Catalytic synthesis of thiophene from the reaction of n-butanol and carbon disulfide over K₂CO₃-promoted Cr₂O₃/γ-alumina catalyst

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Abstract−The synthesis of thiophene from the reaction of n-Butanol and carbon disulfide was performed in a fixed-bed reactor in the presence of promoted chromia on γ-alumina. A high selectivity to thiophene (87%) and a long life-time of the catalyst (55 hour) was obtained at 450 °C with a 1 : 6 n-Butanol to carbon disulfide molar ratio and LHSV 1 h^{-1} over γ-Al₂O₃ promoted by 7% K₂CO₃ with 15% Cr₂O₃ loaded. The catalytic behavior of these catalysts can be attributed to their dual-functional acidity and dehydrogenating and cyclized properties.

Key words: n-Butanol, Carbon Disulfide, Thiophene, γ-Alumina Based Catalyst, K₂CO₃

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, as polythiophene is a conducting polymer with potential application in electro-chemistry [2-5]. Thiophene as a model compound for clean fuel research has attracted more attention in recent decades [6-8].

Thiophene is produced on an industrial scale via four heterogeneous catalytic processes. The first involves the reaction of C₄$^+$ alcohols or carbonyls with CS₂ over alkali-promoted alumina [2,9-14]. The second is based upon the reaction of an α,β-unsaturated aldehyde with H₂S over an alkali-promoted alumina [15]. The third is through the reaction of C₄$^+$ alkyl hydrocarbon or olefins with CS₂, S, and H₂S over alkali-promoted alumina [16-23]. The fourth relates to the manufacture of thiophene by catalytic dehydrogenation of tetrahydrothiophene [24].

Previously, thiophene synthesis from furan was seldom reported. Only several papers concerned this reaction and they did not have detailed information [25-27]. More recently, the thiophene synthesis from furan and hydrogen sulfide has been studied in detail [28]. A high selectivity to thiophene and a long life-time of the catalyst were obtained in this process. However, furan involved in preparing thiophene was limited in industrial quantities due to commercial profit. Hydrogen sulfide as a reactant has a limited availability due to its inconvenient transportation. With the consideration of commercial profit, thiophene synthesis from the reaction of n-Butanol and carbon disulfide has attracted more attention.

EXPERIMENTAL

1. Materials

All starting materials were reagent grade. Carbon disulfide and n-Butanol were used without further purification.

2. Catalyst Preparation and Characterization

A number of catalysts were investigated for the reaction of n-Butanol and carbon disulfide. The pseudo-boehmite was mixed with diluted nitric acid and extruded into sticks 3.0 mm in diameter and 2.0-4.0 mm in length. K₂CO₃-Cr₂O₃/γ-Al₂O₃ was prepared by impregnation of γ-Al₂O₃ with an aqueous solution of K₂CO₃ and Cr(NO₃)₃ by using the incipient wetness method, then dried (120 °C, 12 h) and calcined (550 °C, 5 h).

X-ray diffraction (XRD) analysis was carried out with a Rigaku D/Max-RB diffractometer with a CuKα monochromatized radiation source (λ=1.54178 Å), operated at 40 KV and 100 mA.

Acid sites on the catalyst surface were characterized by an FTIR spectrum of pyridine adsorbed on its surface. The samples were prepared as follows: The catalysts were dehydrated by calcination at 400 °C for 4 hour, then put into a saturated vapor of pyridine and maintained for 24 hour, and then the pyridine that was physically adsorbed was removed under vacuum at 200 °C.

3. Procedure and Analysis

The catalytic tests were conducted in a stainless steel tubular fixed-bed reactor 10 mm I.D. and 40 cm in length. The reactants were uniformly distributed by carrier gas N₂ (n-Butanol : N2=1 : 100 (V)). The liquid products in the ice trap were identified with a GC/MS, and the contents were determined by an Agilent 6890N (Agilent, HP) equipped with a flame ionization detector (FID) and an HP-5 (30 m×0.32 m) column. Product concentrations were calculated by using the normalization method as shown in Eq. (1), (2), (3) and (4).

$$X_i = \frac{A_i f_i}{\sum\limits_{i}^{n} A_i f_i} \times 100\% \qquad (1)$$

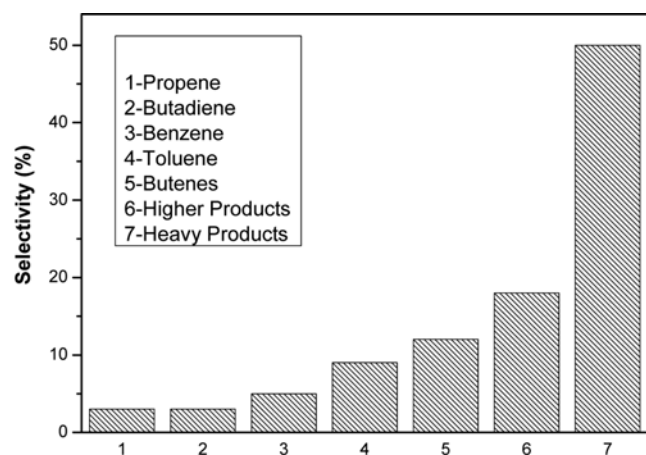†To whom correspondence should be addressed.
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Fig. 1. Product distribution from the reaction of n-Butanol without carbon disulfide over γ-Al$_2$O$_3$ at 500 °C.

