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Catalytic oxidation of aromatic alcohols and alkylarenes with molecular oxygen over Ir/TiO_2

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ABSTRACT

A TiO_2 supported Ir catalyst prepared by the conventional impregnation method exhibited efficient catalytic activity toward the oxidation of organic compounds with molecular oxygen. Aromatic alcohols and alkylarenes selectivity afforded the corresponding carbonyl compounds in high yield under mild conditions. The reaction was quenched by removing the catalyst with filtration suggesting that the catalytic reaction proceeded heterogeneously. The highly dispersed Ir metal particles on TiO_2 surface was considered to be responsible for the catalysis.

1. Introduction

Carbonyl compounds are one of the important classes of the compounds not only in chemical industries but also in laboratories. The most common way to produce carbonyl compounds is the oxidation of the corresponding alcohols and alkanes. In spite of the formation of toxic by-products and large amount of heavy metal wastes, these oxidation reactions have been performed mainly in non-catalytic systems with stoichiometric amount of oxidants [1]. However, from environmental and economic points of view, formation of above mentioned by-products and wastes is undesirable. Therefore, the catalytic systems which can utilize greener and cheaper oxidants, namely molecular oxygen, have attracted much attention [2]. To date, various kinds of catalytic systems have been reported in the catalytic oxidation of alcohols utilizing transition metal complexes [3–5], nitroxy radicals [1], and heterogeneous supported metal catalysts [6–9]. However, degradation of organic moieties as well as deposition of inactive metal particles was the inevitable problems in some homogeneous systems [5].

Recently, nicely working systems have been developed for alcohol oxidation utilizing supported Pd and Ru catalysts, which is robust enough to achieve high TON and also to provide the recyclability. For example, the nano-sized palladium clusters supported on hydroxyapatite was reported by Kaneda et al. [6] Mizuno et al. also reported the nice heterogeneous catalyst of $Ru(OH)_x/Al_2O_3$ which exhibited high catalytic activity to the aerobic oxidation of alcohols [7] as well as alkylarenes [8] and amines [9]. The key step in the oxidation reactions by these catalysts is hydride elimination from substrates to form M–H species (M: Pd, Ru).

Iridium has been attracted much attention as alternative materials for platinum especially in the field of electro catalysts [10]. However, only few works were reported in the field of aerobic oxidation catalysts, while there have been various reports of both homogeneous and heterogeneous catalytic oxidation utilizing other group 8–10 metal elements such as Pd, Pt, Ru, Os and Au [3–9,11]. Ison et al. reported the aerobic oxidation of alcohols to the corresponding aldehydes and ketones catalyzed by $[Cp^{*}IrCl_2]_2$ [12]. Ishii et al. reported the aerobic oxidation of primary alcohols to esters catalyzed by $[IrCl(cod)_2]_2$ [13]. Those reported systems were utilizing the Ir complexes in homogeneous reaction conditions. Therefore, the applicability of supported Ir catalysts to the oxidation reaction of alcohols or alkylarenes have still been an unexplored area. In this manuscript, we firstly report the oxidation of aromatic alcohols and alkylarenes with molecular oxygen catalyzed by supported Ir catalysts.

2. Experimental

2.1. Instruments

GC analyses were performed on a Shimadzu GC-2010 gas chromatograph with a FID detector equipped with a TC-WAX capillary column. Mass spectra were recorded on a Shimadzu GCMS2010 spectrometer equipped with a TC-WAX capillary column at an ionization voltage of 70 eV. Liquid-state NMR spectra were recorded on a JEOL JNM-ECA-600 spectrometer. ^{1}H and ^{13}C NMR spectra

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were measured at 600.17 and 150.92 MHz, respectively. A transmission electron microscope (JEM2010, JEOL) with an acceleration voltage of 200 kV and LaB_6 cathode was applied for the observation of the images of supported catalysts. Samples were prepared by suspending the catalyst powder ultrasonically in 2-propanol and depositing a drop of the suspension on a standard copper grid covered with carbon monolayer films. The X-ray photoelectron spectra were recorded on a JEOL JPS-9010 spectrometer with Mg Kα X-ray source (10 kV, 10 mA). Prior to the measurement, the sample was reduced by H_2 at 573 K in the preparation chamber and transferred to the analysis chamber without exposure to air. The adsorption amount of hydrogen was measured by a static volumetric adsorption apparatus (Omnisorp 100CX, Beckmann Coulter) at 298 K. Before measurement, the catalysts were dried at room temperature and reduced at 573 K for 3 h in a flow of atmospheric pressure of hydrogen. The dispersion (D(%); percentage of metal atoms exposed to the surface) of supported metal particles was evaluated from the amount of chemisorbed carbon monoxide with assuming the adsorption stoichiometry of CO to an surface metal atom is unity.

