Article

Efficient Cross-Coupling of Acetone with Linear Aliphatic Alcohols over Supported Copper on a Fluorite-Type Pr$_2$Zr$_2$O$_7$

Suhyun Lim 1,*, Minseok Kim 1,*, Sang Hyeok Ko 1, Jae-Hong Lee 1, Joon Hyun Baik 2,* and Young-Woong Suh 1,3,*

1 Department of Chemical Engineering, Hanyang University, Seoul 04763, Korea
2 Department of Chemical and Biological Engineering, Sookmyung Women’s University, Seoul 04310, Korea
3 Research Institute of Industrial Science, Hanyang University, Seoul 04763, Korea
* Correspondence: ywsuh@hanyang.ac.kr
† These authors contributed equally to this work.

Abstract: In cross-coupling of biomass-derived acetone and alcohols contributing to the production of carbon-elongated chemicals and fuels, the essential catalyst components are metal dispersion for alcohol dehydrogenation and, more importantly, basicity for carbon–carbon coupling. Herein, we report the potential of co-precipitated praseodymia–zirconia solid solution (Pr$_2$Zr$_2$O$_7$) as a support of Cu catalyst for the conversion of acetone and butanol into C$_7$ and C$_{11}$ products. Cu/Pr$_2$Zr$_2$O$_7$ exhibits a high yield of C$_7$ and C$_{11}$ (ca. 84%) compared to Cu/ZrO$_2$ and Cu/PrO$_x$.83. Moreover, it is robust under the employed solvent-free conditions owing to a solid solution of Pr$_2$Zr$_2$O$_7$ compared to PrO$_{1.83}$ showing phase transition to PrOHCO$_3$. It is also tolerant to up to 5 wt % water of the reactant mixture, recyclable once adequate post-treatment is employed after the reaction, and can convert the acetone–butanol–ethanol mixture into C$_5$–C$_{11}$ products at the nearly equivalent yield (82%) to the acetone–butanol mixture. Therefore, the Cu/Pr$_2$Zr$_2$O$_7$ reported herein is an efficient catalyst for the coupling of acetone with linear aliphatic alcohols into biofuel precursors.

Keywords: cross-coupling; acetone; linear aliphatic alcohols; copper; Pr$_2$Zr$_2$O$_7$

1. Introduction

The acetone–butanol–ethanol (ABE) fermentation using the genus Clostridium has a long history because it produces fuels (ethanol and butanol) and chemicals (acetone, butyric acid, 1,3-propanediol, etc.) from various substrates such as glycerides, glycerol, carbon monoxide, and cellulose [1]. The first industrial ABE fermentation using the Weizmann process focused on acetone and butanol during World War I [2], and was then modified to meet the increasing demand of butanol [3]. However, its prominence declined in the middle of the twentieth century because of rapid advances in the petrochemical industry. In recent years, the ABE fermentation has gained renewed interest owing to the outstanding potential of bio-butanol as drop-in fuel [4,5]. Furthermore, Toste and coworkers suggested that the ABE mixture could be catalytically converted into hydrocarbon precursors of ketones and alcohols through carbon–carbon coupling [6]. Because the carbon number of these products possibly ranges from C$_5$ to C$_{11}$, they are compatible with existing fuel oils after oxygen removal.

In the first attempt, supported noble metal catalysts and basic K$_3$PO$_4$ were used together for the C–C coupling reaction [6]. The former component acts as a dehydrogenation site for the conversion of alcohols into aldehydes on the surface, and the latter’s basicity initiates coupling of the formed aldehyde with acetone. When a mixture of acetone and butanol is used as the substrate, 2-heptanone and 6-undecanone are the products formed when acetone reacts with butanol in a mole ratio of 1:1 and 1:2, respectively. These ketones can be hydrogenated into alcohols by the hydrogen released by butanol dehydrogenation. Among the formed products, 6-undecanone and 6-undecanol are more desired than the C$_7$...
products in terms of fuel efficiency. To produce C\textsubscript{11} products selectively, the dehydrogenation reaction occurs at a higher rate, followed by coupling with acetone at a high efficiency. Therefore, a catalyst would be endowed with suitable metal dispersion and strong basicity, along with guaranteed catalyst stability under reaction conditions.

Sreekumar et al. [7] compared the activities of Pd, Ni, and Cu catalysts in alcohol dehydrogenation. Pd, along with soluble bases, is effective for the coupling of ketones with alcohols [7,8], yet the precious metal Pd needs to be replaced by first-row transition metals such as Cu and Ni. Zhu et al. [9] reported the improved water resistance of Ni-MgO-SiO\textsubscript{2} in the cross-coupling of the ABE mixture. Fridrich et al. [10] used Raney Ni catalyst with hydrotalcite-derived Mg–Al porous metal oxide (PMO) in the coupling of acetone with butanol. Moreover, supported Cu catalysts were effective in the reaction, where the formation of butyl butyrate caused by Lewis acidic Cu can be prevented by employing the supports with strong metal–support interaction, e.g., CeO\textsubscript{2}–ZrO\textsubscript{2} [11] and CeO\textsubscript{2} [12].

