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Catalytic Synthesis of Thiophene from the Reaction of Furan and Hydrogen Sulfide

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Abstract The catalysts were prepared from pseudo-boehmite mixed with dilute nitric acid and calcined at different temperatures. The vapour-phase reaction of furan and hydrogen sulfide was performed in a fixed-bed flow in the presence of catalyst. The catalysts were characterized by XRD, N_2 adsorption, FT-IR techniques. The Al_2O_3 calcined at 550 °C has large surface areas which resulted in high yield of thiophene under the conditions: at atmosphere, reaction temperature 500 °C, the ratio of H_2S to Furan about 10 (mol) and LHSV 0.2 h^{-1}. The reaction mechanism was proposed for the synthesis of thiophene from furan and hydrogen sulfide over Al_2O_3.

Keywords Furan · Hydrogen sulfide · Thiophene · Al_2O_3 · Lewis acid

1 Introduction

The synthesis of thiophene and its homologues has received serious consideration since their discovery in 1882. Prior to the 1950s, thiophene was available only in limited quantities at prohibitive prices [1]. At the present time, thiophene is prepared in industrial quantities and plays an important role in the synthesis of drugs, herbicides, silicone liquids, etc. Moreover, since the 1980s, the polymerization of thiophene has been extensively studied, polythiophene being a conducting polymer with potential application in electro-chemistry [2–5].

Thiophene is produced on an industrial scale via four heterogeneous catalytic processes. The first involves the reaction of C_4^+ alcohols or carbonyls with CS_2 over alkali-promoted alumina [2, 6–11]. The second is based upon the reaction of an α,β-unsaturated aldehyde with H_2S over an alkali-promoted alumina [12]. The third is through the reaction of C_4^+ alkyl hydrocarbon or olefins with CS_2, S, and H_2S over alkali-promoted alumina [13–20]. The fourth relates to the manufacture of thiophene by catalytic dehydrogenation of tetrahydrothiophene [21]. However, all of these procedures suffer from various disadvantages, such as short run time and low yields of thiophene.

Thiophene synthesis from furan was seldom reported. Only several papers concerned this reaction without detail information [22–24]. Previously, furan involved in preparing thiophene was limited in industrial quantities due to commercial profit. At present, furan can be available at moderate price. The selectivity of thiophene prepared from furan with H_2S was higher than it of other procedures. Then thiophene can be separated from product easily without complicate equipment applied. The study of reaction mechanism of furan and H_2S over catalysts plays an important role in selecting catalyst and technology.

2 Experimental

2.1 Catalyst Preparation

The pseudo-boehmite was mixed with dilute nitric acid and extruded into sticks 3.0 mm in diameter. The sample was

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dried at 110 °C overnight, and then was calcined at different temperatures for 5 h.

2.2 Catalyst Characterization

N_2 adsorption–desorption isotherms were measured on a Quanta Chrome NOVA1000 Sorptomatic apparatus. The BET specific surface area (S_{BET}) was calculated by using the standard BET method on the basis of the adsorption data.

X-ray diffraction (XRD) analysis was conducted with a BRUKER-AXSD8Adance X-ray Diffractometer using Cu-Kα radiation, operated at 40 KV and 40 mA in the scanning angle (2θ) range of $5°-80°$ at scanning speed of 4°.

FT-IR analysis of catalysts with absorbed pyridine was carried out, for measuring the acidity of the catalyst, with a Spectrum One spectrometer (PE Co., USA). The sample was calcined at 500 °C for 4 h or was only heated at 120 °C for 4 h in order to test the change of acidity on the inactivated catalyst; pyridine was adsorbed at room temperature overnight and subsequently vacuum desorbed at 100 °C in order to remove physically adsorbed pyridine. The IR spectra were recorded in the ranges 1,000–3,000 cm^{-1} at room temperature.

2.3 Catalytic Activity Testing

All starting materials were reagent grade. Furan was used without further purification. Catalytic activity measurements were carried out in a stainless steel tubular fixed-bed micro-reactor of 10 mm I.D., 40 cm in length. The product was sampled after stabilizing for 2 h at each reaction condition. The compositions of the products were analyzed using a Varian 3800 gas chromatograph equipped with a FID detector and a 100 m PIONA capillary column.

