Dehydrogenative Oxidation of Alcohols Catalyzed by Highly Dispersed Ruthenium Incorporated Titanium Oxide

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Abstract: Ruthenium incorporated titanium oxides (Ru x TiO 2 ) were prepared by a one-step hydrothermal method using Ti(SO 4 ) 2 and RuCl 3 as the precursor of Ti and Ru, respectively. X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), transmission electron microscope (TEM), Energy-dispersive X-ray spectroscopy (EDS) mapping, and BET were applied for the analyses of catalysts. Ruthenium atoms are well dispersed in the anatase phase of TiO 2 and the crystallite size of Ru x TiO 2 (∼17 nm) is smaller than that of pure TiO 2 (∼45 nm). In particular, we found that our homemade pure TiO 2 exhibits a strong Lewis acid property. Therefore, the cooperation of ruthenium atoms playing a role in the hydride elimination and the Lewis acid site of TiO 2 can efficiently transfer primary alcohols into corresponding aldehydes in an oxidant-free condition.

Keywords: ruthenium catalyst; titanium oxide; dehydrogenative oxidation

1. Introduction

The oxidation of alcohols into their carbonyl compounds by a cost effective and environmentally benign means is important in synthetic chemistry. Particularly, many researchers have made concentrated efforts on the development of catalytic oxidation reactions using molecular oxygen (O 2 ) as an oxidant instead of using stoichiometric amounts of expensive and harmful oxidizing reagents [1–3]. Moreover, there have been lots of studies seeking the novel oxidation catalytic systems of alcohols in which alcohol oxidation is accomplished by a dehydrogenation pathway under oxidant-free conditions. In homogeneous catalytic systems, iridium complexes, osmium, or ruthenium pincer-type complexes, and Grubbs’ catalyst were commonly applied for the dehydrogenative oxidation [4–7]. Recently, nickel complexes were also reported [8]. In heterogeneous dehydrogenative catalytic systems, mainly noble metals catalysts were reported: alumina-supported silver cluster, hydrotalcite supported silver nanoparticles, ceria supported gold nanoparticles, alumina-supported Pt nanoparticles, alumina-supported Re nanoparticles [9–13]. Particularly, high reactivity was reported for the oxidation of aliphatic alcohols in anaerobic condition [12]. While aerobic oxidation generates water as byproduct, anaerobic conditions produce hydrogen gas. Therefore, the dehydrogenative oxidation prevents the deactivation of catalysts by water and is safely applied to substrates containing water sensitive functional groups.
Nanocrystalline TiO$_2$ has been intensively investigated in a wide range research fields due to its practical applications, such as photocatalysts, solar cells, materials for water or air purification, and so on [14–17]. It is the chemical, physical, and photo-stability of TiO$_2$ that all applications mentioned above make possible. Therefore, besides the catalytic properties of TiO$_2$, it can be a suitable material for supporting catalytic active centers in heterogeneous catalysts. Particularly, TiO$_2$ supported ruthenium catalysts were utilized for diverse oxidation reactions including aerobic oxidation [18,19], catalytic wet air oxidation of various chemicals [20–22], and electro-oxidation of alcohols [23]. However, to the best of our knowledge, ruthenium incorporated TiO$_2$ has not been applied to the oxidation of alcohols under oxidant-free conditions. Here we report the dehydrogenative oxidation of benzylic, allylic, and aliphatic alcohols into their corresponding aldehydes using ruthenium incorporated TiO$_2$ under oxidant-free conditions. We found that benzylic and allylic alcohols exhibited enhanced catalytic activity compared to aliphatic alcohol. Particularly, our homemade pure TiO$_2$ is a strong Lewis acid catalyst enough to form the Lewis acid-catalyzed Friedel-Craft alkylation products in a benzyl alcohol reaction. Therefore, the dehydrogenative oxidation pathway is accomplished by the synergistic catalysis of the Lewis acidic TiO$_2$ surface and the highly dispersed ruthenium species acting as the hydride elimination of α-carbon.

