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The effect of N-containing compounds on oxidative desulphurization of liquid fuel

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ABSTRACT

The oxidative removal of organic sulfur compounds from model fuel with H_2O_2 over Ti-containing molecular sieves in the presence of N-containing compounds had been studied. The effect of the types and amounts of nitrides on oxidative desulphurization were investigated. It has been shown that pyridine and pyrrole have adverse impact on the oxidation of thiophene and lead to the decrease of corresponding removal rate. The pyridine has stronger influence than pyrrole. Quinoline and indole have no impact on the final removal rate of thiophene. However, the two kinds of nitrides, as well as carbazole, have obvious impact on the oxidation removal of benzothiophene and 4,6-dimethyl dibenzothiophene. The effect of nitrides on oxidative desulphurization can be attributed to the strong adsorption of nitrides and their oxidized products on the active sites of catalysts. For pyridine and quinoline, which are basic nitrides, their adsorptions on catalysts are even stronger than that of sulfides.

1. Introduction

Following the stringent request of the world's gasoline and diesel fuel legislation on sulfur, increasing technical and operational challenges are imposed to the traditional hydrodesulphurization (HDS). HDS is an important part in clean fuel technology; to meet the new emission control standard, HDS technique must be operated at higher temperature and pressure and consuming larger amount of hydrogen. Therefore, the non-HDS technologies such as catalytic oxidative desulphurization (ODS) as a new desulphurization technology develop quickly. In this process, benzothiophene (BT), dibenzothiophene (DBT), and their corresponding alkyl derivatives can be oxidized over various catalysts such as organic acids [1–3], polyoxometalate [4,5], Ti-containing molecular sieves [6,7], $[C_{18}H_{37}N(CH_3)_3]_4[H_2NaPW_{10}O_{36}]$ [8,9]. Ma et al. [10] explored a novel oxidative desulphurization method of liquid hydrocarbon fuels, which combines a catalytic oxidation step of the sulfur compounds directly in the presence of molecular oxygen and an adsorption step of the oxidation-treated fuel over the activated carbon. Even thiophene (Th), a kind of highly stable sulfide, can be oxidized effectively by H_2O_2 over TS-1 under the mild conditions [11].

In addition, it has been observed that the N- and S-containing compounds are coexisting in many kinds of fuel oil. Although the concentration of nitrides in fuel is usually much lower than that of sulfides, the former will inhibit the ultra-deep HDS process [12–16]. How about the effect of the N-containing compounds on oxidative desulphurization? Denitrogenation is considerably more difficult than desulphurization, because the organonitrogen compounds are much less reactive than the organosulfur compounds [17–20]. N-containing compounds such as indole, quinoline, acridine, carbazole in light gas oil can be oxidized over the MoO_3/Al_2O_3 [21]. Shiraishi et al. [22] showed the activities of the compounds on V-HMS lies in the order of DBT > aniline > indole > BT > carbazole. Carbazole is the most difficult compound to be removed over the Ti-HMS using H_2O_2 as the oxidant. The oxidized products of aniline and carbazole were identified as azoxybenzene and carbazole-1,4-dione. As to indole, polymerized material was obtained after oxidation. Luis et al. [23] reported when nitrogen compounds present the ODS activity decrease in this order: quinoline > indole > carbazole. To understand the effect of the N-containing compounds on oxidative desulphurization reactions, the removals of the typical sulfur compounds in the presence of nitrides were studied in this paper.

2. Experimental

2.1. Materials

Thiophene , analytical grade (Parent Medicament Company of China), benzothiophene , analytical grade (Acros organics), 4,6-dimethyl dibenzothiophene (4,6-DMDBT), 95% (Acros organics)

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were used without further treatment. 10 ml *n*-octane containing certain amount of sulfides and nitrides were used as model fuel. The toluene was used in the case of carbazole because of its infusibility in *n*-octane. Hydrogen peroxide (aqueous solution 30 wt%, Shanghai Yuanda Peroxide Company Ltd., China) was used as oxidant. Its concentration was determined by iodometric titration. Deionized water or methanol was used as solvent. Pyridine (99.5%), pyrrole (99%), indole (99%), quinoline (99%) and carbazole (96%) were purchased in China, and they were used as the model N-containing compounds without treatment.