Another important catalyst property is the basicity of supports used for metal loading. Basic sites of the aforementioned supports greatly influence the catalytic performance, although their acidity has moderate contribution. In pursuit of a new support, praseodymium oxide (praseodymia) is interesting because of its stronger basicity and metal–support interaction than CeO\textsubscript{2} [13–15]. Thus, it was used as a bulk catalyst for soot combustion [15], decomposition of 1,3-butanediol [16], and CO oxidation [17], and it could be employed as the support to load Pt [13], Ru [18], and Pd [19]. Furthermore, the cubic fluorite-type structure of praseodymia is facile in forming solid solutions by mixing with ceria [19–21], alumina [22], and zirconia [19,23], which can contribute to enhancement in catalyst stability. Despite these benefits, praseodymia and its mixed oxides have never been used for carbon–carbon coupling reactions.

Herein, the praseodymia–zirconia mixed oxide with the Pr/Zr mole ratio of 1:1 is prepared by co-precipitation together with single zirconia and praseodymia, where it is identified as disorder-defective fluorite-type Pr\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7}. The Cu catalysts supported on these supports are evaluated in the coupling of acetone with butanol. Their activities are discussed on the basis of physicochemical properties. Then, the effects of Cu loading, reaction time, and H\textsubscript{2}O content present in the feed on the catalytic performance of Cu/Pr\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7} are investigated. Furthermore, the recyclability of Cu/Pr\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7} is examined, along with the possibility to use the ABE mixture as a feed. Consequently, the Cu/Pr\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7} reported herein is assessed to be a possible catalyst system for efficient coupling of acetone with linear aliphatic alcohols.

2. Results and Discussion
2.1. Characteristics of Supported Cu Catalysts

The prepared Cu catalysts were characterized by X-ray diffraction (XRD) analysis for phase identification. As shown in Figure 1a, the fresh Cu/zirconia shows the major reflections assigned to monoclinic ZrO\textsubscript{2} (m-ZrO\textsubscript{2}), along with a small reflection of tetragonal ZrO\textsubscript{2} (t-ZrO\textsubscript{2}) at the 2θ of 30.3°. This is a result of using a strong basic solution for precipitation of zirconium species. At the same time, the reflection of Cu (111) is observed at the 2θ of 43.3°. In the case of the fresh Cu/praseodymia, the Cu (111) reflection is positioned at the same diffraction angle as for Cu/zirconia, whereas additional peaks are detected at the 2θ of 28.3°, 32.7°, 47.0°, 55.7°, and 58.4°. The measured XRD pattern was compared with the reference patterns of pure praseodymia phases, where praseodymium forms several stoichiometric and non-stoichiometric sub-oxides with formula PrO\textsubscript{x} (x ≤ 2) [13–15]. As a result of thorough examination, the XRD pattern turned out to be closer to the standard reflections of PrO\textsubscript{1.83} (JCPDS #06-0329) and Pr\textsubscript{6}O\textsubscript{11} (JCPDS #42-1121) than to those of PrO\textsubscript{2} (JCPDS #24-1006). The same finding was also reported for the praseodymia prepared by precipitation [24].

On the other hand, the fresh Cu/praseodymia–zirconia shows the reflections at the 2θ of 28.9°, 33.5°, 48.1°, 50.6°, 56.9°, and 60.0°, aside from the Cu peak at the 2θ of 43.3°. These peaks match the standard diffraction pattern of Pr\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7} (JCPDS #19-1021). The
formula A$_2$B$_2$O$_7$, where A is a larger trivalent metal cation in eightfold coordination and B is a smaller tetravalent metal cation in sixfold coordination, represents a family of phases isostructural to the mineral pyrochlore [25]. The compound is normally observed when the radius ratio of A$^{3+}$ to B$^{4+}$ ranges from 1.46 to 1.78 [26]. The radius ratio of Pr$^{3+}$ to Zr$^{4+}$ in Pr$_2$Zr$_2$O$_7$ is 1.56 (=1.126 Å/0.72 Å), explaining that the reflections of Pr$_2$Zr$_2$O$_7$ are shifted toward high angles compared to pure praseodymia because the ionic radius of Zr$^{4+}$ is smaller than that of Pr$^{3+}$. In addition, it was reported that Pr$_2$Zr$_2$O$_7$ exists in a disorder-defective fluorite or ordered pyrochlore structure [25], depending on the preparation method and annealing temperature [27,28]. In the XRD pattern of Cu/praseodymia–zirconia, superstructure diffraction peaks are absent, suggesting the formation of fluorite-type structure. From the above discussion, the Cu catalysts prepared in this work are hereafter denoted as Cu/m-ZrO$_2$, Cu/PrO$_{1.83}$, and Cu/Pr$_2$Zr$_2$O$_7$.