2.2. *Materials and catalyst preparation*

The TiO_2 support (P25) was purchased from Nippon Aerosil Co. Ltd. The solvents used for the catalytic reaction were dried with activated molecular sieves 4A. For other material, the commercially available reagents of the highest grade were used without further purification.

A TiO_2 supported Ir catalyst was prepared from an aqueous solution of H_2IrCl_6 by the conventional impregnation method. The loading amount of Ir was adjusted to 5 wt%. The impregnated sample was dried at 373 K and then reduced in H_2 flow at 573 K for 3 h. The Ir catalysts supported on other oxide materials were prepared by the same procedure.

2.3. *Procedures for catalytic oxidation*

The oxidation reaction was carried out as follows: 75 mg of the reduced 5 wt% Ir/TiO_2 (Ir: 20 μmol, 1.25 mol% to substrates), the solvent (1.5 mL), and the substrate (1.5 mmol) were charged into a glass vial (volume: 17 mL). The reaction mixture was stirred at 353 K, 393 K or 423 K under atmospheric pressure of molecular oxygen. The products were identified by the comparison of mass and NMR spectra with those of authentic samples. The yields of the products were determined by GC analyses with internal standard technique. TON values were calculated by dividing the number of the mole of the products by the amount of surface Ir atoms estimated from the CO chemisorption results. The inter-molecular competitive oxidation of the primary and secondary alcohols was examined by using the mixture of benzyl alcohol (1.5 mmol) and 1-phenylethanol (1.5 mmol) as substrates under the same reaction conditions described above.

3. Results and discussion

3.1. *Characterization of Ir supported on TiO_2*

After hydrogen reduction, highly dispersed Ir particles were formed on TiO_2 support. From TEM observation, the mean diameter of the particles was 1.7 nm (Fig. 1), which corresponded well to that estimated from the amount of chemisorbed hydrogen (1.8 nm). In a X-ray photoelectron spectrum of $Ir4f_{7/2}$ transition, the larger peak at 60.4 eV and the smaller one at 61.7 eV were observed (Fig. 2). The binding energy of the former peak is slightly lower than that of the reported value for Ir metal (60.8 eV) [14], therefore it should be assignable to metallic Ir species. The binding energy of the latter one at 61.7 eV is close to the value for IrO_2 (62.0 eV) [14]. These results indicate that most of the Ir atoms on Ir/TiO_2 are almost zero valent after hydrogen reduction.

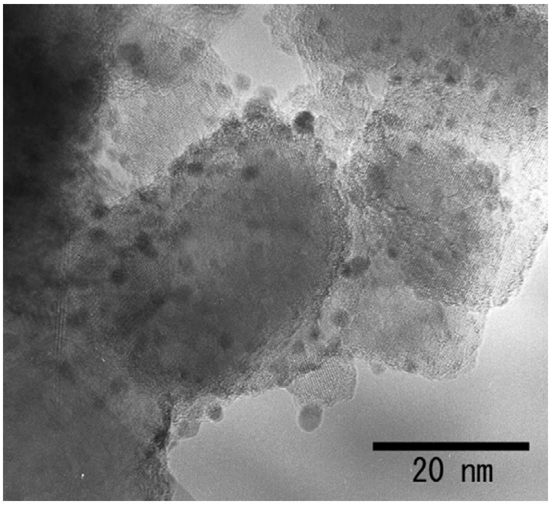


Fig. 1. TEM image of 5 wt% Ir/TiO_2.

