

Chemical equilibrium controlled synthesis of polyoxymethylene dimethyl ethers over sulfated titania

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Abstract

The chemical equilibrium and reaction kinetic behavior in the synthesis of polyoxymethylene dimethyl ethers (DMM_n) were investigated over sulfated titania in order to reveal the decisive factor controlling the reaction. The results showed that the molar ratio of adjacent DMM_n products in equilibrium solution had the same value, which depended absolutely on the reaction temperature. Meanwhile, the reactions had the same DMM_n products distributions under varied reaction conditions. The equilibrium constants of the related step-wise reactions for DMM_n formation were equal, which were calculated based on the bulk compositions of the reaction solution. And thus, the selectivity to DMM_n was mainly controlled by the chemical equilibrium, i.e., thermodynamic control. In brief, the present results provide some guidance for future synthesis of DMM_n.

Key words

polyoxymethylene dimethyl ethers; sulfated titania; chemical equilibrium; reaction kinetic; molar ratio

1. Introduction

Polyoxymethylene dimethyl ethers (DMM_n) with the structure of CH₃–O–(CH₂O)_n–CH₃ are promising blending components for clean oils, especially for diesel fueled engines, due to their lower vapor pressures, higher oxygen contents, higher viscosities, and higher cetane numbers [1], compared with dimethyl ether (DME) [2] and methylal (DMM) [3]. In addition, DMM_n can be produced from methanol and its downstream products (formaldehyde, trioxane, DMM, etc.), thus having potential scientific values and application prospects for petrochemical and methanol industry.

Although the synthesis of DMM_n ($n > 1$) has received much attention [4–8], there is only little reports that focused on the investigation of reaction mechanism [8–11], which can provide guidance for catalyst design. In fact, the thermodynamic feasibility for DMM_n synthesis was studied from methanol, DME, formaldehyde and trioxane etc., based on

theoretical calculations [12]. Initially, Arvidson et al. [13] speculated that lithium halides might promote the thermal depolymerization of paraformaldehyde and thus increasing the yield of DMM_n in homogeneously catalyzed reactions. Burger et al. [9] investigated the chemical equilibrium and reaction kinetics of DMM_n formation from trioxane and DMM, using ion-exchange resin Amberlyst 46 as catalyst, and they suggested that the sorption processes were the rate determining steps, according to an adsorption-based kinetic mode. In addition, the DMM_n products were found to follow the Schulz-Flory distribution law [8]. Also, the elimination mechanism was proposed, in order to explain the reaction rate and kinetic model in the synthesis of DMM_n [11]. However, most of the proposed reaction models were only applied to the specific reaction systems and catalysts, and thus more additional experimental data are required to further understand the DMM_n formation processes.

We have recently proved that trioxane decomposition process was the rate-determine step in the synthesis of DMM_n

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from methanol and trioxane over the designed sulfated iron oxides [10]. In this work, the chemical equilibrium and kinetic study of DMM_n formation from dimethoxymethane (DMM) and trioxane over sulfated titania has been conducted, in order to probe the important and decisive factors involved in this reaction.

2. Experimental

2.1. Catalyst preparation

Conventionally, $\text{SO}_4^{2-}/\text{TiO}_2$ catalysts were synthesized by the two-step method as described elsewhere [10,14]. Typically, 34.38 g TBOT was mixed with 100 mL ethanol, followed by the addition of 50 mL water under vigorous stirring. The precipitate was further aged for 6 h in the mother liquid, then filtrated and washed with water, the resultant solid was dried at 373 K for 12 h. Subsequently, the precursor of titania was suspended in ammonium sulfate solution (0.5 mol/L, 15 mL for 1 g of the powder) for 1 h, filtered and dried at 373 K overnight, and then calcined at 773 K for 6 h in atmosphere.

2.2. Characterization

Power X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance X-ray diffractometer using $\text{Cu } K_\alpha$ radiation operated at 40 kV and 40 mA. X-ray photoelectron spectroscopy (XPS) was taken on an ESCALAB 250Xi spectrometer (ThermoFisher Scientific) with $\text{Al } K_\alpha$ radiation. Fourier transform infrared (FT-IR) spectra were recorded at room temperature on a Nicolet 6700 spectrometer (ThermoScientific), operating in 4000–400 cm^{-1} range with a resolution of 4 cm^{-1} .