3 Results and Discussion

3.1 X-ray Diffraction Analysis and N_2 Adsorption/Desorption Characterization

A series of $A1_2O_3$ were calcined at a tmperature from 550 to 1,300 °C in air for 5 h. As it can be seen from Fig. 1, a series of crystallograms show the alumina changed from γ-$A1_2O_3$ to α-$A1_2O_3$ as the temperature increased. As illustrated in Table 1, the surface areas of alumina were dramatically decreased as the calcination temperature increased.

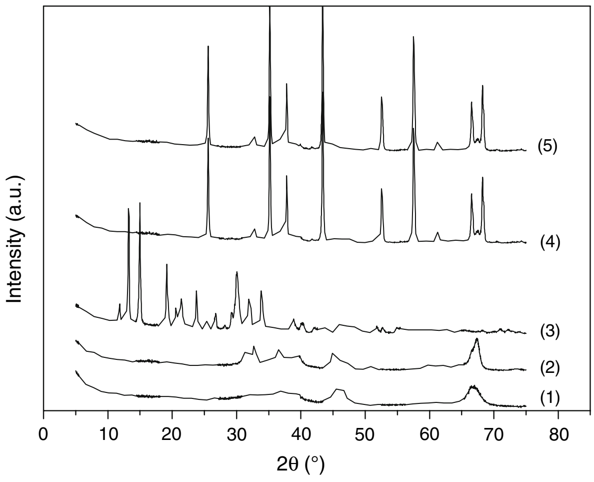


Fig. 1 XRD patterns for Al_2O_3 calcined at (1) 550 °C (2) 1,000 °C (3) 1,100 °C (4) 1,200 °C (5) 1,300 °C

3.2 Catalytic Performance on $A1_2O_3$ Calcined at 550 °C

The reaction of furan and H_2S was performed at the temperature from 260 to 500 °C, ratio of H_2S to Furan from 2 to10 (molar) and LHSV from 0.1 to 1.0 h^{-1} over catalyst at atmosphere. The catalyst was prepared from Al_2O_3 calcined at 550 °C for 5 h.

3.2.1 Effect of Reaction Temperature

Figure 2 illustrates the effect of reaction temperature on the yield of thiophene. The reaction of furan and H_2S was performed at ratio of H_2S to Furan 2 and LHSV 0.2 h^{-1}. It can be seen that temperature enhancement can improve the yield of thiophene.

3.2.2 Effect of Ratio of H_2S to Furan

Figure 3 illustrates the effect of LHSV on the yield of thiophene. The reaction of furan and H_2S was performed at 500 °C and LHSV 0.2 h^{-1}. It can be seen that the ratio of H_2S to furan enhancement can improve the yield of thiophene. The yield of thiophene was slightly improved as the ratio of H_2S to Furan changed from 8 to 10. There were probably two reasons for slight improvement. The first was

Table 1 The surface area of Al_2O_3 calcined at different temperature

$A1_2O_3$ calcined at different temperature (°C)	550	1,000	1,100	1,200	1,300
BET surface area (m^2/g)	226.13	93.12	18.07	4.19	2.22

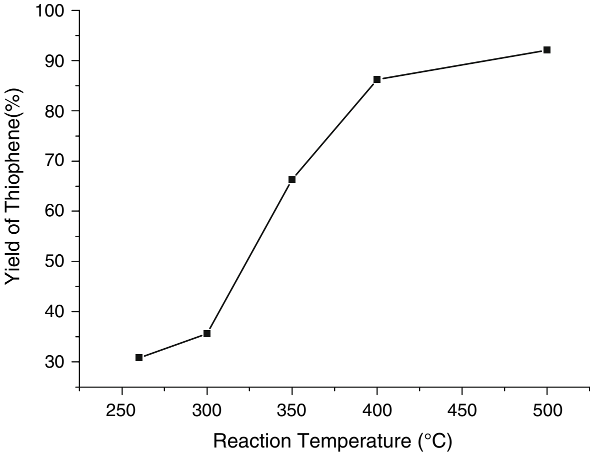


Fig. 2 Effect of reaction temperature on the yield of thiophene

that the conversion of furan can be improved while the enhancement of the ratio of H_2S to Furan. The second was that the reaction of H_2S and Furan can be favored due to the decrease of active site occupation by thiophene while the enhancement of the ratio of H_2S to furan.