3.2. *Oxidation of benzyl alcohol with Ir/TiO_2*

The catalytic activity of Ir/TiO_2 toward the oxidation of benzyl alcohol with molecular oxygen was examined. After 7 h at 353 K, more than 99% of benzyl alcohol was converted to benzaldehyde with 99% selectivity without base addition. The detection of only a trace amount of benzoic acid indicates that the oxidation proceeded selectively. Low valent or metallic Ir should be the active species because the catalyst without hydrogen reduction showed almost no activity. The reaction was quenched by removing the catalyst with filtration, suggesting that the catalytic reaction proceeded heterogeneously. In addition, Ir/TiO_2 was recyclable at least for three times as follows; after the separation of the spent Ir/TiO_2 catalyst by filtration, and the reduction by hydrogen stream, the recovered catalyst showed almost the same catalytic activity as a fresh one even after the three times recovering (the yields of the

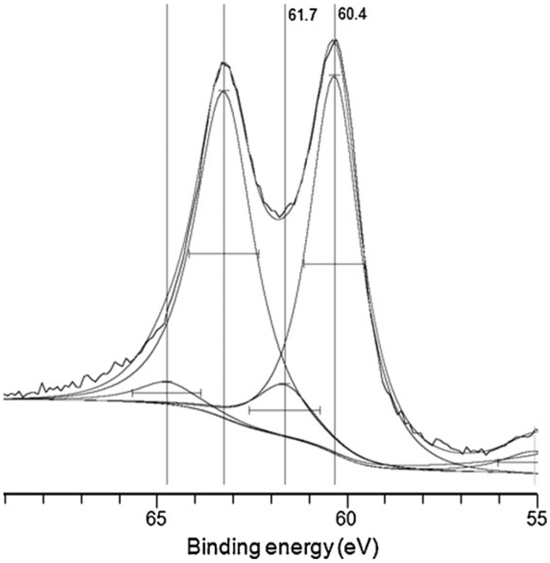
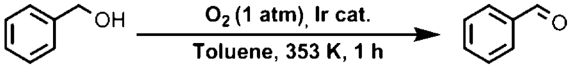


Fig. 2. X-ray photoelectron spectrum of Ir4f transition of Ir/TiO_2.

Table 1
Oxidation of benzyl alcohol with molecular oxygen catalyzed by various supported Ir catalysts.



Support	Conv./%	Yield/%	Selec./%	Disp./%[a]	TON
TiO_2	77	76	98	48	128
ZrO_2	33	26	79	60	44
Al_2O_3	23	18	79	53	35
SiO_2	23	18	78	19	97
CeO_2	14	10	69	80	14
MgO	12	6	54	23	42
TiO_2[b]	73	2	3	–	–

[a] Determined by the amount of chemisorbed carbon monoxide.
[b] The catalyst without hydrogen reduction was used.

benzaldehyde were 94% (the fresh catalyst), 93% (2nd run), 92% (3rd run), and 92% (4th run) after 4 h at 353 K).

The Ir catalysts supported on other oxide materials, such as Al_2O_3, SiO_2, MgO, ZrO_2, and CeO_2 also exhibited the catalytic activity, but were less active than Ir/TiO_2 (Table 1). Among these catalysts, the dependency was not found between the catalytic activity and the dispersion of Ir particles or the acid/base properties of the supports. The intrinsic role of TiO_2 support in this reaction is under investigation.

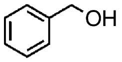
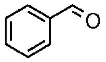
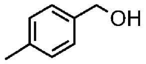
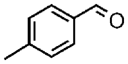
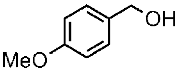
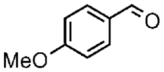
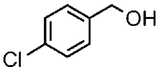
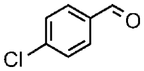
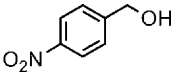
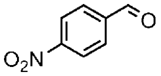
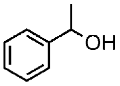
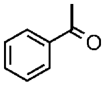
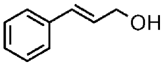
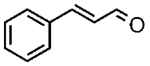
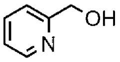
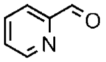
3.3. Oxidation of various alcohols with Ir/TiO_2