2. Results and Discussion

2.1. Catalyst Characterization

Figure 1 shows the crystal phases of ruthenium incorporated titanium oxides (Ru$_x$TiO$_2$, x represents the molar ratio of Ru with respect to Ti) obtained by hydrolysis of Ti(SO$_4$)$_2$ in aqueous solution with the different amount of RuCl$_3$. The pure TiO$_2$ and Ru$_x$TiO$_2$ represent the anatase phase of TiO$_2$ (JCPDS data file No. 00-21-1272). It was reported that TiO$_2$ prepared by a hydrothermal method using Ti(SO$_4$)$_2$ as a precursor exhibited the anatase phase [24]. The reflection peaks originated from RuO$_2$ are not presented for all the samples obtained from a hydrothermal condition (160 °C). After annealing the Ru$_{0.07}$TiO$_2$ sample (A-Ru$_{0.07}$TiO$_2$) at 700 °C for six hours, we find the appearance of Bragg’s reflection of RuO$_2$ (JCPDS file No. 00-040-1290) and phase transformation of TiO$_2$ from anatase to rutile. This result suggests that ruthenium atoms are randomly incorporated into the crystallite of TiO$_2$ before annealing. However, the phase segregation of TiO$_2$ (rutile) and RuO$_2$ takes place at an elevated temperature. The crystallite sizes of samples in Table 1 was calculated from X-ray line broadening by the Scherrer equation ($D = 0.89\lambda/(\beta \cos \theta)$), where $D$, $\lambda$, $\beta$, and $\theta$ represent the average crystal size, the Cu Kα wavelength (0.15406 nm), the full-width at half-maximum, and the diffraction angle, respectively. The calculated size of the pure TiO$_2$ is 26.4 nm which is bigger than that of Ru$_x$TiO$_2$ (13–15 nm). The surface area of the pure TiO$_2$ obtained by the BET method is approximately two-times smaller than that of Ru$_x$TiO$_2$ (Table 1).

| Samples       | Size (nm) | Surface Area (m$^2$/g) | Ru Content (µmol/g) |
|---------------|-----------|------------------------|---------------------|
| Pure TiO$_2$  | 26.4      | 45.7 ± 5.3             | -                   |
| Ru$_{0.01}$TiO$_2$ | 13.2      | 16.7 ± 0.9             | 9                   |
| Ru$_{0.03}$TiO$_2$ | 13.3      | 16.9 ± 1.0             | 24                  |
| Ru$_{0.05}$TiO$_2$ | 13.4      | 17.0 ± 1.4             | 37                  |
| Ru$_{0.07}$TiO$_2$ | 14.7      | 17.3 ± 1.1             | 51                  |

Table 1. The physical properties of the samples.
The elemental surface analyses of samples were done by X-ray photoelectron spectroscopy (XPS). A survey spectrum verify the presence of titanium, oxygen, ruthenium, and carbon contaminant without other species (Figure S1). The Ru 3d XPS spectra of Ru$_{0.07}$TiO$_2$ is shown in Figure 2. It is mainly composed of two parts which corresponds to the Ru 3d$_{5/2}$ (280.7 eV) and Ru 3d$_{3/2}$ (284.6 eV) band originated from spin-orbital coupling. Ru$_{0.07}$TiO$_2$ was synthesized under highly acidic aqueous conditions because no base was added in the hydrolysis of Ti(SO$_4$)$_2$. Therefore, we attributed the binding energy of 3d$_{5/2}$ (280.7 eV) to the Ru species with +4 oxidation state considering the above mentioned synthetic condition and previous literature data [25–27]. It was known that the Ru 3d$_{3/2}$ band overlaps with carbon 1s band and therefore, the Ru 3d$_{5/2}$ band is used for quantitative analysis [23,28]. The amount of Ru in Ru$_{0.07}$TiO$_2$ is 0.58 atomic percent and the ratio of Ru to Ti is 0.026 which is smaller than the added molar ratio (0.07) (In quantitative analysis, the relative sensitivity factor (RSF) of Ti 2p and Ru 3d$_{5/2}$ is 2.077 and 2.705, respectively.). The XPS peak intensities of 3d Ru of other Ru$_x$HAP are too weak to analyze quantitatively.

