Base-Free Catalytic Aerobic Oxidation of Mercaptans for Gasoline Sweetening over HTLcs-Derived CuZnAl Catalyst

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An aerobic oxidative removal of mercaptans from gasoline in the absence of liquid base has been demonstrated for gasoline sweetening over CuZnAl catalyst. This process could proceed at large WHSV of gasoline (50–70 h^{-1}) with >95% mercaptan conversion at 150°C (or 300°C) using an O_2/S molar ratio of 20–40. At 150°C, dimerization of mercaptans occurred dominantly to form their disulfides. At 300°C, deep oxidation of the mercaptans to SO_2 was the dominant process in the first tens of hours, but it decreased then with prolonged time on stream and meanwhile the dimerization increased. The spent catalyst could be restored to its fresh activity level only through a calcination treatment in air. This process was also demonstrated to be effective and efficient for sweetening of a real cracking gasoline. © 2009 American Institute of Chemical Engineers *AIChE J,* 55: 3214–3220, 2009

Keywords: catalysis, gasoline sweetening, aerobic oxidation, mercaptan, hydrotalcite, copper, zinc

Introduction

Mercaptans are widely distributed in petroleum products, especially in light oil like gasoline. They cause foul odor, deterioration of additives in finished products except being corrosive. Therefore, it is necessary to remove them from the fuels, which is usually called sweetening in the petroleum industry.[1] The mercaptan removal technology widely used so far is the Merox process developed by UOP. The process is based on the ability of a metal chelate, i.e., sulfonated cobalt phthalocyanine (CoPcS), to catalytically oxidize the mercaptans to their corresponding disulfides in alkaline medium by molecular oxygen. It has been widely accepted that mercaptan reacts with a base to form mercaptide anion and the mercaptide is then oxidized with O_2 to disulfide in the presence of catalyst such as CoPcS; note that the mercaptide formation is of primary importance since mercaptide ion (as a ligand) can bind to CoPcS more strongly than mercaptan.[2] The reaction mechanism can be summarized as overall reaction: $2RSH + 1/2O_2 \rightarrow RSSR + H_2O$.

In the Merox process, an aqueous base, such as sodium hydroxide or ammonia, is used to fulfill the purpose. But the aqueous bases always cause an environmental problem of spent caustic materials. As a consequence, the disposal of the spent caustics has become more and more difficult and expensive. One possible way to solve this problem is to use inorganic[1–11] solid bases or polymeric[9–13] as carriers to support CoPcS for the fuel sweetening. Extended studies[1–7] have been devoted to the MgO-based solid catalysts, investigating the basicity and textural/structural properties as well as the synergistic effect between basic sites and CoPcS. The previous efforts make the Merox process much cleaner (i.e., the aqueous bases are only required for catalyst regeneration), but we should bear in mind that a typical refinery handles 100,000–200,000 barrels a day. This means that bulk amount of spent caustics is still a problem on a long view.

Herein, an aerobic oxidation of mercaptans (AOM)[14] for high efficiency gasoline sweetening, without any spent caustic emission, has been demonstrated by mixing small amount of air with the fuel and passing through a fixed bed packed

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with CuZnAl catalysts derived from hydrotalcite-like compounds (HTLcs). Copper-zinc oxide composites have been widely used in methanol synthesis industry and have been receiving growing interest due to their potential applications in the hydrogen production from methanol steam-/autothermal-reforming[15,16], catalytic wet oxidation of phenol and CO oxidation.[17] Very recently, it has been demonstrated that the HTLcs-derived CuZnAl catalysts can selectively and efficiently convert thiophene and its derivatives in the gasoline fuel into SO_2 at near 300°C and the atmospheric pressure using a high O_2/S molar ratio of 50–200.[18,19] The promotive effects have been observed clearly over the HTLCs-derived CuZnAl oxide composites for aforementioned reaction processes.[15–17] The promoted catalytic performance of HTLcs-derived CuZnAl catalysts, especially the catalytic oxidation, is likely assignable to the increase of the surface concentration of ionized oxygen vacancies.[20] As this is sensible, we asked ourselves whether they can directly catalyze the oxidation of mercaptan with O_2 to form disulfide with omitting the formation of mercaptide ion[2] from mercaptan with a base. In the present work, we investigated the effects of reaction parameters, such as weight hourly space velocity, O_2/S molar ratio and reaction temperature, on the performance of the HTLcs-derived CuZnAl catalysts for the aerobic oxidation of mercaptans in gasoline. The regenerability of CuZnAl catalysts was also studied, showing that the spent catalyst could be restored to its fresh activity level only through a calcination treatment in air.

