Chemical Engineering and Processing 64 (2013) 48–56

Contents lists available at SciVerse ScienceDirect

Chemical Engineering and Processing: Process Intensification

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

Enhancing p-xylene productivity for disproportionation of toluene in microstructured reactors

Brishti Mitra [1], Deepak Kunzru *

Department of Chemical Engineering, Indian Institute of Technology Kanpur, Kanpur 208 016, India

ARTICLE INFO

Article history:
Received 31 March 2012
Received in revised form 17 October 2012
Accepted 21 October 2012
Available online 28 November 2012

Keywords:
Monoliths
Washcoating
Toluene disproportionation
Washcoat thickness
p-xylene productivity

ABSTRACT

Microstructured monolith reactors washcoated with ZSM5 and La_2O_3-loaded ZSM5 (LaZSM5) were used for disproportionation of toluene for studying the effect of washcoat thickness on reactor productivity and yield of the commercially important p-xylene isomer. The toluene conversion and p-xylene yield in the ZSM5 washcoated monolith reactor was superior to that in a packed bed reactor using ZSM5 pellets. Modification of the surface properties of ZSM5 due to addition of La_2O_3 reduced the toluene conversion but resulted in a substantial enhancement in p-xylene yield. The decrease in catalytic activity and p-xylene yield with increase in washcoat thickness was attributed to the lengthening of the diffusional path length. The reactor productivity was highest with thin washcoats and low conversion on La_2O_3-loaded ZSM5 washcoated monoliths. The advantage of higher p-xylene productivity using monoliths is offset by the increase in the cost of recycling unreacted toluene.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Microstructured reactors are frequently used for process intensification. Monoliths, a class of microstructured reactors, have narrow, straight, parallel channels with cell density varying between 100 and 1200 cells per square inch [1]. The catalyst in a monolith reactor is located as a thin layer on the walls of the monolith, and typically the washcoat thickness is less than 100 μm. This thin washcoat helps in reducing the diffusional resistance in the catalytic layer thus enhancing the activity and altering the selectivity of the catalyst [2]. Because of the straight channels, the pressure drop in monoliths is significantly lower in comparison to packed bed reactors. In monolith reactors it is, thus, possible to simultaneously operate with a low pressure drop and high catalyst effectiveness [3].

The catalyst can be deposited on the walls of the monolith channels by different methods such as hydrothermal synthesis, sol–gel deposition, slurry washcoating etc. [4,5]. Amongst these, the slurry washcoating method allows direct coating with readymade catalysts and affords better control of the thickness of the catalyst layer. There are some studies on the effect of washcoat thickness on activity and selectivity of monolith catalysts. Rebrov et al. [6] compared the performance of CeZSM-5 coated plate type microreactors with internal recycle type Berty reactors containing CeZSM-5 pellets for selective catalytic reduction of NO with NH_3. Under similar conditions, higher reaction rate was observed for the microreactor owing to the absence of mass transfer limitations and the increase in the use of the internal surface of the catalyst. Kapteijn et al. [7] obtained an improvement in the C_{5+} selectivity and olefin/paraffin ratio for the Fischer–Tropsch process using thin washcoats up to 50 μm. For the selective hydrogenation of benzene to cyclohexene on Ru/Al_2O_3 on cordierite monoliths, Zhao et al. [8] reported a sharp decrease in cyclohexene selectivity from 60.3 to 30.8% with an increase in washcoat thickness from 7 to 19 μm. Metkar et al. [9] studied the effect of washcoat thickness on selective catalytic reduction of NO with NH_3 on Fe/ZSM5 monoliths. They observed that washcoat diffusion limitations exist in Fe/ZSM5 monoliths at temperatures higher than 573 K and the conversion on the monolith with 11 wt.% loading was higher than that on a monolith with 21.7% loading.

