



# Preparation of amorphous silica-alumina using polyethylene glycol and its role for matrix in catalytic cracking of *n*-dodecane



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## ABSTRACT

For catalytic cracking, mixed catalysts of zeolite as a main catalyst and matrix with large pore capable of reacting large molecules, which cannot enter into the tiny pore of zeolite, are used. Hence the selection of matrix is quite important for the activity and product selectivity of catalytic cracking. Therefore, this paper reports the preparation and the analysis of reactivity of amorphous silica-alumina as a matrix, which has not been studied in catalytic cracking extensively and academically.

Amorphous silica-alumina matrices were prepared by the sol-gel method using polyethylene glycol (PEG) as an organic template. Further, catalytic cracking of *n*-dodecane was performed in order to explore their reactivity as matrices. Silica-aluminas prepared had only moderate amounts of mesopore and larger amounts of micropore, of which the pore size was larger than that of zeolite. The surface area and the pore volume of prepared silica-aluminas increased with increasing the amount of PEG added. The amounts of  $\text{NH}_3$  desorbed and the conversions of *n*-dodecane using mixed catalysts with zeolite also increased with increasing the amount of PEG added. The results suggested that larger amounts of micropores as well as moderate amounts of mesopores would affect the higher conversions. The conversion increased, gasoline fraction decreased and gas fraction increased with decreasing particle size of silica-aluminas. The ratio of multi-branched products to single-branched products (multi/single ratio) decreased when the conversion increased by increasing PEG content. The result indicates that although the addition of PEG increased the surface area and the activity, sizes and amounts of mesopores prepared using PEG were not enough large to increase multi-branched products improving the selectivity.

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## 1. Introduction

Catalytic cracking is a significant process to convert from lowly demanded vacuum gas oil (VGO) or atmospheric residue (AR) to highly demanded gasoline or propylene. Recently, the increase of heavy oil fraction and the rise in oil price require the efficient process of the conversion. There are some techniques to overcome the problem, and catalytic process is one of the most hopeful techniques. The developing and modifying zeolites as a main catalyst have been extensively studied by various preparation methods and by exploring the reactivity. Further, since zeolite consists of the micropores, many researchers have tried to introduce mesopores in zeolite to eliminate the problem of slow diffusion of the heavy oils. Siddiqui et al. investigated the effect of addition of newly developed TNU-9, SSZ-33 and ZSM-5 with mesopores, and compared them with common ZSM-5 in catalytic cracking of VGO using USY FCC

catalyst [1]. Lately, many works have been carried out for ZSM-5 [2–13], and, on the other hand, other zeolites such as mordenite [14,15], MCM-22 [16], beta [15,17], ITQ [18], MCM-68 [19] and ZSM-12 [20] have also been studied. Wei et al. prepared ZSM-12 using carbon black and found the higher ratio of  $\text{C}_8$ ,  $\text{C}_9$  and blanch products to  $\text{C}_3$  and  $\text{C}_4$  in the reaction of tridecane compared to conventionally prepared ZSM-12 by the creation of mesopores with crystalline structure [20]. On the other hand, Groen et al. tried to introduce mesopores using alkali treatment for desilylation for MFI, BEA, MOR and FER zeolites [21]. Further, the combinations of the zeolites with different pore sizes have been investigated to prepare the catalyst with high conversion efficiency [22–31].

The other important factor characterizing catalytic cracking is the matrix. As indicated above, zeolites commonly contain micropores and thus diffusion of big molecules of VGO and AR greatly influences the catalytic cracking. Therefore, matrices usually applied contain relatively large pores such as silica-alumina. The matrix accelerates the diffusion of substances because of large pore size and distributes zeolites properly resulting in controlling acid sites concentration. Thus, the structure and activity of the

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**Table 1**  
Composition of chemicals used to prepare amorphous silica-aluminas using PEG as an organic template and mixed catalysts with zeolite.

Catalyst	PEG		Composition (wt%)		
	Ave. MW	Amount (g)	SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	Zeolite	Binder
P30	400	7.0	100	0	0
P30(sp)	400	7.0	100	0	0
P30(6000)(sp)	6000	7.0	100	0	0
MAT-P30	400	7.0	56	26	18
MAT-P30(sp)	400	7.0	56	26	18
MAT-P30(6000)(sp)	6000	7.0	56	26	18
P183	400	42.6	100	0	0
P183(sp)	400	42.6	100	0	0
P183(6000)(sp)	6000	42.6	100	0	0
MAT-P183	400	42.6	56	26	18
MAT-P183(sp)	400	42.6	56	26	18
MAT-P183(6000)(sp)	6000	42.6	56	26	18

sp, small particle.

matrix play an important role in catalytic cracking as well [32–45]. Hence, the control of the structure and reactivity of the matrix as well as stability and activity of zeolite are indispensable in order to develop new catalysts for catalytic cracking. However, relatively few reports on the academic study on matrix have been carried out in comparison with those of zeolites [32–34,42–44]. We previously reported the preparation of various matrices and investigated catalytic cracking of saturated hydrocarbon [32–39]. In specific, we used malic acid as organic template or reinforced structure by post treatment with tetraethyl orthosilicate (TEOS) for the preparation of silica-alumina mixed with zeolites as catalysts resulting in superior activity and selectivity.