Conversion of n-butanol (%)

$$=1-\frac{X_{n\text{-}butanol}}{X_{n\text{-}butanol}+X_{Thiophene}\times\frac{74}{84}+X_{CS_2}+X_{other}}\times100\% \qquad (2)$$

Selectivity to thiophene $(\%)=\dfrac{X_{Thiophene}}{X_{Thiophene}+X_{other}}\times100\% \qquad (3)$

Yield of thiophene (%)=Conversion×Selectivity … $\qquad (4)$

RESULTS AND DISCUSSION

1. Study of the Reactivity of the Individual Initial Compounds

n-Butanol is known to be relatively easily dehydrated, especially at high temperatures. A stream of n-Butanol was passed as a single component through the catalyst bed (γ-Al$_2$O$_3$) at 500 °C and LHSV 1 h^{-1}. As can be seen from Fig. 1, the products of the reaction of n-Butanol without carbon disulfide are partially those considered as by-products of the reaction between n-Butanol and carbon disulfide. There was also a large amount of heavy products and tars. Under these conditions, the catalyst was completely de-activated within 1 hour of reaction.

Carbon disulfide does not react when passed as a single reactant through the catalyst bed. However, in the presence of n-Butanol in the reaction mixture, carbon disulfide reacts with some of the primary by-products formed to give substituted thiophenes and other sulfur-containing by-products.

2. The Reaction over γ-Al$_2$O$_3$

Fig. 2 illustrates the effect of the reaction temperature on the conversion of n-Butanol. The mole ratio of CS$_2$ to n-Butanol was 6 and LHSV was 1 h^{-1}. It can be seen that temperature enhancement can improve the conversion of n-Butanol. Fig. 3 illustrates products' distribution resulting from the reaction. As shown, a selectivity to thiophene of 70.5% was achieved at 500 °C. Also, the alkylthiophenes were detected above 300 °C. Temperature enhancement favors thiophene formation but inhibits butanethiol formation from 300 to 500 °C. These results are consistent with those of Atanas Tomov and Claude Moreau [15], who have claimed that both lower and higher temperatures tend to reduce both selectivity and yield in primary butanethiol.
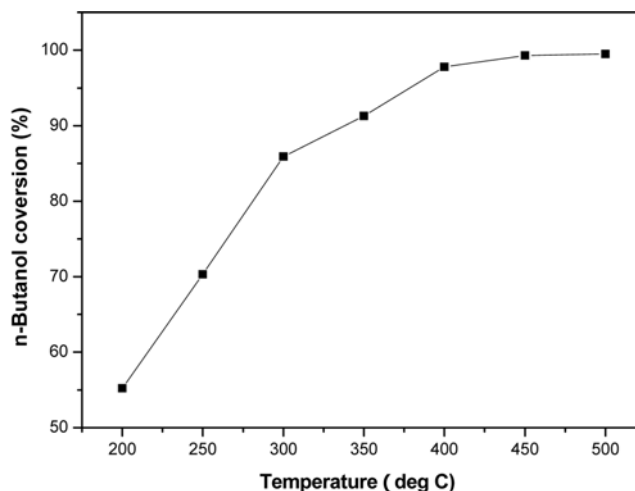
Fig. 2. Effect of reaction temperature on the n-Butanol conversion over γ-Al$_2$O$_3$ (mole ratio of CS$_2$ to n-Butanol: 6, LHSV: 1 h^{-1}).
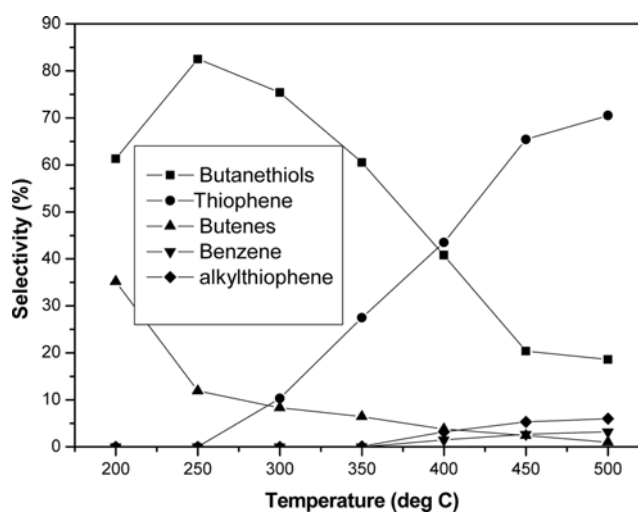

Fig. 3. Products distribution resulting from the reaction of n-Butanol and carbon disulfide over γ-Al$_2$O$_3$.