Experimental

Preparation of HTLcs-derived CuZnAl catalyst

CuZnAl HTLcs were obtained by coprecipitation method first. An aqueous solution of sodium carbonate (0.5 mol/L) and sodium hydroxide (2.0 mol/L) is used as precipitant. The aqueous solution dissolving Cu/Zn/Al nitrates at a Cu/Zn/Al atom ratio of 37:15:48 to a total metal concentration of 2.0 mol/L was dropped, in parallel with the precipitant, into 100 mL deionized water to form precipitate at 60°C under vigorously stirring and controlled pH of about 9. The resulting precipitate was aged under continuous stirring in the mother liquor at the same temperature overnight. After filtering, the precipitate was washed thoroughly with deionized water until Na^+ elimination and dried overnight at 100°C to form HTLcs. CuZnAl oxide-composite catalysts were then obtained by thermal decomposition of the HTLcs in air. The decomposition procedure was programmed from room temperature to 600°C at a heating ramp of 1°C/min with a hold time of 3 h at the set point. Decomposition of CuZnAl HTLcs at 600°C has proven to be able to endow the resulted catalysts with highly dispersed CuO (copper dispersion: 23.7%), large specific surface area (102 m^2/g), improved CuO–ZnO interaction and promoted catalyst reducibility/re-oxidability.[15] That is why a temperature of 600°C was selected to decompose the CuZnAl precursor for the catalyst preparation.

Catalyst test

The AOM testing was performed with catalyst particulates (150–250 μm) packed into a fixed-bed continuous-flow quartz tube reactor (14 mm i.d.). Loading amount of the catalysts was 1.0 g if not specified. The CuZnAl catalysts were directly heated and exposed to a feed stream at atmospheric pressure. Mercaptan-containing gasoline was fed continuously using a high-performance liquid pump, in parallel with air (as oxidant) feeding by a calibrated mass flow controller, into the reactor heated to the desired reaction temperature. Reaction temperature, weight hourly space velocity (WHSV) and O_2/S molar ratio were varied in range from 150 to 300°C, 20 to 70 h^{-1}, and 5 to 40, respectively. The control experiments throughout the temperature and O_2/S ratio range of interest showed that the quartz tube reactor induced negligible conversion (<5%). Feed stream was the retail gasoline (390 μg/g S) blended with various mercaptans such as 1-pentanthiol to total sulfur content of 890 μg/g or a real cracking gasoline (218 μg/g S from mercaptans; taken from SINOPEC Shanghai Petrochemical Company.).

The residual mercaptan level in gasoline were monitored by sampling at regular time intervals and analyzed by silver nitrate titration method[4,13] combined with a Varian CP 3800 gas chromatography-pulsed flame photometric detector (GC-PFPD, with a 60-m CP-sil 8 CD capillary column). The sulfur contents in the liquid effluent before and after silver nitrate titration were detected using a WK-2D microcoulometry analyzer (Jiangsu Electroanalysis, China), and therefore the difference value is the content of mercaptans in the liquid effluent. The effluent gas was analyzed with the GC-PFPD combined with a HP 6850 gas chromatography-thermal conductivity detector (GC-TCD, with a 30 m AT-plot capillary column) for identification of the gaseous sulfur-containing product and CO/CO_2, respectively.

Results and Discussion

Effects of weight hourly space velocity and O_2/S molar ratio

The effect of WHSV on the performance of aerobic oxidation of 1-pentanthiol blended in a retail gasoline over the HTLcs-derived CuZnAl catalysts has been investigated with the results shown in Figure 1. Clearly, decrease of 1-pentanthiol conversion could be observed with the increase of WHSV at reaction temperature of 150°C using an O_2/S molar ratio of 20. 1-pentanthiol conversion remained at ~100% with the WHSV at or below 30 h^{-1} and then decreased slowly with further increasing WHSV up to 70 h^{-1}. Note that high 1-pentanthiol conversion could remain at ~94% when operating the reaction with a high WHSV of 70 h^{-1}. For comparison, the space velocity for the traditional Merox process is generally 1–5 h^{-1}, being much lower than the space velocity of our new process.[1–13,21] Obviously, the reaction efficiency is at least 10 times higher than the Merox process. In other words, in equivalent bed volume, to sweeten equivalent gasoline that can be done via AOM within 100 h at 70 h^{-1}, traditional Merox process will need >3000 h with a WHSV of 2 h^{-1}.[5]

