# Competitive oxidation of 1- and 2-propanol catalyzed by titanium silicalite-1 and the application for selective oxidation of 1-methoxy-2-propanol to 1-methoxy-2-propanone

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Received 24 July 1995; accepted 20 September 1995

Oxidation of 2-propanol with hydrogen peroxide catalyzed by TS-1 was strongly retarded in the presence of an equimolar 1-propanol to a level of 1-propanol oxidation, and the competitive oxidation behavior was applied for the selective oxidation of 1-methoxy-2-propanol to afford 1-methoxy-2-propanone in a high yield of 85%.

**Keywords:** TS-1; competitive oxidation; 1- and 2-propanol; 1-methoxy-2-propanol

## 1. Introduction

Titanium silicalites (TS-1) with MFI topology [1] provided new opportunities during the last decade in catalytic oxidation [2]. A general reactivity trend in alcohol oxidation, secondary > primary ≫ methanol, and competition kinetics with pairs of secondary alcohols in methanol have been recently reported [3]. 3-pentanol reacted approximately ten times slower than 2-pentanol [2,3]. An interesting competitive oxidation behavior is demonstrated in the present communication with TS-1 catalyzed 1- and 2-propanol oxidation. The secondary 2-propanol was oxidized much more quickly than the primary 1-propanol as anticipated from the above general trend. However, the rate of oxidation of 2-propanol was strongly retarded in the presence of an equimolar 1-propanol to a level of 1-propanol oxidation. Application of the competitive oxidation behavior at the primary and secondary hydroxyl sites for the selective oxidation of 1-methoxy-2-propanol was successful to give a high yield of 85% of 1-methoxy-2-propanone, which was 30–45% on lead- or bismuth-modified palladium-on-carbon catalysts [4].

## 2. Experimental

Titanium silicalite was prepared by the literature procedure [5,6]. To a solution of 1.5 g tetraethyltitanate in 45 g of tetraethylsilicate was added 200 ml of an alkali-free tetra-*n*-propylammonium hydroxide (TPAOH) under stirring in a beaker. The resultant mixture was heated at 70–80°C on a hot-plate to evaporate ethanol formed by the hydrolysis of ethoxides. After evaporating 6 h, no ethanol was detected by gas chromatography, and an appropriate amount of water was added to make up, adjusting to a composition of Ti : Si : TPAOH : $H_2O$ = 3.04 : 100 : 45.7 : 3500. The ingredients were transferred into a Teflon-lined autoclave, kept static for 4 days at 175°C, separated and washed by repeated centrifuge, and then calcined at 550°C in air for 5 h. Silicalite S-1 was prepared similarly without titanium.

Powder X-ray diffraction(XRD) was measured by a MXP system of MacScience Co., Tokyo. Infrared (IR) spectra were recorded for catalyst powder tabletted with KBr on a spectrometer, model FTIR-3 of Japan Spectroscopic Co. Scanning electron microscopic (SEM) observation was made by an electron probe microanalyzer of type JXA-840A of JEOL, Tokyo. Surface area was measured by a conventional BET nitrogen adsorption apparatus of Shibata P-700. Bulk composition was ana-

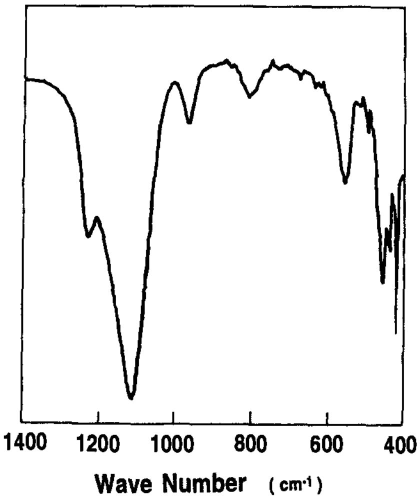

Fig. 1. IR spectrum of titanium silicalite-1.

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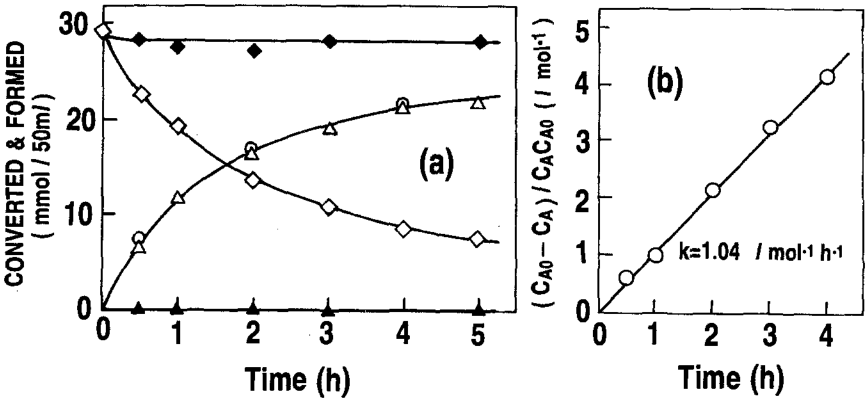


Fig. 2. Oxidation of 2-propanol with equimolar $H_2O_2$. (a) Temperature, 40°C; catalyst, 0.5 g/50 ml; 2-propanol, 30 mmol; open symbols, TS-1; closed symbols, S-1; squares, 2-propanol; circles, $H_2O_2$ consumed; triangles, acetone. (b) Verification of second-order kinetics.

lyzed for Ti and Si by an inductively coupled plasma (ICP) apparatus of Seiko SPS-1700.

