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The Direct Synthesis of Hydrogen Peroxide from H_2 and O_2 over Au/TS-1 and Application in Oxidation of Thiophene in Situ

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Au supported on TS-1 exhibits high activity in hydrogen peroxide formation from H_2 and O_2 under mild conditions (ambient temperature, low pressure about 1.5 MPa, water as solvent, 2 h); and thiophene dissolved in *n*-octane (as model gasoline) is oxidized in situ over Au/TS-1, about 82% removal of thiophene can be achieved.

Gold has received more and more attention for its catalytic activity in some chemical reactions, and lots of studies have been and being done on CO oxidation, gas-phase propylene epoxidation, water-gas-shift reaction, and so forth over supported Au catalysts.[1–4] Recently, it has also been proved that supported Au nanopaticles has catalytic activity on the direct synthesis of hydrogen peroxide with H_2 and O_2.[5–10] In these reactions of hydrogen peroxide synthesis, metal oxides (TiO_2, Al_2O_3, SiO_2, Fe_2O_3, MgO, ZnO, ZrO_2, Gr_2O_3, and Bi_2O_3) and molecular sieves (MCM-41, H-ZSM-5, and H-Y) were used as supports. Titanium silicate (TS-1) has been used widely in selective oxidation, using hydrogen peroxide as oxidant.[11] Some studies have reported that sulfides, such as thioether, thiophene, and methylthiophene, can also be oxidized efficiently over TS-1, using hydrogen peroxide as oxidant.[12–16] Considering the wide use of TS-1, Au supported on TS-1 have been investigated for the oxidation of propene to propene oxide using O_2/H_2 mixtures,[17,18] and it is considered that a surface hydroperoxy species may be formed as the oxidant. However, to date, there are no reported studies concerning the use of Au/TS-1 catalyst for the direct synthesis of hydrogen peroxide with H_2/O_2. We have now addressed this point and, in this communication, we show that over supported Au on TS-1, hydrogen peroxide can be synthesized directly from H_2 and O_2, using de-ionized water as solvent, under ambient temperature, and low pressure (about 1.5 MPa). Furthermore, considering the amount of hydrogen peroxide formed, oxidative desulfurization is studied, and results show that thiophene (dissolved in *n*-octane as model gasoline) can be oxidized efficiently in situ with H_2 and O_2 over Au/TS-1.

Gold supported on TS-1 with 2 wt % loading was prepared by homogeneous deposition–precipitations (prepared according to the Ref. 19). TS-1 support of 1 g (prepared following Ref. 20) was suspended in 50 mL of aqueous solution of chloroauric acid (2.0×10^{-3} mol/L). Excessive urea (0.8 g) was added. The solution was stirred for 30 min, and the initial pH was about 2. The temperature of suspension was gradually increased up to 80 °C under vigorous stirring and was maintained 3 h. Thereafter, the mixture was aged at 30 °C for 3 h, and then the solid was centrifuged, washed with de-ionized water till no white floc produced when the washing water contacted with solution of $AgNO_3$, dried at 100 °C, and calcined at 400 °C for 4 h.

The synthesis of hydrogen peroxide was performed using a stainless autoclave with Teflon lining and a nominal volume of 100 mL. The autoclave was equipped with magnetic stirrer, water bath, and provisions for measuring pressure and charging gases. Typically, 0.13–0.14 g Au/TS-1 and 10 mL de-ionized water (solvent) were fed into the reactor. The autoclave was purged with N_2 (0.2 MPa) for three times and then charged with H_2/N_2 and O_2/N_2 to give the required O_2/H_2 ratio. The partial pressure of H_2 was 0.3 MPa, and the total pressure was 1.5 MPa. The temperature was controlled with water bath. The concentration of H_2O_2 was determined by iodometric titration. The oxidation of thiophene was performed in the conditions similar to synthesis of hydrogen peroxide, additional 10 mL model gasoline (thiophene in *n*-octane) added. The content of thiophene before and after reaction was analyzed by Agilent GC-6890 with FPD detector.

Table 1 shows the effect of partial pressure of O_2/H_2 and reaction temperature on H_2O_2 synthesis, and Figure 1 shows the effect of reaction time. It is apparent that Au/TS-1 catalyst exhibits the high activity for hydrogen peroxide synthesis. Furthermore, in the absence of gold, no hydrogen peroxide is detected. The molar ratios of O_2/H_2, reaction temperature and reaction time have effect on the productivity of hydrogen peroxide synthesis. In particular, the rate of hydrogen peroxide is more dependent upon reaction time and temperature. For all data presented in Table 1, both the productivity and concentration of H_2O_2 synthesis increase together with increase of O_2/H_2 ratio. It is considered that increasing the O_2/H_2 ratio can inhibit the decomposition of H_2O_2.[5] The low temperature benefits H_2O_2 synthesis, for hydrogen peroxide decomposition and/or hydrogenation to water can be enhanced with the temperature increasing.