Figure 2 shows the effect of O_2/S molar ratio on the performance of HTLcs-derived CuZnAl catalyst for the aerobic oxidation of 1-pentanthiol blended in the retail gasoline. It is clear that high O_2/S molar ratio facilitated the conversion of 1-pentanthiol at 150°C using a WHSV of 50 h^{-1}. 1-pentanthiol conversion was promoted from 87 to 93% when the

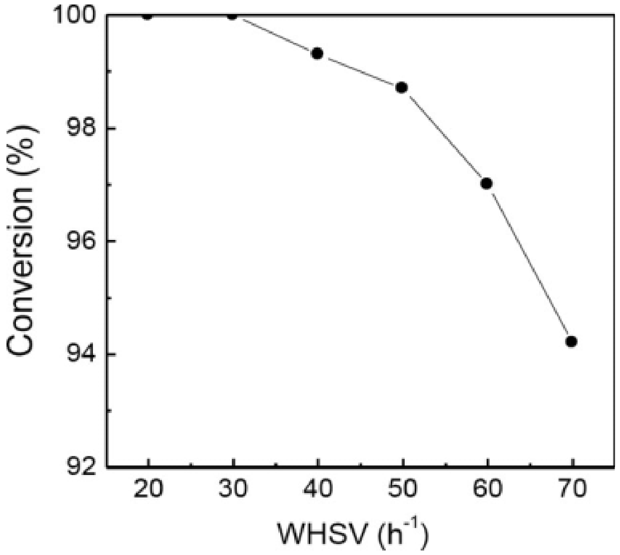

Figure 1. Conversion of 1-pentanthiol vs. gasoline WHSV over the HTLcs-derived CuZnAl catalysts for sweetening of gasoline with 500 μg/g sulfur from 1-pentanthiol.

Reaction conditions: 150°C, 0.1 MPa, and O_2/S molar ratio of 20.

O_2/S molar ratio is increased from 5 to 10. Nevertheless, higher O_2/S molar ratio (e.g., 20–30) was required for achieving >98% conversion of 1-pentanthiol.

In addition, CO and CO_2 were formed only in trace amounts throughout the temperature and O_2/S ratio range of interest, indicating that non-sulfur-containing hydrocarbon fuel was left untouched in this AOM process.

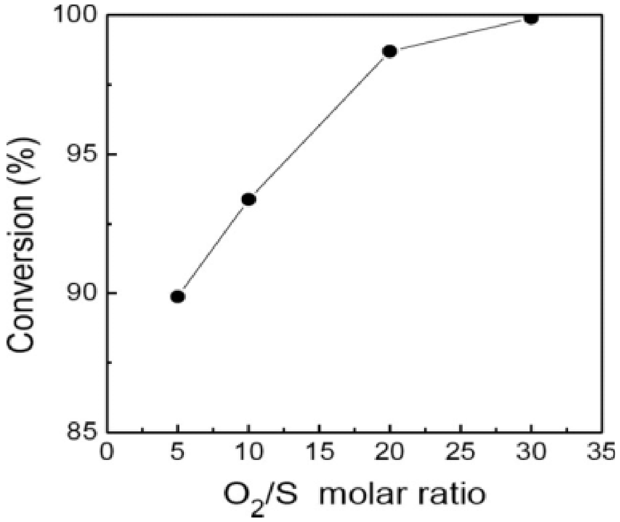

Figure 2. Conversion of 1-pentanthiol vs. O_2/S molar ratio over the HTLcs-derived CuZnAl catalysts for sweetening of gasoline with 500 μg/g sulfur from 1-pentanthiol.

Reaction conditions: 150°C, 0.1 MPa, and WHSV of 50 h^{-1}.

Effect of reaction temperature

Figure 3 shows the 1-pentanthiol conversion vs. reaction temperature over the HTLcs-derived CuZnAl catalysts using O_2/S molar ratio of 20 and WHSV of 50 h^{-1}. In the reaction temperature range of 100–300°C, the CuZnAl catalysts demonstrated excellent initial activity with the 1-pentanthiol conversion of >98%. However, the activity maintenance evolution with prolonged reaction time was quite different at varied reaction temperatures. At 150 and 300°C, clearly, 1-pentanthiol conversion was sustained at >95% within 80 h and then was decreased to ~85% within another 20 h. At 200 and 250°C, however, 1-pentanthiol conversion declined quickly from ~100 to 85% and ~75% within only 30 h test, respectively. At 100°C, a high 1-pentanthiol conversion of ~94% could be obtained at the beginning of the reaction but it declined quite fast to ~49% after 3 h run (not profiled in Figure 3).