Oxidation of alcohols was carried out at 40°C in aqueous phase under magnetical stirring with 0.5 g of catalyst, 30 mmol of each alcohol and $H_2O_2$ (equimolar) in 50 ml in a three-necked, flat-bottom flask equipped with a reflux condenser. An aliquot (each 2 ml) of the reaction liquor was taken intermittently, and analyzed for $H_2O_2$ by iodometric titration [7] and for organic compounds by gas chromatography. Column packings of Gaskuropack 56 (3⌀ × 1 m) was used at 160°C for 1-propanol, propionaldehyde and propionic acid, and 15% PEG 4000/Uniport B (3⌀ × 2 m) at 80°C for 2-propanol, acetone, 1-methoxy-2-propanol and 1-methoxy-2-propanone.

## 3. Results and discussion

Titanium content of the calcined TS-1 was analyzed as 2.00 mol% (Ti/(Ti + Si)) by ICP. The powder XRD pattern agreed well with literature [5]. An IR band characteristic of TS-1 [8] was detected at 960 $cm^{-1}$ as shown in fig. 1. Cubic crystals of 0.1–0.2 μm in size were observed by SEM and the BET surface area was 435 $m^2/g$ for the present TS-1.

Fig. 2a illustrates TS-1 catalyzed oxidation of 2-propanol with an equimolar hydrogen peroxide (open symbols), where the amount of acetone formed and $H_2O_2$ consumed were super-imposed on a single curve, showing the active oxygen in $H_2O_2$ was consumed selectively to give acetone, and the excellent fit of data with over-all second-order kinetics was verified as in fig. 2b. Attempted oxidation at the same condition in the presence of S-1 (black symbols, fig. 2a) shows the framework reference to be inactive.

Comparing with 2-propanol (fig. 2a), TS-1 catalyzed oxidation of 1-propanol was extremely slow as given in fig. 3a. The results are as anticipated in reference to the general reactivity trend in alcohol oxidation [2,3]. Thus the oxidation of 1,2-propylene glycol would give a product oxidized in preference at the secondary hydroxyl site as the major product. Hydroxyacetone was obtained, but the rate of oxidation of 1,2-propylene glycol was slow in the level of 1-propanol rather than 2-propanol oxidation in contrast to the expectation. Com-

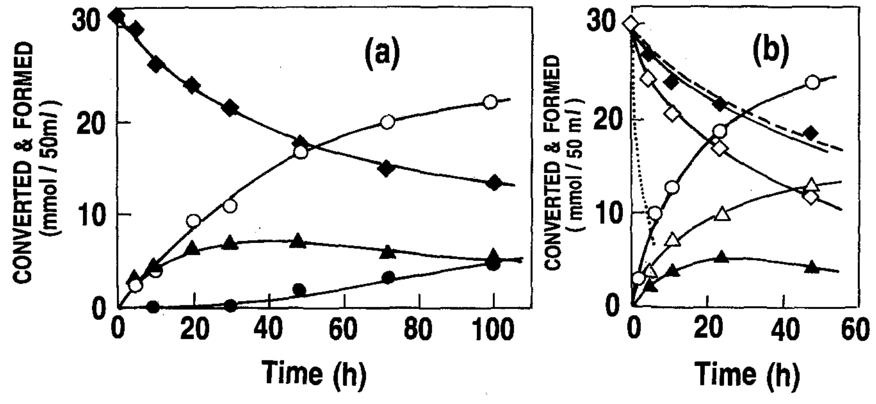


Fig. 3. Oxidation of 1-propanol in the absence (a) and presence of equimolar 2-propanol (b). Temperature, 40°C; catalyst, TS-1 0.5 g/50 ml; (◆) 1-propanol, (▲) propionaldehyde, (●) propionic acid, (◇) 2-propanol, (△) acetone, (○) $H_2O_2$ consumed. Dotted line: oxidation of 2-propanol in the absence of 1-propanol, taken from fig. 2a for reference. Dashed line: oxidation of 1-propanol in the absence of 2-propanol, taken from fig. 3a.