p-Xylene, a raw material for making terephthalic acid, can be produced by the disproportionation of toluene using solid acid catalysts such as zeolites [10–13]. The composition of xylene isomers obtained in a packed bed reactor is close to the equilibrium value (25.6% o-xylene, 51.3% m-xylene and 23.1% p-xylene at 800 K) [10], while the worldwide market demand is roughly in the ratio: 18% o-xylene, 2% m-xylene and 80% p-xylene [13]. As the expected average market growth rate of p-xylene from 2010 to 2015 is ~4.6% [14], the p-xylene produced industrially is below the market demand. Consequently, improving the yield of p-xylene is one of the major challenges of this process. Previous studies have shown that p-xylene selectivity in packed beds can be improved by modifying

* Corresponding author. Tel.: +91 512 2597193; fax: +91 512 2590104.
E-mail addresses: brishti_mitra@hotmail.com (B. Mitra), dkunzru@iitk.ac.in (D. Kunzru).
[1] Present address: Department of Chemical Engineering, University Institute of Engineering & Technology, CSJM University, Kanpur 208 024, India.

0255-2701/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.cep.2012.10.016

the zeolite with additives such as boron, magnesium, phosphorous, calcium, lanthanum or cerium oxides, coke or silica [12,15,16]. The enhancement in p-xylene selectivity was, however, accompanied by a decrease in the toluene conversion, leading to low p-xylene yields. Our earlier studies [17,18] have shown that, in comparison to pellets and powder catalysts, the p-xylene selectivity was higher on zeolite washcoated monoliths. Moreover, the selectivity could be further enhanced by washcoating with metal oxide modified ZSM5. The highest selectivity was obtained with La_2O_3-loaded ZSM5.

In the above-mentioned studies, the emphasis was on improving the selectivity to p-xylene. However, industrially, it is more relevant to enhance the yield of p-xylene and the reactor productivity. The objective of this study was to investigate the effect of washcoat thickness on the reactor productivity and yield of p-xylene for the disproportionation of toluene on ZSM5 and La_2O_3-loaded ZSM5 (LaZSM5) washcoated ceramic monoliths.

2. Experimental

The monolith catalysts were prepared by coating small pieces (diameter: 19.5 mm, length: 30 mm) of 400 cpsi cordierite monoliths by the slurry washcoating procedure. The details of washcoating have been presented earlier and are only briefly summarized here [18]. The cordierite pieces were coated by immersing these in slurries of ZSM5 (NH_4 form, Si/Al = 34) or LaZSM5 powder of 30 wt.% concentration. The particle size of the zeolite powder was reduced to 2–3 μm from an initial size (d_{50}) of 5.3 μm by wet ball milling. This powder was mixed with demineralized water in a ball-mill to obtain a stable uniform slurry of pH ~7. The monolith sections were pretreated at 873 K for 2 h to remove adsorbed impurities and then vertically immersed in the slurry for 3 min each. The pieces were taken out and the excess slurry removed by blowing compressed air at constant speed through the channels by means of an air knife. The excess slurry was removed from all the channels simultaneously in order to achieve uniformity of coating in the channels. They were dried at 383 K for 2 h and weighed. The washcoating procedure was repeated to achieve washcoat loadings between 10 and 60 wt.%. The zeolite loading is estimated as the weight of zeolite coated per unit weight of the bare monolith. The washcoated monoliths were finally calcined at 823 K for 4 h at a heating rate of 2 K/min. In case of the LaZSM5 coated monoliths, the 10 wt.% La_2O_3 loaded ZSM5 powder was prepared by wet impregnation method prior to washcoating. The La/Al ratio in the prepared LaZSM5 powder was 0.61.

The adherence of the ZSM5 and LaZSM5 washcoat was determined by measuring the weight loss on subjecting the monoliths to ultrasonication in acetone for 1 h at 33 kHz. The morphologies of the washcoated monoliths were examined by means of a scanning electron microscope (Model No JEOL 840A) operating at an accelerating voltage of 20 keV. The XRD patterns of the ZSM5 and LaZSM5 powders were obtained on a Panalytical (Netherland) X'pert PRO MRD X-ray diffractometer using Cu Kα radiation. The final lanthanum content in the LaZSM5 powder was estimated by inductively coupled plasma optical emission spectroscopy in Thermo Scientific X Series 2 ICP-MS analyzer. The BET surface area and pore volume of ZSM5 and LaZSM5 powder was determined by N_2-physisorption using a Quantachrome Autosorb-1C system. Degassing of the samples was carried out at 623 K for 8 h prior to measurement. The acidity of the ZSM5 and LaZSM5 catalysts were measured by temperature programmed desorption (TPD) of ammonia using a Micrometrics Pulse Chemisorb 2720 unit.