2.2. Catalysts

The microporous titanosilicate TS-1 was hydrothermal synthesized with tetra-propyl ammonium bromide (TPABr) as the template according to the reference [24]. The mesoporous Ti-HMS was prepared with dodecylamine as the structure director, and the detailed procedure referred to the published literature [25].

2.3. Oxidative desulphurization

The sulfides and nitrides were dissolved in 10 ml *n*-octane/toluene to act as the model fuel, in which the concentrations of the sulfides and nitrides were 1000 $\mu g\ g^{-1}$ and about 200–700 $\mu g\ g^{-1}$, respectively. The oxidative reactions were performed under vigorous stirring in the water bathed jacket flask equipped with a condenser. In a typical run, 100 mg catalyst, 10 ml model fuel and 10 ml solvent containing H_2O_2 were added to the reactor. The oxidation was carried out at 333 K for some time. The oil phase was analyzed by GC-HP6890 equipped with a HP-5 capillary column (30 m × 0.25 mm, 0.32 μm film thickness) and FPD/FID detector.

2.4. Adsorption

10–20 mesh granules of Ti-containing molecular sieves were prepared, and dried at 623 K for 1 h in nitrogen circumstance firstly. Nitrogen containing sulfide or nitride drew through U tube (made by ourselves) at 298 K for some time, in which the catalyst was loaded. The weight of the catalyst was confirmed on the electronic balance at interval to obtain the adsorption amount of the catalyst.

3. Results and discussion

3.1. The effect of N-containing compounds on oxidative removal of Th

Figs. 1–4 show the effects of different N-containing compounds on oxidative removal of Th. It can be seen that different nitrides have different influences on the removal of Th, and the rational order is pyridine > pyrrole > quinoline ≈ indole. Th removal rate increased with reaction time, and it was almost stable after 5 h. The influences from pyridine and pyrrole are very distinct, especially the pyridine. They had decreased the removal rate of Th, and the more the nitrides was, the greater the effect was. The reason might be that the molecules of pyridine and pyrrole are undersized to the pore size of TS-1, so they could access the micropores of TS-1 and adsorb on the active sites. As a result, the adsorption of Th molecules on the catalysts was inhibited to a certain degree.

In order to verify this explanation, the tests of the adsorption of Th, pyridine and pyrrole over TS-1 had been performed. The result was displayed in Fig. 5. It is obvious that both pyridine and pyrrole have larger adsorption amounts than Th on TS-1 and pyridine can be adsorbed faster. This result indicated that the competition of adsorption between nitride and sulfide existed indeed in our reaction system. In addition, the catalytic performances of pyridine and pyrrole dipped TS-1 on the Th oxidation was shown in Fig. 6. It can be seen that the nitrides dipped catalysts exhibited the lower Th removal rate than the fresh one. Such results further indicated that the effects of pyridine and pyrrole on the oxidative removal of Th were due to the competitive adsorptions of nitrides on catalyst, which inhibited the adsorption of sulfide and the later oxidation.

According to the published report, the presences of N-containing compounds have no influence on the oxidative desulphurization mechanism [23], and slightly diminishing the decomposition of H_2O_2 [26,27]. There are still some other factors such as the extraction of solvent and competitive oxidation between nitrides and sulfides will affect the oxidative desulphurization. Deioned water was used as solvent in this oxidation system. Considering the infusibility of Th in the water, the contribution from the extraction of solvent is little. On the other hand, pyridine could also be oxidized [28] in our reaction systems. However, excessive H_2O_2 was added to the reaction system to ensure enough oxidant in this system and the effect from the