The results for the oxidation of aromatic alcohols with Ir/TiO_2 are summarized in Table 2. The *p*-substituted benzyl alcohols afforded the corresponding benzaldehyde derivatives in excellent yield, while *p*-chloro and *p*-nitro substituted ones required more severe reaction conditions for achieving complete conversion. Furthermore, Ir/TiO_2 also catalyzed the oxidation of 2-pyridine methanol, which contains the nitrogen atom being able to coordinate to the metal center, to the corresponding aldehyde. All the reaction above mentioned proceeded without base addition. Comparing to the Ir complex, the catalytic activity of Ir/TiO_2 was ten times higher. The TOF value for the oxidation of 4-methoxybenzyl alcohol by Ir/TiO_2 was 33 h^{-1} at 353 K for 5 h (TON: 166), while that for $[Cp^*IrCl_2]_2$ at the same reaction temperature was 3.2 h^{-1} for 12 h (TON: 38) [12]. In the oxidation of benzyl alcohol, the TOF value of $Ru(OH)_x/Al_2O_3$, which is known to exhibit high activity to the oxidation of alcohols, was 40 h^{-1} (TON: 40) under the almost same reaction conditions of ours (at 356 K, 1 mmol of benzyl alcohol in 1.5 mL of $PhCF_3$) [7], while that for Ir/TiO_2 was 24 h^{-1} (TON: 166). Although the catalytic activity of Ir/TiO_2 was a little lower than $Ru(OH)_x/Al_2O_3$, Ir/TiO_2 showed much better performance than the previously reported homogeneous Ir complex.

The primary cinnamyl alcohol and the secondary 1-phenyl ethanol also afforded the corresponding aldehyde and ketone, respectively, although, the secondary 1-phenyl ethanol required longer reaction period than the primary alcohols for achieving full conversion. To investigate the lower reactivity of the secondary alcohol, the competitive reaction of benzyl alcohol and 1-phenylethanol was carried out as shown in Fig. 3. The reaction rate of 1-phenylethanol was remarkably decreased under the competitive condition, while that of benzyl alcohol was almost the same. The diminishment of the reaction rates of secondary alcohols in the presence of the primary alcohols was also observed in the $Ru(OH)_x/Al_2O_3$ catalyzed system, where the formation of metal alcoholate species were expected [7]. Since the formation of metal alcoholate intermediate is well known for the selective oxidations of primary hydroxyl groups [15,16], the formation of alcoholate species from alcohol with M–OH moiety (M: Ir or Ti) should be taken part in the present Ir/TiO_2 catalyzed reaction and this is probably a reason for the slower reaction rate of 1-phenylethanol.

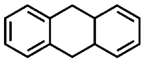
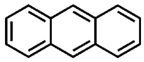
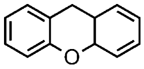
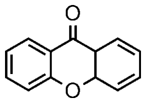
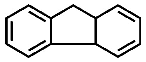
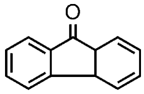
In the presence of 2-octanol with a catalytic amount of Ir/TiO_2, acetophenone was converted to 1-phenylethanol under an Ar atmosphere and the comparable amount of 2-octanone was formed at the same time (Fig. 4). This result suggests that β-hydride elimination of alcohol may take place on Ir/TiO_2 with the formation of Ir–H, which has also been confirmed in the alcohol oxidation reaction catalyzed by Ir complexes [12,17]. On the basis of these results, same as the $Ru(OH)_x/Al_2O_3$ and Pd/hydroxyapatite systems [6,7], the formation of alcoholate and Ir–H species are possibly concerned to the present Ir/TiO_2 catalyzed aerobic oxidation of alcohols.

Table 2
Oxidation of aromatic alcohols with molecular oxygen catalyzed by 5 wt% Ir/TiO_2.

Substrate	Product	Time/h	Conv./%	Yield/%	Selec./%	TON
		7[a]	>99	>99	>99	166
		6[a]	>99	>99	>99	166
		5[a]	>99	>99	>99	166
		3.5[b]	99	85	86	143
		80[b]	98	95	97	161
		48[a]	97	95	97	161
		20[a]	>99	86	86	143
		7[b]	99	94	95	158

[a] Reaction temperature (solvent): 353 K (toluene).
[b] Reaction temperature (solvent): 393 K (o-xylene).

