

EXPERIMENTAL AND THEORETICAL RESEARCH ON CATALYTIC SYNTHESIS OF THIOPHENE FROM FURAN AND H₂S

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Abstract - The yield of thiophene from furan and H₂S was investigated using selected catalyst carriers (alumina, active carbon and silica gel) and active ingredients (silicotungstic, phosphomolybdic and phosphotungstic acids) to obtain the optimized synthesis parameters. The experimental results indicated that the yield of thiophene reached a maximum when the supported catalyst was alumina and the active ingredient was phosphotungstic acid. Furthermore, the reaction mechanism of the optimized reactive system was studied by the density functional theory (DFT) method. The calculated energy profile indicated that there were four transition states in the reaction process.

Keywords: Furan; Thiophene synthesis; Supported catalyst; Density functional theory.

INTRODUCTION

Thiophene is an important heterocyclic organic material. It is mainly used in sensitive materials, precursors for making pharmaceuticals, additives of photoluminescent materials, pigments and herbicides, etc. (Rivers et al., 2002; Peregichka et al., 2005; Barbarella et al., 2005; Barbarella et al., 2005). In addition, it is also adopted as a raw material and intermediate in the chemical industry (Zhang et al., 2008).

The synthesis and application of thiophenes have been thoroughly studied (Navacchia et al., 2008; Melucci et al., 2007; Zekai et al., 2008). The methods of synthesizing thiophene include the reactions of ring-closure and isomerization of the 5-membered ring (Li et al., 2008). The ring-closure reaction was a general route to synthesize thiophene

in the past decades. For example, alkanes and hydrogen sulfide have been used as raw material for obtaining thiophene through the ring-closure reaction, but the yield of thiophene is rather low and there is no efficient method to improve it (Voronkov et al., 1981). In contrast to the ring-closure reaction, the isomerization reaction has the advantages of high yield and low cost (Southward et al., 1998). Many researches have indicated that the catalyst plays an important role in the synthesis of thiophene. The catalyst can induce the chemical reaction and improve the yield of target product. In the isomerization reactions between furan and H₂S, the catalytic reaction using supported catalysts (active ingredient loaded on the surface of a carrier) drew more attention because of the high yield and high purity of the products. However, the high cost of furan prohibited the widespread use of this method in

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the past decades (Southward et al., 1998). With the development of industrial technology, the cost of furan has been greatly reduced in recent years. Moreover, the reaction can utilize the waste H_2S gas produced in the chemical industry. Therefore, this method is being used again to produce thiophene.

The literature on the optimization of the synthesis parameters and related mechanism for this reaction are scarce (Li et al., 2008). In this paper, the yields of thiophene were investigated to obtain optimized synthesis parameters. The supported catalysts consisted of several selected catalyst carriers and active ingredients. Furthermore, the reaction mechanism of the optimized reactive system was studied by the DFT method. Our experimental studies provide important guidance for increasing the yield. The following theoretical study was helpful for understanding the reaction mechanism and may serve as a reference for analyzing similar reaction mechanism.

EXPERIMENTAL

Alumina, activated carbon and silica gel have typically been used as carriers in the synthesis of thiophene (Li et al., 2008; Li et al., 2009). Therefore, these three carriers were selected in our experiments to study their influence on the yield of thiophene.

Carrier Pretreatment

Three selected carriers were pretreated to ensure the best catalytic effect. As for the alumina carrier, it was obtained via the thermal treatment of pseudo-boehmite by the following processes. The pseudo-boehmite powder ($AlOOH \cdot nH_2O$, $n = 0.08 \sim 0.62$) was mixed with dilute nitric acid (2 wt%) and extruded into thin cylinders with a diameter of 3.0 mm. The sample was dried at $110^\circ C$ for 12 h and then calcined at $550^\circ C$ for 5 h. After that, the pseudo-boehmite was dehydrated to form alumina. As for activated carbon, it was immersed in dilute nitric acid (2 wt%) for 4 ~ 5 h to remove the ash and alkaline matter absorbed onto its surface and then washed repeatedly with deionized water. Finally, it was dried at $120^\circ C$ for 8 h. As for silica gel ($xSiO_2 \cdot yH_2O$), it was calcined at $500^\circ C$ for 4 h, immersed in deionized water for 12 h, and then dried at $150 \sim 200^\circ C$ for 6 h.