The support materials and supported Cu catalysts were characterized by X-ray photoelectron spectroscopy (XPS) analysis (Figure 2). In the spectra of the Zr 3d core level, m-ZrO$_2$ shows the binding energies of Zr 3d$_{3/2}$ and 3d$_{5/2}$ peaks centered at 184.1 eV and 181.8 eV, respectively. The doublet is shifted to 183.7 eV and 181.4 eV for Pr$_2$Zr$_2$O$_7$. Such a shift is similarly observed in between Cu/m-ZrO$_2$ and Cu/Pr$_2$Zr$_2$O$_7$. The shift towards a lower binding energy indicates electron enrichment of Zr$^{4+}$ by Pr species. In the spectra of the O 1s core level, the peak around 531 eV represents the loosely bound surface oxygen species (O$_{ads}$) and the peak at the lower binding energy can be assigned to the surface lattice oxygen (O$_{lat}$) [29]. While the peak of O$_{ads}$ at 530.9 eV is negligibly changed, the peaks of O$_{lat}$ in the spectra of m-ZrO$_2$, Pr$_2$Zr$_2$O$_7$, and PrO$_{1.83}$ are positioned around 529.2 eV, 528.6 eV, and 528.1 eV, respectively. The similarity is found in the O 1s spectra of the supported Cu catalysts. The trend in the binding energy of O$_{lat}$ is attributed to the higher electronegativity of Zr$^{4+}$ (1.3) than Pr$^{3+}$ (1.13).

The more interesting result is that the fraction of O$_{ads}$ increases with the Pr composition. This is in accordance with the results reported for Pr-doped CeO$_2$ [30] and In$_2$O$_3$ [31]. When the two deconvoluted curves are integrated, the area ratio O$_{ads}$/(O$_{ads}$ + O$_{lat}$) increases from 28.9% of m-ZrO$_2$ to 51.2% of Pr$_2$Zr$_2$O$_7$ and further to 91.2% of PrO$_{1.83}$, which is similarly observed in the spectra of the supported Cu catalysts. In the report of Zhang et al. [32], this ratio was used to estimate the amount of oxygen vacancy. In the case of Pr-containing samples, the O$_{ads}$ peak originates from the oxygen species in O–Pr$^{3+}$.

**Figure 1.** XRD patterns of (a) fresh and (b) spent Cu/m-ZrO$_2$, Cu/Pr$_2$Zr$_2$O$_7$, and Cu/PrO$_{1.83}$ catalysts. The symbol represents the diffraction peak of Cu (111) and the bar plots are the reference XRD patterns of PrO$_{1.83}$, Pr$_3$O$_{11}$, PrO$_2$, PrOHCO$_3$, Pr$_2$Zr$_2$O$_7$, m-ZrO$_2$, and t-ZrO$_2$. 

The support materials and supported Cu catalysts were characterized by X-ray photoelectron spectroscopy (XPS) analysis (Figure 2). In the spectra of the Zr 3d core level, m-ZrO$_2$ shows the binding energies of Zr 3d$_{3/2}$ and 3d$_{5/2}$ peaks centered at 184.1 eV and 181.8 eV, respectively. The doublet is shifted to 183.7 eV and 181.4 eV for Pr$_2$Zr$_2$O$_7$. Such a shift is similarly observed in between Cu/m-ZrO$_2$ and Cu/Pr$_2$Zr$_2$O$_7$. The shift towards a lower binding energy indicates electron enrichment of Zr$^{4+}$ by Pr species. In the spectra of the O 1s core level, the peak around 531 eV represents the loosely bound surface oxygen species (O$_{ads}$) and the peak at the lower binding energy can be assigned to the surface lattice oxygen (O$_{lat}$) [29]. While the peak of O$_{ads}$ at 530.9 eV is negligibly changed, the peaks of O$_{lat}$ in the spectra of m-ZrO$_2$, Pr$_2$Zr$_2$O$_7$, and PrO$_{1.83}$ are positioned around 529.2 eV, 528.6 eV, and 528.1 eV, respectively. The similarity is found in the O 1s spectra of the supported Cu catalysts. The trend in the binding energy of O$_{lat}$ is attributed to the higher electronegativity of Zr$^{4+}$ (1.3) than Pr$^{3+}$ (1.13).