Table 3
Oxidation of alkylarenes with molecular oxygen catalyzed by 5 wt% Ir/TiO_2.

Substrate	Product	Time/h	Conv./%	Yield/%	Selec./%	TON
		12	>99	94[a]	94	156
		12	>99	98	98	163
		50	>99	62	62	103

Reaction temperature (solvent): 423 K (mesitylene).

[a] 5% of anthrone was yielded.

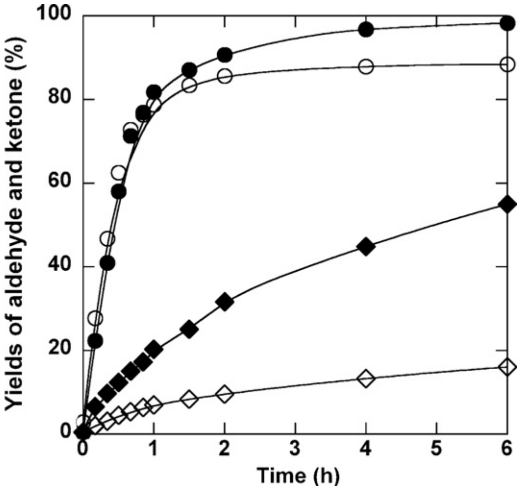


Fig. 3. Time courses of the oxidation of benzyl alcohol (solid circles), 1-phenylethanol (solid diamonds), and their competitive reaction (open marks).

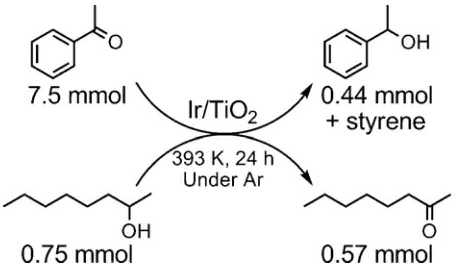


Fig. 4. Ir/TiO_2 catalyzed hydrogen transfer reaction from 2-octanol to acetophenone.

3.4. Oxidation of alkylarenes with Ir/TiO_2

Ir/TiO_2 also exhibited the catalytic activity toward the oxidation of alkylarenes. Only few examples have been reported for the liquid-phase oxidation of alkylarenes with molecular oxygen as a solo oxydant [8,18]. Xanthene and fluorene afforded the oxygenated products of xanthone and 9-fluorenone, respectively, while 9,10-dihydroanthracene afforded the dehydrogenated product of anthracene (Table 3). The oxygenation of xanthone and fluorene, and the dehydrogenation of 9,10-dihydroanthracene were also reported by Mizuno et al. in the oxidation of alkylarenes catalyzed by $Ru(OH)_x/Al_2O_3$ with molecular oxygen [8]. They suggested that the oxygenated products were formed by the successive oxidation of initially formed hydroxylated products of xanthydrol and 9-fluorenol. On the other hand, the dehydrogenated products were suggested to be formed by the successive dehydration of hydroxylated products of 9-hydroxy-9,10-dihydroanthracene, which may be promoted by the Al_2O_3 support. In the present alkylarene oxidation catalyzed by Ir/TiO_2, the oxygenation and dehydrogenation are expected to proceed in the similar manner to the Ru/Al_2O_3 catalyzed reactions.

4. Conclusion

The TiO_2 supported Ir catalyst prepared by the conventional impregnation method exhibited excellent activity toward the oxidation of aromatic alcohols and alkylarenes. Various kinds of alcohols including the benzyl alcohol derivatives, the secondary 1-phenylethanol and the nitrogen containing 2-pyridine methanol selectively afforded the corresponding aldehydes and ketones without addition of base or acid. Ir/TiO_2 showed the catalytic activity to the hydrogen transfer reaction from 2-octanol to acetophenone suggesting the oxidation reaction of alcohols proceeded through the formation of Ir–H species. In addition, Ir/TiO_2 also catalyzed the oxidation of alkylarenes with molecular oxygen affording xanthone and 9-fluorenone from xanthene and fluorene, respectively. While 9,10-dihydroanthracene afforded the dehydrogenated product of anthracene.

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