The morphology of samples was characterized by transmission electron microscopy (Figure 3). The pure TiO$_2$ is similar to corn-shape (Figure 3a). The average size of pure TiO$_2$ is 45.7 ± 5.3 nm, standard deviation. The shape of Ru$_x$TiO$_2$ is similar to pure TiO$_2$, however, the average size is...
smaller, approximately 16–27 nm (Figure 3b,e). This result agrees with the crystallite size calculated by Scherrer’s equation based on the full width at half maximum (FWHM) of the (101) facet of anatase. It was reported that the addition of metal ions—such as Na+, Zn2+, and Fe3+—influence the crystal phase resulting in a decrease of the crystal size of TiO2 [29–32]. We believe that incorporation of Ru in the TiO2 lattice causes lattice deformation which might inhibit the crystals growth of TiO2. After annealing the Ru0.07TiO2 at 700 °C, several crystallites aggregate with each other to be the size of a few hundred nanometers (Figure 3f and Figure S2) with rutile phase. Particularly, dark spots (red circle in Figure 3f) are embedded in the crystallite. These dark spots seem to be RuO2 crystallites observed in XRD data.

Figure 3. TEM image of Ru0.07TiO2. (a) TiO2; (b) Ru0.01TiO2; (c) Ru0.03TiO2; (d) Ru0.05TiO2; (e) Ru0.07TiO2; and (f) A-Ru0.07TiO2. Red circles: RuO2.

The elemental mapping of Ru0.07TiO2 was investigated by energy dispersive X-ray spectroscopy (Figure 4). Individual mapping of Ti, O, and Ru is shown Figure 4b–d, respectively. Figure 4e represents the elemental mapping with Ti, O, and Ru overlaid. We found that Ru is homogeneously dispersed within TiO2. This result is in good accordance with the previous XRD data of samples in which the reflection peak from RuO2 does not observed before annealing Ru0.07TiO2. In addition, high resolution
TEM image also showed no aggregation of Ru species (Figure 4f). Therefore, combining XRD and TEM data, we conclude that ruthenium species are highly dispersed in TiO$_2$ in monomeric form.

![TEM image showing dispersed ruthenium species](image)

**Figure 4.** TEM image and Energy-dispersive X-ray spectroscopy (EDS) element mapping of Ru$_{0.07}$TiO$_2$. (a) TEM image of Ru$_{0.07}$TiO$_2$; (b) Ti mapping; (c) O mapping; (d) Ru mapping; (e) overlapping of Ti, O, and Ru; (f) high resolution TEM image of Ru$_{0.07}$TiO$_2$ (insert: interlayer spacing of d(101) = 0.35 nm).

