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Oxidative Desulfurization of Model Oil over Au/Ti-MWW

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Abstract Au/Ti-MWW catalysts were prepared by the impregnation of $HAuCl_4$ on Ti-MWW. Its structure and properties were characterized by X-ray diffraction, N_2 adsorption and UV-visible. The oxidation reactions of thiophene (TH), benzothiophene (BT), dibenzothiophene (DBT) and 4,6-dimethyl-dibenzothiophene (DMDBT) were investigated at mild reaction conditions using H_2O_2 as oxidant. The results showed that Au loading could significantly promote the activity of Ti-MWW for oxidative desulfurization.

Keywords Au/Ti-MWW · Oxidative desulfurization · Sulfur compounds · H_2O_2

1 Introduction

The removal of sulfur compounds in fuels has been a challenge for many years, due to the more stringent emission restriction standards in most countries [1–3]. Presently, the commercial process for desulfurization is hydrogenation desulfurization (HDS), which is carried out at high temperatures and elevated pressures. However, HDS is difficult to remove polyaromatic sulfur compounds, such as benzothiophene (BT), dibenzothiophene (DBT) and their derivatives, owing to their steric hindrance and stronger C–S bond energy, which make them difficult to broken down by hydrotreatment [4].

To overcome the limitations of HDS, several new approaches such as oxidation desulfurization (ODS) [5–10], adsorption desulfurization [3], and extraction desulfurization [11, 12] have been studied in recent years. Among those methods, oxidative desulfurization combined with extraction/adsorption has been paid more and more attention due to its mild reaction conditions and high sulfur removal. As high active oxidation catalysts, Ti-containing molecular sieves were used to catalyze the oxidation of sulfur compounds at mild conditions. Although the catalytic activity of TS-1 for the oxidation of thiophene using hydrogen peroxide is high [5, 8, 9], whereas the catalytic activity for the oxidation of benzothiophene and dibenzothiophene is very low due to the small pore size of TS-1. Other titanium-containing zeolites such as Ti-beta [5], Ti-HMS [6, 8] with larger pore size have been used as catalysts for the oxidation of thiophenes, they were also found with low activity or poor stability. We found that Ti-MWW [13] had high oxidative activity for benzothiophene and dibenzothiophene. The superior activity probably due to the structure of Ti-MWW. It consists of 12-membered ring side cups and two independent interlayer and intralayer 10-membered ring channels, one of which contains supercages of 0.71 × 1.8 nm in dimension [13, 14].

In view of the disadvantage of zeolites, there is an increasing interest to catalytic potential of noble meal modified zeolites catalysts in the last few years, Ag/TS-1 has been showed higher active for thiophene oxidation than TS-1 [15]. Especially gold-modified catalysts including Au/MCM-41 [16, 17], Au/TS-1 [18, 19], Au/SBA-15 [20, 21] have been also shown to be highly active to perform many oxidation reactions. Here, we would like to report Ti-MWW supported gold and other metals catalysts for the oxidation of benzothiophene (BT), dibenzothiophene (DBT) and 4,6-dimethyl dibenzothiophene (DMDBT).

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2 Experimental

2.1 Materials

Thiophene (99%), BT (97%), DBT (99%) and 4,6-DMDBT (99%) from ACROS. ORGANICS were used as supplied. Hydrogen peroxide (aqueous solution 30 wt.%) was used as oxidizing agent. Iso-octane (2,2,4-trimethypentane) and acetonitrile were used as solvents.

2.2 Catalyst Preparation and Characterization

Ti-MWW was synthesized by referring to literature [14, 22]. The M/Ti-MWW catalysts with different metal loadings were prepared by impregnation method. In a typical preparation procedure, a suitable amount of chloroauric acid tetrahydrate (47.8% Au) dissolved in 7 mL deioned water was added to 2 g of Ti-MWW at room temperature. The resulting solid catalysts were dried in an oven at 373 K for 12 h, and calcined at 823 K for 6 h. The Si/Ti ratio was found to be 43 using inductively coupled plasma spectroscopy, the specific surface areas were obtained from N_2 adsorption using the Brunauer–Emmett–Teller method (Quancachrome Autosorb-3B), the crystallinity and structure were determined by X-ray diffraction (Bruker D8 ADVANCE), and UV-Vis (UV-2550) measurements were carried out at room temperature.