GC-PFPD analyses of the gasoline samples before and after mercaptan oxidation for the different reaction time lengths were performed with the results shown in Figure 4. At 150°C, the dimerization of 1-pentanthoil proceeded dominantly to form the corresponding disulfide during 100 h test; only a little amount of 1-pentanthoil was deeply oxidized to form SO_2 in the first several hours (i.e., 5 h) as only trace SO_2 was detected to be dissolved in the gasoline effluent (Figure 4A). At 150°C, the oxidation of 1-pentanthoil to form disulfide is absolutely the main process but is not analogous to Merox chemistry. It is suggested that HTLcs-derived CuZnAl catalysts could directly catalyze the oxidation of mercaptan with O_2 to form disulfide, unlike the Merox chemistry that the mercaptan has to be reacted with a base to form mercaptide ion firstly. In addition, our previous

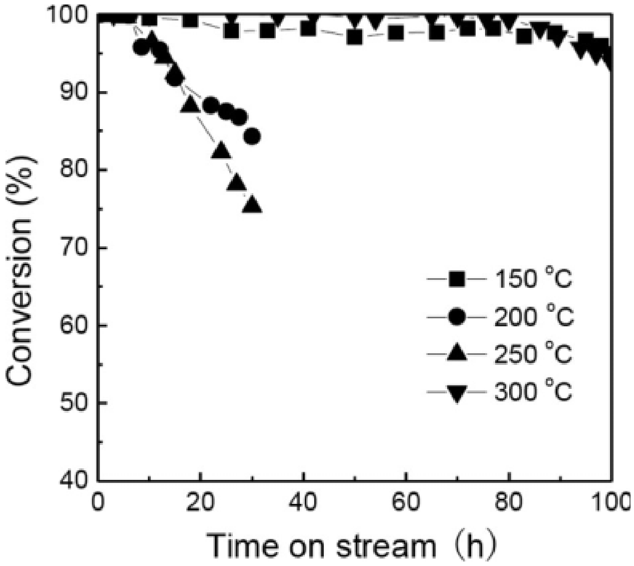

Figure 3. Conversion of 1-pentanthiol vs. time on stream over the HTLcs-derived CuZnAl catalysts for sweetening of gasoline with 500 μg/g sulfur from 1-pentanthiol at various reaction temperatures.

Reaction conditions: O_2/S molar ratio of 20, WHSV of 50 h^{-1}, and 0.1 MPa.