The more interesting result is that the fraction of O$_{ads}$ increases with the Pr composition. This is in accordance with the results reported for Pr-doped CeO$_2$ [30] and In$_2$O$_3$ [31]. When the two deconvoluted curves are integrated, the area ratio O$_{ads}$/(O$_{ads}$ + O$_{lat}$) increases from 28.9% of m-ZrO$_2$ to 51.2% of Pr$_2$Zr$_2$O$_7$ and further to 91.2% of PrO$_{1.83}$, which is similarly observed in the spectra of the supported Cu catalysts. In the report of Zhang et al. [32], this ratio was used to estimate the amount of oxygen vacancy. In the case of Pr-containing samples, the O$_{ads}$ peak originates from the oxygen species in O–Pr$^{3+}$.
bonds. When deconvoluted using the curve fitting reported for Pr₆O₁₁ [33], the presence of Pr⁵⁺ is identified at 932 eV and 927.2 eV in Pr₂Zr₂O₇, PrO₁.₈₃, and their supported Cu catalysts. Therefore, a number of oxygen vacancies are present in PrO₁.₈₃ due to the high basicity of Pr. However, this might be problematic in CO₂-releasing reactions because the oxygen vacancy can contribute to the adsorption of CO₂ [34]. Since the transformation of CeO₂ to CeOHCO₃ was found in Cu–CeO₂ [12], the number of oxygen vacancies in PrO₁.₈₃ may need to be reduced by mixing with Zr⁴⁺, that is, Pr₂Zr₂O₇. In contrast, zirconia with the low O_ads/(O_ads + O_lat) is not highly basic for the reaction studied in this work.

Figure 2. XPS spectra of (a) support materials and (b) supported Cu catalysts. Each panel represents the regions of Zr 3d (left), O 1s (middle), and Pr 3d (right).

To confirm the presence of oxygen vacancy, Raman spectra were acquired for the three support materials. In general, fluorite-type CeO₂ shows two absorption bands in the ranges of 400–500 and 500–600 cm⁻¹ that can be assigned to a symmetric breathing mode of the oxygen ions coordinating the tetravalent cations and a defect mode caused by oxygen vacancy, respectively [24,35–37]. Similar absorption bands centered at 430 and 540 cm⁻¹ were observed for PrO₁.₈₃ and Pr₂Zr₂O₇, but not for m-ZrO₂ (Figure 3). The Raman intensity ratio I₅₄₀/I₄₃₀ was lower for Pr₂Zr₂O₇ than for PrO₁.₈₃. This indicates that Pr₂Zr₂O₇ has a lower concentration of oxygen vacancy than pure PrO₁.₈₃ because of the stabilizing effect of Zr ions, which is in agreement with the finding identified in the XPS O 1s spectra.
The activity results of Cu/m-ZrO$_2$ vacancy) and higher Cu dispersion compared to the other catalysts (Table 1). Additionally, version of acetone was mainly used for activity comparison. Note that the cross-coupling which are identified in m-ZrO$_2$ products (selectivities of 6C$_{11}$-one, 2-heptanol (2C$_7$-one), 6-undecanone (6C$_{11}$-one), 2-heptanol (2C$_7$-ol), and 6-undecanol (6C$_{11}$-ol) were quantified with respect to the molar selectivity of each species among all products converted from acetone. In particular, the mono-/di-coupling products (2C$_7$-one, 2C$_7$-ol, 6C$_{11}$-one, and 6C$_{11}$-ol) were summed to represent the total yield of cross-coupling products. Thus, the conversion of acetone was mainly used for activity comparison. Note that the cross-coupling products are formed by the consumption of one and two moles of butanol per mole of acetone, which makes it complicated to understand the conversion of butanol (listed in Table S1).

Among the prepared catalysts, Cu/m-ZrO$_2$ showed the lowest acetone conversion of 73.9%, along with the butanol conversion of 56.2%. The yields of the cross-coupling products (C$_7$ and C$_{11}$) were only 27.9%, while the IPA selectivity was high at 59.6% (Figure 4). The activity results of Cu/m-ZrO$_2$ are explained by the lower basicity (i.e., lower oxygen vacancy) and higher Cu dispersion compared to the other catalysts (Table 1). Additionally, its acidity can affect the poor yield of coupling products. The highly dispersed copper particles of Cu/m-ZrO$_2$ (Cu dispersion of 30.4%) not only affect butanol dehydrogenation into butyraldehyde but also convert acetone into IPA by the hydrogen transferred by the dehydrogenation reaction. Moreover, the mono-coupling products, 2C$_7$-one (selectivity = 19.9%) and 2C$_7$-ol (selectivity = 14.8%), were more selectively formed than the di-coupling products (selectivities of 6C$_{11}$-one and 6C$_{11}$-ol = 3.0%), attributed to the lower basicity of Cu/m-ZrO$_2$ because CO$_2$ desorption was observed at ca. 100 °C (Figure 5a). This was also identified in m-ZrO$_2$ (Figure 5b).