Fig. 4 illustrates the effect of LHSV (h^{-1}) on the conversion of n-Butanol. The reaction of n-Butanol and CS$_2$ was performed at 450 °C and the mol ratio of CS$_2$ to n-Butanol was 6. It can be seen that the conversion of n-Butanol decreased as the LHSV (h^{-1}) increased from 0.5 to 5. With the consideration of commercial production, the LHSV (h^{-1}) was selected at 1.

Fig. 5 illustrates the effect of the ratio of CS$_2$ to n-Butanol on the selectivity to thiophene. The reaction of n-Butanol and CS$_2$ was performed at 450 °C and LHSV 1 h^{-1}. It can be seen that the ratio of CS$_2$ to n-Butanol enhanced from 1 to 6 can improve selectivity to thiophene. The selectivity to thiophene was slightly inhibited as the ratio of CS$_2$ to n-Butanol changed from 7 to 9. There were probably two reasons for the tendency displayed in Fig. 5. First, the O/S exchange reaction can be improved with the enhancement of the ratio of CS$_2$ to n-Butanol by increasing CS$_2$ concentration. Second, the reaction of n-Butanol and CS$_2$ can be inhibited due to the occupation of a catalytic active site by CS$_2$ dissociative adsorption, when the ratio of CS$_2$ to n-Butanol is increased.
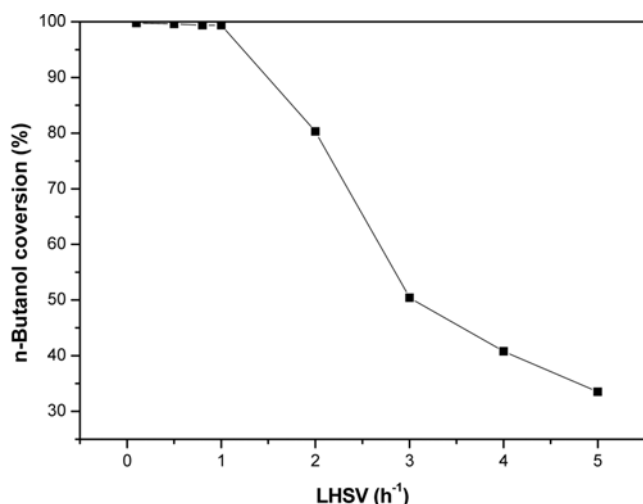
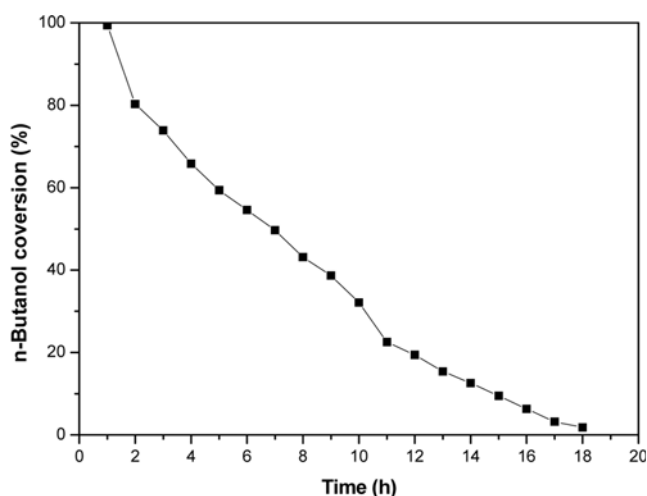**Fig. 4. The effect of LHSV (h^{-1}) on the n-Butanol conversion at 450 °C (mole ratio of CS_2 to n-Butanol: 6).**

Fig. 6. The conversion of n-Butanol on a time-stream of γ-Al_2O_3 at 450 °C.
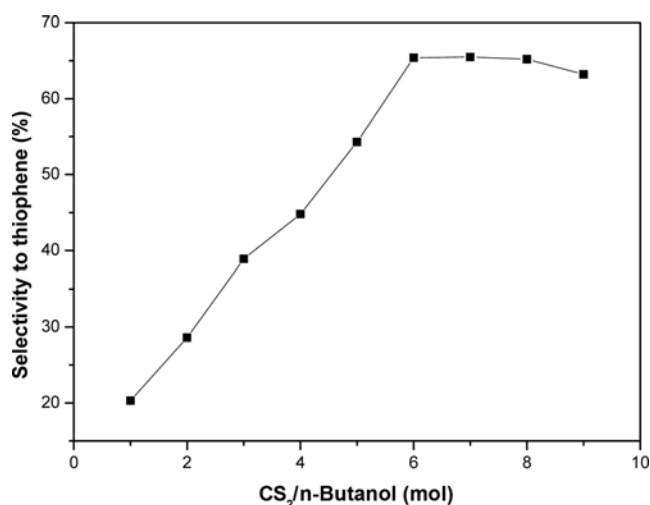