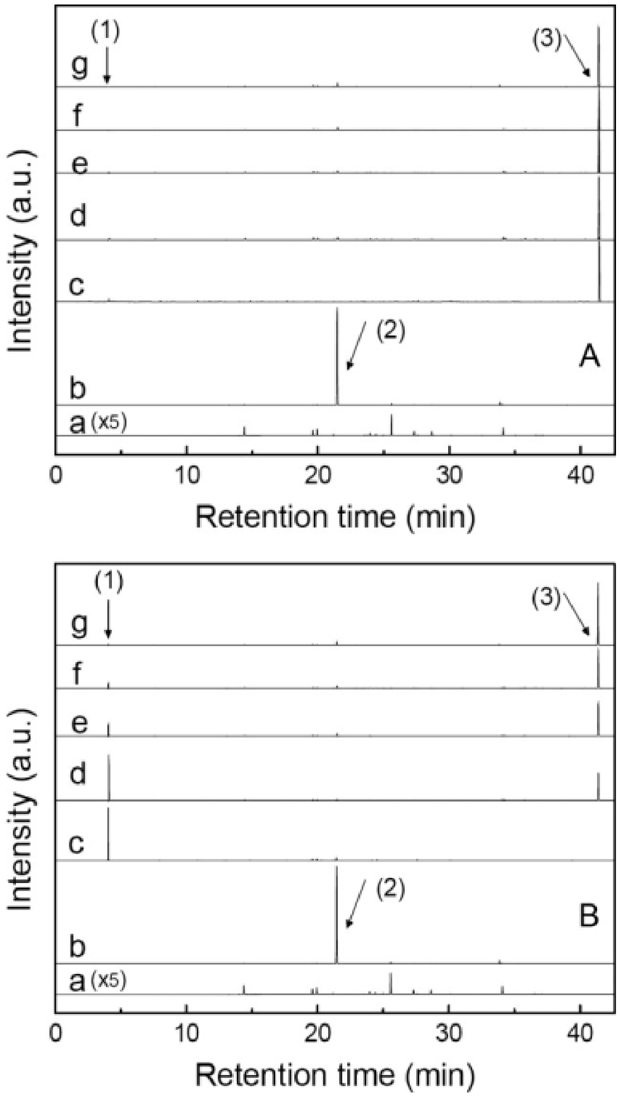

Figure 4. GC-PFPD chromatogram for sulfur compounds in (a) retail gasoline, (b) sample *a* blended with 500 μg/g 1-pentanthiol sulfur, and after sweetening reaction for (c) 5 h, (d) 25 h, (e) 50 h, (f) 75 h, and (g) 100 h at (A) 150°C and (B) 300°C, respectively.

Reaction conditions: O_2/S molar ratio of 20, WHSV of 50 h^{-1}, and 0.1 MPa. Note: (1) SO_2, (2) 1-pentanthiol, and (3) disulfide of 1-pentanthoil.

work has shown that the HTLcs-derived CuZnAl catalysts permitted stronger interaction between CuO and ZnO mini-crystal and larger CuO-ZnO contact interface.[15] According to Frost,[20] this would provide a significant increase of surface concentration of the ionized oxygen vacancies as a consequence of promoted Cu–Zn interaction. Moreover, both CuAl-HTLcs-derived and ZnAl-HTLcs-derived catalysts were found not active for the titled process, likely due to the absence of the Cu–Zn interaction. Consequently, it is suggested that the ionized oxygen vacancies are likely the active sites for the AOM process.

At 300°C, deep oxidation of 1-pentanthiol to SO_2 became the dominant process in first tens of hours. After that, it was decreased fast with the prolonged time on stream and meanwhile the dimerization of 1-pentanthoil was increased rapidly (Figure 4B). GC-PFPD analyses of the gas effluents corresponding to the cases in Figure 4B were also performed. The amount of SO_2 in the gas effluent was decreased likewise with the prolonged time on stream, being consistent with the degradation evolution of the deep oxidation process as shown in Figure 4B. At 200 or 250°C, the dimerization and deep oxidation processes almost equably presented to form disulfides and SO_2 as evidenced by GC-PFPD analyses (not shown). The amount of SO_2 and disulfide formed from 1-pentanthoil almost remained unchanged within first 10 h run, but then declined continuously within another 20 h. This observation is in good agreement with the 1-pentanthiol conversion evolution behavior at 200 and 250°C as shown in Figure 3.

SO_2 poisoning

According to the foregoing studies, it is thought that the formation of SO_2 is likely the main cause of the different evolution of the activity maintenance with the prolonged reaction time at varied reaction temperatures. Thus, we proceed to perform the aerobic oxidation of 1-pentanthoil in the presence of SO_2 (5 vol % in air) with the results as shown in Figure 5. As expected, CuZnAl catalysts deactivated fast when operating the reaction at and below 250°C (Stages a,c,e in Figure 5) in the presence of SO_2. Interestingly, such deactivated catalysts could deliver the 1-pentanthiol conversion of >98% when increasing the reaction temperature to 300°C (stages b,d,f in Figure 5) in the presence of SO_2. For instance, at 150°C 1-pentanthoil conversion was decreased quickly from >98 to 78% in the presence of SO_2 within 7 h.