Among the prepared catalysts, Cu/m-ZrO$_2$ showed the lowest acetone conversion of 73.9%, along with the butanol conversion of 56.2%. The yields of the cross-coupling products (C$_7$ and C$_{11}$) were only 27.9%, while the IPA selectivity was high at 59.6% (Figure 4). The activity results of Cu/m-ZrO$_2$ are explained by the lower basicity (i.e., lower oxygen vacancy) and higher Cu dispersion compared to the other catalysts (Table 1). Additionally, its acidity can affect the poor yield of coupling products. The highly dispersed copper particles of Cu/m-ZrO$_2$ (Cu dispersion of 30.4%) not only affect butanol dehydrogenation into butyraldehyde but also convert acetone into IPA by the hydrogen transferred by the dehydrogenation reaction. Moreover, the mono-coupling products, 2C$_7$-one (selectivity = 19.9%) and 2C$_7$-ol (selectivity = 14.8%), were more selectively formed than the di-coupling products (selectivities of 6C$_{11}$-one and 6C$_{11}$-ol = 3.0%), attributed to the lower basicity of Cu/m-ZrO$_2$ because CO$_2$ desorption was observed at ca. 100 °C (Figure 5a). This was also identified in m-ZrO$_2$ (Figure 5b).

Table 1. Characteristics of the prepared Cu catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Cu loading * (wt %)</th>
<th>$S_{\text{BET}}$ b ($\text{m}^2 \text{ g}^{-1}$)</th>
<th>$V_p$ b ($\text{cm}^3 \text{ g}^{-1}$)</th>
<th>$S_{\text{Cu}}$ c ($\text{m}^2 \text{ g}^{-1}$)</th>
<th>$D_{\text{Cu}}$ c (%)</th>
<th>$N_{\text{CO}_2}$ d ($\mu$mol g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu/m-ZrO$_2$</td>
<td>5.75</td>
<td>22.4</td>
<td>0.07</td>
<td>3.9</td>
<td>30.4</td>
<td>37 (33)</td>
</tr>
<tr>
<td>Cu/Pr$_2$ZrO$_7$</td>
<td>5.63</td>
<td>29.7</td>
<td>0.23</td>
<td>2.5</td>
<td>19.3</td>
<td>785 (418)</td>
</tr>
<tr>
<td>Cu/Pr$_2$Zr$_2$O$_7$</td>
<td>6.13</td>
<td>13.6</td>
<td>0.30</td>
<td>2.0</td>
<td>15.8</td>
<td>187 (109)</td>
</tr>
</tbody>
</table>

* Measured by inductively coupled plasma–mass spectrometry (ICP-MS) analysis. b Brunauer–Emmett–Teller (BET) surface area ($S_{\text{BET}}$) and pore volume ($V_p$) measured by N$_2$ physisorption. BET isotherms and pore size distribution curves are presented in Figure S1. c Cu surface area ($S_{\text{Cu}}$) and dispersion ($D_{\text{Cu}}$) measured by N$_2$O reactive frontal chromatography experiments. d Number of adsorbed CO$_2$ measured by CO$_2$ temperature-programmed desorption experiments, where the value in parentheses indicates the N$_{\text{CO}_2}$ of Cu-free support materials.
As presented in Figure 5, PrO\textsubscript{1.83} catalyst nearly catalyzes the hydrogenation of acetone to IPA. Furthermore, it should be highlighted that Cu/Pr\textsubscript{1.83} shows superior catalytic performance to the previously reported Cu/CeO\textsubscript{2}–ZrO\textsubscript{2} [11] and Cu–CeO\textsubscript{2} [12].

In contrast, the conversion of acetone over Cu/PrO\textsubscript{1.83} was high at 96.4% while the selectivity to IPA was only 4.9%. The conversion of butanol was 91.0% and the cross-coupling reaction preferentially took place, which was examined by the higher selectivity of 6C\textsubscript{11}-one (55.2%) and 6C\textsubscript{11}-ol (15.1%). As a result, the yield of C\textsubscript{7} and C\textsubscript{11} was 3-fold larger for Cu/PrO\textsubscript{1.83} (90.9%) than for Cu/m-ZrO\textsubscript{2}, possibly caused by the high basicity of Cu/PrO\textsubscript{1.83} resulting from the large amount of oxygen vacancy, in which acid sites were nearly absent. As presented in Figure 5, PrO\textsubscript{1.83} and Cu/PrO\textsubscript{1.83} showed broad CO\textsubscript{2} desorption profiles, where the peaks below 200 °C, between 200 and 500 °C, and above 500 °C are assigned to weak base OH groups, medium-strength metal–oxygen pairs, and low-coordination oxygen anions, respectively [22]. On the other hand, Cu/Pr\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7} exhibited acetone conversion of 91.0%, lower than Cu/PrO\textsubscript{1.83}. The selectivity of the di-coupling products (59.9%) was also slightly lower due to the lower basicity (i.e., lower oxygen vacancy) of Cu/Pr\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7} than Cu/PrO\textsubscript{1.83}. However, the formation of IPA was suppressed in comparison with Cu/m-ZrO\textsubscript{2} because of the lower Cu dispersion of Cu/Pr\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7} (15.8%). Therefore, the mixed oxide Pr\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7} prefers the coupling of acetone with butanol to the Cu-catalyzed hydrogenation of acetone to IPA. Furthermore, it should be highlighted that Cu/Pr\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7} shows superior catalytic performance to the previously reported Cu/CeO\textsubscript{2}–ZrO\textsubscript{2} [11] and Cu–CeO\textsubscript{2} [12].