2.3. Catalytic tests

The reaction activity tests were carried out in a 100 mL stainless steel autoclave (model parr-5500, Parr Instrument Co., Moline, IL) equipped with a mechanical stirrer, at a stirring speed of 500 rpm under the following typical reaction conditions: 10.8 g trioxane, 9.2 g DMM, 0.2 g catalyst, unless otherwise stated. The products were analyzed by a HP 7890 gas chromatograph (GC) equipped with a SE-54 capillary column (60 m \times 0.25 mm \times 0.25 μm) connected to a flame ionization detector. Meanwhile, tetrahydrofuran was used as the internal standard, the trioxane conversion (X_{TRIO}), dimethoxymethane conversion (X_{DMM}), and the products selectivity, e.g., DMM_n selectivity (S_{DMM_n} , $n > 1$) were calculated based on the total carbon atom numbers that converted (including dimethoxymethane and trioxane) [10]. And, $\text{DMM}_n/\text{DMM}_{n-1}$ ($n \geq 2$) molar ratio ($x_{n/n-1}$ for simplicity) in the final products was obtained by normalizing the DMM_n products only.

3. Results and discussion

3.1. Structural feature of sulfated titania

As shown in Figure 1(a), $\text{SO}_4^{2-}/\text{TiO}_2$ catalyst with the structure of TiO_2 anatase phase (confirmed by XRD pattern, not shown) exhibited only one peak at about 169.0 eV ($\text{S } 2p_{3/2}$), which was associated with S=O bond in sulfate species, indicating that sulfur existed in S^{6+} oxidation state [15]. Figure 1(b) shows the IR spectrum of the sample. The broad bands in the range of 500–900 cm^{-1} were ascribed to the Ti–O bonding vibrations of anatase [16], while the maxima appeared at about 590 cm^{-1} . As is well known, the peak centered at 1630 cm^{-1} was due to the bending mode of adsorbed water and the broad band centered at 3441 cm^{-1} characterized the stretching vibrations of adsorbed water and hydroxyl groups on sample surface [17]. The bands at 1389, 1206 and 1134 cm^{-1} were assigned to asymmetric stretching frequencies of S=O bond, while the bands at 1043 and 985 cm^{-1} were ascribed to symmetric stretching frequencies of S–O bonds coordinated to Ti^{4+} [18], respectively. The results were in good consistency with S 2p XPS spectrum that sulfur atoms existed in S^{6+} oxidation state and thus forming $\text{SO}_4^{2-}/\text{TiO}_2$ solid superacid.

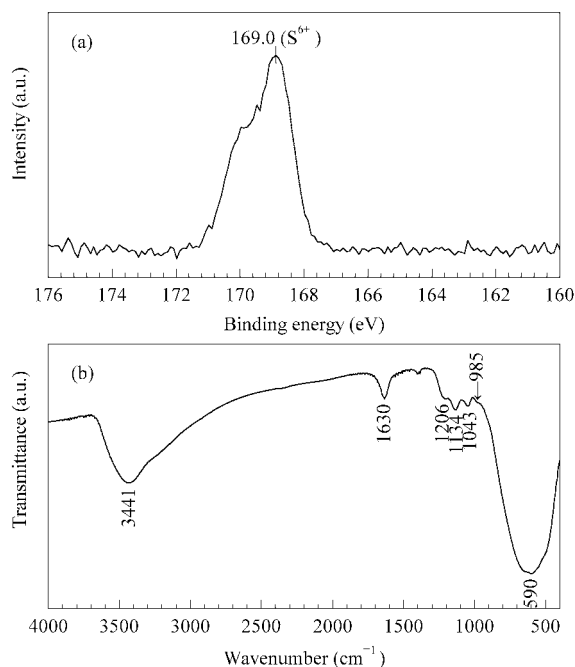


Figure 1. S 2p XPS (a) and IR (b) spectra of $\text{SO}_4^{2-}/\text{TiO}_2$ solid acid

3.2. Catalytic evaluation

3.2.1. Screening of the catalysts

Table 1 lists the catalytic performance on the synthesis of DMM_n over the typical catalysts. Pure TiO_2 exhibited the

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