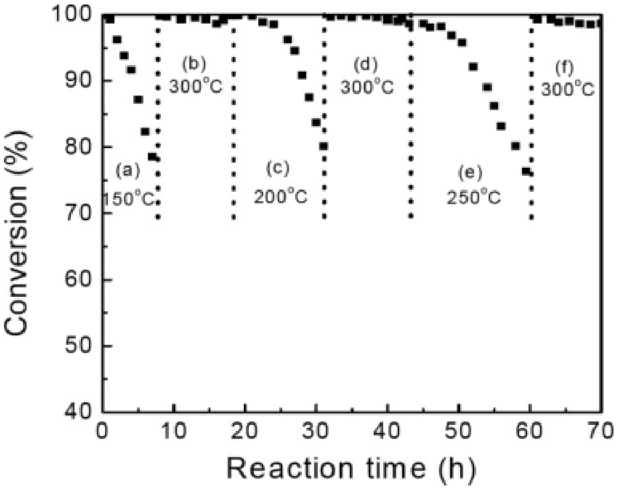

Figure 5. Conversion of 1-pentanthiol vs. time on stream over the HTLcs-derived CuZnAl catalysts for sweetening of gasoline with 500 μg/g sulfur from 1-pentanthiol in the presence of 5 vol % SO_2 in air at (a) 150°C, (b) 300°C (increased from 150°C), (c) 200°C (decreased from 300°C), (d) 300°C (increased from 200°C), (e) 250°C (decreased from 300°C), and (f) 300°C (increased from 250°C).

Afterwards, the catalyst bed was heated to 300°C and as a result 1-pentanthiol conversion of >98% was obtained again and was sustained until the bed temperature was reduced designedly to 200 or 250°C.

By combining the above information with the observation that the CuZnAl catalysts went on quite different reactivity maintenance evolution with the prolonged reaction time in the temperature range from 150 to 300°C, it is suggested that the SO_2 poisoning was the main cause for the fast deactivation of the CuZnAl catalysts at 200 or 250°C. At 150°C, the dimerization of 1-pentanthiol was dominant only with trace SO_2 formation just within first 5 h. As a result, SO_2 poisoning was avoided thereby ensuring the activity maintenance with the prolonged reaction time. At 200 or 250°C, deep oxidation of 1-pentanthiol occurred obviously and the SO_2 product was relatively difficult to sneak away from the catalyst surface[18]; therefore, quick amassment of sulfite deposits took place to poison the catalyst. At 300°C, SO_2 product could escape easily from the catalyst surface, but a slow and continuous SO_2 deposition on the catalyst surface still took place until to a adsorption/desorption equilibrium.[18] Obviously, this SO_2 deposition resulted in a degradation of the oxidative ability of the catalyst, and as a result, the deep oxidation of 1-pentanthoil was decreased with the prolonged time (see Figure 4B). Even so, such partially poisoned catalyst surface was still active at 300°C to catalyze the oxidative dimerization of 1-pentanthoil to form disulfide (see Figure 4B).

However, it is not clear why the fast deactivation of CuZnAl for the oxidation of 1-pentathiol occurred at 100°C. Likely, the reaction temperature is too low to activate the oxygen molecular as we observed a similar deactivation evolution at 100°C in the case of using inert N_2 to replace air.

Aerobic oxidation of ethanethiol and 1-octyl-mercaptan

We also proceed to perform the aerobic oxidation of ethanethiol and 1-octyl-mercaptan blended in a retail gasoline at the mercaptan sulfur content of 500 μg/g over the HTLcs-derived CuZnAl catalysts. The results clearly indicate that the aerobic oxidation reactivity improved in the order of 1-octyl-mercaptan < 1-pentanthiol < ethanethiol. At 150°C with the WHSV of 50 h^{-1} and the O_2/S (mercaptan sulfur) molar ratio of 40, their conversions remained at: 98.3, 99.0 and >99.9% after 20 h run; 90.2, 95.4 and 99% after 100 h run. This order of reactivity is consistent with that in Merox process.

Reactivity and regenerability of the CuZnAl catalysts for sweetening real cracking gasoline

Tentative sweetening experiments on a real cracking gasoline containing 218 μg/g sulfur from mercaptans were performed over the HTLcs-derived CuZnAl catalysts (5 g) with the results as shown in Figure 6. The feed was directly introduced into the catalytic bed without washing using a NaOH solution for removal of the acidic compounds. It is clear from the results in Figure 6A that the CuZnAl catalysts showed excellent mercaptan oxidation performance for the real cracking gasoline under reaction conditions: 150°C, O_2/S ratio of 30, WHSV of 50 h^{-1} and 0.1 MPa. The mercaptan removal efficiency was retained at >98% within first 70 h and then was reduced slightly to ~94% and sustained within another 70 h. Afterwards, the mercaptan removal efficiency