Fig. 5. The effect of the ratio of CS_2 to n-Butanol on the selectivity to thiophene at 450 °C.
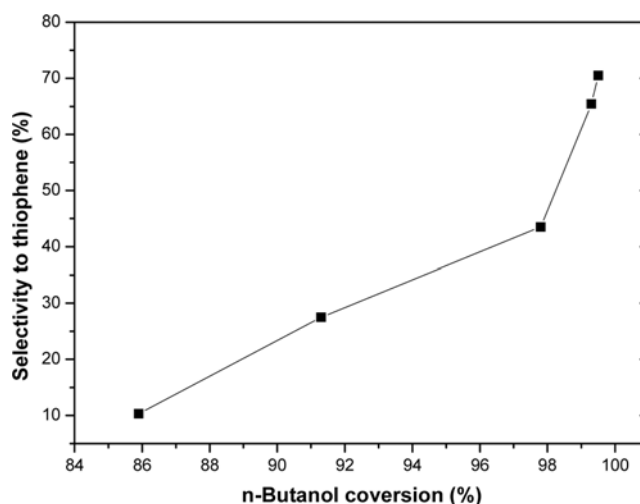

Fig. 7. Selectivity to thiophene as a function of n-Butanol conversion over γ-Al_2O_3 at 450 °C.

Fig. 6 illustrates n-Butanol conversion on a time-stream. From Figs. 2 to 5, the results show that γ-Al_2O_3 was probably an effective catalyst in the thiophene synthesis from n-Butanol and CS_2 due to the high n-Butanol conversion and selectivity to thiophene. However, the n-Butanol conversion decreased dramatically on the time-stream. The catalyst employed must be regenerated in industry at a one-way conversion below 20%. As shown in Fig. 6, there was only about a 10 hour lifetime above 20%. The short lifetime of the catalyst was due to the carbon deposition on the surface of catalyst. So, the strong acid site on the surface of γ-Al_2O_3 should be covered by alkaline salt to inhibit carbon deposition.

Fig. 7 illustrates the selectivity to thiophene as a function of n-Butanol conversion. As shown, an increase in the conversion of n-Butanol leads to an increase in the selectivity to thiophene, which is typical for thermodynamically preferred products. The same relationship was also observed for aromatic hydrocarbons.

3. The Reaction over γ-Al_2O_3 Promoted by K_2CO_3

Carbonic potassium, a kind of alkaline salt, was frequently employed in catalyst preparation to prolong the duration of catalytic reaction. In this part, the catalysts with 1%, 3%, 5%, 7%, 9%, 11%, 13%, and 15% K_2CO_3 were studied. The reaction was conducted at 450 °C, LHSV 1 h^{-1} and the ratio of CS_2 to n-Butanol (mol) was 6.

Fig. 8 illustrates the effect of K_2CO_3 on n-Butanol conversion and the lifetime of the catalyst. As shown in Fig. 8, n-Butanol conversion was inhibited due to γ-Al_2O_3 promoted by K_2CO_3. The reaction of n-Butanol dehydrogenation was most easily carried out in the presence of an acid catalyst. So, n-Butanol conversion over γ-Al_2O_3 promoted by K_2CO_3 was lower than without K_2CO_3 promoting. As shown in Fig. 8, K_2CO_3 promoting can prolong the reaction time at the expense of n-Butanol conversion. The reaction time was increased when K_2CO_3 was added, and reached its max when 7% K_2CO_3 was added. The reaction time was decreased as more than 7% K_2CO_3 was added. With the consideration of n-Butanol conversion and reaction time, 7% K_2CO_3 was selected to modify γ-Al_2O_3 for further study.
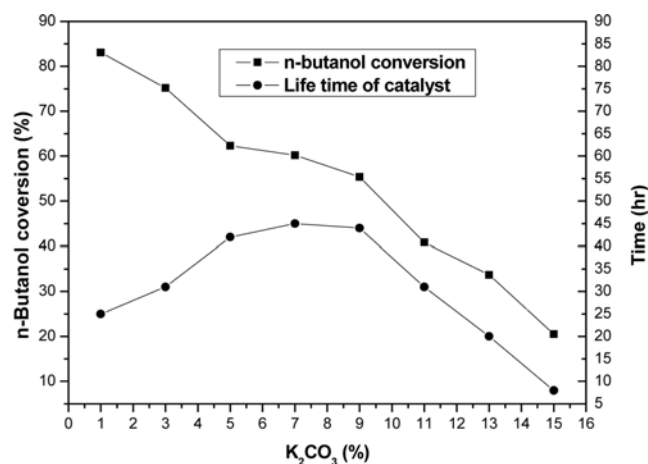
Fig. 8. The effect of K_2CO_3 on n-Butanol conversion and the life-time of the catalyst at 450 °C (mole ratio of CS_2 to n-Bu-tanol: 6, LHSV: 1 h^{-1}).
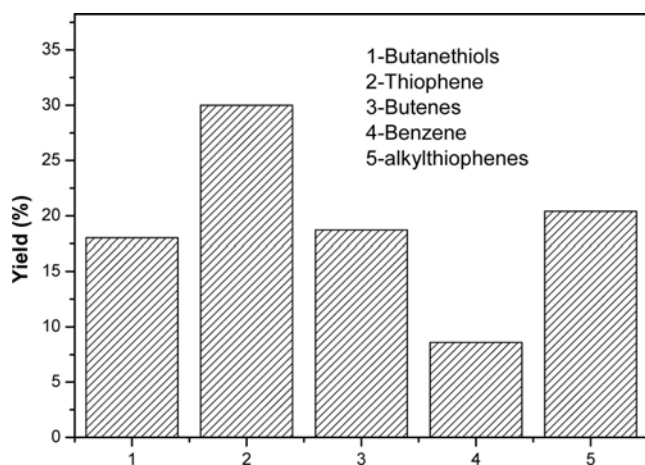