In this study, polyethylene glycol (PEG) was used as an organic template [46,47] to prepare mesopores in amorphous silica-alumina and to clarify the influence of the amount of PEG added, the average molecular size of PEG and the particle size of silica-alumina on the characteristics of silica-alumina and the catalytic cracking reactivity.

## 2. Experimental

### 2.1. Preparation of amorphous silica-alumina derived by sol-gel technique using PEG as organic template

Analytical grade and commercially available tetraethyl orthosilicate (TEOS, Nacalai Tesque Co. Ltd.) of 23.304 g and aluminum tri-sec-butoxide (ASB, Tokyo Kasei Kogyo Co. Ltd.) of 1.724 g, ethanol (GR, Nacalai Tesque Co. Ltd.) and ion-exchange water (prepared with Auto still AW 200, Yamato Co. Ltd.) of 8.071 g were used as starting materials. Tartaric acid (TA, Nacalai Tesque Co. Ltd.) of 0.672 g was used for hydrolysis and polymerization catalyst. The molar ratio of TEOS:ASB:H<sub>2</sub>O:C<sub>2</sub>H<sub>5</sub>OH:TA was 1:0.06:4:7:0.04 for all the samples. PEG of 6.991 g or 41.947 g (average molecular weight = 400 or 6000, Nacalai Tesque Co. Ltd.). The catalysts prepared using these amounts of PEG were named P30 and P183, respectively, because these weights of PEG corresponded to 30% and 183% of weights of TEOS used (23.304 g), respectively. The detail flow chart for the preparation is shown in Fig. 1. Firstly, TEOS was dissolved into ethanol and stirred at room temperature for 30 min, and tartaric acid with water was dropped for 15 min. Subsequently, mixed liquid of ASB and ethanol was dropped at room temperature for 15 min and stirred for 1 h. Then, after PEG was added for 15 min and stirred for 1 h, the derived solution was further stirred at 60 °C in oil bath. After gelation, the product was dried at 60 °C for 24 h. The gel after crushed was heat-treated under 600 mL/min air flow up to 600 °C by raising temperature of 2.4 °C/min. The derived silica-alumina was pulverized by alumina mortar and pestle, and divided into four parts of less than 45, 45–75,

75–125 and 125–355, using 45, 75, 125 and 355 μm sieves. These four parts of particles were combined to prepare two groups of relatively large size particles and relatively small size particles (sp) and to investigate the effect of particle sizes of a matrix on catalytic cracking. The detail particle size distributions of silica-aluminas and mixed catalysts (see next section) in weight ratio are shown in Table 2.

### 2.2. Preparation of mixed catalyst and molding pellets

Mixed catalyst was prepared from 56 wt% amorphous silica-alumina mentioned above, 26 wt% zeolite (β-zeolite, HSZ940HOA, Tosoh Co. Ltd.) and 18 wt% alumina sol (Cataloid AP-1, Shokubaikasei Co. Ltd.) as a binder [34]. After adding proper amount of distilled water to have suitable viscosity, pellets were prepared by compressor (NP-1, Miki Ind. Co. Ltd.) and heat-treated in air at 600 °C for 3 h by elevating temperature of 3 °C/min. In naming of the mixed catalyst, MAT was put in front of P30 or P183 because P30 and P183 silica-aluminas were used as matrices in the mixed catalysts.

Table 1 summarizes all the sample names of amorphous silica-aluminas and mixed catalysts and their preparation conditions.

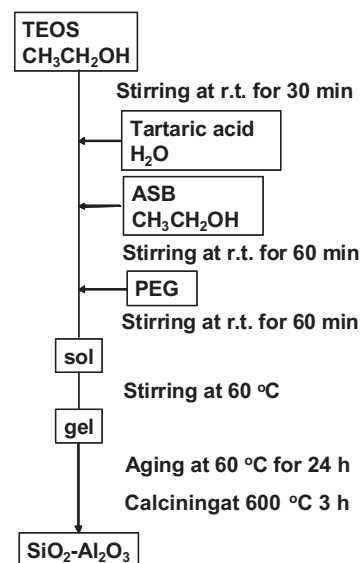


Fig. 1. Flow chart of preparation of amorphous silica-alumina using PEG as organic template.

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