3.2.3 *Effect of LHSV*

Figure 4 illustrates the effect of LHSV (h^{-1}) on the yield of thiophene. The reaction of furan and H_2S was performed at 500 °C and the ratio of H_2S to Furan (mol) 10. It can be seen that the yield of thiophene was decreased as the LHSV (h^{-1}) increased from 0.1 to 1. With the consideration of commercial production, the LHSV (h^{-1}) was selected at 0.2.

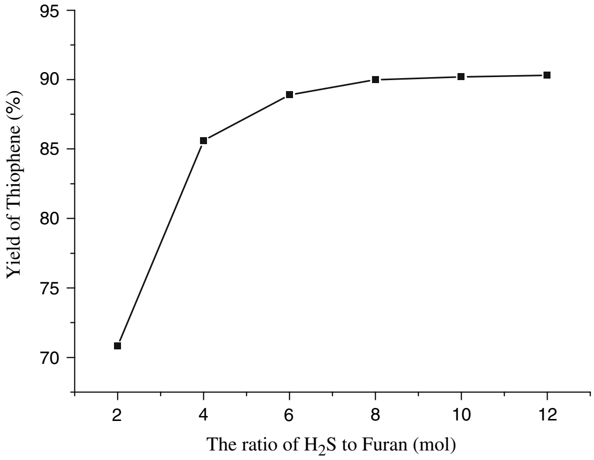


Fig. 3 Effect of ratio of H_2S to Furan (mol) on the yield of thiophene

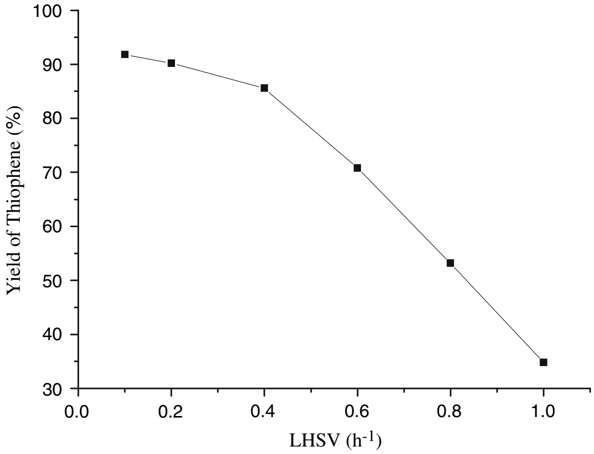


Fig. 4 Effect of LHSV (h^{-1}) on the yield of thiophene

3.3 Mechanism of Catalytic Synthesis of Thiophene

3.3.1 *Catalytic Performance on $A1_2O_3$ Calcined at Different Temperatures*

With the purpose of elucidation of reaction mechanism, a series of alumina calcined at different temperatures were prepared and tested for their efficacy in the synthesis of thiophene, giving the results shown in Table 2. As can be seen from Table 2, the conversion of furan was increased with the temperature enhanced and the catalysts activity seems relation to the surface area. With observation of the product, the color of product was darker due to more polymeric compound involved in as the conversion of furan increased. Products distribution resulting from the reaction of furan and H_2S over α-Al_2O_3 at 500 °C, the ratio of H_2S to Furan (mol) 10 and LHSV 0.2 h^{-1} was shown in Table 3. As can be seen from Table 3, there was small molecule compound observed in the product from the reaction over α-$A1_2O_3$ at 500 °C. However small molecule compound was not observed from the reaction on γ-$A1_2O_3$ at 500 °C. Probably due to large area of γ-$A1_2O_3$, small molecule compound cracked from furan was adsorbed on

Table 2 Reaction of furan and H_2S over various Al_2O_3

Al_2O_3 calcined at different temperature (°C)	Yield of thiophene (%) at different reaction temperature (°C)			
	300	350	400	500
550	35.5	65.8	85.3	90.2
1,000	15.4	39.9	69.8	80.7
1,100	12.7	35.1	44.0	55.6
1,200	4.3	6.6	12.1	19.2
1,300	2.9	3.3	7.7	10.4

Table 3 Products distribution resulting from the reaction of furan and H_2S over α-Al_2O_3

Ingredients	Retention time (min)	Content (%)
Butane	3.51	0.91
2-butene	3.68	0.23
n-butene	3.96	0.18
1,3-butadiene	4.25	2.07
Thiophene	10.85	96.61

the surface of γ-$A1_2O_3$, then aggregated and desorbed from the surface of γ-$A1_2O_3$.