Fig. 10. The effect of Cr_2O_3 on n-Butanol conversion and the life-time of the catalyst at 450 °C.

Fig. 9. Products' distribution from the reaction of n-Butanol and CS_2 over γ-Al_2O_3 promoted by 7% K_2CO_3 at 450 °C.

Fig. 11. Products resulting from the reaction of n-Butanol and CS_2 over γ-Al_2O_3 with 15% Cr_2O_3 loaded at 450 °C.

Fig. 9 illustrates product distribution from the reaction of n-Butanol and CS_2 over γ-Al_2O_3 promoted by 7% K_2CO_3. Compared to the results shown in Fig. 3, the selectivity to thiophene was decreased from 68% to 30% due to K_2CO_3 promoting under the same reaction conditions. However, the selectivity to alkylth-iophenes was increased from 5% to 21%, butenes were increased from 3% to 16%, and benzene was increased from 3% to 9%. K_2CO_3 increased n-Butanol cracking due to the acid site on γ-Al_2O_3 covered. Alkylthiophenes were formed through the thiophene alkylation with small moleculars. Benzene was formed through butene aromatization with small molecules at high temperatures. The processes of both aromatization and alkylation were possible in the presence of small molecules under high tempera-tures.

4. The Reaction over γ-Al_2O_3 with Cr_2O_3 Loaded

It is well known that chromia catalysts are active for dehydroge-nation, dehydrocyclization and dehydroisomerization of paraffins or olefins, and isomerization of substituted aromatic hydrocarbons, as well as for dehydroalkylation of aromatics. In this part, the cata-
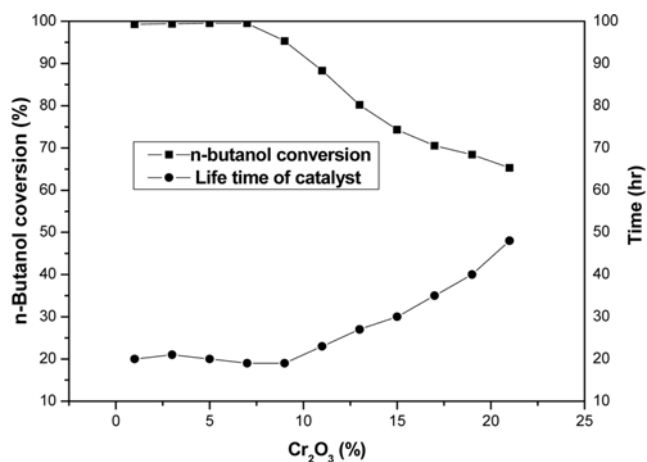
lysts with 1%, 3%, 5%, 7%, 9%, 11%, 13%, 15%, 17%, 19%, and 21% Cr_2O_3 (wt) were studied.

Fig. 10 illustrates the effect of Cr_2O_3 on n-Butanol conversion and the lifetime of the catalyst. The initial n-Butanol conversion over Cr_2O_3 promoted γ-Al_2O_3 was similar to the reaction over γ-Al_2O_3 with less than 9% Cr_2O_3 added. With more than 9% Cr_2O_3 added, the n-Butanol conversion was decreased. γ-Al_2O_3 with the same amount of Cr_2O_3 was more active than K_2CO_3 promoted. The lifetime was very similar for Cr_2O_3 and K_2CO_3 promoted due to their strong acidic site on the γ-Al_2O_3 covered surface.