Loading of Active Intergradient on the Carriers

First, the carriers were immersed in the solution containing the active intergradient for several hours.

Afterward, the immersed carriers were filtered and washed repeatedly with deionized water, and finally dried. Secondly, these carriers were activated under a certain temperature. The quantity of active ingredient loaded on the carrier could be controlled through adjusting the concentration of the active intergradient in solution and the immersion time.

EXPERIMENTAL RESULTS

Selection of Optimized Experimental Parameters

In order to improve the yield of thiophene, two critical experimental parameters, catalyst carrier and active ingredient, were systemically investigated.

Catalyst Carrier

With phosphotungstic acid as active ingredient, the yields of thiophene with the three catalyst carriers are shown in Fig.1. The yields of thiophene with the catalyst carriers of alumina, activated carbon and silica gel were 84.2%, 33.5% and 21.8%, respectively. Thus, the yield with alumina was much higher than that with the other two catalyst carriers. The results indicated that alumina was the best carrier among the three selected catalyst carriers.

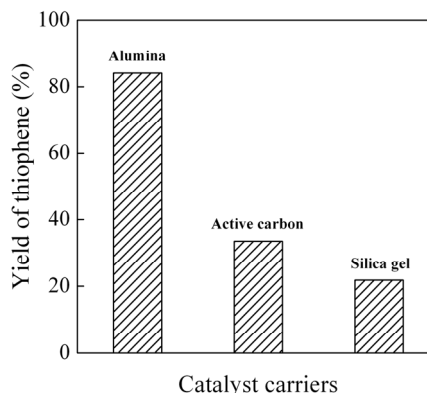


Figure 1: The yields of thiophene with phosphotungstic acid as active ingredient and the catalyst carriers of alumina, active carbon and silica gel.

Active Ingredient

Based on the optimization of catalyst carrier above, alumina was adopted as the carrier in the following experiments to optimize the active ingredient. Silicotungstic, phosphotungstic and phosphomolybdic acids have been commonly used as the active ingredients in the catalytic reaction (Brooker, et al.,

2009; Singh, et al., 2009). So, these three acids were selected as active ingredients for the catalytic reaction, and the alumina carrier was immersed in these three acid solutions with the same mass percentage of 2 wt%. The yields of thiophene with the active ingredients of silicotungstic, phosphotungstic and phosphomolybdic acids are shown in Fig. 2. The yield of thiophene with phosphotungstic acid (84.2%) was a little higher than that with silicotungstic acid (83.5%) and phosphomolybdic acid (82.7%).

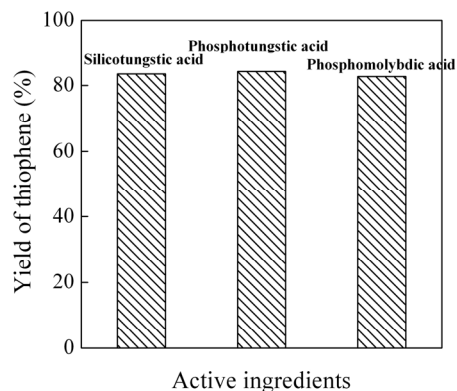


Figure 2: The yields of thiophene with the active ingredients of silicotungstic, phosphotungstic and phosphomolybdic acids with alumina as catalyst carrier

In addition, to evaluate the efficiency of the catalyst, the BET surface areas of alumina treated with the three different acids were investigated. The corresponding results are listed in Table 1. The alumina carrier activated by phosphotungstic acid has a relatively higher BET surface area. Thus, phosphotungstic acid was selected as the optimized active ingredient in the following studies.