### 2.2. Catalytic Tests

Catalytic properties were tested by the oxidation reaction of alcohols (benzyl alcohol, cinnamyl alcohol, and 1-octanol) under oxidant-free condition (Table 2). The entries 1–10 showed the oxidative catalytic activities of benzyl alcohol. Compared to the short reaction period (30 min) under O$_2$ atmosphere (Table 3), reaction time was adjusted to 3 h in N$_2$ environment. The conversion was less than 2% in the absence of catalyst or in the presence of Degussa, P25 (entries 1 and 2). However,
the conversion of benzyl alcohol with homemade pure TiO₂ (entry 3) was 49% which is high compared to the commercial Degussa P25 (Degussa, Frankfurt, Germany) (entry 2). Importantly, the conversion into benzoaldehyde is only 2%. Instead, o, m, p-benzyltoluenes (the molar ratio of ortho/meta/para = 43:6:51) and dibenzyl ether were produced as the major products. These o, m, p-benzyltoluenes were produced by the acid catalyzed Friedel-Crafts alkylation of toluene (solvent) with benzyl alcohol (Figure S3). Dibenzyl ether is produced by the homo-coupling of benzyl alcohol. Both reactions are proceeded by the same intermediate that is benzylic carbocation as indicated in the Scheme 1. Therefore, the surface of homemade pure TiO₂ acts as a Lewis acid catalyst. It was reported that TiO₂ and sulfated TiO₂ are applied to Friedel-Crafts acylation or Beckman rearrangement in which these solid catalysts act as Lewis acid catalysts [33,34]. In the case of Ru₄TiO₂, the major product is benzoaldehyde, however, still approximately 7% of benzyl toluene and benzyl ether are remained (entries 4–9). As the Ru content increases, the catalytic activity increases (entries 4–7 in Table 2). For example, Ru₀.₀⁵TiO₂ exhibits 98% conversion with 93% selectivity within 3 h (entry 7). In addition, Ru₀.₀⁷TiO₂ exhibited the catalytic activity to be retained without significant loss for up to three cycles (entries 7–9). However, after annealing Ru₀.₀⁷TiO₂ at 700 °C, the catalytic activity decreased dramatically (entry 10), and the Lewis acid catalyzed products (o, m, p-benzyltoluenes and dibenzyl ether) were not produced by A-Ru₀.₀⁷TiO₂ in the same reaction conditions. Based on the previous mechanistic studies using the single crystal of TiO₂ (typically rutile (110) surface) in vacuum conditions, the reactivity of alcohol on TiO₂ is strongly dependent on the surface defects of TiO₂, such as oxygen vacant sites [35–37]. Besides the reduction of surface area and the aggregation of Ru into RuO₂ during annealing process, the decrease of the surface defects after annealing at 700 °C might result in the low reactivity of A-Ru₀.₀⁷TiO₂.

**Table 2.** Catalytic properties of alcohol oxidation under oxidant-free conditions.

| Entry | Catalysts | Substrates | Products | Conversion (%) | Yield to Aldehyde (%) | Selectivity (%) |
|-------|-----------|------------|----------|----------------|------------------------|----------------|
| 1     | None      |            |          | 0              | -                      | -              |
| 2     | Degussa, P25 |          |          | 2              | 1                      | 60             |
| 3     | pure TiO₂ |            |          | 49             | 1                      | 2              |
| 4     | Ru₀.₀⁵TiO₂ |            |          | 41             | 34                     | 86             |
| 5     | Ru₀.₀⁵TiO₂ |            |          | 79             | 72                     | 93             |
| 6     | Ru₀.₀⁵TiO₂ |            |          | 88             | 82                     | 93             |
| 7     | Ru₀.₀⁷TiO₂ |            |          | >99            | 92                     | 93             |
| 8     | Reuse 7   |            |          | 99             | 92                     | 93             |
| 9     | Reuse 8   |            |          | 98             | 90                     | 92             |
| 10    | A-Ru₀.₀⁷TiO₂ |          |          | 2              | 2                      | 99             |
| 11    | None      |            |          | 0              | -                      | -              |
| 12    | Degussa, P25 |          |          | 3              | 3                      | 99             |
| 13    | pure TiO₂ |            |          | 44             | 43                     | 98             |
| 14    | Ru₀.₀⁵TiO₂ |            |          | 78             | 78                     | >99            |
| 15    | Ru₀.₀⁵TiO₂ |            |          | 85             | 84                     | >99            |
| 16    | Ru₀.₀⁷TiO₂ |            |          | 96             | 94                     | 98             |
| 17    | Ru₀.₀⁷TiO₂ |            |          | >99            | 98                     | 99             |
| 18    | None      |            |          | 0              | -                      | -              |
| 19    | Degussa, P25 |          |          | 3              | 2                      | 93             |
| 20    | pure TiO₂ |            |          | 4              | 4                      | 98             |
| 21    | Ru₀.₀⁵TiO₂ |            |          | 12             | 12                     | >99            |
| 22    | Ru₀.₀⁵TiO₂ |            |          | 23             | 22                     | 97             |
| 23    | Ru₀.₀⁷TiO₂ |            |          | 23             | 22                     | >99            |
| 24    | Ru₀.₀⁷TiO₂ |            |          | 24             | 23                     | 98             |