Fig, 11 illustrates the products resulting from the reaction of n-Butanol and CS_2 over γ-Al_2O_3 with 15% Cr_2O_3 loaded. As shown, the difference is easily observed compared to Fig. 9. The selectivity to thiophene was dramatically improved with Cr_2O_3 loaded. The selectivity to other components was decreased with Cr_2O_3 loaded. γ-Al_2O_3 with Cr_2O_3 loaded can favor the dehydrogenation, dehydro-cyclization and dehydroisomerization of n-Butanol. A new active site for dehydrogenation, dehydrocyclization and dehydroisomer-ization was formed as Cr_2O_3 was loaded. These three processes were key steps for thiophene formation. γ-Al_2O_3 with Cr_2O_3 loaded can
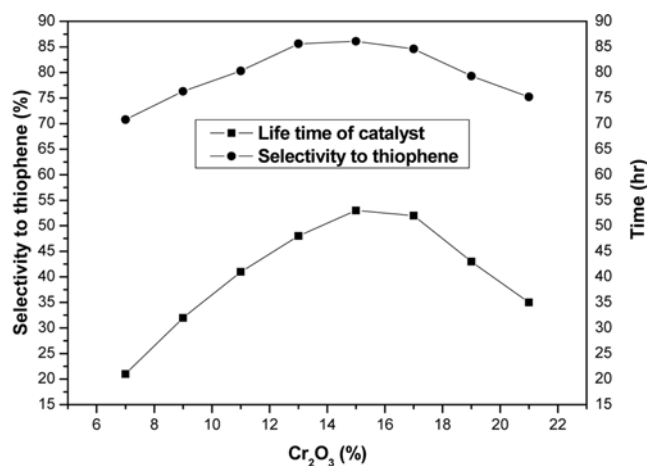
Fig. 12. The effect of loading of Cr$_2$O$_3$ on γ-Al$_2$O$_3$ promoted by 7% K$_2$CO$_3$ on the selectivity to thiophene and life time at 450 °C.
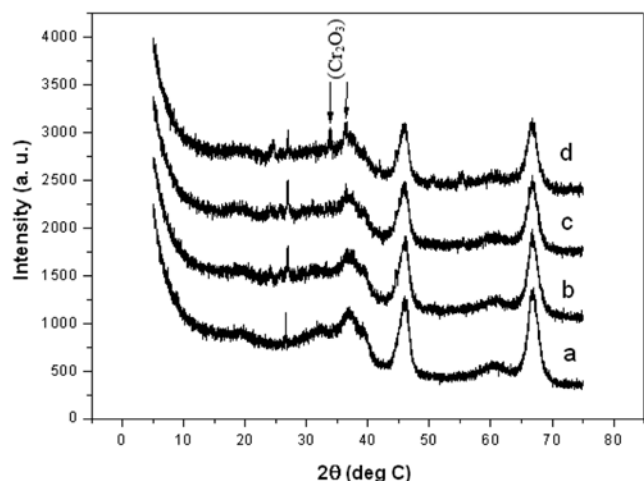

Fig. 14. FTIR spectroscopy of pyridine adsorbed on γ-Al$_2$O$_3$ with 7% of K$_2$CO$_3$ promoted and different Cr$_2$O$_3$ loaded: a: 11%, b: 13%, C: 15%, d: 17%.

Fig. 13. XRD patterns for γ-Al$_2$O$_3$ with 7% of K$_2$CO$_3$ promoted and different Cr$_2$O$_3$ loaded: a: 11%, b: 13%, c: 15%, d: 17%.

Fig. 15. The effect of γ-Al$_2$O$_3$ promoted with different K$_2$CO$_3$ and 15% Cr$_2$O$_3$ loaded at 450 °C.

decrease thiophene hydroalkylation due to dehydrogenation, dehydrocyclization and dehydroisomerization being enhanced and n-Butanol's cracking being inhibited.

5. The Reaction over γ-Al$_2$O$_3$ with Cr$_2$O$_3$ and K$_2$CO$_3$ Loaded

In this part, the catalysts with 7%, 9%, 11%, 13%, 15%, 17%, 19%, and 21% of Cr$_2$O$_3$ supported on γ-Al$_2$O$_3$ with 7% of K$_2$CO$_3$ promoted were studied.

Fig. 12 illustrates the selectivity to thiophene and the lifetime on γ-Al$_2$O$_3$ with 7% of K$_2$CO$_3$ promoted and different Cr$_2$O$_3$ loaded. As shown, the selectivity to thiophene can be improved when less than 15% Cr$_2$O$_3$ is loaded. Cr$_2$O$_3$ loaded more than 15% inhibits the selectivity to thiophene, possibly due to the poor dispersion of Cr$_2$O$_3$ on γ-Al$_2$O$_3$. Poor dispersion of Cr$_2$O$_3$ can block the channel of γ-Al$_2$O$_3$ and decrease the surface area. Fig. 13 illustrates XRD patterns for γ-Al$_2$O$_3$ with 7% of K$_2$CO$_3$ promoted and different Cr$_2$O$_3$ loaded: a: 11%, b: 13%, c: 15%, d: 17%. As shown in Fig. 13, the crystal phase peak was obviously observed at a position of 33.71 and 36.76°.