Table 1: BET surface area of the alumina carrier activated by different catalysts

Carrier activated with different acids	BET surface area (m ² /g)
Al ₂ O ₃ / 2 wt% silicotungstic acid	243
Al ₂ O ₃ / 2 wt% phosphomolybdic acid	237
Al ₂ O ₃ / 2 wt% phosphotungstic acid	252

REACTION MECHANISM USING THE DFT METHOD

Alumina and phosphotungstic acid were selected as the carrier and active ingredient, respectively, to investigate the reaction mechanism. Alumina was prepared by the dehydration of aluminum hydroxide.

Surfaces of Al₂O₃ consist of coordinatively unsaturated cations (Al³⁺) and oxide (O²⁻) ions. The surfaces are usually terminated by OH groups unless they are treated at elevated temperatures (Li et al., 2008). In order to simplify the calculation, hydrafil was substituted by Structure 1, as shown in Fig. 3.

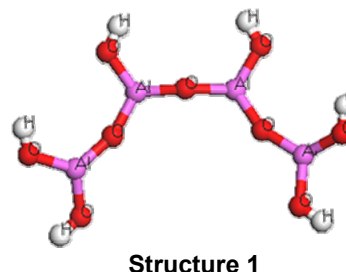


Figure 3: Schematic illustration of optimized molecular geometry of pseudo-boehmite

To investigate the reaction mechanism of thiophene, furan and hydrogen sulfide were the starting materials (Mashkina and Khairulina, 2008) and all of the reactive pathways were calculated by the self-consistent DFT method. The calculations were performed with the program package DMol³ in Material Studio 4.0. The exchange-correlation energy was calculated within the generalized gradient approximation (GGA) using the form of the functional RPBE proposed by Hammer et al. (Hammer et al., 1999). All of the atoms were treated with an all-electron basis set. The valence electron functions were expanded into a set of numerical atomic orbitals by a double-numerical basis with polarization functions (DNP). All computations were performed using spin-polarization with Fermi smearing of 0.005 Hartree. The transition state (TS) searches were performed at the same theoretical level via the completely linear synchronous transit (LST) with quadratic synchronous transit (QST) method (Halgren and Lipscomb, 1977). In this method, LST maximization was performed to obtain an approximate TS and then an energy minimization was conducted to obtain an optimized TS. The optimized TS was further optimized using QST maximization and another conjugated gradient minimization. This cycle was repeated until a stationary point was located. The convergence criterion of the TS searches was set as 0.01Hartree/Å for the root mean square of atomic forces. All the simulation work was carried out on Dell Pentium PC computer (2.49 GHz, 2.00 GB).

All reaction processes including the thermal decomposition of aluminum hydroxide, the absorption of H₂S and furan, and the desorption of thiophene.

First, alumina was formed by the thermal decomposition of aluminum hydroxide. Second, hydrogen sulfide adsorbed on Al_2O_3 . Then, the proton was transferred to an oxygen atom of Al_2O_3 , and the SH^- group adsorbed on the unsaturated cation (Al^{3+}). The anion S^- was formed by the dehydration reaction between OH^- and SH^- . Furan would adsorb on the alumina surface through its O atom and combine with molecule 7 (see in Figure 4) via the formation of C-S and Al-O bonds after the cleavage of the C-O bond in

furan. After that, thiophene would desorb from molecule 9 to finally form thiophene.

The corresponding energy changes in the whole reaction process are shown in Fig. 4 (a) and (b). There were four transition states in the reaction process including Ts1-2, Ts4-5, Ts5-6 and Ts8-9, with the energy barriers 242.1, 116.6, 150.4, and 15.3 kJ/mol, respectively. The highest energy barrier (242.1 kJ/mol) is in the first step in which a H_2O molecule was formed.