¹ Reaction conditions: substrate amount: 0.04 mmol, catalyst amount: 5 mg, reaction time: 3 h. Conversion is calculated by an internal standard method. Yield to aldehyde is calculated by calibration curves (Figure S4). Selectivity is calculated by the peak area of aldehyde divided by the total peak area of product.
Table 3. Catalytic properties of alcohol oxidation using O₂ as an oxidant.

| Entry | Catalysts    | Substrates | Products | Conversion (%) | Selectivity (%) |
|-------|--------------|------------|----------|---------------|-----------------|
| 1     | None         |            |          | 0             | -               |
| 2     | Degussa, P25 |            |          | 3             | >99             |
| 3     | pure TiO₂    |            |          | 3             | >99             |
| 4     | Ru₀.₀₁TiO₂   |            |          | 38            | >99             |
| 5     | Ru₀.₀₃TiO₂   |            |          | 77            | >99             |
| 6     | Ru₀.₀₅TiO₂   |            |          | 94            | >99             |
| 7     | Ru₀.₀₇TiO₂   |            |          | >99           | >99             |

Scheme 1. Lewis acid (TiO₂ surface) catalyzed an electrophilic aromatic substitution and homo-coupling of benzyl alcohol.

RuₓTiO₂ can be successfully applied oxidation of allylic alcohol (cinnamyl alcohol) into corresponding a α,β-unsaturated carbonyl compound (cinnamaldehyde) with high selectivity (>98%). In the case of cinnamyl alcohol, the by-products from the electrophilic aromatic substitution or acid catalyzed homo-coupling were not produced (entries 14–17 in Table 2). Similar to benzyl alcohol oxidation, homemade pure TiO₂ showed the high conversion compared to Degussa, P25 (entries 12 and 13 in Table 2). In addition, pure TiO₂ exhibits high selectivity in transformation into the cinnamaldehyde (entry 13 in Table 2). We want to point out that the conversion of alcohol into aldehyde in our catalytic system is not a common phenomenon because the dehydration of various alcohols into alkenes is a more general reaction on TiO₂ surface instead of dehydrogenation reaction [35,38]. Unfortunately, the kinetics of primary aliphatic alcohol (1-octanol) were not as efficient as that of benzyl alcohol and cinnamyl alcohol in the given conditions (entries 19–24 in Table 2). In the case of the oxidation of secondary alcohol (1-phenyl ethanol), the major product is styrene instead of acetophenone, which indicates that secondary benzyllic alcohols are prone to elimination under the same experimental conditions (Table S1).

In our initial experiment set-up, the role of TiO₂ is catalyptic supports to incorporate ruthenium atoms that are catalytic active centers. However, our homemade TiO₂ itself significantly involves in the reaction (entries 3 and 13 in Table 2). For the conversion of alcohol into aldehyde, two hydrogen atoms (one is attached to oxygen, the other is attached to α-carbon) are detached. A previous high resolution STM study verified that adsorption process of alcohol on TiO₂ surface induces the detachment of the hydroxyl hydrogen in which the regular surface Ti sites of TiO₂ enable alcohols to be adsorbed molecularly and dissociatively (deprotonated alkoxide) at room temperature [37]. Particularly, our homemade highly acidic surface of pure TiO₂ facilitates alcohol adsorption on the surface to form deprotonated alkoxide species. The hydrogen elimination of the α-carbon seems to take place on exclusively ruthenium species (Figure 5). This interpretation is supported by a dramatic change of major products from o, m, p-benzyltoluene to benzaldehyde when pure TiO₂ is replaced Ru₀.₀₁TiO₂ (entries 3 and 4 in Table 2). Similarly, Yamaguchi et al. proposed that in an alcohol oxidation reaction on RuₓTiO₂ using molecular oxygen as oxidant, the reaction was accomplished by
the ruthenium alcoholate formation followed by hydride elimination and the rate determining step is the hydride abstraction step [18].