Figure 4. Catalytic performance of Cu/m-ZrO\textsubscript{2}, Cu/Pr\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7}, and Cu/PrO\textsubscript{1.83} in the cross-coupling of acetone with butanol. Reaction conditions: 20 g reactant with the butanol/acetone mole ratio of 2, catalyst 1 g, 240 °C, and 20 h.

Figure 5. CO\textsubscript{2} temperature-programmed desorption (TPD) profiles of (a) supported Cu catalysts and (b) support materials.
Catalyst stability in this reaction is an important issue, as studied with Cu/CeO$_2$–ZrO$_2$ and Cu–CeO$_2$. After the activity tests under the reaction conditions stated in Figure 4, the spent catalysts were characterized by XRD analysis. The phase change was remarkable for Cu/Pr$_{1.83}$ in which PrO$_{1.83}$ was transformed into PrOHCO$_3$ (JCDPS #24-1006), as shown in Figure 1b. This was confirmed when the calcined Pr$_{1.83}$ support was subjected to the identical reaction conditions (not shown here for brevity). A similar transformation was reported for Cu–CeO$_2$, showing the formation of CeOHCO$_3$ from CeO$_2$ [12]. This carbonate species is attributed to metal complexation with CO$_2$ that is possibly produced by ketonization of the dehydrogenation product of butanal (i.e., butyraldehyde). Therefore, Pr$_{1.83}$ is not considered to be useful due to its inferior stability, although the cross-coupling activity was high.

On the other hand, the XRD patterns of the fresh and spent Cu/m-ZrO$_2$ were similar, except the intensity of Cu (111) reflection at the 2θ of 43.3° was slightly weakened, meaning that copper leaching occurs during the reaction. The leaching was confirmed by the ICP result (ca. 140 ppm) obtained from the reaction mixture collected after the reaction over Cu/m-ZrO$_2$. Such catalyst instability was rarely observed with Cu/Pr$_2$Zr$_2$O$_7$ because the fresh and spent forms showed nearly identical XRD patterns. The same observation was found with the supported Cu on Pr$_2$Zr$_2$O$_7$ prepared with the Pr/Zr mole ratio of 3:7 though showing the C$_7$–C$_{11}$ yield of 45.6%. This is a beneficial effect of mixing ZrO$_2$ with praseodymium oxide in terms of catalyst stability. Therefore, the Cu/Pr$_2$Zr$_2$O$_7$ with the Pr/Zr mole ratio of 5:5 is suggested to be an effective and stable catalyst in the coupling of acetone with butanol.

2.3. Catalytic Performance of Cu/Pr$_2$Zr$_2$O$_7$ with Different Cu Loadings

The acetone conversion and product selectivities were investigated in terms of Cu loading (Figure 6). In the case of Cu-free Pr$_2$Zr$_2$O$_7$ tested in the coupling of butyraldehyde with acetone at the mole ratio of 2 and 240 °C for 20 h, the acetone conversion approached 72.4%, but a variety of unidentified products were obtained along with IPA. This means that the cross-coupling reaction does not involve free aldehyde but rather the acyl species adsorbed on surface Cu particles, which was previously confirmed with Cu/CeO$_2$–ZrO$_2$ [11]. As the Cu loading increased from 1 to 5 wt %, the conversion of acetone became higher, from 82.6% to 91.0%, along with the increase in butanol conversion from 60.2% to 82.6%. More importantly, the cross-coupling products were more formed (i.e., increase in C$_7$–C$_{11}$ yield from 66.9% to 83.8%), whereas the selectivity of IPA decreased from 17.7% to 6.7%. This means that the rates of butanol dehydrogenation and subsequent reaction with acetaldehyde of 5 wt % Cu/Pr$_2$Zr$_2$O$_7$ were retarded for large CuO particles. This explains the lowered transfer hydrogenation activity of 5 wt % Cu/Pr$_2$Zr$_2$O$_7$. The increase in Cu particle size with the Cu content was confirmed by Cu reflections in XRD patterns (Figure S2) and transmission electron microscopy (TEM) results (Figure S3). When calculated from the diffraction peak of Cu (111) using the Scherrer equation, Cu particle size increased from 37 (1 wt % Cu) to 42 nm (5 wt % Cu).
2.4. Catalytic Performance of Cu/Pr₂Zr₂O₇ with Respect to the Reaction Time and H₂O Content

