



Research article

Identification of the rate-determining step for the synthesis of polyoxymethylene dimethyl ethers from paraformaldehyde and dimethoxymethane

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ABSTRACT

Polyoxymethylene dimethyl ethers (PODE_n, CH₃O(CH₂O)_nCH₃, where $n \geq 1$) are environmentally friendly diesel fuel additives because they can significantly reduce the emission of engine exhaust during combustion. It is an efficient way to synthesize PODE_n from dimethoxymethane (DMM) and paraformaldehyde (PF) over solid acid catalysts. The synthesis process consisted of two steps: the depolymerization of PF and the polymerization of PODE_n. In this work, the first step was proved to be the rate-determining step by analyzing the product distribution and the rate of reactions with and without PF. NKC-9 resins of different size were used to prove that the internal diffusion in catalyst was a key factor to affect the depolymerization process. The SO₄²⁻/TiO₂ and SO₄²⁻/TiO₂-ZrO₂ catalysts were used to further prove that the catalysts with larger pores were more active for the synthesis of PODE_n.

1. Introduction

Polyoxymethylene dimethyl ethers (PODE_n, CH₃O(CH₂O)_nCH₃, where $n \geq 1$) are a kind of ideal diesel fuel additives receiving much attention because they can significantly reduce the emission of smoke and engine exhaust during combustion [1–3]. They have many advantages over other fuel additives such as methanol, dimethyl ether and dimethoxymethane (DMM) [4,5].

The synthesis of PODE_n is a complicated process, and many works have been carried out to study the thermodynamics [6–10] and reaction kinetics [11–16]. A consensus has been reached on the thermodynamics of this process that the product distribution follows the Schulz-Flory distribution [6,8,9], and a detailed thermodynamics concerning homogenous CH₃OH, DMM, H₂O and CH₂O as reactants has been developed [10]. However, the kinetics of the process was still unclear due to the different reactants, different reaction mechanisms and different catalysts.

Terminal group suppliers, such as methanol and DMM, and methoxyl group suppliers, such as formaldehyde solution, paraformaldehyde (PF) and trioxane, are needed for PODE_n synthesis [4]. Because water produced in the system has negative effects on the PODE_n synthesis, DMM is a preferred terminal group supplier than methanol, and PF or trioxane is a preferred methoxyl group supplier than formaldehyde solution. Compared with PF, trioxane is dissolvable and has a simple

and certain structure, so it is used as methoxyl group suppliers in many researches [9,17–19]. However, PF is preferred in the industrial process because it is much cheaper than trioxane. The behaviour of PF in the reaction is so complicated and unclear that most literatures omitted it.

There are two kinds of mechanisms proposed for the reaction of PODE_n synthesis: the sequential reaction mechanism [4,6,11,20] and simultaneous reaction mechanism [8,21]. The two mechanisms were in dispute. In addition, both mechanisms only focused on the synthesis process of PODE_n, and did not include the decomposition of PF/trioxane.

The reaction is catalyzed by acid catalysts, and several kinds of homogenous and heterogeneous acid catalysts have been investigated. The behaviours of homogenous catalysts are relatively simple, and the mechanism for homogenous reaction of PODE_n synthesis is clear [21,22]. However, the mechanism for heterogeneous catalyst is still in dispute for this system [20,23,24], because the process is more complicated, involving phase change, external mass transfer, internal diffusion, adsorption, desorption and chemical reactions [7]. Heterogeneous acid catalysts are preferred for the industrial production of PODE_n because they are noncorrosive and easy to separate and reuse [12,14,25], therefore it is important to understand the mechanism and identify the rate-determining step in the heterogeneous reaction system.

In our previous work, the reaction kinetics for the production of

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PODE_n from PF and DMM were proposed [11,12], and the synergistic effect of Brønsted and Lewis acid sites on the solid acid catalyst was proved by experiments [20]. These mechanisms explained the Schulz-Flory distribution of PODE_n and the role of different acid sites. Nevertheless, in previous work the effect of depolymerization of PF was not considered in detail, and the CH₂O concentration in the PODE_n solution was simplified as a constant. Schmitz et al. [15] and Oestreich et al. [26] did detailed works of the kinetics for synthesis of PODE_n from CH₂O and methanol. They proposed a detailed kinetics involving mass transfer and reaction over the catalyst. Their work focused more on the reaction in solution, but did not study the reaction involving solid PF. This work aimed to investigate the process of PODE_n synthesis with the consideration of PF depolymerisation and identify the rate-determining step. The key factors of the catalyst affecting the rate-determining step were found out and studied, and the process intensification solution was proposed based on these results.

2. Experimental

2.1. Materials

DMM (analytic reagent grade, AR), PF (analytic reagent grade, AR) and Zirconium *n*-butoxide (> 80%, dissolved in butanol) were purchased from Alfa Aesar-Johnson Matthey. Tetrabutyl titanate (analytic reagent grade, AR) was purchased from Tianjing Yongda Chemical Reagent Co., Ltd. The NKC-9 cation exchange resins were dry resins of H⁺ type provided by Tianjin Bohong Resin Technology Co., Ltd.

PODE₃₋₄ (industrial grade, > 95%) were provided by a 10 kt/a PODE_n industrial plant in Shandong Yuhuang Chemical (Group) Co., Ltd., China, which used the technology developed by our research group. In this technology, a fluidized-bed reactor was used to produce PODE_n from DMM and PF over solid acid catalysts.