![Figure 5. The proposed mechanism for the dehydration of benzyl alcohol by Ru\textsubscript{x}TiO\textsubscript{2}.](image)

The turnover frequency (TOF) based on Ru for benzyl alcohol oxidation using Ru\textsubscript{0.01}TiO\textsubscript{2} amounts to 130 h\textsuperscript{-1} where the total amount of ruthenium obtained from Inductively coupled plasma mass spectrometry (ICP) data are used for TOF calculation. In comparison with other heterogeneous catalytic systems in oxidant-free conditions (Au/CeO\textsubscript{2}, (TOF = 125 h\textsuperscript{-1}) [7], Ag/Al\textsubscript{2}O\textsubscript{3} (>2 h\textsuperscript{-1}) [9], Ru/AlO(OH) (7 h\textsuperscript{-1}) [39], Cu\textsubscript{2}/hydrotalcite (1.5 h\textsuperscript{-1}) [40], Cu/Al\textsubscript{2}O\textsubscript{3} (8.3 h\textsuperscript{-1}) [41]), our value is higher except for the silver nanoparticles on the hydrotalcite system (590 h\textsuperscript{-1}) [11].

3. Materials and Methods

3.1. Synthesis of TiO\textsubscript{2} and Ruthenium-Incorporated TiO\textsubscript{2} (Ru\textsubscript{x}TiO\textsubscript{2})

Ti(SO\textsubscript{4})\textsubscript{2} and RuCl\textsubscript{3} nH\textsubscript{2}O were purchased from Kanto and Sigma-Aldrich, respectively. TiO\textsubscript{2} and Ru\textsubscript{x}TiO\textsubscript{2} were synthesized by a hydrothermal method using Ti(SO\textsubscript{4})\textsubscript{2} and RuCl\textsubscript{3} nH\textsubscript{2}O as the precursor of Ti and Ru, respectively. 15 mL of 24% Ti(SO\textsubscript{4})\textsubscript{2} (Ti: 20 mmol) was added dropwise into the 60 mL of aqueous solution containing the different amount of RuCl\textsubscript{3} (Ru: 0, 0.2, 0.6, 1, 1.4 mmol) under vigorous stirring. The samples are labeled Ru\textsubscript{x}TiO\textsubscript{2}, in which x represents the mole ratio of ruthenium with respect to titanium. The solution was transferred to a Teflon-lined autoclave reactor and treated at 160 °C for 6 h. After the reaction vessel was cooled down to room temperature, the samples were separated by centrifugation and purified by washing with distilled water three times. Finally, the precipitates were obtained by drying under vacuum at room temperature. A-Ru\textsubscript{0.07}TiO\textsubscript{2} was prepared by annealing the Ru\textsubscript{0.07}TiO\textsubscript{2} at 700 °C for 6 h.

