective catalysts for direct aldol reactions. Besides, accompanied with the green chemistry principles voice growing, works focused on polystyrene-supported proline [17,18] were reported on purpose of taking the advantages of both polymer and amine as catalysts. Compared to sophisticated immobilization strategies and the fragility of industrial applications of using proline, ion exchange resins are superb for the simplicity, easy to use and recycle, low cost as well as good modularity-proper combination of the resin type and immobilization strategy allowing a systematic design of new heterogeneous catalysts [17].

In order to increase the catalytic activity, which generally related to and limited by the carrier's solubility, works for polymer-supported catalysts modifications often focused on copolymerizing soluble materials [19–22] such as polyethylene glycol (PEG) or crown-ethers, while long alkyl chain addition normally acted as functional spacer groups [18,23,24].

In addition, the microenvironment of the polymer support played a crucial role in controlling the reaction's selectivity through adjusting the diffusion. Kouzu et al. [25] pointed out that

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[*] Corresponding author. Tel.: +86 592 2185253; fax: +86 592 2184822.
E-mail address: chenbh@xmu.edu.cn (B.H. Chen).

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http://dx.doi.org/10.1016/j.apcata.2012.11.028

gelular resins were catalytically superior to macro resins, due to the larger number of the catalytical acidic site. However, the internal mass transfer was slower for the gelular resins than that of the macro-reticular resins. Furthermore, Rios et al. [26] mentioned that polystyrene-based resins with a DVB content higher than 8% are too crosslinked to allow the contacts between the epoxide and the inner acid sites. Xu et al. [27] synthesized a nanostructured solid acid resin possessed a higher catalytic activity in the second step of the formation of dioctyl phthalate from phthalic anhydride than Amberlyst^{TM}-15. Wu and Lin [28] pointed out that the immobilized chloride density (active site) in the resins was decreased with the increasing carbon number of tertiary amines. However, the reactivity of the catalyst was increased with increasing carbon number of tertiary amine.

In this work, the aldolization selectivity was focused by bringing the conception of steric hindrance effects where polystyrene type ion exchange resin was modified with long alkyl chains around the polystyrene aromatic ring as well as active amine groups. Accordingly a long chain acyl group was directly introduced onto the polystyrene aromatic ring and/or tertiary amine through the Menshutkin N-alkylation and Friedel–Crafts alkylation reactions. Although ion exchange resins have been used for alkaline-catalyzed reactions [12,29,30], to the best of our knowledge, the direct modifications of the commercial tertiary amine resins, particularly introducing one or two long akyl chains onto selected position to improve the catalytic activity/selectivity has rarely been reported. As approximately 8% solid base catalysts, a large proportion of them is resin-based catalysts, are being used in the industrial applications of solid acid–base catalytic reactions [31], the attempt of this work has a great significance to expand the applications of resin especially polystyrene type catalysts.

2. Experimental

2.1. General

The polystyrene resins were supplied in the chloride form by Nankai Hecheng Co. Ltd. in China. In this work, three kinds of resins denoted as D27, D301 and D296 corresponding to strong acid, weak basic and strong basic macro resins were selected and used. The reason for choosing these three type of polystyrene resins (not gel resins) was based on the fact that macro resins normally have relatively predominant mechanical strength and chemical stability, these are the favorite properties for industrial applications. Other commercial reagents used in this work were purchased in analytical pure generally from China Sinopharm Chemical Reagent Co. Ltd. and used as received unless otherwise stated.

2.2. Catalysts pretreatment and modification

2.2.1. Resins pretreatment

The resins need pretreatments for impurity removal before they can be used as the modification substrate. The resins were firstly washed with 5 wt.% HCl and 1 M NaOH in sequence to get rid of the impurity. Each step immediately followed deionized water washing until neutral. Finally, the resin was washed by THF and then dried at 50 °C for 4 h.

2.2.2. Menshutkin N-alkylation

The Menshutkin N-alkylation reaction to add alkyl group on copolymer tertiary amine is shown in Fig. 1a. The dried resin D301 (2.5 g) was swelled for 2 h in the different selected solvent (25 mL), which could be one of those listed here: 1,2-dichloroethane (EDC),

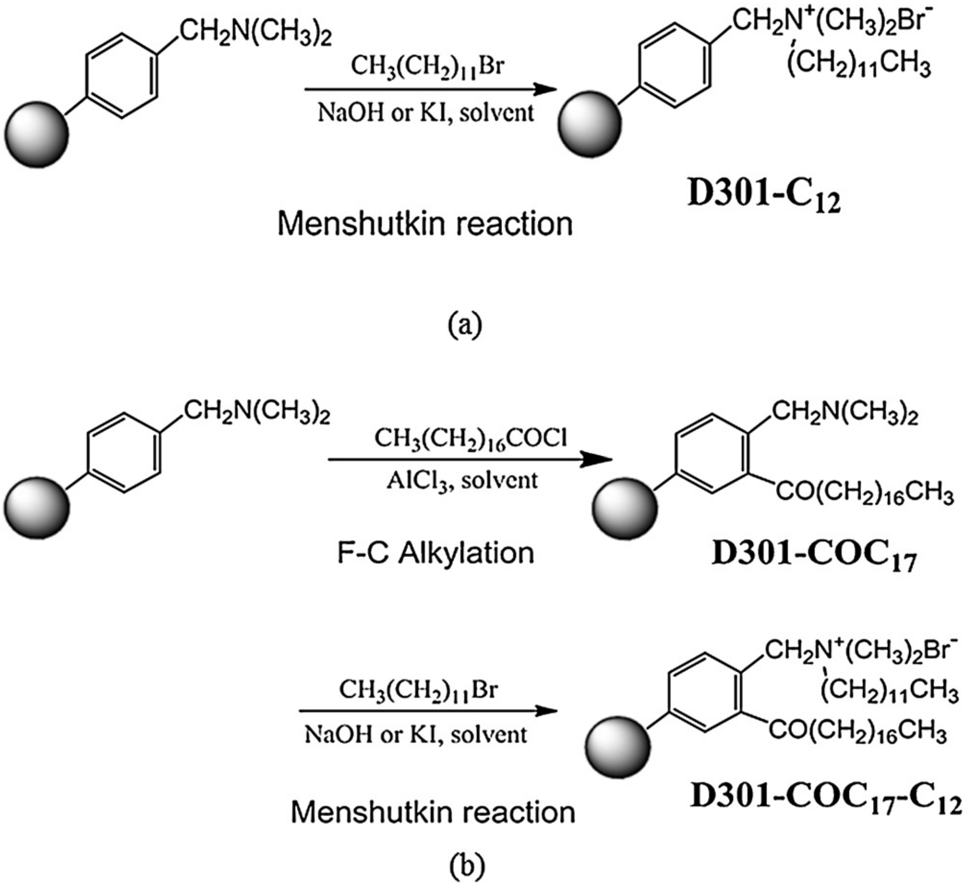

Fig. 1. The reactions used to modify resin D301 adding long alkyl groups (a) Menshutkin N-alkylation and (b) the Friedel–Crafts alkylation follows Menshutkin N-alkylation.