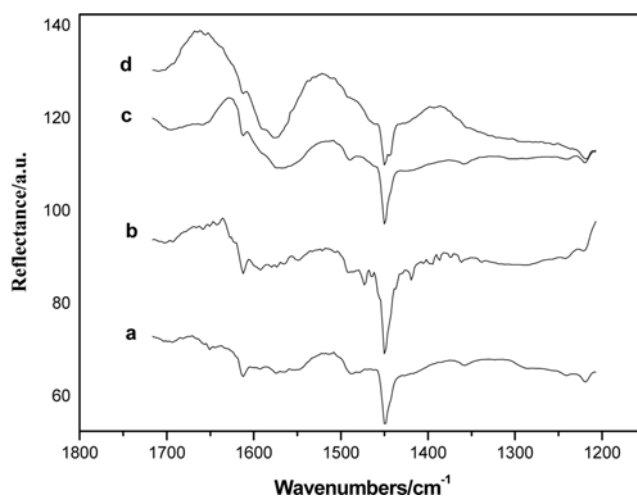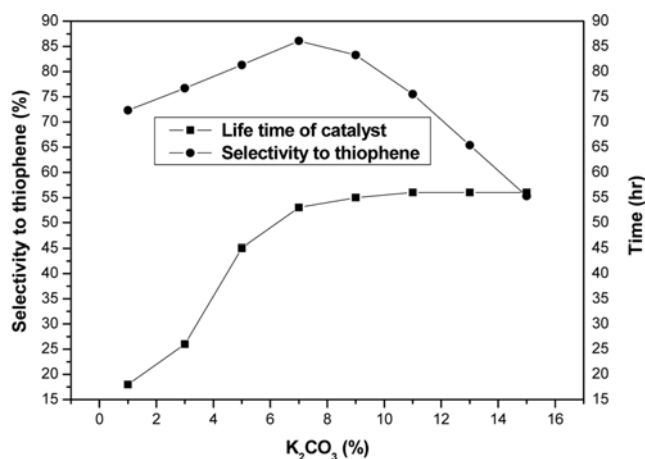Fig. 14 illustrates FTIR spectroscopy of pyridine adsorbed on γ-

Al$_2$O$_3$ with 7% of K$_2$CO$_3$ promoted and different Cr$_2$O$_3$ loaded. As shown, only the Lewis acid site (in the 1,450 cm^{-1} frequency range) was observed on the surface of γ-Al$_2$O$_3$. The amount of Lewis acid was slightly affected with different Cr$_2$O$_3$ loaded.

Fig. 15 illustrates the effect of γ-Al$_2$O$_3$ promoted with different K$_2$CO$_3$ and 15% Cr$_2$O$_3$ loaded. As shown, the selectivity to thiophene can be improved with less than 7% K$_2$CO$_3$ promoted. The improvement of selectivity to thiophene was attributed to the strong acid site covered by K$_2$CO$_3$ added. Further K$_2$CO$_3$ added will cover the acid site on the surface and inhibit the O/S exchanged reaction. The reaction time was also improved with less than 7% K$_2$CO$_3$ promoted. With more than 7% K$_2$CO$_3$ promoted, the reaction time did not change markedly.