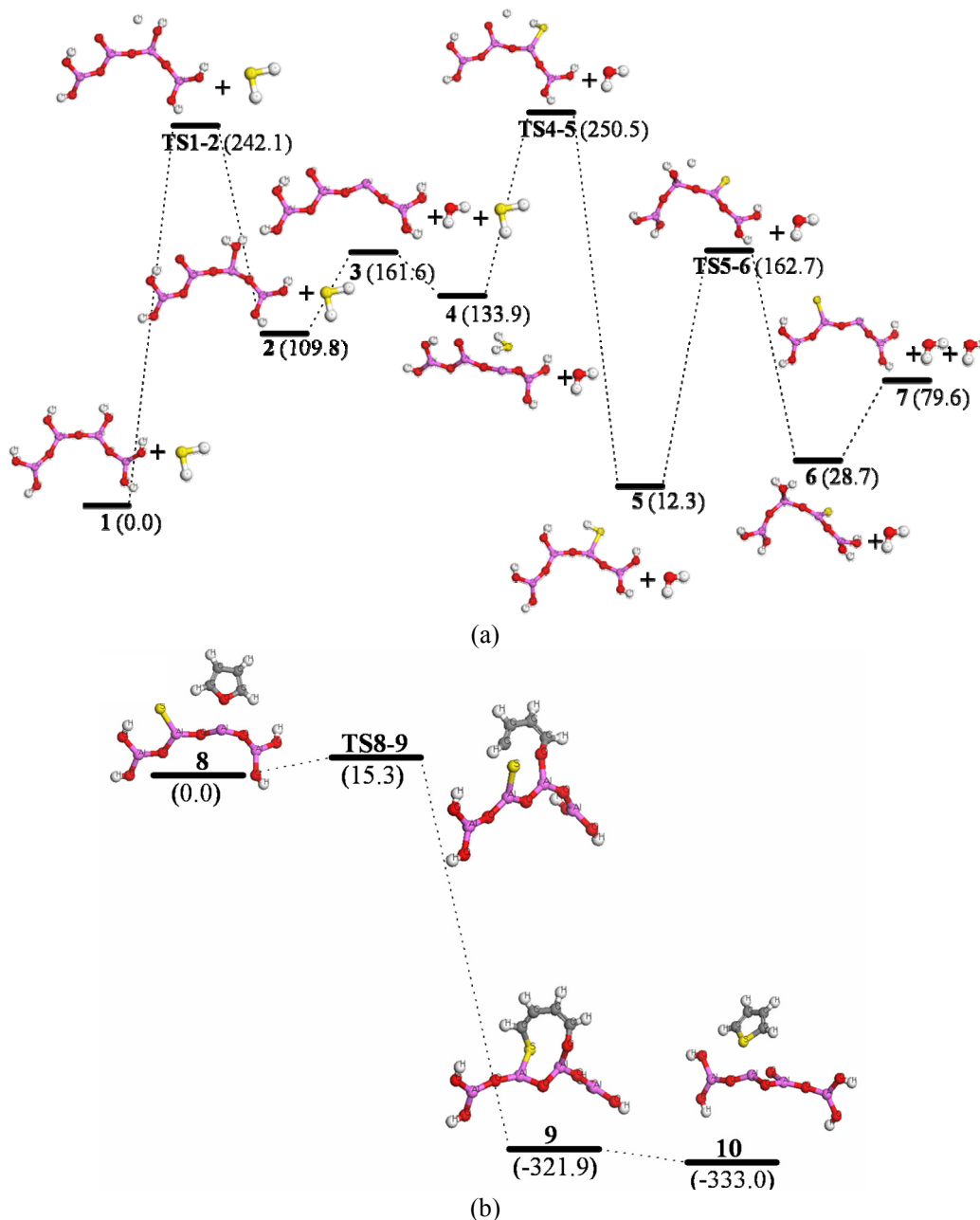


Figure 4: (a) Energy diagram (kJ/mol) of the thermal decomposition of aluminum hydroxide and the absorption of H_2S ; (b) Energy diagram of the absorption of furan and the desorption of thiophene.

CONCLUSIONS

The yield of thiophene was investigated using selected catalyst carriers (alumina, active carbon and silica gel) and active ingredients (silicotungstic, phosphomolybdic and phosphotungstic acids) to obtain the optimized synthesis parameters. The yield of thiophene reached a maximum when the supported catalyst was alumina and the active ingredient was phosphotungstic acid. The reaction mechanism of the optimized reaction system was studied by the density functional theory (DFT) method. The calculated energy indicated that there were four transition states in the reaction process (Ts1-2, Ts4-5, Ts5-6 and Ts8-9) and the energy barriers were 242.1, 116.6, 150.4, and 15.3 kJ/mol, respectively.

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