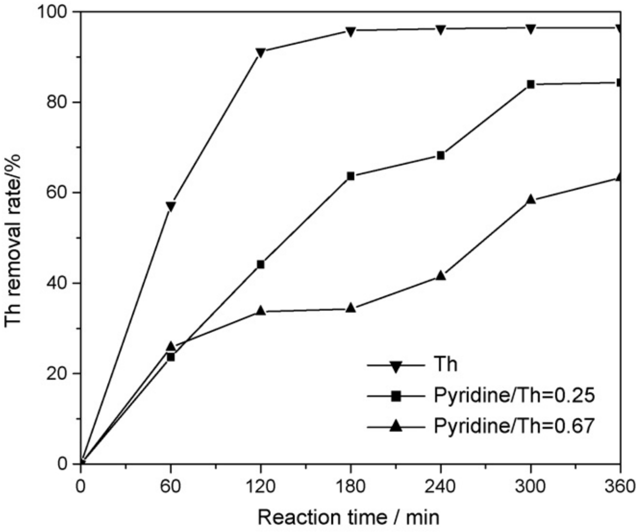

Fig. 1. Effect of pyridine on oxidative removal of Th over TS-1 using hydrogen peroxide oxidant. Reaction conditions: TS-1, 5 g L^{-1}; 333 K; 101 kPa; initial sulfur content 1000 $\mu g\ g^{-1}$; H_2O_2:(Th + nitrides) = 4; solvent, deioned water; model fuel, (Th + nitrides)/*n*-octane.

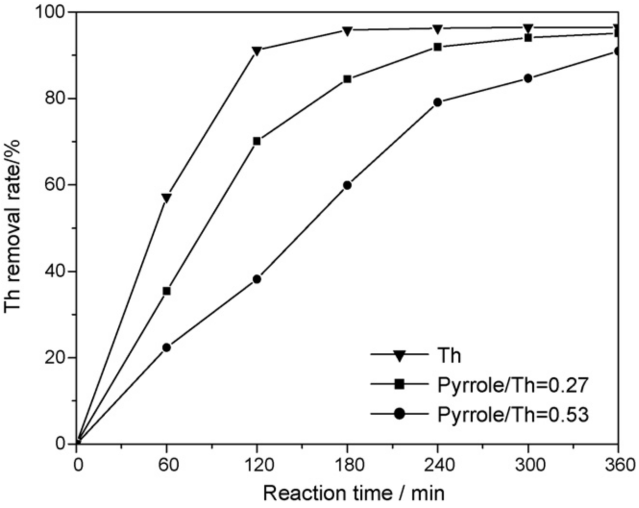

Fig. 2. Effect of pyrrole on oxidative removal of Th over TS-1 using hydrogen peroxide oxidant. Reaction conditions are the same as Fig. 1.

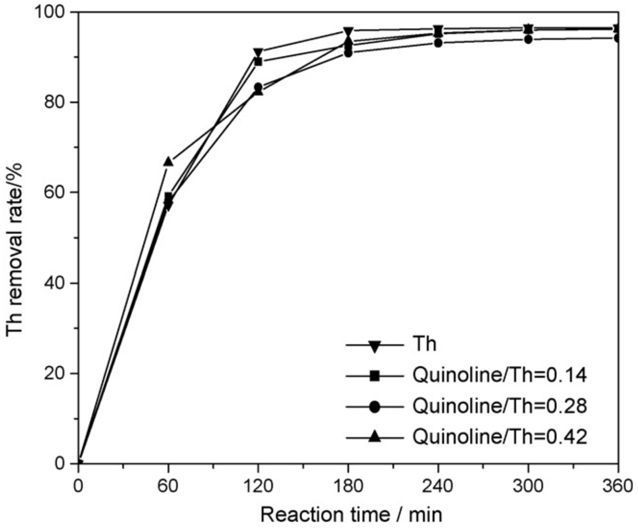

Fig. 3. Effect of quinoline on oxidative removal of Th over TS-1 using hydrogen peroxide oxidant. Reaction conditions are the same as Fig. 1.