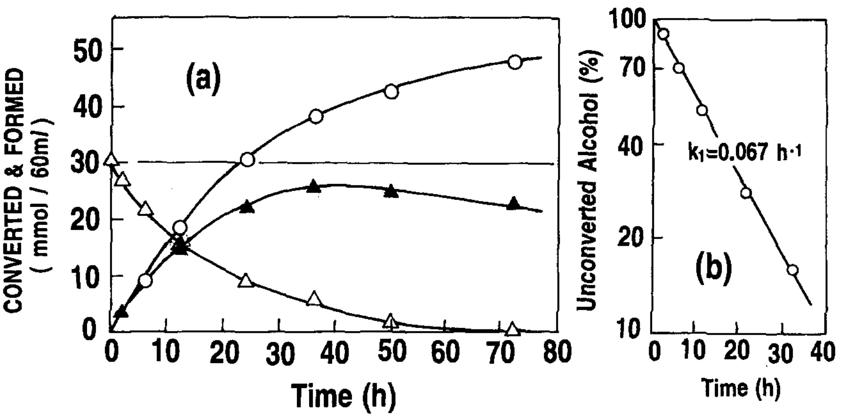


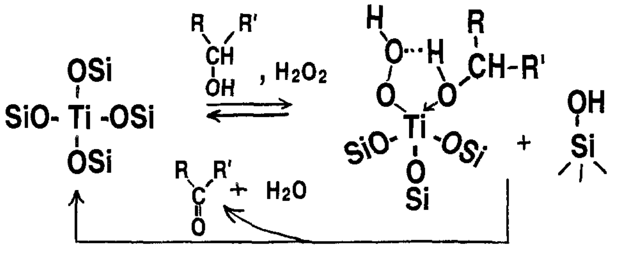
Fig. 4. Oxidation of 1-methoxy-2-propanol (a) and the apparent first-order kinetics (b). Temperature, 40°C; catalyst, TS-1 0.5 g/60 ml, (△) 1-methoxy-2-propanol (MP), (▲) 1-methoxy-2-propanone, (○) $H_2O_2$ consumed. Initial molar ratio, $H_2O_2$/MP = 2.19.

petitive oxidation with a pair of 1- and 2-propanol also revealed strong retardation on the oxidation of 2-propanol in the presence of 1-propanol as given in fig. 3b, where the dotted line shows oxidation of 2-propanol in the absence of 1-propanol, taken from fig. 2a for reference, and the dashed line shows that oxidation of 1-propanol was unaffected in the presence of 2-propanol.

It seems to be generally accepted that tetrahedral framework Ti [9] simultaneously coordinated with both $HO_2$- and alkoxy-ligands would be the intermediate in alcohol oxidation [3,9] as illustrated in scheme 1, and the results suggest that 1-propanol coordinated strongly on the active site followed by the slow oxidation, while 2-propanol coordinated weakly but was oxidized quickly.

The site occupied with 1-propanol is inert for 2-propanol until the site has been regenerated by the oxidative desorption of 1-propanol, leading to slow oxidation of 2-propanol in the presence of 1-propanol. It appears worthwhile to note that 3-pentanol reacted slower than 2-pentanol, but the former did not retard the oxidation of the latter in the competitive oxidation [3].

Selective oxidation at the secondary hydroxyl site of lactic acid to pyruvic acid in aqueous phase catalyzed by lead-modified palladium-on-carbon and related systems has been carried out in our laboratory [10–12]. Similar catalysts, Pb/Pd/C and Bi/Pd/C, were employed in oxidation also at secondary hydroxyl site of 1-methoxy-2-propanol to 1-methoxy-2-propanone [4]. The substrate was oxidized with great ease, but the product yield passed through a maximum at most 30–45% [4].



Scheme 1.

An attempted application of TS-1 catalyzed oxidation of 1-methoxy-2-propanol is given in fig. 4. The rate was slow but rather selective, and a prolonged reaction under mild condition resulted in a high yield of 1-methoxy-2-propanone of 85%. The TS-1 catalyzed oxidation of 1-methoxy-2-propanol with hydrogen peroxide at equimolar condition was again overall second order, but was first order with respect to the substrate in the presence of a slight excess of $H_2O_2$ as shown in fig. 4b. Assuming consecutive first-order reactions of 1-methoxy-2-propanol to 1-methoxy-2-propanone followed by the further oxidation at 1-methoxy site with rate constant of $k_1$ and $k_2$, respectively, the time $t_{\max}$ at which 1-methoxy-2-propanone shows the maximum yield, is

$$t_{\max} = \frac{\ln(k_1/k_2)}{k_1 - k_2} .$$

The values of $t_{\max} = 40$ h and $k_1 = 0.067\ \mathrm{h}^{-1}$ obtained in figs. 4a and 4b give $k_2 = 0.0056\ \mathrm{h}^{-1}$, signifying preferential oxidation at the secondary hydroxyl site.

## 4. Conclusion

Oxidation of 2-propanol with hydrogen peroxide catalyzed by TS-1 in aqueous phase was carried out with great ease as compared with that of 1-propanol. However, oxidation of 2-propanol in the presence of 1-propanol was strongly retarded to a level of 1-propanol oxidation. The competitive oxidation behavior was applied for preferential oxidation at the secondary hydroxyl site of 1-methoxy-2-propanol to afford 1-methoxy-2-propanone in a high yield of 85%.

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