2.3 Catalytic Oxidation of Thiophenes

The oxidation desulfurization experiments were carried out in an electrothermostatic glass flask equipped with a magnetic stirrer and a condenser. In a typical oxidation reaction, the solid catalyst was stirred with 10 mL model organic sulfur compounds in iso-octane (1,000 µg/mL of sulfur), 10 mL acetonitrile and hydrogen peroxide (H_2O_2/sulfur molar ratio of 2:1–4:1). After the reaction, the catalyst was recovered by centrifuge; the model oil phase and the solvent phase were analyzed by GC-MS (Agilent 6890-5973N) and GC-FID with a capillary column (Shimadzu GC-14B, CBP1-M25-0.25).

3 Results and Discussion

3.1 Catalyst Characterization

3.1.1 X-ray Diffraction of the Different Amount Au Loadings of Ti-MWW

The XRD of Ti-MWW and Au-modified Ti-MWW were shown in Fig. 1. All catalysts have representative structure with single-phase X-ray diffraction patterns, corresponding to the (100), (101), (102), (220) and (310) Bragg reflections [22], which represent structure of MWW. No peak for Au particles at 38.19° was observed in the XRD patterns [21]. This indicates that Au was highly dispersed on the surface of Ti-MWW.

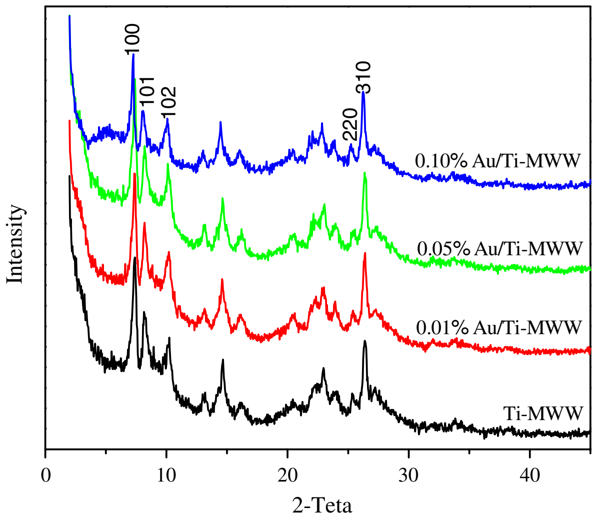

Fig. 1 XRD of the different Au-modified Ti-MWW

3.1.2 UV-Visible Spectra of Au-modified Ti-MWW Catalysts

The UV-vis spectra of Ti-MWW, 0.01% Au/Ti-MWW, 0.05% Au/Ti-MWW, 0.1% Au/Ti-MWW were listed in Fig. 2. It was found that the UV-vis spectra of Ti-MWW and Au-modified Ti-MWW catalysts showed an absorption band around 220 nm, which indicates titanium incorporated as tetrahedral Ti species in the framework of zeolite.

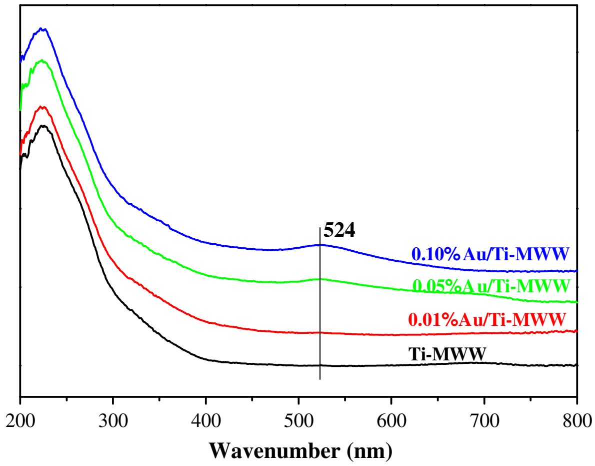

Fig. 2 UV-vis spectrum of the different Au-modified Ti-MWW catalysts

Table 1 The specific surface areas of Au/Ti-MWW

Catalysts	Au content (wt.%)	S_{BET} ($m^2\ g^{-1}$)
Ti-MWW	0	441
Au/Ti-MWW	0.01	398
Au/Ti-MWW	0.05	385
Au/Ti-MWW	0.10	371

Different content Au-modified Ti-MWW catalysts have a characteristic absorption band at 556–510 nm. The intensity of the spectra increased with the increase of Au loading. This absorption band was due to the gold plasmon vibrations [23].