The activity and product distribution of 5 wt % Cu/Pr₂Zr₂O₇ were studied as the reaction time varied (Figure 8). In the early time of 3 h, the conversion of acetone was 66.9%, while IPA and 2C₇–one were the major products with selectivities of 28.9% and 43.4%, respectively. As the experiment progressed to 12 h, the acetone conversion increased to 90.6%, and 6C₁₁–one (48.6%) and 6C₁₁–ol (6.0%) were more formed with the decreases in the selectivities of IPA (9.8%) and 2C₇–one (26.0%). This product distribution was slightly changed for the longer reaction period—specifically, the total yield of C₇–C₁₁ was 83.8% and 85.9% at 20 and 24 h, respectively. Therefore, the reaction needs to be performed for at least 20 h to preferentially produce the C₁₁ products instead of the IPA and C₇ products.

Additionally, the effect of water on the activity of 5 wt % Cu/Pr₂Zr₂O₇ was investigated because water is released by the cross-coupling reaction and is detrimental to catalytic activity [11]. Figure 9 shows that the activity and product distribution strongly depend on the content of water added into the reaction. When the water content was 3 and 5 wt % relative to the reactant mixture (i.e., acetone plus butanol), the acetone conversion and C₇–C₁₁ yield were maintained at the levels of 91% and 82 ± 2%, respectively.
However, the selectivity of 6C_{11}-one declined from 53.9% (no water) to 42.6% (5 wt % H_{2}O), whereas the selectivities of the C_{7} products (2C_{7}-one and 2C_{7}-ol) increased from 32.2% (no water) to 38.9% (5 wt % H_{2}O) and that of IPA also increased to 10.9%. In other words, water lowers the cross-coupling ability of Cu/Pr and shifts the catalytic function towards the transfer hydrogenation of acetone to IPA. This can be explained by the probable reason that water blocks the oxygen vacancy of Pr_{2}Zr_{2}O_{7}, thereby reducing its basic strength [31,34], and forms surface oxidized copper species (i.e., Cu^{1+}) resulting in the formation of a Cu^{0}/Cu^{1+} interface favorable for enhanced hydrogenation activity [12]. This phenomenon was more obvious when more than 5 wt % H_{2}O was added; the major product was not 6C_{11}-one but 2C_{7}-one under these conditions. Moreover, the acetone conversion and C_{7}–C_{11} yield were greatly reduced to ca. 80% and 63 ± 1%, respectively, at the water content of 10 wt %. Particularly, the decrease in the C_{7}–C_{11} yield was attributed to the higher selectivity of IPA (21%). Therefore, Cu/Pr_{2}Zr_{2}O_{7} is resistant to water of up to 5 wt % relative to the reactant mixture. When compared with the catalysts reported in the literature, this catalyst has an advantage over Ni–MgO–SiO_{2} [9] and is comparable to Ni–MgO–SBA-16 [38].

![Figure 8](image1.png)

**Figure 8.** Effect of reaction time on the catalytic performance of 5 wt % Cu/Pr_{2}Zr_{2}O_{7} in the cross-coupling of acetone with butanol. Reaction conditions: 20 g reactant with the butanol/acetone mole ratio of 2, catalyst 1 g, and 240 °C.

![Figure 9](image2.png)

**Figure 9.** Effect of water on the catalytic performance of 5 wt % Cu/Pr_{2}Zr_{2}O_{7} in the cross-coupling of acetone with butanol. Reaction conditions: 20 g reactant with the butanol/acetone mole ratio of 2, catalyst 1 g, 240 °C, and 20 h.
2.5. Catalyst Recyclability of Cu/Pr$_2$Zr$_2$O$_7$

The spent Cu/Pr$_2$Zr$_2$O$_7$ catalyst was separated from the product mixture by filtration, dried at 105 °C, and activated by H$_2$ reduction at 250 °C. When this catalyst was tested under the same conditions as in the first cycle, the acetone conversion and product distribution were negligibly changed, resulting in the C$_7$–C$_{11}$ yield of 84.0% (cycle 2 in Figure 10a). When the spent catalyst was subjected to the identical post-treatment, the acetone conversion dropped to 78.7%, along with the decrease in C$_7$–C$_{11}$ yield to 64.2% (cycle 3 in Figure 10a). Moreover, the selectivity of 6C$_{11}$-one was significantly declined, and vice versa for IPA and the C$_7$ products. This was also observed in further cycles only when H$_2$ activation was performed.