The toluene disproportionation reaction was conducted in a vertical stainless steel downflow reactor (diameter: 19.7 mm, length: 320 mm) at atmospheric pressure and a temperature range of 573–773 K. The details of the experimental set-up are available elsewhere [16]. Liquid toluene was vaporized in a preheater (473 K), mixed with hydrogen (inlet toluene partial pressure = 33.44 kPa) and introduced into the monolith reactor. The catalyst washcoat was pretreated in nitrogen at 823 K for 2 h before exposing it to the reactant. The W/F_{Ao} was varied between 5 and 20 g h/mol. Reactions were carried out for monoliths with different average washcoat thickness for both ZSM5 and LaZSM5.

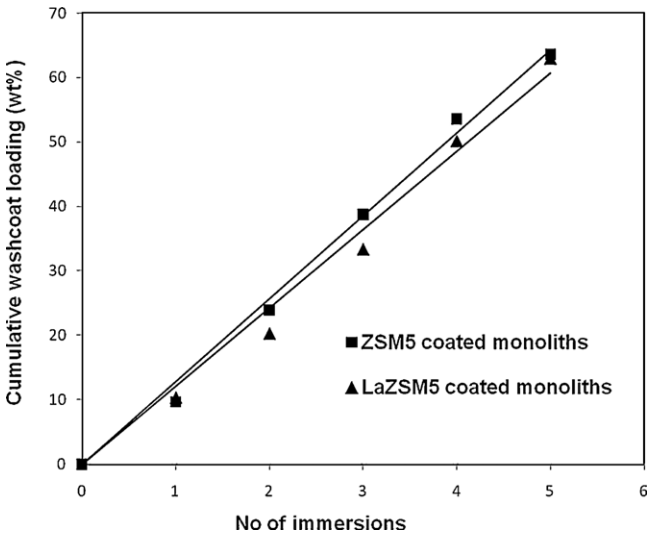

Fig. 1. Variation of cumulative zeolite loading with number of immersions.

3. Results and discussion

Monolith reactors coated with ZSM5 and LaZSM5 were prepared by the slurry washcoating method. This is a simple procedure which allows for washcoats of any desirable thickness. Previous studies have reported that uniform, reproducible and stable washcoats on the walls of the monolith channels can be obtained by using small particle sizes, slurries of low to medium concentration and multiple immersions [19,20]. The particle size of the powder used for preparing the slurry was maintained between 2 and 3 μm so that most of the coating is deposited on the channel walls and the maximum washcoat loading is independent of the micro-pore volume of the monolith [4]. The use of a slurry concentration of 30 wt.% resulted in uniform coating in the monolith channels without any plugging of channels.

As shown in Fig. 1, the cumulative loading achieved on the monoliths increased more or less linearly with the number of

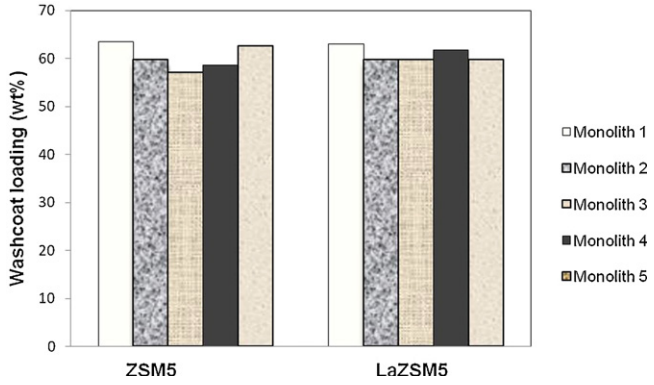

Fig. 2. Variation of washcoat loading for different monoliths (slurry concentration = 30 wt.%).

Download English Version:

https://daneshyari.com/en/article/687163

Download Persian Version:

https://daneshyari.com/article/687163

Daneshyari.com