3.1.3 The Specific Surface Area of Au/Ti-MWW

The specific surface area of Ti-MWW and Au/Ti-MWW were listed in Table 1. From Table 1, the specific surface area of Ti-MWW, 0.01% Au/Ti-MWW, 0.05% Au/Ti-MWW and 0.10% Au/Ti-MWW was 441, 398, 385 and 371 m^2/g, respectively. As the amount of Au increased on Ti-MWW, the specific surface area decreased slightly.

3.2 Catalytic Oxidation of Sulfur Compounds

3.2.1 Effect of H_2O_2/S Ratios and Temperature on DBT Oxidation over Au/Ti-MWW

The effect of H_2O_2/S ratios on the conversion of DBT was listed in Fig. 3. The conversion of DBT increased with the increase of H_2O_2/S ratio. When the H_2O_2/S ratio exceeded 3, the conversion of DBT increased slightly. The main oxidative product was corresponding sulfone (90%). Other products were identified as sulfuric acid (about 5%), sulfoxide and biphenyl. It is interested that Au/Ti-MWW with different gold loading has higher activity for DBT oxidation than Ti-MWW. Among these catalysts, Au/Ti-MWW with 0.05% gold gives the highest activity. The conversion of DBT reaches 93–99% at 313 K under the H_2O_2/S ratio of 3, being 26% higher than Ti-MWW.

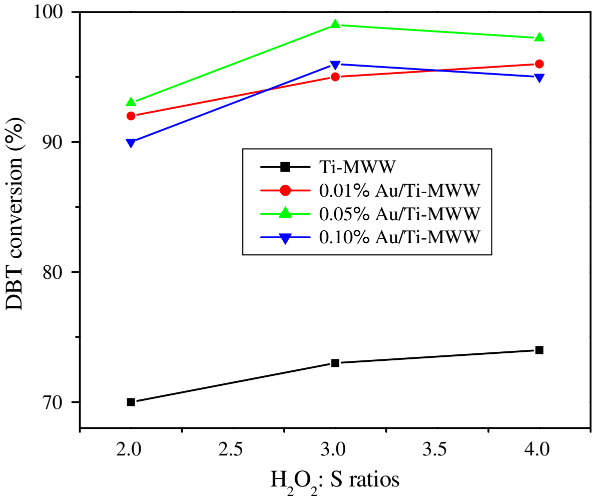

Fig. 3 DBT oxidation at different H_2O_2/S ratios. Reaction conditions: DBT (1,000 ppm): 10 mL, acetonitrile: 10 mL, catalyst: 100 mg, 313 K, 3 h

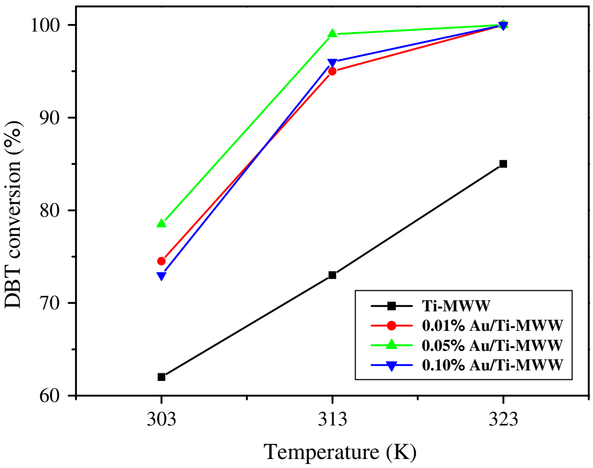

Fig. 4 Effect of Au loading on selective oxidation of DBT at different temperatures. Reaction conditions: DBT (1,000 ppm): 10 mL, acetonitrile: 10 mL, catalyst: 100 mg, H_2O_2:S = 313 K, 3 h

The effect of reaction temperature on DBT oxidation was listed in Fig. 4. The results showed that the conversion of DBT increases with the increase of the reaction temperature. The conversion of DBT is 15–26% higher over Au/Ti-MWW than Ti-MWW in the temperature range from 303 to 323 K.

