

Direct Synthesis of H₂O₂ over Ti-Containing Molecular Sieves Supported Gold Catalysts: A Comparative Study for *In-situ*-H₂O₂-ODS of Fuel

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Direct synthesis of H₂O₂ and *in situ* oxidative desulfurization of model fuel over Au/Ti-HMS and Au/TS-1 catalysts has been comparatively investigated in water or methanol. Maximum amount (82%) of active Au⁰ species for H₂O₂ synthesis was obtained. Au/Ti-HMS and Au/TS-1 exhibited the contrary performances in H₂O₂ synthesis as CH₃OH/H₂O ratio of solvent changed. H₂O₂ decomposition and hydrogenation in water was inhibited by the introduction of methanol. Effect of O₂/H₂ ratio on H₂O₂ concentration, H₂ conversion and H₂O₂ selectivity revealed a relationship between H₂O₂ generation and H₂ consumption. The highest dibenzothio-phenone removal rate (83.2%) was obtained over Au/Ti-HMS in methanol at 1.5 of O₂/H₂ ratio and 60 °C. But removal of thiophene over Au/TS-1 should be performed in water without heating to obtain a high removal rate (61.3%). Meanwhile, H₂ conversion and oxidative desulfurization selectivity of H₂ were presented.

Key Words : Hydrogen peroxide, Gold catalyst, Molecular sieve, Framework titanium, Oxidative desulfurization

Introduction

Hydrogen peroxide has always been regarded as an environmentally friendly oxidizing agent. Small-scale, distributed H₂O₂ production process is highly desirable because of the costs and hazards associated with transportation and handling of concentrated H₂O₂. The liquid-phase direct H₂O₂ process offers an attractive green technology to replace the currently practised anthraquinone process.^{1,2} For economic reasons, attempts have been made to substitute H₂O₂ by employing a mixture of H₂ and O₂ that generates H₂O₂ *in situ*.³⁻⁶ In these cases, active support is modified with precious metals such as palladium and platinum to catalyze the direct synthesis of H₂O₂. Up until 2002, Pd is the most active metal for the direct synthesis of H₂O₂. Recently, more and more research shows that Pd-Au alloys supported catalysts can give rather significant improvements in the rate of hydrogen peroxide formation when compared with the Pd-only catalyst.^{1,7,8} However, halide ions is usually added to the reaction medium for the sake of inhibiting an unwanted catalysis of Pd for H₂ oxidation to H₂O, as well as decomposition and hydrogenation of H₂O₂.⁹ A more serious problem is that palladium is also a kind of metal with the hydrogenation performance,^{10,11} which is possible to cause some side reactions during the *in situ* oxidation of substrates. Therefore, the above-mentioned problems are possible to restrict the *in situ* using of H₂O₂. After Hutchings and co-workers first reporting that Au/Al₂O₃ were effective for the direct reaction, Au is observed to be a substitute for Pd as

carrying out the reaction of small-scale H₂O₂ formation with dilute H₂ and O₂ mixtures well away from the side reactions. Although monometallic gold used in the direct synthesis of H₂O₂ has been reported many times, there are still several unmentioned problems to be solved. First of all, very few investigations has been concentrated on mesoporous molecular sieves supported gold for H₂O₂ synthesis, even the microporous molecular sieves supported gold. Secondly, the valence of active Au species determined H₂O₂ generation has been rarely studied. Finally, searching for a suitable solvent for different support of gold in the direct synthesis of H₂O₂ is important to the final yield of H₂O₂.

The direct process can provide an *in situ* oxidant for several catalytic oxidation reactions which need small-scale and dilute H₂O₂. Combined with the active center on the support of gold or palladium catalyst, the H₂ and O₂ mixture can accomplish a H₂O₂-free process. Most of the reports have concentrated on the gas-phase propylene epoxidation over Ti-containing materials supported gold catalysts in recent years.¹²⁻¹⁶ In addition, some organic substrates, such as cyclohexane or cyclooctene can be oxidized by the *in situ* H₂O₂ over zeolites supported noble metal catalysts.⁵ Methane can be directly converted into a methanol derivative and formic acid by the *in situ* H₂O₂ in the presence of Pd/C.^{17,18} However, there are still few reports on the *in situ* use of H₂O₂, especially in the liquid-phase reactions. In our preliminary studies, oxidative desulfurization (ODS) of fuel oil *in situ* using the H₂O₂ generated from H₂ and O₂ (*in-situ*-H₂O₂-ODS) over Au/Ti-containing molecular sieves provid-

ed a feasibility of commercial H₂O₂-free process.¹⁹⁻²³ Interestingly, a high removal rate of bulky reactants such as benzo-thiophene (BT) and dibenzothiophene (DBT) over Au/Ti-HMS could be obtained in methanol solvent, while the suitable solvent for the oxidation of smaller thiophene (Th) over Au/TS-1 is not methanol but water. But the reason for the different behavior of *in-situ*-H₂O₂-ODS has not yet been discussed.

In this work, we present some interesting regularities in the direct synthesis of H₂O₂ and *in-situ*-H₂O₂-ODS from H₂ and O₂ over Ti-containing molecular sieves supported gold catalysts prepared by deposition-precipitation (DP) method. Type of the gold active center for H₂O₂ synthesis was confirmed by a TPR quantitative analysis. Au/Ti-HMS and Au/TS-1 exhibited the different catalytic behavior in H₂O₂ synthesis when using H₂O, CH₃OH, or their mixture as solvent. The solvent effect would be associated with the further *in situ* using H₂O₂ to oxidize DBT and Th over the suitable catalyst and in the suitable solvent. In addition, the behavior of H₂O₂ decomposition and hydrogenation over the two catalysts in solvent with different H₂O/CH₃OH ratio could provide insight into the solvent effect on H₂O₂ synthesis. The effect of O₂/H₂ pressure ratio on H₂O₂ generation and *in-situ*-H₂O₂-ODS was investigated, and the valuable results including removal and conversion rate of sulfur compound, H₂ conversion, H₂O₂ selectivity, as well as the ODS selectivity of H₂ were also presented and discussed in detail.