3.3.2 *Acid Properties on $A1_2O_3$ Calcined at Different Temperatures*

Control experiments using SiC or glass wool, without the addition of a catalyst, gave no thiophene, confirming that the formation of thiophene was due to the presence of Al_2O_3 and thiophene synthesis from the reaction of furan and H_2S was catalytic reaction.

Alumina was prepared by aluminum hydroxide dehydration. The formation of isomer crystal of alumina was through thermal decomposition of aluminum hydroxide, like α-Gibbsite, β_1-, and β_2-Gibbsite. These isomer crystals of alumina can be change to α-$A1_2O_3$ as the temperature of thermal decomposition higher than 1,200 °C.

Surfaces of Al_2O_3 consist of coordinatively unsaturated cations (Al^{3+}) and oxide (O^{2-}) ions, and are usually terminated by OH-groups unless they are treated at elevated temperatures. The OH-groups are formed as a result of dissociative adsorption of H_2O molecules. The process of acid site on alumina surface generated by dehydration was illustrated in Fig. 5. FTIR spectroscopy of small adsorbed base molecules, often NH_3, pyridine, CH_3CN, NO or CO molecule, has been well established as a powerful surface analytical technique for characterization of nature, strength and concentration of acid sites. Pyridine has been preferred as an IR probe molecule of finely divided metal oxide surfaces at room temperature. The spectra show the ring vibration of pyridine detected in the frequency range of 1,400–1,650 cm^{-1} commonly used to characterize the concentrations of Brønsted and Lewis acid sites. The Brønsted acid sites correspond to the 1,545 cm^{-1} band (pyridinium ion). The Lewis acid sites give rise to the 1,450 cm^{-1} band attributed to pyridine coordinatively bound to accessible Al^{3+}. As can be seen from Fig. 6, the properties of acid sites on the surfaces of Al_2O_3 were changed as Al_2O_3 treated at the elevated temperature. The strength and concentration of acid sites on the surface were dramatically decreased as Al_2O_3 calcined at above 1,200 °C. As can be seen from Table 1 and Table 2 with Fig. 6, the catalysts activity was related to acid sites on the surface of Al_2O_3. The lower conversion of furan was due to a drop in the total surface area with lower total amount of acid. The Brønsted acid sites were almost disappeared with small amount of Lewis acid on the surface of Al_2O_3 calcined at 1,300 °C. Then it has been conclude that the active sites for this reaction are Lewis acid.

3.3.3 *Reaction Pathway*

To determine the "key step" of the thiophene synthesis reaction, the matrix of possible reactions was established (Scheme 1). From this matrix it is apparent that there are six steps that furan can undergo:

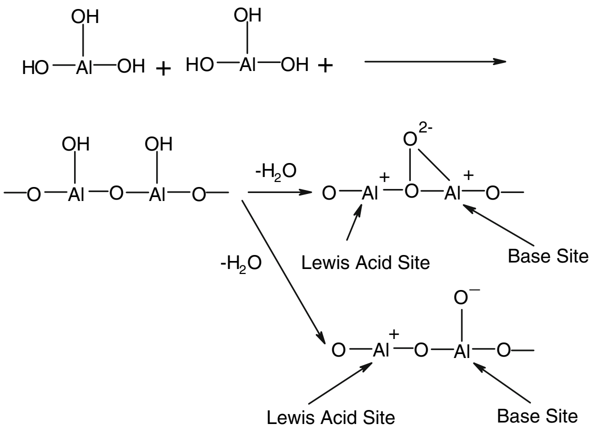


Fig. 5 The process of acid site on alumina surface was generated by dehydration

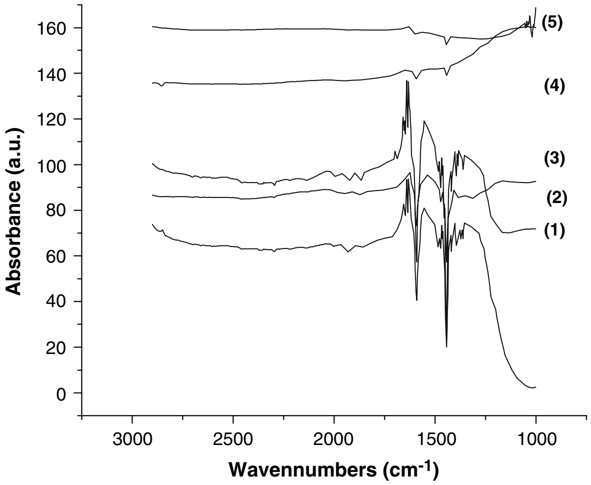
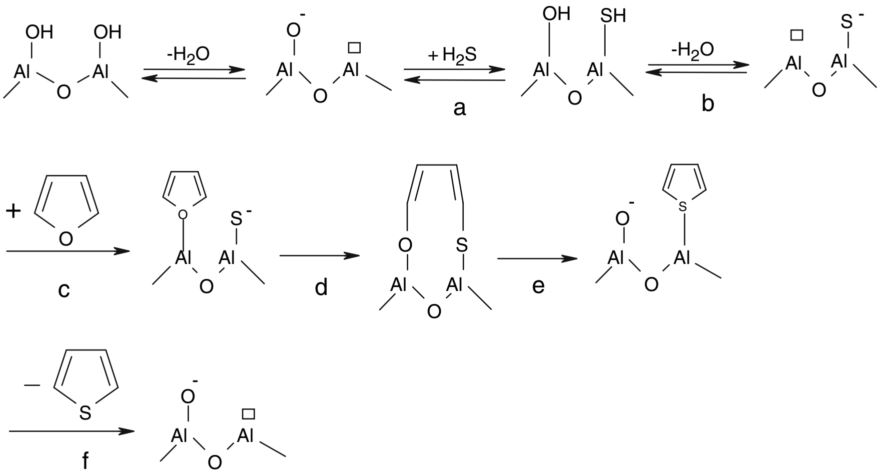


Fig. 6 FTIR spectroscopy of pyridine adsorbed on alumina calcined at (1) 550 °C (2) 1,000 °C (3) 1,100 °C (4) 1,200 °C (5) 1,300 °C

Scheme 1 Reaction mechanism proposed for the synthesis of thiophene from furan and H_2S on the surface of alumina



(a) *Dissociative adsorption of hydrogen sulfide*. The dissociative adsorption can be described as a Brønsted acid–base reaction where H_2S is the acid. The proton is transferred to an oxygen atom of Al_2O_3 and the SH group is adsorbed on the unsaturated cations (Al^{3+}).

(b) *Dehydration*. Unsaturated cations (Al^{3+}) and S^- on the surfaces was formed by the reaction of –OH group and –SH group through dehydration.

(c) *Adsorption*. Furan was adsorbed on the surfaces as the O atom of furan filled in the unsaturated cations (Al^{3+}).

(d) *Ring opening*. Chemisorption of furan leads to cleavage of C–O and C–S formation. Semicyclic molecule was adsorbed by the bond of C–O and C–S. The 1,3-butadiene was appeared in product as shown in Table 3 due to cleavage of C–O without C–S formation. Butane, *n*-butene and 2-butene were produced from 1,3-butadiene hydrogenation.

(e) *Cyclization*. The bond of C–O among the semicyclic molecule cleavage and C–S formation leads to chemisorption state thiophene. In this step, Butane, *n*-butene, 2-butene and 1,3-butadiene can also be produced due to cleavage of C–O without C–S formation.

(f) *Desorption*. The desorption of thiophene from the surface of Al_2O_3 leads to thiophene formation and Al_2O_3 recovery for new reaction.

4 Conclusion

The Al_2O_3 calcined at 550 °C has large surface areas which resulted in high yield of thiophene under the conditions: at atmosphere, reaction temperature 500 °C, the ratio of H_2S to Furan about 10 (mol) and LHSV 0.2 h^{-1}.

From this Scheme 1 it is apparent that *Ring opening* and *Cyclization* were key steps for thiophene synthesis.

The active sites for thiophene synthesis from furan and hydrogen sulfide over Al_2O_3 are Lewis acid.

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