

# Enhancement of catalytic activity of Ir/TiO<sub>2</sub> by partially reduced titanium oxide in oxidation of alcohols with molecular oxygen

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## Introduction

In spite of the formation of toxic by-products and large amount of heavy metal wastes, oxidation reactions of alcohols have been performed mainly in non-catalytic systems with stoichiometric amount of oxidants [1]. From environmental and economic points of view, the catalytic systems which can utilize greener and cheaper oxidants, namely molecular oxygen, have attracted much attention [2].

We have already reported that supported Ir catalysts prepared by the conventional impregnation method exhibited catalytic activity to the oxidation of alcohols with molecular oxygen [3]. Among them, TiO<sub>2</sub> supported catalyst showed the best performance. In this work, we report that the catalytic activity of Ir/TiO<sub>2</sub> is enhanced by partially reduced titanium oxide.

## Experimental

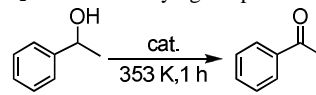
A TiO<sub>2</sub> supported Ir catalyst was prepared from aqueous solution of H<sub>2</sub>IrCl<sub>6</sub> and commercial TiO<sub>2</sub> (Aerosil, P25) by the conventional impregnation method. The loading amount of Ir was adjusted to 2 wt%. The impregnated sample was dried at 373 K and then reduced in H<sub>2</sub> flow for 3 h. The reduction temperature was varied from 353 K to 873 K. The oxidation reaction was carried out as follows: the reduced 2 wt% Ir/TiO<sub>2</sub> catalyst (75 mg, 20 μmol of Ir), toluene (1.5 mL), and the substrate (1.5 mmol) were charged to glass vials followed by introduction of atmospheric pressure of oxygen. The reaction was started by heating the reaction mixture at 353 K. The yields of the products were determined by GC analyses.

## Results/Discussion

By the TEM analysis of the catalyst reduced at 573 K, highly dispersed Ir particles on TiO<sub>2</sub> support were observed. The mean diameter of the metal particles was 1.5 nm. This value was well corresponding to the result of CO chemisorption (dispersion: 68%, mean particle diameter: 1.9 nm). The CO chemisorption amount was decreased with increasing the temperature of

hydrogen reduction due to the Strong Metal Support Interaction (SMSI) effect (Table 1) [4]. This phenomenon is caused that the Ir metal surface is covered with partially reduced titanium oxide, which is formed by hydrogen reduction at high temperature. In order to investigate the relation between catalytic activity and reduction temperature, the aerobic oxidation of 1-phenylethanol was carried out (Table 1). In spite of the covering of surface Ir atoms with partially reduced titanium oxide, the catalysts reduced at higher temperature (> 573 K) showed higher activity. This result indicates that the catalytic activity was enhanced by partially reduced titanium oxide. The catalyst reduced at 723 K showed the best performance and the TON value based on the loaded amount of Ir was reached to 75 after 3 h reaction at 353 K. Not only 1-phenylethanol, but the wide variety of alcohols were efficiently oxidized by 2wt%Ir/TiO<sub>2</sub> reduced at 723 K (Table 2). To clarify the role of










Table 1. Oxidation of 1-phenylethanol over Ir/TiO<sub>2</sub> reduced at varying temperature



Red. Temp (K)	Yield of acetophenone (%)	CO chemisorption amount (mL/g)
573	27	1.5
673	62	1.0
723	89	0.35
773	62	0.17
873	57	-

partially reduced titanium oxide for the promotion of catalytic activity, the kinetic analysis was demonstrated. The linear correlation was obtained when the inverse of substrate concentration was plotted against the inverse of the initial reaction rate, suggesting the operation of the Langmuir type reaction kinetics. Langmuir adsorption equilibrium constants determined by the above mentioned plot was 6.7 and 13.5 mol<sup>-1</sup> for 573 K and 723 K reduced catalysts, respectively. This result suggests that the catalyst reduced at 723 K has higher affinity to substrates than the catalyst reduced at 573 K. It is supposed that partially reduced titanium oxide formed in the vicinity of Ir metal particle worked as coordination sites to bind alcohols and enhance the catalytic activity.

Table 2. Oxidation of various alcohols over 2wt% Ir/TiO<sub>2</sub> reduced at 723 K

Entry	Substrate	Time / h	Yield / %	Selec. / %
1		1	>99	>99
2		1	>99	>99
3		30	65	72
4		7	>99	>99
5		3	>99	>99
6		7	92	98
7		9	80	88
8		7	95	98
9		21	94	96

## References.

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