Experimental

Catalyst Preparation. Two types of Ti-containing molecular sieves (Ti-HMS and TS-1) were used as the supports of gold nanoparticles. Ti-HMS was synthesized according to literature.²⁴ TS-1 was synthesized according to literature,²⁵ and then modified by TPAOH. Au/Ti-HMS and Au/TS-1 were prepared by a DP method using H₂AuCl₄·4H₂O as gold precursor and diluent ammonia as precipitator. In detail, a solution of H₂AuCl₄·4H₂O was slowly added to a mixture of support (1 g) and water (50 mL) under stirring. The pH of the mixture was adjusted to 9 (unless otherwise noted) with aqueous ammonia (0.24 M), and aged at room temperature for 5 h. After filtration and washing, the resulting solid was dried at 80 °C, and then calcined at 300 °C (unless otherwise noted) for 4 h.

Catalyst Characterization. Powder X-ray diffraction (XRD) patterns were recorded using a Rigaku D/Max 2400 diffractometer employing Cu K α radiation. UV-visible (UV-vis) spectra were obtained on a JASCO UV550 spectrometer using BaSO₄ as the internal standard. Transmission electron microscopy (TEM) images were taken on Tecnai G₂ 20 S-twin instrument (FEI Company) with an acceleration voltage of 200 kV. H₂ temperature programmed reduction (H₂-TPR) was carried out on a quartz fixed-bed reactor, in which the sample (0.1 g) was dried in a N₂ flow (40 mL/min) under a desired temperature for 1 h and then cooled to ambient temperature. The flowing rate of H₂/N₂ (10% pressure ratio) was 40 mL/min and the temperature increased at the rate of

10 °C/min. H₂ signals were analyzed by means of GC-7890T with a TCD detector.

Direct Synthesis of H₂O₂. Direct synthesis of H₂O₂ was performed using a stainless steel autoclave charged with catalyst (0.13 g), solvent (10 mL) and mixed gas (total pressure of 1.5 MPa) of H₂/N₂ and O₂/N₂ under stirring. The composition of reaction gas with different O₂/H₂ pressure ratio is shown in Table 1. After reaction for 2 h (unless otherwise noted), H₂O₂ concentration was determined by an iodometric titration method.²⁶ H₂ consumption was measured by means of GC-7890T with a TCD detector using Ar as carrier gas, and H₂ content was analyzed using N₂ as internal standard. Total H₂ conversion and H₂O₂ selectivity of H₂ are expressed as Eqs. (1) and (2), respectively.

$$C(\text{H}_2) = \frac{[\text{H}_2]_1 - [\text{H}_2]_2}{[\text{H}_2]_1} \times 100\% \quad (1)$$

$$S(\text{H}_2\text{O}_2) = \frac{[\text{H}_2\text{O}_2]_1 - [\text{H}_2]_1}{C(\text{H}_2)} \times 100\% \quad (2)$$

C (H₂): H₂ conversion; S (H₂O₂): H₂O₂ selectivity of H₂; [H₂]₁: Initial H₂ content; [H₂]₂: H₂ content after reaction; [H₂O₂]₁: H₂ content converted to H₂O₂.

Catalytic Decomposition and Hydrogenation of H₂O₂. Testing for catalytic H₂O₂ decomposition over Ti-HMS or TS-1 was carried out in the same reactor as H₂O₂ synthesis with the catalyst (0.03 g) and initial H₂O₂ solvent (10 mL, 0.04 M) under stirring, while for H₂O₂ hydrogenation was charged with H₂ (0.3 MPa) and N₂ (0.2 MPa). After reaction for 0.5 h, H₂O₂ concentration was also determined by the iodometric titration method.

***In-situ*-H₂O₂-ODS.** Dibenzothiophene (DBT) and thiophene (Th) with 500 ppm of S were respectively dissolved in n-octane as model oil. *In-situ*-H₂O₂-ODS was performed based on the reaction system of H₂O₂ synthesis with addition of 10 mL model oil, and heated to a desired temperature by a water bath. After reaction for 1 h, the oil and solvent phase were respectively analyzed by means of Agilent GC-6890N (HP-5 capillary column, 30 μm \times 320 μm \times 0.25 μm , FID). The removal and conversion rate of sulfur compound are expressed as Eqs. (3) and (4), respectively. The total H₂ conversion in ODS and ODS selectivity of H₂ are expressed as Eqs. (1) and (5), respectively, and the measurement for H₂ is similar to that in H₂O₂ synthesis.

