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An effective tri-phasic catalytic system for oxidation of benzyl alcohol under phase transfer conditions

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A tri-phasic catalytic system consisting of aqueous hydrogen peroxide, benzyl alcohol and a solid catalyst such as tungsten trioxide has been proved effective for the oxidation of benzyl alcohol in the presence of cetyl trimethyl aniline bromide (CTMAB). At first, the oxide reacts with CTMAB to form a complex, which can be oxidized by aqueous hydrogen peroxide to form a peroxide which effectively oxidizes benzyl alcohol.

Keywords: Tungsten trioxide; tri-phasic catalytic system; oxidation of benzyl alcohol; hydrogen peroxide

1. Introduction

While studying the effect of calcination temperature on structure and catalytic property of 12-heteropoly-tungstophoric acid, we found that the tungsten oxide formed from the decomposition of the heteropoly anion $[PW_{12}O_{40}]^{3-}$ calcined at 600°C has very good catalytic activity in the oxidation of benzyl alcohol under phase transfer conditions [1]. The interesting fact is that the reaction is carried out in a tri-phasic catalytic system constituted of aqueous hydrogen peroxide, benzyl alcohol and a solid catalyst. So far this kind of tri-phasic catalytic system has never been reported. It may be also benificial to the elucidation of general relationships between heterogeneous and homogeneous catalysis. For this purpose, we report here the result of an investigation of the catalytic behaviour of tungsten trioxide in the oxidation of benzyl alcohol under phase transfer conditions.

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2. Experimental

Materials. Unless otherwise stated, the materials were obtained from commercial suppliers and used without further purification. Benzaldehyde in the benzyl alcohol was removed by using the Cannizzaro reaction [2].

Preparation. WO_3 (2.32 g, 10 mmol) was added to a solution of CTMAB (a kind of phase transfer catalyst, 3.64 g, 10 mmol) in 150 ml of water, and the mixture was stirred at 85°C for 2 h. The mixture was cooled to room temperature and a white precipitate was obtained. After centrifuging, the precipitate was washed repeatedly with distilled water and dried in vacuo to give the product (abbreviated as TTCB).

TTCB (12.0 g) was added to a solution of 30% H_2O_2 (40 ml). After the mixture had been stirred at 90°C for a few minutes, a pale yellow foam was formed, which was collected until its production stopped. The foam was cooled to room temperature and put aside for at least 4 h. After centrifuging, a powdery product was obtained. After this powdery product was washed repeatedly with distilled water and dried in vacuo, the peroxide of TTCB (abbreviated as PTTCB) was obtained.

Analysis. TG (thermogravimetric) analysis was performed with a Delta Series TGA7 type instrument. The splitting products of PTTCB or TTCB formed in the TG analysis were determined by a Quattro type MS. GC analysis was performed by employing a 3 mm × 1 m stainless steel column packed with silicone JXR on chamelite 101.

The reaction procedure for the oxidation of benzyl alcohol is given in ref. [3].

3. Results and discussion

The catalytic activity of oxides of transition metals of the VIB group and of the fourth period (from Ti to Cu), and of some rare earth metal oxides has been studied in the oxidation of benzyl alcohol under phase transfer conditions. Except for the oxides listed in table 1, the oxides show no catalytic activity. From the results in table 1, we obtain the order of catalytic activity: $WO_3 \gg MoO_3 \gg$

Table 1
Catalytic activity of various oxides. Reaction conditions: H_2O_2 (30 wt%) 3 ml, oxide 2.5×10^{-3} mol, CTMAB 7.5×10^{-3} mol, benzyl alcohol 2 ml, temperature 90°C, time 120 min. The selectivity of benzaldehyde is near 100%

	Oxide			
	WO_3	MoO_3	V_2O_5	CrO_3
yield of benzaldehyde(%)	74.3	25.4	6.8	trace

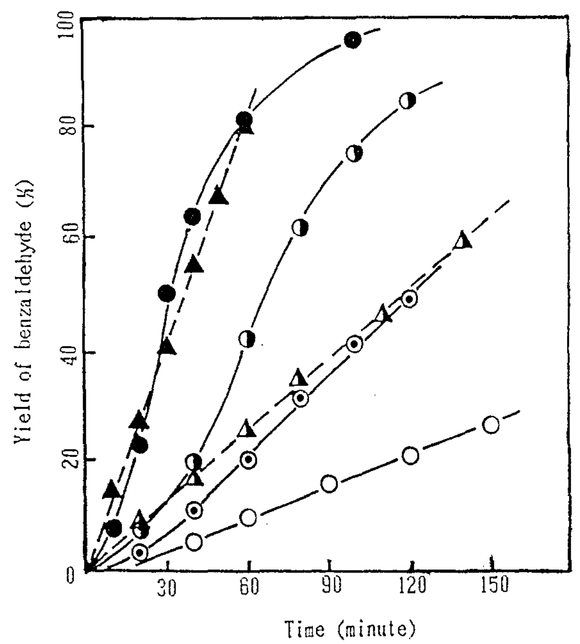
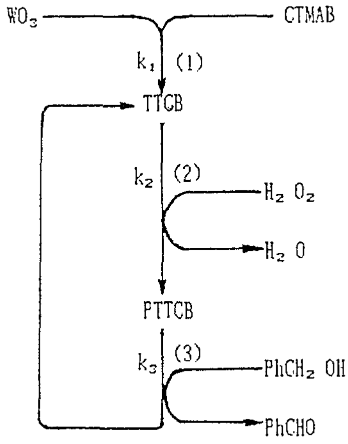


Fig. 1. Time-dependence curves of the oxidation of benzyl alcohol with hydrogen peroxide catalyzed by the WO_3/CTMAB system under different catalyst concentrations. Reaction conditions: H_2O_2 (30 wt%) 3 ml, CTMAB 27.3 mg, benzyl alcohol 2 ml, temperature 90°C. WO_3 as catalyst: (○) 2.9 mg, (⊙) 5.8 mg, (◑) 8.7 mg, (●) 11.6 mg. TTCB as catalyst directly: (△) 13.5 mg, (▲) 27.0 mg.