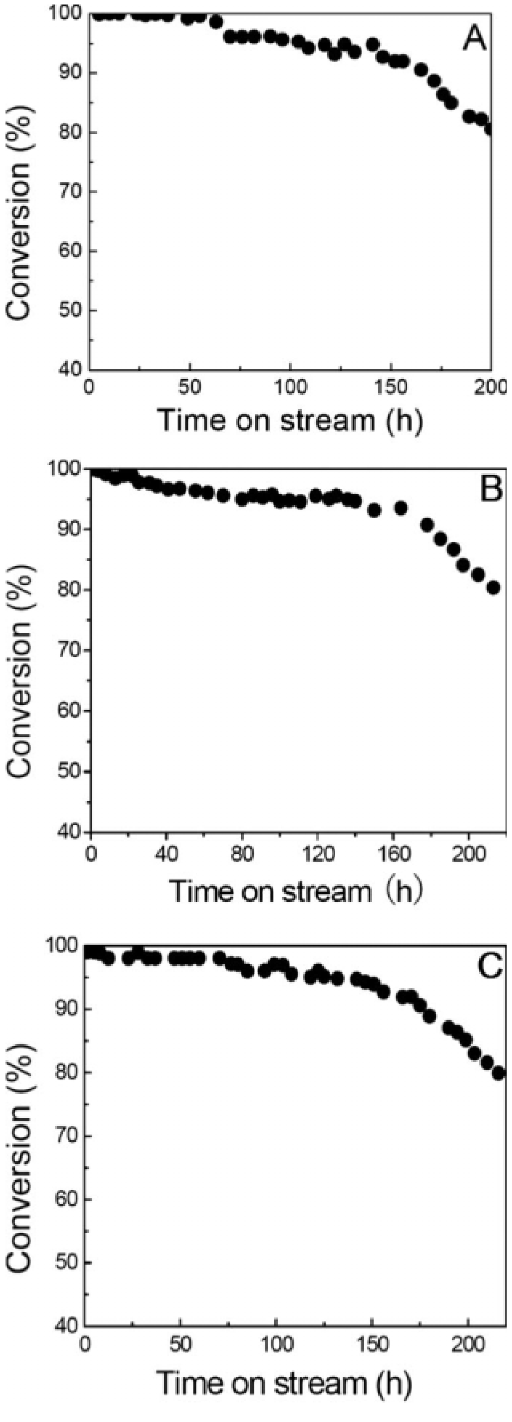

Figure 6. Reactivity and regenerability of the HTLcs-derived CuZnAl catalyst for sweetening of a real cracking gasoline with 218 μg/g mercaptan sulfur.

Mercaptan conversion vs. time on stream for (A) fresh catalyst, (B) after 1st regeneration, and (C) after 3rd regeneration. Sweetening reaction conditions: 150°C, WHSV of 50 h^{-1}, O_2/S molar ratio of 30, 0.1 MPa. Regeneration conditions: 400°C for 3 h in air.

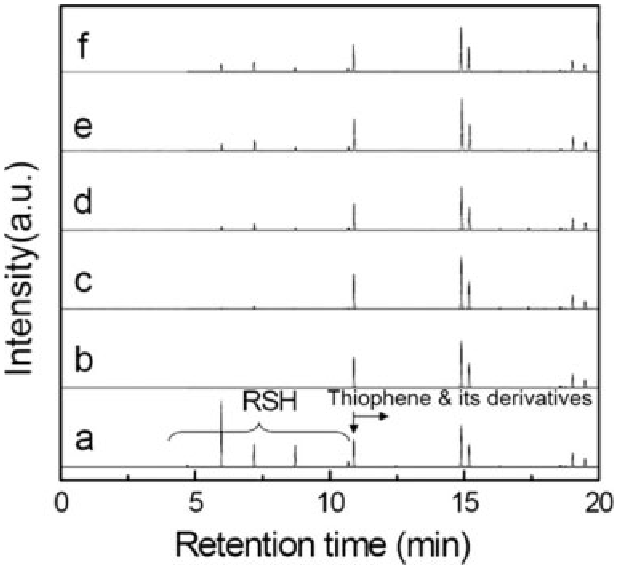

Figure 7. GC-PFPD chromatogram for sulfur compounds in (a) real cracking gasoline, (b) sample *a* after complexation by $AgNO_3$, and liquid-phase effluent in the case of Figure 6A at (c) 50 h, (d) 100 h, (e) 150 h, and (f) 200 h.