Table 1. Partial pressure of reaction gas under different O₂/H₂ pressure ratio

O ₂ /H ₂ pressure ratio	H ₂ partial pressure (MPa)	O ₂ partial pressure (MPa)	N ₂ partial pressure (MPa)
1	0.54	0.54	0.42
1.5	0.45	0.675	0.375
1.9	0.40	0.75	0.35
3	0.30	0.90	0.30
6	0.18	1.08	0.24

$$R(S) = \frac{M_0 C_0 - M_0 C_{t,1}}{M_0 C_0} \times 100\% = \frac{C_0 - C_{t,1}}{C_0} \times 100\% \quad (3)$$

$$C(S) = \frac{M_0 C_0 - M_0 C_{t,1} - M_0 C_{t,2}}{M_0 C_0} \times 100\% \quad (4)$$

$$S(S) = \frac{[S]/[H_2]_1}{C(H_2)} \times 100\% \quad (5)$$

R (S): Removal rate of sulfur compound; C (S): Conversion rate of sulfur compound; S (S): ODS selectivity of H₂; M₀: Mass of model oil; M₁: Mass of solvent; C₀: Initial mass concentration of sulfur compounds; C_{t,1}: Mass concentration of sulfur compounds in model oil after reacting t h; C_{t,2}: Mass concentration of sulfur compounds in solvent after reacting t h; [S]: H₂ content converted for the *in-situ*-H₂O₂-ODS.

Results and Discussion

Catalyst Characterization and Direct Synthesis of H₂O₂.

Catalyst Characterization: Powder XRD patterns are shown in Figure 1. Typically, four peaks should appear at 38.3°, 44.5°, 64.7° and 77.7°, which are assigned to the face-centered cubic metal gold structure. But in the figure, only one peak (38.3°) can be observed for Au/Ti-HMS and Au/TS-1, showing that the gold species exist as highly dispersed particles in nanoscale. UV-visible spectra are shown in Figure 2. For each sample, the peak at 210-220 nm proves the existence of framework Ti species in tetrahedral coordination. The peak at 520-550 nm can be attributed to the absorption of surface plasmon vibration in gold nanoparticles. The broad gold absorption peak shows the generation of uniformly dispersed gold particles. TEM images are shown in Figure 3. The gold particles are highly dispersed on the surface of Ti-HMS or TS-1 support. The average size of gold is about 5-6 nm. In addition, the pore size and BET surface area of Au/Ti-HMS is 2.5 nm and 770.1 m²/g, respectively. The pore size and BET surface area of Au/TS-1 is 0.55 nm and 369.7 m²/g, respectively. The preparation method did not show influence on the physical properties of

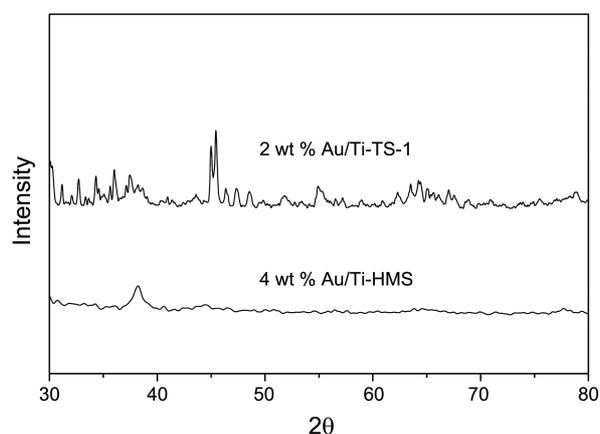


Figure 1. XRD patterns of 4 wt % Au/Ti-HMS and 2 wt % Au/TS-1.

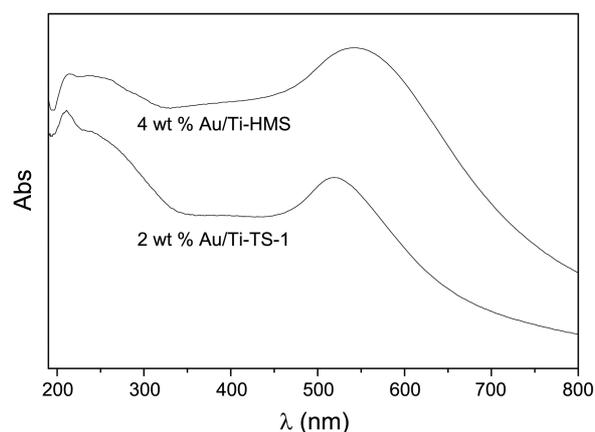


Figure 2. UV-visible spectra of 4 wt % Au/Ti-HMS and 2 wt % Au/TS-1.

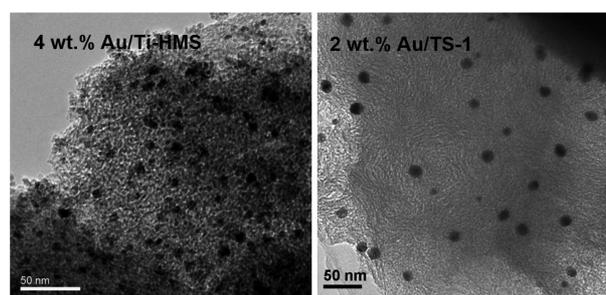


Figure 3. TEM images of 4 wt % Au/Ti-HMS and 2 wt % Au/TS-1.

support.

