



Dramatic change of methylenedianiline activity and selectivity in different pore geometry of zeolites



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ABSTRACT

The activity and isomers selectivity of the synthesis of methylenedianiline (MDA) from aminal on the various zeolites with different topology structure have been investigated. The poor activity in H-ZSM-5 and H-mordenite contributed to the narrow porous and scarcity of pore intersections or supercages in the MOR structure, respectively. H-beta zeolite shown high activity for the rearrangement reaction can take place in the pore intersections of zeolite BEA. For the dealuminated USY catalysts, the highest activity and selectivity to 4,4'-MDA is attributed to the rearrangement of aminal in the supercages and mesoporous, which the mass transport limitation can be overcome.

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1. Introduction

As an important raw material for production of the polyurethane, methylenedianiline (MDA) is produced by the reaction of formaldehyde with aniline in presence of HCl [1,2]. However, use of mineral acid leads to several problems like, corrosion, difficulty in separation and recovery of products, etc. Many efforts have been devoted to replace the mineral acid by more safe and environmentally friendly catalyst. Hence, the several patents concerning MDA production over solid acid catalysts with hydrochloric acid, such as ion-exchanged resins, clays and zeolite have been disclosed [3–5]. Among them, ion-exchange resins have shown excellent selectivity to the para-isomer, although their activity per gram of catalyst is low and regeneration of used catalyst has not been solved.

For its acidity and structure can be tailored, several studies on the use of zeolites in the production of MDA have been published. Apart from MFI-, BEA-, FAU and MOR-type zeolites with varying Si/Al ratio, the delaminated materials, such as ITQ-2, ITQ-6, ITQ-18 and MCM-36, the dealuminated Y-types and the desilicated BEA-types were applied. Furthermore, the optimized process conditions to accomplish the manufacture of crude MDA to industrial production specifications were provided both in batch and continuous flow reactor systems [6–12].

Pore size is the key factor for zeolites to function as shape selective catalysts. Besides reactant and product selectivity, transition state shape selectivity has gained increasing attentions because the intermediate species formed at the transition state are critical to elucidate a reaction mechanism [13–16]. As rearrangement limitation of the intermediate species in the microporous is believed to be the limiting factor for the activity and selectivity of catalyst, several zeolites with different pore structures were proposed as catalysts. In the present paper, the activity and selectivity of zeolites have been explored to identify the physicochemical properties of the catalyst. The dramatic changes in the MDA yield and isomers selectivity were observed among these zeolites. On H-ZSM-5 and H-Mordenite

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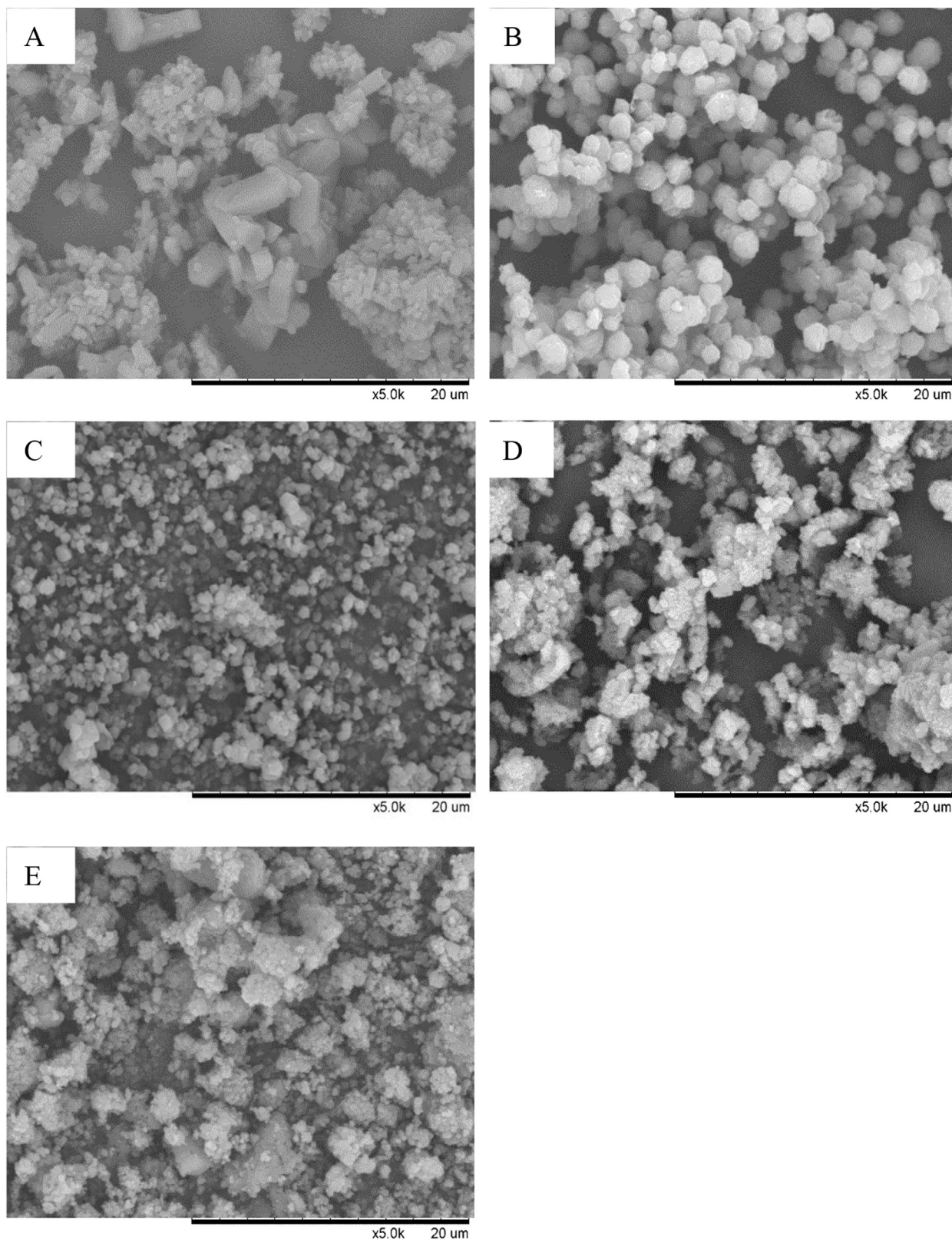


Fig. 1. SEM images of zeolites: (A) H-ZSM-5, (B) Na-Y, (C) USY, (D) H-Mordenite and (E) H-beta.

zeolite, essentially low MDA was produced. While on Na-Y and H-beta zeolites, higher activity of MDA was formed. The USY zeolites, which modified by hydrothermal treatment and acid leaching, shown the highest activity and 4,4'-MDA isomer selectivity.

2. Experimental

Aniline and ca. 37% formaldehyde aqueous solution were obtained from Aldrich. Aniline is purified by the distillation over

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