Figure 1 shows the change of productivity and concentration of H_2O_2 formed as a function of reaction time. As increasing the reaction time, the productivity of H_2O_2 synthesis decreases significantly and concentration of H_2O_2 increases. It demonstrates that the oxidation rate of H_2 is fast in initial 30 min, and as the

Table 1. Hydrogen peroxide formation over Au/TS-1 from H_2 and O_2[a]

Catalyst	Temperature /°C	O_2/H_2 mol ratio	$R[H_2O_2]$[b] mmol kg-(catalyst)$^{-1}$ h^{-1}	H_2O_2 mmol/L
TS-1	25	3	—	—
2 wt %Au/TS-1	25	1.2	109.26	2.95
2 wt %Au/TS-1	25	2	111.85	3.02
2 wt %Au/TS-1	25	3	125.93	3.40
2 wt %Au/TS-1	2	3	134.44	3.63
2 wt %Au/TS-1	60	3	89.63	2.42

[a]Reaction conditions: 10-mL de-ionized water as reaction medium, 0.3 MPa H_2, total pressure 1.5 MPa, 135 mg catalyst. [b]Productivity of H_2O_2.

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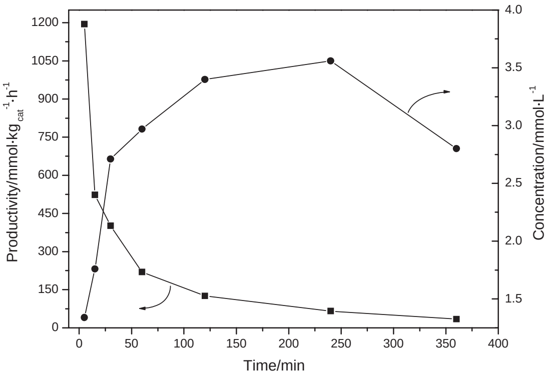

Figure 1. Effect of reaction time on H_2O_2 formation over Au/TS-1. (0.135 g catalyst, 25 °C, $O_2/H_2 = 3$).

Table 2. Thiophene oxidation over Au/TS-1 in the presence of H_2 and O_2

Catalyst	Thiophene /μg g^{-1}	Removal /%	Actual removal /μmol
TS-1	100	15.16	—
Au/TS-1[b]	100	20.48	0.24
Au/TS-1[c]	100	19.80	0.23
Au/TS-1	100	81.96	8.40
Au/TS-1	300	69.14	17.30
Au/TS-1	600	56.54	28.30
Au/TS-1[d]	600	73.97	36.98

[a]Reaction conditions: 10-mL de-ionized water, 10-mL model gasoline (thiophene in *n*-octane), 0.3 MPa H_2, 0.9 MPaO_2, and additional N_2 to a total pressure 1.5 MPa, 135 mg catalyst, 25 °C. [b]No gas charged. [c]Only 1.0 MPa O_2, no H_2. [d]For 4 h.

extending of reaction time, the hydrogenation and decomposition of H_2O compete with H_2O_2 synthesis, and the total synthesis rate of H_2O_2 decreases.

Subsequently, in situ oxidation of thiophene was investigated with H_2 and O_2 over Au/TS-1, and the results are shown in Table 2. It is apparent that, the TS-1 catalyst has no oxidative activity for thiophene in the presence of O_2/H_2, only 15.16% absorption on TS-1.[15] Absorption of thiophene over Au/TS-1 is 20.48%, and if only O_2 charged, no more thiophene is oxidized besides absorption. Previous studies have confirmed that thiophene can be oxidized efficiently over TS-1/H_2O_2.[15,16] From Table 2, it is apparent that thiophene can be also oxidized efficiently over Au/TS-1 in the presence of O_2 and H_2, as hydrogen peroxide is synthesized in situ over Au supported on TS-1 catalyst. The oxidative removal of thiophene is 81.96, 69.14, and 56.54%, respectively for the 100, 300, and 600 µg/g thiophene in *n*-octane, and extending reaction time to 4 h, 73.97% oxidative removal can be achieved for 600 µg/g thiophene. The actually removed thiophene is 36.98 µmol for 600 µg/g, which has exceeded the actual H_2O_2 formation amount at the same reaction time in the synthesis of H_2O_2 (as Figure 1, 36.5 µmol for 4 h). It is considered that the H_2O_2 synthesized in situ is used for oxidation of thiophene at once, inhibiting H_2O_2 hydrogenation or decomposition, and further H_2O_2 synthesis and oxidation of thiophene can be carried out.

The primary product of in situ oxidation of thiophene is SO_4^{2-}, which can be identified by analyzing water phase after reaction. Dropping $Ba(NO_3)_2$ solution to water phase, white deposit $BaSO_4$ can be found. According to our earlier research on thiophene oxidation over TS-1/H_2O_2,[15] the carbons of thiophene molecule were transferred mainly to styrene and can be detected in oil phase using GC-MS.

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