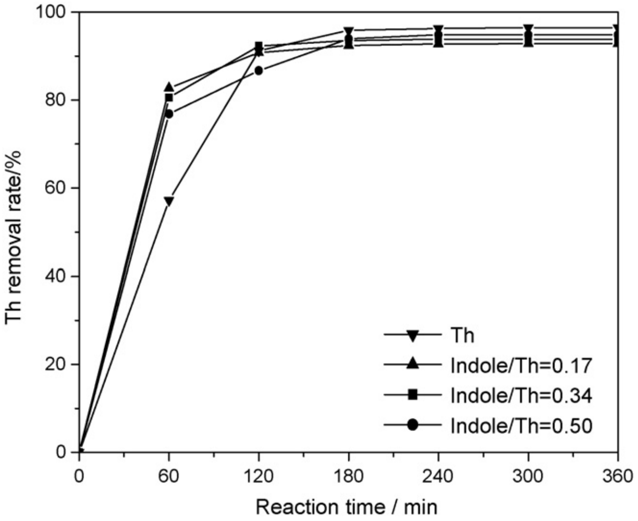

Fig. 4. Effect of indole on oxidative removal of Th over TS-1 using hydrogen peroxide oxidant. Reaction conditions are the same as Fig. 1.

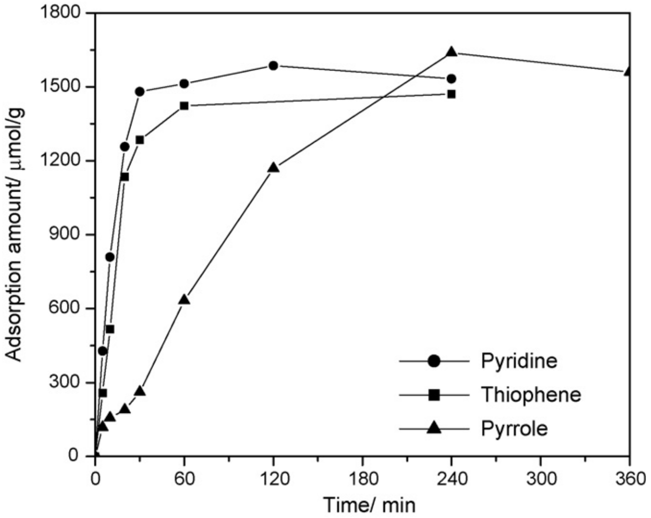

Fig. 5. Adsorptions of Th, pyridine and pyrrole over TS-1.

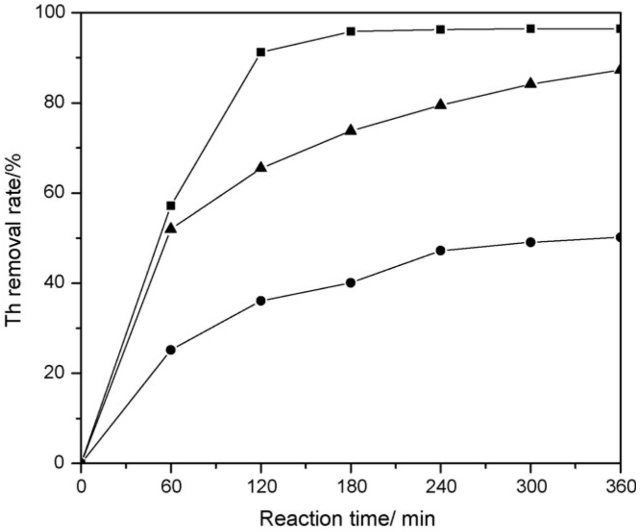

Fig. 6. Oxidation of thiophene over TS-1 (■), pyridine-dipped TS-1(●) and pyrrole-dipped TS-1 (▲) using hydrogen peroxide oxidant. Reaction conditions: TS-1, 5 g L^{-1}; 333 K; 101 kPa; initial sulfur content 1000 μg g^{-1}; H_2O_2:Th = 4; solvent, deioned water; model fuel, Th/*n*-octane.

competitive oxidation was weak. Therefore, it can be proposed that the decreased removal rate is mainly due to the competitive adsorption between nitrides and Th. In addition, pyridine has stronger impact than pyrrole on Th oxidation. The possible reason is that TS-1 catalyst contains acid site [29–31]. Basic pyridine is more easily to be adsorbed on. Quinoline and indole have scarcely impact on the final removal rate of Th because these large molecules cannot access the micropores of TS-1.