3.2. Characterization of Catalysts

X-ray diffraction (XRD) patterns were obtained using a Bruker D8 Advance X-ray diffractometer with Cu Kα radiation (Bruker, Karlsruhe, Germany). Diffraction patterns were taken over the 2θ range 20°–75°. The XPS results were obtained on a PHI 5000 Versaprobe instrument (ULVAC-PHI Inc., Chigasaki, Japan) in which monochromated Al Kα radiation (hν = 1486.6 eV) is illuminated as the light source. The X-ray anode was run at 25 W and the voltage was maintained at 15 kV. The pass energy was fixed at 23.5 eV to ensure sufficient resolution to determine peak positions accurately. The binding energies were calibrated by using the Au 4f\textsubscript{7/2} signal at 84.0 eV. The prepared sample morphology was characterized by a TITAN G2 60-300 (FEI, Hillsboro, OR, USA) transmission electron microscopy (TEM) equipped with CETCOR corrector and 4-silicon drift detector system energy dispersive X-ray spectrometry (EDS) with a Bruker AXS (Bruker, Karlsruhe, Germany).
spectroscopy (Super-X EDS, Bruker) operating at an accelerating voltage of 80 kV. The quantitative EDS area mapping was carried out using a scanning electron probe (Bruker) with a size of 1 nm over the sample. The surface area of samples was measured by Brunauer-Emmett-Teller (BET) method. \( \text{N}_2 \) adsorption-desorption isotherms of samples at liquid nitrogen temperature (77 K) were obtained using Belsorp Mini II (BEL Japan, Osaka, Japan).

3.3. Catalytic Tests

2 mL of alcohols (benzyl alcohol, 1-octanol, cinnamyl alcohol, 20 mM) dissolved in toluene was added to 16 mL test tubes containing 5 mg of catalysts. To ensure oxygen-free conditions, nitrogen gas was flowed for 20 min in the reaction mixture for degassing, followed by connection of an \( \text{N}_2 \) balloon that was connected to a syringe needle, which was inserted into the septum covering the test tube. The reaction mixture was heated 105\( ^\circ \text{C} \) for 3 h. After cooling the reaction mixture to room temperature, the solid catalysts were separated from solution phase by centrifugation. The solution phase was analyzed by gas chromatography (GC, aglient 7890A, Agilent Technologies, Santa Clara, CA, USA) with a flame ionization detector (FID). Dodecane was used as an internal standard for the calculation of conversion. The catalytic property of the commercial Degussa P25 was also tested for comparison.

4. Conclusions

In summary, we prepared the highly dispersed ruthenium incorporated TiO\(_2\) by a one-pot hydrothermal method. Ru\(_x\)TiO\(_2\) can transfer the benzylic, allylic, and alkyl alcohols into corresponding carbonyl compounds in oxidant-free conditions. In our catalytic system, particularly, TiO\(_2\) acts as not only the catalytic support but also a Lewis acid catalytic site which improves reactivity by facilitating the deprotonated adsorption of alcohols on the catalysts. Therefore, the synergistic effect of hydride elimination by ruthenium and the Lewis acid site on TiO\(_2\) can efficiently transfer primary alcohols into corresponding aldehydes in oxidant-free conditions.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4344/7/1/7/s1, Figure S1: The survey XPS spectrum of Ru\(_{0.07}\)TiO\(_2\), Figure S2: TEM image of A-Ru\(_{0.07}\)/TiO\(_2\). After annealing, crystallites aggregate each other to form large crystallites without particular shape. (a) TEM image; (b) aggregation of crystallites, Figure S3: (Top) Conversion data from analysis of gas chromatography (GC, Agilent 7890A, Agilent Technologies, Santa Clara, CA, USA). Dodecane was used as internal standard for the calculation of conversion (middle); the main products by pure TiO\(_2\) were o, m, p-benzyltoluenes which are produced by Friedel-Crafts alkylation of toluene (solvent) with benzyl alcohol. In addition dibenzyl ether is also produced by the acid catalyzed homo-coupling of benzyl alcohol (bottom), Figure S4: The calibration curves of alcohols and aldehydes. The flame ionization detector was used. (a) Benzyl alcohol and benzaldehyde; (b) 1-octanol and 1-octanal; (c) cinnamyl alcohol and cinnamaldehyde, Table S1: Catalytic properties of 1-phenyl ethanol oxidation under oxidant-free condition.

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Conflicts of Interest: The authors declare no conflict of interest.

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