Effect of Active Au Species on Direct Synthesis of H₂O₂:

The active center for H₂O₂ synthesis is converted from the Au species precipitated on the support by calcination. In order to confirm the type of active Au species and its influence, the evolution of H₂O₂ generation with the thermal treatment temperature for catalysts was investigated combined with a H₂-TPR quantitative method. Figure 4 shows the H₂-TPR profiles of uncalcined 4 wt % Au/Ti-HMS pretreated at 100-400 °C. Only the 100 °C sample shows an intense reduction peak (P₁) at 162 °C, whereas other samples calcined at higher temperature gives no reduction signal at this region. Each

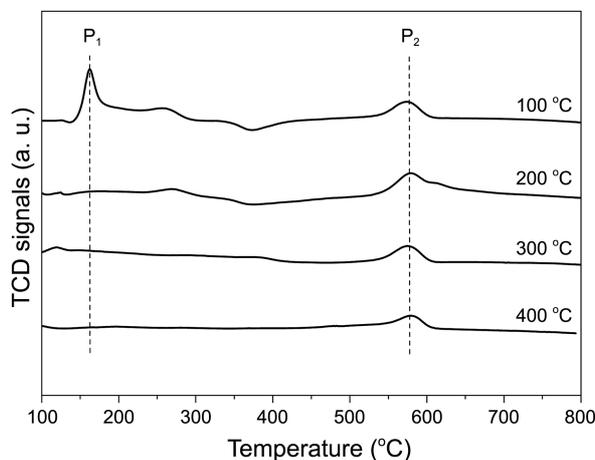


Figure 4. H₂-TPR profiles of 4 wt % Au/Ti-HMS calcined at different temperatures.

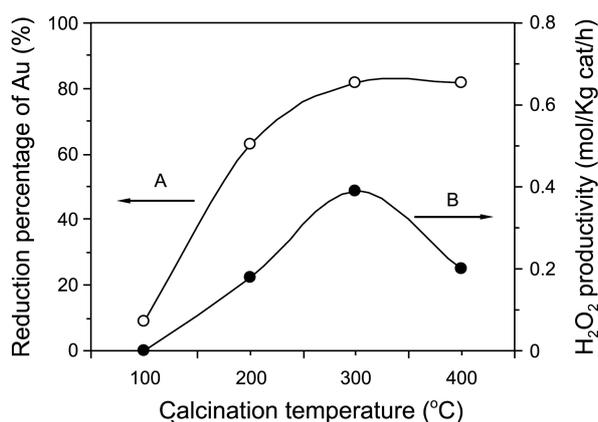


Figure 5. Reduction percentage of Au on Ti-HMS and catalytic performance of 4 wt % Au/Ti-HMS calcined at different temperatures.

sample shows a reduction peak (P_2) around 577 °C. The low temperature reduction peak around 162 °C is related to the reduction of Au^{3+} to Au^+ ($Au^{3+} + 2H_2 \rightarrow Au^+ + 2H_2O$), and the reduction peak at 577 °C can be attributed to the reduction of Au^+ to Au^0 ($Au^+ + H_2 \rightarrow Au^0 + H_2O$), which well agrees with other reports.^{27,28} As described in the literature,²⁷ the intensity and position of the reduction peak depend on Au particle size and shape, as well as the presence of other metal (such as Ti and Ce). As a result, the reduction at high temperature is a little different from the reported one. The partial reduction percentage of Au species during H_2 -TPR operation was calculated according to the H_2 consumption determined by the integral of reduction peak in Figure 4. Figure 5 reveals a relationship between the H_2O_2 generation rate and the thermal treatment temperature of the catalysts on which different valence of Au species exists. The amount of non-zero valent Au converted to Au^0 increases with the calcination temperature (curve A in Fig. 5). The yield of H_2O_2 increases as the calcination temperature increases until 300 °C, and then decreases (curve B in Fig. 5). This observation reflects that Au^0 particle is the active center for the direct synthesis in H_2O_2 , and pretreatment of the catalyst under a proper temperature (300 °C for Au/Ti-HMS) helps to

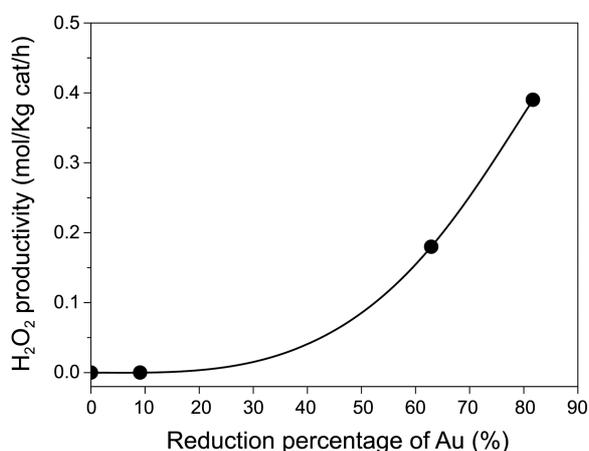


Figure 6. Effect of reduction percentage of Au on H_2O_2 productivity over 4 wt % Au/Ti-HMS.

generate the active Au species. However, calcination at a higher temperature will lead to the agglomeration of gold nanoparticles, although more Au^0 species generates. In Figure 5 and 6, it can be seen that the H_2O_2 yield is mainly decided by the amount of active Au^0 . However, the productivity will reach a highest value of 0.39 mol/Kg cat/h and not increase, because the amount of active Au^0 has reached a maximum of 82%. In this respect, it is quite the same as Au/TS-1, which has been investigated *via* the X-ray photoelectron spectra (XPS) technique in our previous study.²⁰