3.2.2 Oxidation of Thiophene, BT, DBT and DMDBT over 0.05% of Au/Ti-MWW

The catalytic activity of 0.05% Au/Ti-MWW for oxidation of sulfur compounds (TH, BT, DBT and DMDBT) in acetonitrile at 313 K was listed in Fig. 5. In comparison, the oxidation activity of Ti-MWW, 0.05% Au/Ti-MWW gave higher activity for TH, BT, DBT and DMDBT than Ti-MWW. The conversion of TH BT, DBT and DMDBT increased from 55% to 71%, 68% to 90%, 60% to 84% and 50% to 68%, respectively. Considering that the content of DMDBT in diesel oil is not very high, we also investigated the DMDBT oxidation activity with 100 µg/mL sulfur content at same reaction conditions. It was found that DMDBT conversion reached to 94% over 0.05% Au/Ti-MWW. In contrast, the conversion of DMDBT is only 68% over Ti-MWW.

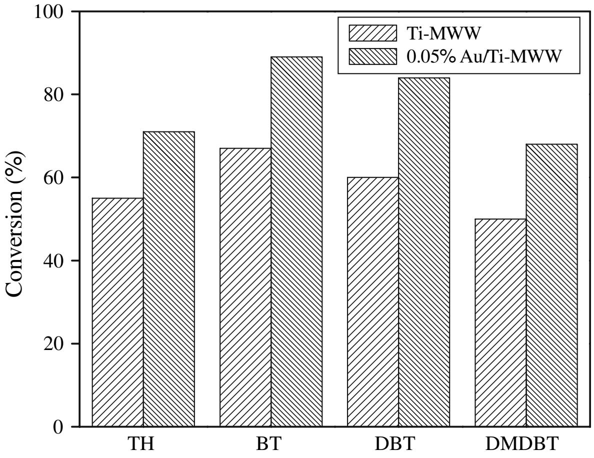

Fig. 5 The oxidation of sulfur compounds over Au/Ti-MWW. Reaction conditions: DBT (1,000 ppm): 10 mL, acetonitrile: 10 mL, catalyst: 100 mg, T = 313 K, 3 h

Table 2 Oxidation of DBT with H_2O_2 over various catalysts

Catalysts	DBT conversion (%)		
	303 K	313 K	323 K
Ti-MWW	60	72	85
0.05% Cr/Ti-MWW	65	83	95
0.05% Fe/Ti-MWW	61	81	89
0.05% Cu/Ti-MWW	65	73	77
0.05% Ag/Ti-MWW	71	93	95
0.05% Pd/Ti-MWW	79	93	100
0.05% Au/Ti-MWW	84	93	100

Reaction condition: DBT (1,000 μg/mL): 10 mL, catalysts: 100 mg, acetonitrile: 10 mL, $n(H_2O_2)$:n(S) = 3, 3 h

3.2.3 Effect of Different Metal Loading on Ti-MWW

In order to investigate metal loading effect, the catalysts with different metal loading on Ti-MWW were used to catalyze the oxidation of DBT. The results were listed in Table 2. The oxidation activity of Cr, Fe and Cu modified Ti-MWW increased slightly compared with Ti-MWW. Basically, the increase of conversion of DBT was less than 10% at different reaction temperature. However, noble metal such as Ag, Pd, and Au modified Ti-MWW showed much higher activity than that of Ti-MWW. The increase of the conversion of DBT was as high as 20% at different reaction temperature. In the case of Pd/Ti-MWW and Au/Ti-MWW, the conversion of DBT was 100% at 323 K. Further studies found that MCM-22, Pd/MCM-22 and Au/MCM-22 had no activity for DBT oxidation at same reaction conditions. The results showed that Ti atoms play decisive role in the oxidation of sulfur compounds. Au and other transition metals were as co-catalyst to improve the activity of Ti-MWW. The improvement was probably due to the adsorption of sulfur on the metal. Further studies of the mechanism are under investigated.

4 Conclusion

Au/Ti-MWW prepared by impregnation of Ti-MWW with $HAuCl_4$ has very high activity for TH, BT, DBT and DMDBT oxidation with H_2O_2. The conversion of BT, DBT and DMDBT was 90%, 84% and 68%, respectively, which is much higher than that of Ti-MWW.

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