$V_2O_5 \gg CrO_3$. Thus we selected WO_3 as catalyst to investigate its catalytic mechanism.

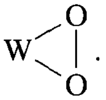
Fig. 1 shows typical time-dependent curves for the oxidation of benzyl alcohol catalyzed by WO_3 in the presence of CTMAB. The rate of oxidation increases with the concentration of the catalyst. The maximum rate of oxidation is about 111 mmol/min, the yield of benzaldehyde can be up to 98% with a selectivity of near 100%. The shape of the kinetic curves tends to become linear with decreasing catalyst concentration. The induction period of the reaction decreases with the reduction of catalyst concentration. Using TTCB or PTTCB directly as catalyst, there will be no inducting period during the reaction and the kinetic curves will have the shape of a line (see also fig. 1).

It was found that WO_3 can react with CTMAB to form a new compound TTCB which can be oxidized by aqueous hydrogen peroxide to yield a peroxide peroxo-TTCB (PTTCB). Because of the difficulty of obtaining a single crystal, the detailed structure of TTCB or PTTCB was not revealed. The results of XPS showed that there exist W and C elements, but no Br element is detected in the TTCB. So TTCB seems to be a new compound. The IR spectrum of PTTCB indicated that the characteristic absorption peaks at 538, 572 and 904 cm^{-1}



Scheme 1. Conceivable path of oxidation of benzyl alcohol catalyzed by the WO_2/CTMAB system with aqueous hydrogen peroxide.

could be assigned respectively to the vibration and trans-vibration of the W–O bond and the vibration of the O–O bond in



The active oxygen found by iodometry in PTTCB was estimated to be 0.32 mmol per gram PTTCB. The results of TG and MS analysis indicated that TTCB or PTTCB split to produce $N(CH_3(CH_2)_{14}CH_3)(CH_3)_2$ when heated at 105–305°C, and $N(CH_3)_3$ at 305–430°C. The ratio of WO_3 and $(CH_3)_3(CH_3(CH_2)_{14}CH_3)N^+$ in PTTCB or TTCB was determined to be 1 : 1 by thermogravimetry of PTTCB. This fact showed that WO_3 coordinated with CTMAB in equal molar quantities.

PTTCB or TTCB is almost insoluble in either water or benzyl alcohol, even if the temperature is raised to 90°C. However, the conversion of benzyl alcohol can become very high in the tri-phasic catalytic system when a small amount of catalyst (WO_3: 2.9 mg) is added to a mixture of aqueous hydrogen peroxide and benzyl alcohol (see also fig. 1). It shows that the reaction is carried out in a tri-phasic catalytic system constituted of aqueous hydrogen peroxide, benzyl alcohol and a solid catalyst.

The catalytic cycle for the oxidation of benzyl alcohol has been outlined in scheme 1. Based on this reaction mechanism, the induction period of reaction is found to be due to the formation of TTCB (the first step of the reaction in scheme 1). This deduction gives a satisfying explanation of the relationship between the induction period of the reaction and the concentration of the catalyst. Formation of PTTCB (the second step of the reaction in scheme 1) is the rate determining step of the reaction; the oxidation of benzyl alcohol by

PTTCB is very fast. So it is reasonable to use the steady-state method for PTTCB:

$$d[\mathrm{PTTCB}]/dt = k_2[\mathrm{TTCB}][\mathrm{H_2O_2}] - k_3[\mathrm{PTTCB}][\mathrm{PhCH_2OH}] = 0,$$

$$k_2[\mathrm{TTCB}][\mathrm{H_2O_2}] = k_2[\mathrm{PTTCB}][\mathrm{PhCH_2OH}].$$

The rate of formation of benzaldehyde is

$$d[\mathrm{PhCHO}]/dt = k_3[\mathrm{PTTCB}][\mathrm{PhCH_2OH}] = K_2[\mathrm{TTCB}][\mathrm{H_2O_2}].$$

The amount of hydrogen peroxide added in the reaction system is excessive; so, if the concentration of the catalyst (WO_3) is very low or if TTCB (or PTTCB) is directly used as catalyst, the concentration of TTCB will remain constant. Then the relationship between [PHCHO] and time is:

$$d[\mathrm{PHCHO}] = K\,dt \quad (K = k_2[\mathrm{TTCB}][\mathrm{H_2O_2}] = \text{constant}),$$

$$[\mathrm{PHCHO}] = Kt \quad \text{(initial concentration of PHCHO was zero)}.$$

This means that the yield of benzaldehyde increases linearly with time. If the concentration of the catalyst (WO_3) is large enough, TTCB produces continually during the reaction, the rate of reaction will increase gradually, and this results in an S shape for the kinetic curves. So these results agree with the kinetic conclusions.

References

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