2.2. Catalyst preparation and characterizations

The NKC-9 resin catalysts of different size were used for experiment: (a) original particles, (b) powder grinded from original particles, (c) powder of (b) sieved by 200-mesh sieves, and (d) powder of (b) sieved by 300-mesh sieves. The four kinds of NKC-9 catalysts were named as N-O, N-P, N-200 and N-300. The particle size distributions of the four kinds of catalysts and the PF used in this work were characterized by Malvern laser particle size analyser (Mastersizer 3000), and the results are shown in Fig. 1.

The SO₄²⁻/TiO₂ catalyst used in this reaction was prepared by the sol-gel and impregnation methods [20]. Typically, 68.76 g of tetrabutyl titanate was mixed with 200 mL ethanol, followed by the addition of 100 mL water under vigorous stirring. The obtained precipitate was

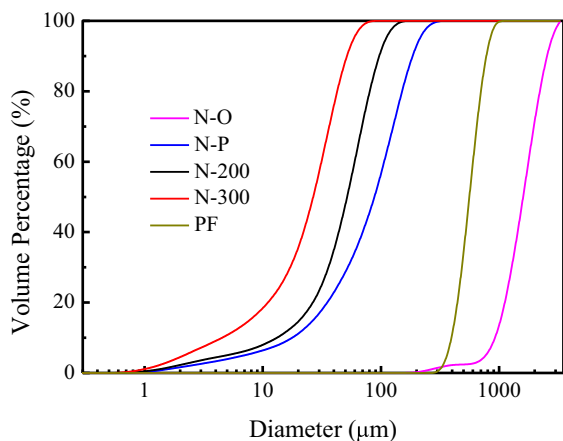


Fig. 1. Particle size distribution of NKC-9 catalysts and PF.

aged for 6 h in the mother liquid, then it was filtrated and dried at 80 °C for 12 h. The obtained powder was suspended in 0.5 mol/L (NH₄)₂SO₄ solution (15 mL solution for 1.0 g of the powder) for 2 h. The solids were then filtered, dried at 80 °C overnight and calcined at 500 °C for 6 h. The SO₄²⁻/TiO₂-ZrO₂ catalyst was prepared similarly, where half moles of tetrabutyl titanate was replaced by zirconium *n*-butoxide.

The specific surface area and pore size distribution of the catalysts were determined by N₂ adsorption-desorption with a Quantachrome autosorb iQ and AsiQwin instrument. The specific area and pore size distribution were calculated by the Brunauer–Emmett–Teller (BET) and density functional theory (DFT) methods, respectively. The concentration of Na⁺ in the solution was characterized by inductively coupled plasma mass spectrometry (ICP-MS) using a Thermo iCAP-Q equipment of ThermoFisher.

The amount of acid sites was determined by temperature-programmed desorption of ammonia (NH₃-TPD), using a Quantachrome ChemBET Pulsar TPR/TPD instrument equipped with a thermal conductivity detector (TCD). For each experiment, the sample of 150 mg was heated to 500 °C at a rate of 20 °C/min and maintained at this temperature for 1 h under He flow (30 mL/min). Then the sample was cooled down to 80 °C followed by introducing a 5% NH₃/He gas mixture (30 mL/min) for 45 min. The sample was purged with He flow of 30 mL/min at 80 °C for 15 min to remove physisorbed ammonia, and then heated to 500 °C at a rate of 5 °C/min under He flow (30 mL/min).

2.3. Reaction and analysis

The catalytic performance was evaluated in a 0.5-L stirred autoclave, as described in our previous works [4,11,20]. Firstly, the reactants were mixed and loaded into the reactor, then the reactor was sealed and heated. When the reactor temperature reached the specific value and kept stable, the catalyst was released from a fragile bottle and uniformly dispersed by stirring at 500 rpm. The effect of gas-liquid and liquid-solid mass transfer was excluded by experiments at different stirring speeds. This moment was considered as the starting time of reaction. It was proved that the effect of external diffusion had been eliminated at 500 rpm for all the catalysts used in this work. The reaction temperature was controlled with an accuracy of ± 0.5 K in steady state. The liquid phase was sampled at different reaction times for analysis.

To carry out the reaction without solid PF, NaOH was used as catalyst for the depolymerization of PF. For such an experiment, PF, DMM and 3 wt% NaOH were mixed in a hydrothermal reactor and heated at 80 °C for 2 h. The mixture was then filtrated to separate the solid NaOH and PF. To ensure the base was not dissolved in the solution, the liquid was tested by pH paper, and the results showed the pH value of the liquid was 7. The concentration of Na⁺ in the liquid was further analyzed by ICP-MS. The results showed that the concentration of Na⁺ was 1.19 ppm, confirming that little base was dissolved in the solution. After filtration, the solution containing DMM and CH₂O was added into the autoclave reactor for the catalytic reaction.

The concentrations of PODE_n were analyzed by a gas chromatography (GC, SHIMADZU GC2010 plus) using undecane as diluent. The concentration of CH₂O in solution was determined using titration by the sodium sulphite method [27,28]. The conversion of paraformaldehyde cannot be directly measured because paraformaldehyde is insoluble. In this work, the conversion of formaldehyde was determined indirectly by:

$$X_{\text{CH}_2\text{O}} = \frac{N_{\text{DMM},0} \sum_{n>1} (n-1) \cdot x_n}{N_{\text{CH}_2\text{O},0}} \quad (1)$$

where $X_{\text{CH}_2\text{O}}$ was the conversion of formaldehyde, x_n was the mole fraction of PODE_n among DMM and PODE_n in the sample, and $N_{\text{DMM},0}$ and $N_{\text{CH}_2\text{O},0}$ were the moles of DMM and formaldehyde loaded in the reactor at the beginning of the reaction, respectively.

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