3.2. The effect of N-containing compounds on oxidative removal of BT

Tables 1 and 2 exhibited the results of BT oxidation with H_2O_2 over Ti-HMS in the presence of quinoline, indole and carbazole. Through comparing with the results of oxidative desulphurization in the absence of nitrides, it can be seen that all the nitrides decreased the initial removal rate of BT and had no impact on the final removal rate. The influences from quinoline and indole were stronger than that of carbazole.

Fig. 7 shows the adsorptions of BT, quinoline and indole over the Ti-HMS. Ti-HMS is a mesoporous material, which possesses the average pore size of 2.0–3.0 nm. Therefore, it is allowable for the quinoline, indole and carbazole to enter the framework channels and they could adsorb on the catalyst surface. Compared with BT and

Table 1
Effect of quinoline/indole on oxidative removal of BT (wt%).

Reaction time (min)	BT	Quinoline/BT = 0.25	Quinoline/BT = 0.44	Indole/BT = 0.28	Indole/BT = 0.47
30	91.80	87.44	82.14	85.40	83.50
90	100.0	100.0	100.0	100.0	100.0

Reaction conditions: Ti-HMS, 5 g L^{-1}; 333 K; 101 kPa; initial sulfur content 1000 μg g^{-1}; H_2O_2:(sulfides + nitrides) = 4; solvent, methanol; model fuel, (sulfides + nitrides)/*n*-octane.

Table 2
Effect of carbazole on oxidative removal of BT (wt%).

Reaction time (min)	BT	Carbazole/BT = 0.55	Carbazole/BT = 0.77
30	96.74	92.88	90.42
90	100.0	100.0	100.0

Reaction conditions: Ti-HMS, 5 g L^{-1}; 333 K; 101 kPa; initial sulfur content 1000 μg g^{-1}; H_2O_2:(sulfides + nitrides) = 4; solvent, methanol; model fuel, (sulfides + nitrides)/toluene.

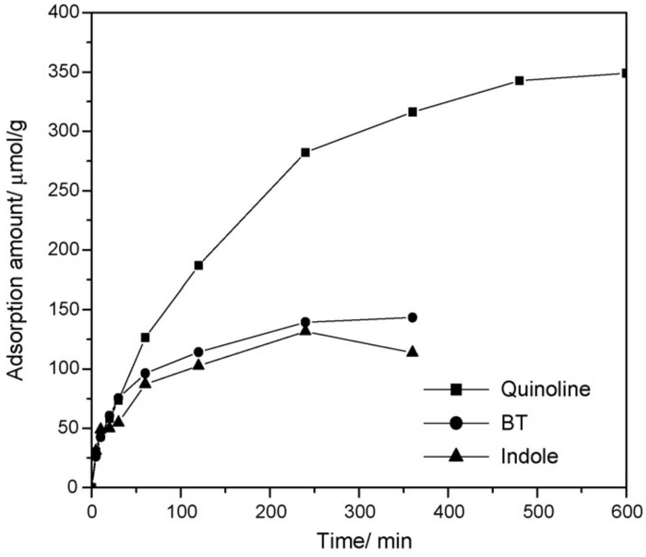

Fig. 7. Adsorptions of BT, quinoline and indole over Ti-HMS.

indole, quinoline gave the largest adsorption amounts, which could also be attributed to its basic nature. However, the removal rates of BT in the presence of quinoline and indole are very similar (Table 1). The reason may be that compared with Th, BT is more active and easy to be oxidized owing to the higher electron density of sulfur atom in it, so the difference of the influence from quinoline and indole cannot be incarnated clearly. For the same reason, both quinoline and indole only inhibit the initial removal rate of BT. In addition, considering the quinoline and indole may be oxidized in this reaction, so a competitive consumption H_2O_2 between BT and quinoline or indole may play a role in the decrease of BT removal rate. To make sure this matter, two reactions with excessive H_2O_2 were performed as shown in Fig. 8. It is obvious that BT removal rate still decreased. Therefore, the effect of nitrides on BT removal derives from the adsorption of nitrides and their oxidized products on the catalyst, rather than the competitive consumption of H_2O_2 between nitrides and sulfides. The preferential adsorptions of nitrides and their oxidized products will cover some active sites. As a result, the adsorption and oxidation of BT were restricted.