Effect of Solvent on Direct Synthesis of H_2O_2 : Since the liquid-phase direct synthesis of H_2O_2 takes place in a three-phase system, the H_2O_2 productivity will strongly depend on the overall mass transfer rate of gaseous reactants to the catalyst surface.²⁹ Further, the H_2O_2 yield will be indirectly increased by using a solvent with high solubility of H_2 and O_2 , as well as with high viscosity and surface tension.²⁹ A comparative investigation on the direct synthesis of H_2O_2 over Au/Ti-HMS and Au/TS-1 has been carried out using the mixed solvent with different H_2O/CH_3OH volume ratio. Interestingly, Figure 7 presents the different trends of H_2O_2 yield when using different types of supports for gold in the same reaction medium. In detail, Au/TS-1 in pure water obtains the highest H_2O_2 yield, and the yield decreases with the increase of methanol content in solvent. By contraries, Au/Ti-HMS obtains a higher H_2O_2 yield in pure methanol than that in methanol/water solvent or in pure water. Herein, two lines of available evidence can be presented to explain the different behavior between Au/Ti-HMS and Au/TS-1. For one thing, it has been reported that TS-1 is a type of hydrophobic material,³⁰ which exhibits an obvious wettability and adsorbability for methanol over water. Therefore, in methanol/water solvent or pure methanol, a number of the active centers on Au/TS-1 would be covered by the adsorbed methanol molecule, resulting in the decrease of catalytic performance. By contraries, Ti-HMS is a type of hydrophilic support.³¹ More and more active centers would be covered by water molecule as the H_2O/CH_3OH volume ratio increases. The adsorption capability of water and methanol on each catalyst can be reversed depending on the adsorption conditions. In the presence of water, the hydrophilic character of Ti-HMS can induce the preferential accessibility and adsorption capability of water, resulting in the increase of intraporous water concentration and its subsequent blocking of catalytic sites. For TS-1, hydrophobic and facilitates the adsorption of low-polar methanol and desorption of the high-polar water. For another, with a hydrophilic Au/Ti-HMS, the surface tension of solvent makes no obvious difference as the H_2O/CH_3OH volume ratio changes. However, the solubility of H_2 in alcohols is 4-5 times higher than in water while that of O_2 may increase up to eightfold,²⁹ which results in the highest reaction rate of H_2/O_2 over Au/Ti-HMS in methanol. But water solvent with the hydrophobic Au/TS-1 would obtain a higher surface tension than methanol, which results in the highest yield of H_2O_2 over Au/TS-1 in water, despite the higher solubility of H_2/O_2 in methanol than in water. In other words, regarding the effect

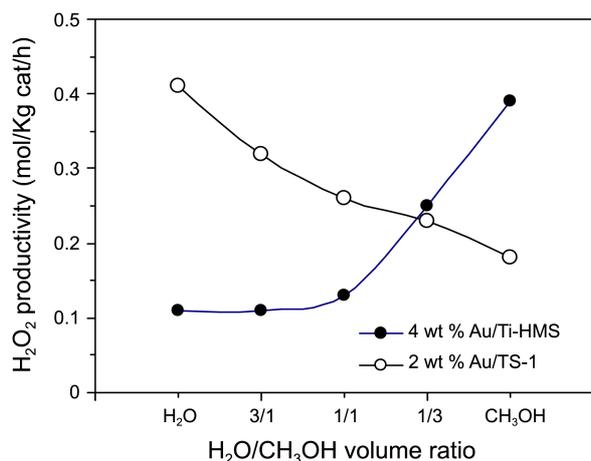


Figure 7. H₂O₂ productivity in H₂O/CH₃OH mixed solvent.

of methanol/water ratio on H₂O₂ yield, the solubility of H₂/O₂ in the reaction medium plays a major role as using Au/Ti-HMS, while the surface tension of the solvent plays a major role as using Au/TS-1. In our previous studies on the ODS with titanosilicates/H₂O₂ system, the small molecule thiophene was more effectively oxidized over TS-1 in water than methanol, while the bulky molecules BT, DBT and 4,6-DMDBT were more effectively oxidized over Ti-HMS in methanol than water.^{32,33} It is an interesting coincidence with the above discussion, which will provide an insight into the fundamental understanding of the matching of sulfur compound, catalyst and solvent in the *in-situ*-H₂O₂-ODS.

Effect of O₂/H₂ Pressure Ratio on Direct Synthesis of H₂O₂. Since H₂O₂ is stable in presence of oxygen but unstable in presence of hydrogen towards its hydrogenation, it is obvious that O₂/H₂ ratio should have a significant effect on the direct synthesis of H₂O₂. The reports on the effect of O₂/H₂ ratio on H₂O₂ synthesis in different reaction systems showed different conclusions, in which the optimal O₂/H₂ ratios were different from each other.^{19,34-36} The effect of O₂/H₂ ratio on H₂ conversion, H₂O₂ selectivity and H₂O₂ concentration was investigated at a constant total pressure of 1.5 MPa. Figure 8 and 9 show the results over 4 wt % Au/Ti-HMS in methanol and 2 wt % Au/TS-1 in water, respectively. The two types of catalysts in their suitable solvent exhibit the similar regularities. With the increase of O₂/H₂ ratio, H₂ conversion increases before 1.9 of O₂/H₂ ratio and then decreases, but H₂O₂ selectivity continuously increases. H₂O₂ concentration reaches a maximum value (7.1 and 9.5 mmol/L in Figs. 8 and 9, respectively) at the O₂/H₂ ratio of 1.5 and then gradually decreases. It is known that the amount of H₂ solving in the catalyst suspending solution increases with H₂ partial pressure, which accelerates the formation rate of H₂O₂. However, the hydrogenation (H₂ + H₂O₂ → 2H₂O) rate is simultaneously accelerated.³⁷ According to Eq. (1), H₂ conversion first increasing with O₂/H₂ ratio is mainly due to the decrease of initial H₂ content and then decreasing is possibly due to the H₂ consumption rate over the decrease rate of initial H₂ content. According to Eq. (2), H₂O₂ selectivity would continually increase because of the obvious