In general, as shown from Figs. 12 to 15, C$_2$O$_3$/γ-Al$_2$O$_3$ promoted by K$_2$CO$_3$ was a bifunctional catalyst which supplied two active sites: one was the Lewis acid site from γ-alumina attributed to the O/S exchange to yield butanethiols. Another was Cr^{3+} attributed to dehydrogenation and dehydrocyclization. The synergistic effect of two active sites would result in the formation of thiophene
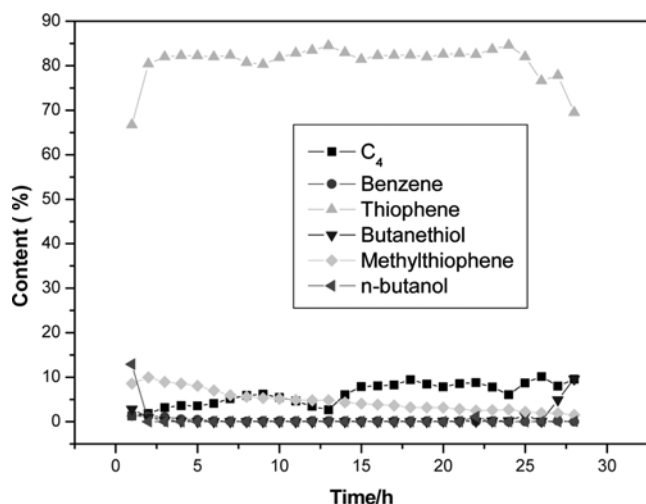
Fig. 16. Products' distribution on a time stream at 450 ℃ (mole ratio of CS₂ to n-Butanol: 6, LHSV: 1 h⁻¹).
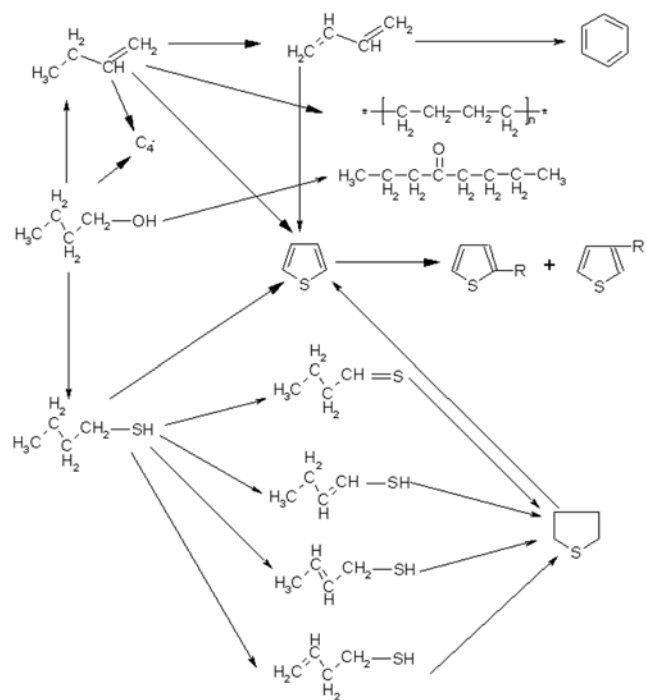

Fig. 17. Thiophene synthesis pathways from the reaction of n-Butanol and carbon disulfide.

from the reaction of n-Butanol and carbon disulfide.

6. Thiophene Synthesis Pathways

As shown in Fig. 16, the main product of the transformation of n-Butanol and carbon disulfide over promoted chromia on γ-Al₂O₃ catalysts was thiophene. However, more than 10 different reaction products were detected. The products which appeared in concentrations up to 1% in every catalytic run were butane, 1-butene, 2-butene, benzene, butanethiol, 1,3-butadiene, 2-methylthiophene, 3-methylthiophene and 2,3-dimethylthiophene. Products such as 2,3-and 2,5-dihydrothiophene, 2,3-dimethylthiophene, butanal, hexenes, benzo [2,3-b] thiophene, thiophenol, etc. were also detected. They appeared in concentrations lower than 1%.

Fig. 17 illustrates thiophene synthesis pathways from the reaction of n-Butanol and carbon disulfide. As shown, the matrix of possible reactions was established. From this matrix it is apparent that there are four processes that n-Butanol can undergo:

(a) *O/S exchange.* A surface mediated or gas phase heteroatom exchange to yield butanethiols.

(b) *Dehydration.* Acid base catalyzed or thermal reaction to form butane, which can be used as feedstock to produce thiophene.

(c) *Cyclization.* Cr³⁺ active site catalyzed butanethiol to form heterocycles which can be dehydrogenated to produce thiophene. Or catalyzed n-Butanol to form tetrahydrofuran, which then acts as a starting material to produce tetrahydrothiophene and then is dehydrogenated to form thiophene.

(d) *Dehydrogenation.* Cr³⁺ active site catalyzed tetrahydrothiophene to form thiophene. Or catalyzed n-Butanol to form butenol, which is then cyclized and O/S exchanged to produce thiophene.

CONCLUSION

Cr₂O₃ loaded on γ-Al₂O₃ can improve the selectivity to thiophene due to enhancement of dehydrogenation and dehydrocyclization of the C4 hydrocarbon. ã-alumina promoted by K₂CO₃ can prolong the catalyst life due to decreased occupation of the active site on the surface of the catalyst by carbon deposition. The catalytic behavior of these catalysts can be attributed to their multi-functional acidic, dehydrogenating and cyclized properties.

The optimization of the operating conditions, by using γ-Al₂O₃ promoted by 7% K₂CO₃ with 15% Cr₂O₃ loaded, leads to an 87% selectivity to thiophene and catalyst stability for 55 h on stream at the following reaction conditions: reaction temperature at 450 ℃, LHSV 1 h⁻¹, and the ratio of CS₂ to n-Butanol (mol) was 6.

O/S exchange can easily be carried out at about 250 ℃ to yield butanethiol. Cyclization of the butanethiol and dehydrogenation to yield thiophene need higher temperatures of about 400 ℃. Cyclization of the butanethiol and dehydrogenation to yield thiophene were key reaction steps for thiophene formation.

ACKNOWLEDGMENT

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