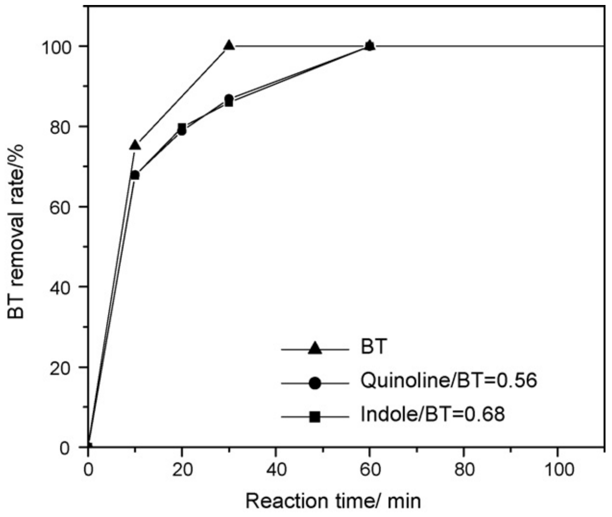

Fig. 8. Effect of indole/quinoline on oxidative removal of BT over Ti-HMS with more hydrogen peroxide oxidant. Reaction conditions: Ti-HMS, 5 g L^{-1}; 333 K; 101 kPa; initial sulfur content 1000 μg g^{-1}; H_2O_2:sulfides = 10; solvent, methanol; model fuel, (sulfides + nitrides)/*n*-octane.

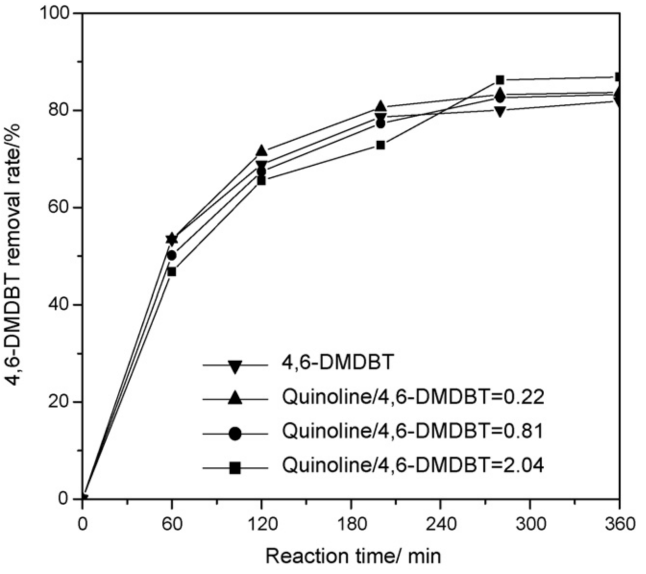

Fig. 9. Effect of quinoline on oxidative removal of 4,6-DMDBT over Ti-HMS with hydrogen peroxide oxidant. Reaction conditions are the same as Table 1.

3.3. The effect of N-containing compounds on oxidative removal of 4,6-DMDBT

The effect of N-containing compounds on oxidative removal of 4,6-DMDBT over Ti-HMS with H_2O_2 was displayed in Figs. 9 and 10.