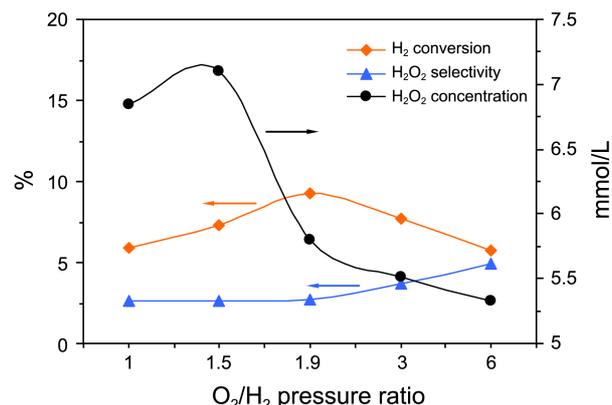


Figure 8. H₂ conversion, H₂O₂ selectivity and H₂O₂ concentration over 4 wt % Au/Ti-HMS in methanol.

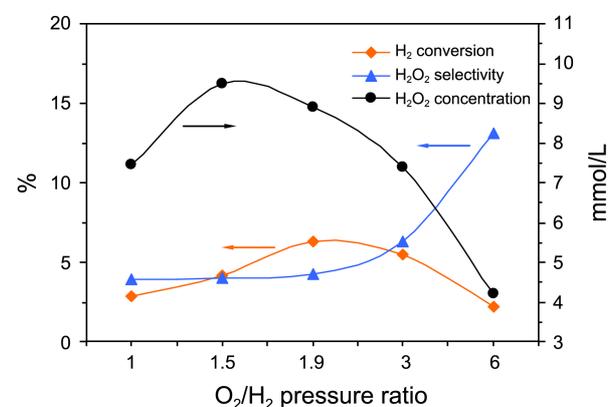


Figure 9. H₂ conversion, H₂O₂ selectivity and H₂O₂ concentration over 2 wt % Au/TS-1 in water.

decrease of H₂ conversion, despite the H₂O₂ formation rate increases slightly. As a result, H₂O₂ concentration is decided by H₂ conversion and H₂O₂ selectivity.

Decomposition and Hydrogenation of H₂O₂: The understanding of H₂O₂ heterogeneous decomposition or hydrogenation catalyzed by gold is very important in the direct synthesis of H₂O₂, especially in the *in-situ*-H₂O₂-oxidation, since the decomposition or hydrogenation results in the H₂O₂ loss during reaction. The decomposition and hydrogenation routes have been reported for many times: decomposition route involves disproportionation to water and oxygen, while hydrogenation route occurs *via* hydrogenation of hydrogen peroxide to water.^{1,38} An explanation to the effect of reaction medium on H₂O₂ yield over different Au/titanosilicates is also presented. As shown in Figure 10, no matter in which solvent, H₂O₂ decomposition amount is always lower than hydrogenation amount. It has been proved that the noble metals, such as Pd and Au, could be present in an oxidised form, resulting in the low decomposition rate in the absence of hydrogen.³⁸ On the other hand, H₂O₂ decomposition or hydrogenation amount in H₂O is much higher than that in CH₃OH or CH₃OH/H₂O solvent. The second observation suggests that gold in water can accelerate the H₂O₂ decomposition or hydrogenation. For Au/Ti-HMS, the lower decomposition and hydrogenation rate of H₂O₂ in methanol

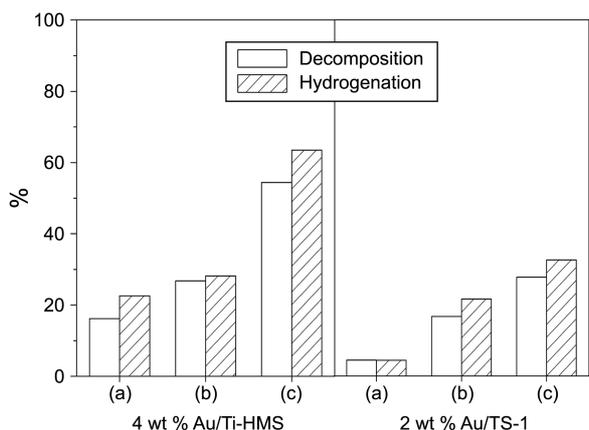
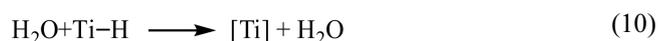
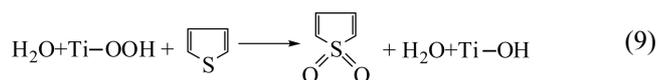
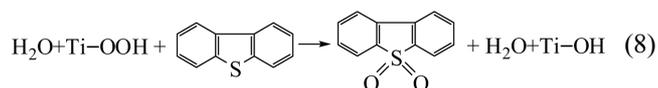


Figure 10. Decomposition and hydrogenation of H₂O₂ in (a) CH₃OH, (b) 1:1 of CH₃OH/H₂O solvent, (c) H₂O.

solvent is possible to become another explanation for the higher H₂O₂ yield in methanol. However, this rule is unsuitable for Au/TS-1. Figure 10 also shows that the decomposition or hydrogenation rate of H₂O₂ over 4 wt % Au/Ti-HMS is rather higher than that over 2 wt % Au/TS-1 in the same type of solvent, which is mainly attributed to the higher gold content accelerating the side reactions.