Sweetening reaction conditions: 150°C, WHSV of 50 h^{-1}, O_2/S molar ratio of 30, 0.1 MPa.

decreased slowly from ~94 to 80% (the lowest acceptable mercaptan conversion by sweetening industry) with the prolonged reaction time from 140 to 200 h (Figure 6A). The regeneration experiments on the spent CuZnAl catalysts after the longer-term tests were carried out. Figures 6B, C show the mercaptan oxidation performance of the CuZnAl catalysts after regenerated first-time and third-time by calcination at 400°C for 3 h in air, respectively (totally regenerated three times in this work). Clearly, the spent catalysts could recover completely only through a simple calcination treatment at 400°C in air. No any degradation of the activity was observed after three reaction-regeneration cycles, suggesting that the HTLcs-derived CuZnAl catalysts possess good reaction and regeneration stability. Extended experiments at higher regeneration temperatures (500 and 600°C) were also carried out for three reaction-regeneration cycles. In all three cycles, the regenerated catalysts did not yield the reactivity for AOM better than that regenerated at 400°C.

The detailed sulfur analyses by GC-PFPD show that the mercaptan compounds were oxidized with high selectivity and high efficiency but thiophene and its alkylated derivatives were left untouched (Figure 7). According to the forgoing results for the oxidation of model compounds, at 150°C the mercaptan compounds in the real cracking gasoline should be selectively oxidized with O_2 to form the corresponding disulfides. Unfortunately, the GC-PFPD analyses failed to distinguish the disulfide products from so many thiophenic sulfur-containing compounds in the real cracking gasoline (Figure 7). Our previous work has shown that thiophene and its derivatives are not so reactive as mercaptan and only can be deeply oxidized to SO_2 in the absence of mercaptan compounds at under more severe conditions: 300°C, high O_2/S molar ratio of 50–200.[18,19]

Moreover, tests on the HTLcs-derived CuZnAl catalysts prepared with the decomposition temperature at or below 500°C, did not yield the activity and durability for such real cracking gasoline sweetening better than the catalysts prepared with the decomposition temperature at 600°C. For comparison, CuAl-HTLcs and ZnAl-HTLcs derived catalysts were also prepared and tested in the sweetening process. Whereas compatible reactivity could be obtained at the beginning of the reaction, fast deactivation presented with the prolonged time. Not surprisingly, the decomposition of CuZnAl HTLcs at 600°C has proven to be able to endow the resulted catalysts with highly dispersed CuO, large specific surface area, especially improved CuO-ZnO interaction and promoted reducibility/re-oxidability.[15] Nevertheless, decomposition of the CuZnAL-HTLcs at or above 700°C results in severe sintering of CuO phase and meanwhile facilitates the formation of $CuAl_2O_4$ spinel,[15] thereby degrading the catalyst activity for the sweetening reaction.

Now, the nature for the CuZnAl catalyst deactivation and regeneration is still not clear, but better understanding of this is particularly desirable for the rational catalyst improvement. The work along this line is in progress in our research group.

Conclusion

Our results establish a promising cost-efficient and base-free gasoline sweetening process, by which mercaptans in gasoline can be selectively converted into disulfides and/or SO_2 when the fuel is mixed with a small amount of air and passes through a fixed bed packed with our HTLcs-derived CuZnAl catalyst. The effects of reaction parameters, such as weight hourly space velocity, O_2/S molar ratio and reaction temperature, have been investigated on the performance of aerobic oxidation of mercaptans in gasoline. It is found that this process could proceed at high throughput with high mercaptan conversion at 150 and 300°C using lower O_2/S molar ratio of 20–40. Dimerization of mercaptan occurs dominantly to form disulfide compounds at 150°C. Interestingly, at 300°C deep oxidation of mercaptan is the dominant process in first tens of hours, but it attenuates with prolonged time on stream and meanwhile the dimerization reaction boosts up.

The CuZnAl-HTLcs-derived catalyst shows excellent mercaptan oxidation performance for real cracking gasoline (containing 218 μg/g mercaptan sulfur) under reaction conditions: 150°C, O_2/S ratio of 30, WHSV of 50 h^{-1} and 0.1 MPa. The mercaptan removal efficiency is retained at >94% within 140 h and then decreases slowly to ~80% at the end of 200 h test. Through entire 200 h test, the mercaptan compounds are selectively oxidized but thiophene and its alkylated derivatives are left untouched. The spent catalyst can recover to its fresh activity level only through a calcination treatment at 400°C in air, and can be regenerated again and again without degradation of the catalyst activity for real cracking gasoline sweetening.

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