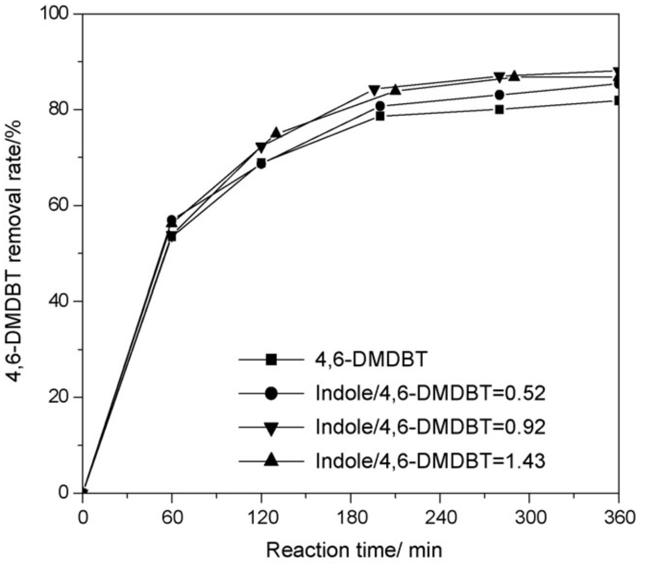

Fig. 10. Effect of indole on oxidative removal of 4,6-DMDBT over Ti-HMS with hydrogen peroxide oxidant. Reaction conditions are the same as Table 1.

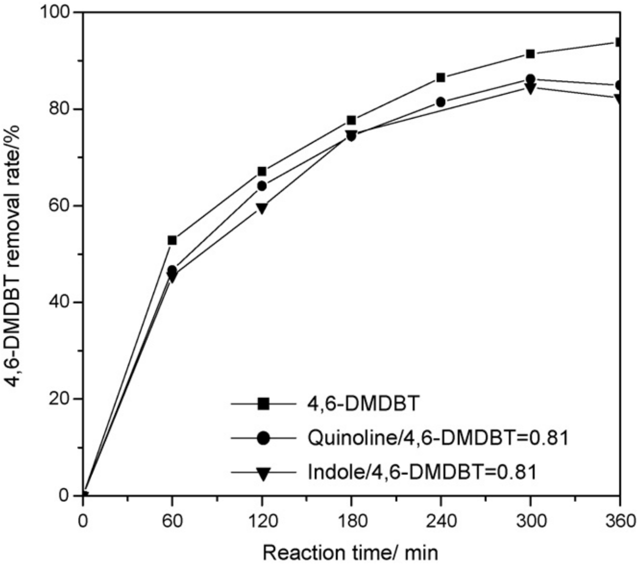

Fig. 11. Effect of quinoline/indole on oxidative removal of 4,6-DMDBT over Ti-HMS with more hydrogen peroxide oxidant. Reaction conditions are the same as Fig. 8.

It can be seen that the removal rate of 4,6-DMDBT in the presence of quinoline or indole decreased slightly at the beginning, and then increased. The enhancement of the removal of 4,6-DMDBT cannot be attributed to N-containing compounds, but the H_2O_2. To prove this effect, two processes of oxidative removal of 4,6-DMDBT when quinoline or indole presented with excessive H_2O_2 were carried out [as shown in Fig. 11]. It has been displayed that when quinoline or indole was added in, the removal rate of 4,6-DMDBT decreased clearly.

The removal rates of 4,6-DMDBT in the presence of quinoline or indole are close. The influence of N-containing compounds may be mostly ascribed to the adsorptions of N-containing compounds and their oxidized products on the active sites. As a result, the molecular of 4,6-DMDBT has less chance to take up the active sites and to be oxidized.

4. Conclusions

The effects of N-containing compounds, such as pyridine, pyrrole, quinoline, indole, and carbazole, on oxidative desulphurization of model liquid fuel were studied, using Ti-containing molecular sieves as the catalyst and hydrogen peroxide as the oxidant. Pyrrole and pyridine can impact the removal rate of Th, and pyridine has stronger influence than pyrrole. Quinoline and indole have no impact on the final removal rate of Th. The influence from quinoline and indole is stronger than that of carbazole on oxidative removal of BT. Quinoline and indole have the similar influences on the oxidative removal of 4,6-DMDBT. The effects of nitrides on oxidative desulphurization may be attributed to the preferential strong adsorption of nitrides and their oxidized products on the active sites of the catalysts.

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