***In-situ*-H₂O₂-ODS.** The H₂O₂ concentration and productivity would directly relate to the coming *in situ* oxidations. *In-situ*-H₂O₂-ODS of DBT and Th in model oil was carried out in different reaction systems according to the different molecular size of sulfur compounds and solvent effect mentioned above. Oxidation of DBT was catalyzed by Au/Ti-HMS in methanol solvent, and oxidation of Th was catalyzed by Au/TS-1 in water. Based on our previous work,²¹ the *in-situ*-H₂O₂-ODS reaction follows a mechanism of bi-metallic (Au-Ti) catalysis, which can be expressed as Eqs. (6)–(10). Briefly, the as-synthesized H₂O₂ over gold is activated by framework Ti to generate a hydroperoxide species (H₂O···Ti-OOH), which is responsible for oxidation of sulfur compounds in a rate determining step. Then the sulfones are generated as the final products of DBT and Th.



***In-situ*-H₂O₂-ODS of DBT over Au/Ti-HMS.** The removal of sulfur compound consists of a H₂O₂ oxidation (*i.e.* conversion of S) process and a solvent extraction process. Figure 11 (a) and (b) show the removal and conversion rate of DBT at 20 and 60 °C, respectively. It can be seen that the removal and conversion rate of DBT both decrease with the

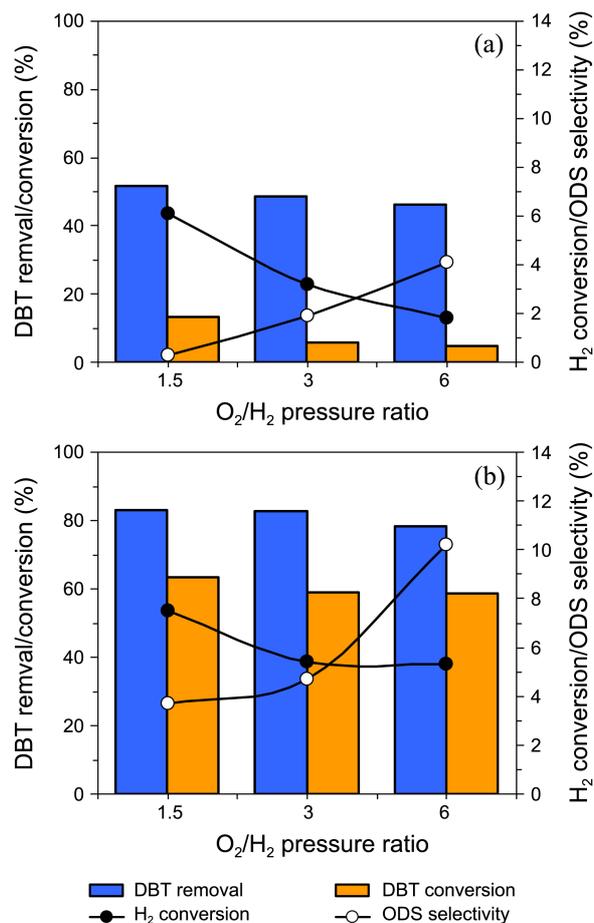


Figure 11. *In-situ*-H₂O₂-ODS of DBT over Au/Ti-HMS in methanol at (a) 20 °C and (b) 60 °C.

increase of O₂/H₂ ratio under a same temperature, but the effect of O₂/H₂ ratio is not so obvious. At 20 °C, the removal amount of DBT mostly comes from the methanol extraction. As the reaction temperature reaches 60 °C, the removal and conversion rate significantly increases, showing that the *in-situ*-H₂O₂-oxidation plays a far more important role than solvent extraction. H₂O₂ productivity is one of the crucial factors that determine the *in situ* oxidation rate of DBT, which needs only a small scale of H₂O₂. However, reaction temperature is more decisive factor. The oxidation of DBT over Ti-HMS/H₂O₂ occurs easily due to the high electron density of DBT and the pore-reactant matching.³³ As reported in our previous work,²¹ the H₂O₂ generation process and sulfides oxidation process occur simultaneously, and the momentary yield of H₂O₂ is theoretically sufficient for DBT oxidation. At 20 °C and the O₂/H₂ ratio of 1.5, the net amount of H₂O₂ (8 × 10⁻⁵ mol) calculated from the momentary yield, plus the decomposition amount of H₂O₂, is over the amount of H₂O₂ (6.7 × 10⁻⁵ mol) oxidizing 300 ppm of DBT in 10 mL noctane. It has also been proved that the activity of framework Ti in Ti-HMS is much lower than that in TS-1.³² Therefore, the key factor that decides the final removal rate of DBT is not the H₂O₂ productivity, but a higher reaction temperature (60 °C) to overcome the energy barrier.

Figure 11(a) and (b) also show the H₂ conversion and *in-*

in-situ- H_2O_2 -ODS selectivity of H_2 over Au/Ti-HMS. The conversion and ODS selectivity of H_2 under 60 °C are much higher than that under 20 °C at a same O_2/H_2 ratio, which can be attributed to more amount of H_2O_2 participating in the oxidation of DBT under a higher temperature. The increased ODS selectivity shows that the as-synthesized H_2O_2 can immediately achieve the conversion of DBT before generation under heating. Therefore, increasing the reaction temperature is beneficial to improve the efficient use of H_2O_2 . In each figure, the *in-situ*- H_2O_2 -ODS selectivity of H_2 obviously increases with the O_2/H_2 ratio, but the H_2 conversion decreases. This result well agrees with the effect of H_2 partial pressure on the H_2O_2 generation (Fig. 8). In addition, the H_2 conversion and selectivity is much higher than that of H_2O_2 synthesis in the absence of ODS, indicating that the introduction of ODS increases the utilization of H_2 and H_2O_2 .

***In-situ*- H_2O_2 -ODS of Th over Au/TS-1.** Figure 12(a) and (b) show the removal/conversion rate of Th at 20 and 60 °C, respectively. It can be seen that the removal and conversion rate of Th both decrease with the H_2 partial pressure at a same temperature, the trend of which well agrees with the H_2O_2 productivity in Figure 9. This result is also similar to that of DBT. But the effect of temperature on the *in-situ*- H_2O_2 -ODS is quite different between Th and DBT. In detail, a higher removal/conversion rate of Th can be obtained at 20

°C than 60 °C. In other words, lower temperature (without heating) is beneficial to the *in-situ*- H_2O_2 -ODS of Th. For removal of Th, H_2O_2 productivity plays a more decisive role than reaction temperature, which is contrary to the removal of DBT. It can be explained that the Th molecular, which is a kind of highly stable organic sulfur, is difficult to be oxidized by $H_2O_2/TS-1$,³³ therefore, quite a little as-synthesized H_2O_2 has decomposed before it participates in the *in-situ*-oxidation, especially under heating. Since H_2O_2 yield becomes a decisive factor, the highest removal rate (61.3%) of Th can be obtained at the O_2/H_2 ratio of 1.5, because the highest concentration of H_2O_2 can be generated under this condition (Fig. 9).

Figure 12 (a) and (b) also show the H_2 conversion and *in-situ*- H_2O_2 -ODS selectivity of H_2 over Au/TS-1. H_2 conversion obviously decreases with the H_2 partial pressure, but the selectivity of H_2 increases, which is similar to the removal of DBT. Interestingly, H_2 conversion shows no increase as the reaction temperature increases from 20 to 60 °C, indicating that the net amount of H_2 participates in oxidation at 20 °C is obviously over that at 60 °C. In addition, the reaction temperature shows no obvious effect on the ODS selectivity of H_2 .

Conclusion

Au/Ti-HMS and Au/TS-1 prepared by DP method showed some different catalytic performances in the direct synthesis of H_2O_2 and *in-situ*- H_2O_2 -ODS from H_2 and O_2 . H_2 -TPR analysis revealed that the content of Au^0 active center decided the H_2O_2 formation, but 82% was a maximum amount for active Au^0 generating. Au/Ti-HMS and Au/TS-1 can effectively catalyze H_2O_2 synthesis in pure methanol and water, respectively. However, the H_2O_2 productivity would seriously decrease once the methanol/water mixed solvent is used, which results from the different properties of the gold supports, solvents and reactant gasses. As the O_2/H_2 ratio increases, the H_2O_2 concentration and H_2 conversion both increase first and then decrease, but the H_2O_2 selectivity continuously increases. This effect of O_2/H_2 ratio is decided by the H_2O_2 decomposition and hydrogenation during reaction. Catalyzed by Au/Ti-HMS or Au/TS-1, H_2O_2 decomposition and hydrogenation rate in H_2O is higher than that in CH_3OH or CH_3OH/H_2O mixed solvent, and the oxidised form of Au results in a lower decomposition rate than hydrogenation rate. In the *in-situ*- H_2O_2 -ODS reaction, a highest removal and conversion rate of DBT, as well as a highest H_2 conversion and ODS selectivity can be obtained at the O_2/H_2 ratio of 1.5 and 60 °C, showing that the effect of reaction temperature on oxidation of DBT is over that of H_2O_2 productivity. But the removal of Th should be performed at room temperature to avoid more H_2O_2 loss under heating because of the difficulty in oxidation of the stable Th.

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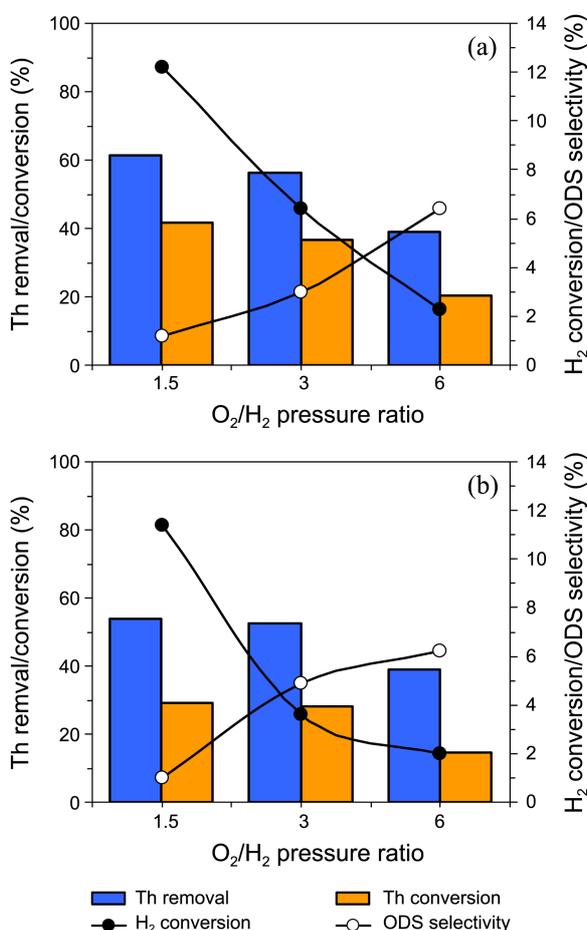


Figure 12. *In-situ*- H_2O_2 -ODS of Th over Au/TS-1 in water at (a) 20 °C and (b) 60 °C.

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