![Catalytic performance of 5 wt % Cu/Pr$_2$Zr$_2$O$_7$ in the cross-coupling of acetone with butanol in recycle runs.](image)

**Figure 10.** Catalytic performance of 5 wt % Cu/Pr$_2$Zr$_2$O$_7$ in the cross-coupling of acetone with butanol in recycle runs. Reaction conditions: 20 g reactant with the butanol/acetone mole ratio of 2, catalyst 1 g. (a) 240 °C and (b) 200 °C, and 20 h. * For cycle 4 in panel (a) and for all the cycles in panel (b), the catalyst was obtained by calcination at 400 °C and H$_2$ reduction at 250 °C, which is different from the other cycles using only H$_2$ reduction at 250 °C for 2 h.

Thus, the spent catalysts obtained after cycles 2 and 3 were characterized by XRD analysis. As depicted in Figure 11, the diffraction peaks of PrOHCO$_3$ were detected in the patterns of the as-obtained samples and even the samples reduced at 250 °C, which is attributed to the oxygen vacancy of Pr$_2$Zr$_2$O$_7$, even though the quantity is lower than...
PrO$_{1.83}$. Once again, the presence of PrOHCO$_3$ is harmful to the reaction. To recover the catalytic activity, calcination at 400 °C, which is usually performed after impregnation of copper species on the prepared supports, was added before H$_2$ activation. As a result, the reflections of PrOHCO$_3$ disappeared by oxidation of hydroxycarbonate species (Figure 11). This catalyst showed improved acetone conversion and C$_7$–C$_{11}$ yield of 84.5% and 72.1%, respectively (cycle 4 in Figure 10a). When the same two-step catalyst regeneration protocol was used for three consecutive runs at 200 °C, the acetone conversion and C$_7$–C$_{11}$ yield were maintained at 50.0% (Figure 10b).

Figure 11. XRD of the fresh and spent catalyst of 5 wt % Cu/Pr$_2$Zr$_2$O$_7$ in recycle runs. The symbol represents the diffraction peak of Cu (111) and the bar plots are the representative reference XRD patterns of PrOHCO$_3$ and Pr$_2$Zr$_2$O$_7$.

2.6. Catalytic Performance of Cu/Pr$_2$Zr$_2$O$_7$ in the Cross-Coupling of the ABE Mixture

Finally, 5 wt % Cu/Pr$_2$Zr$_2$O$_7$ was tested in the conversion of an ABE mixture with the mole ratio of 2.3:3.7:1, which is the general product composition obtained by anaerobic fermentation of real biomass. The acetone conversion was measured to be about 94%. Aside from the products formed from the mixture of acetone and butanol, 2-pentanone (2C$_5$-one) and 4-nonanone (4-C$_9$-one) were produced by the mono-coupling of acetone with ethanol and the di-coupling of acetone with ethanol and butanol, respectively (Figure 12). The overall yield of C$_5$–C$_{11}$ products was 82%, which is nearly equivalent to the yield of C$_7$–C$_{11}$ products (82 ± 2%) obtained from the acetone–butanol mixture.
3. Materials and Methods

3.1. Preparation of Supported Cu Catalysts

Three support materials were synthesized by precipitation. For the synthesis of praseodymia–zirconia, a solution of Pr(NO$_3$)$_3$·6H$_2$O (19.8 g; Sigma-Aldrich, Munich, Germany) and ZrO(NO$_3$)$_2$·xH$_2$O (10.6 g; Strem Chem., Newburyport, MA, USA) in 150 mL of distilled water, with a metal concentration of 0.6 M, was added dropwise into 100 mL of an aqueous ammonia solution (25–28 wt %; Daejung Chem., Seoul, Korea) within 20 min. The resulting suspension was aged at room temperature, filtered three times, and dried at 105 °C overnight. After sieving to 200 µm, the dried co-precipitate was calcined at 600 °C for 5 h. The same procedure was used for the synthesis of zirconia and praseodymia. Then, an aqueous Cu(NO$_3$)$_2$·3H$_2$O solution was impregnated onto the synthesized support samples, where the nominal copper loading was set at 5 wt %. Finally, the supported copper catalysts were calcined at 400 °C for 5 h and finally activated by H$_2$ reduction at 250 °C for 2 h prior to the activity test. The H$_2$ reduction temperature was determined from the preliminary results that the activity of Cu/Pr$_2$Zr$_2$O$_7$ was negligibly changed when the catalyst was reduced at 250, 350, and 400 °C.

3.2. Catalyst Characterization

XRD analysis was performed with a Rigaku MINI Flex 600 (Rigaku Corp., Spring, TX, USA) using a Cu K$_\alpha$ radiation source at 40 kV and 15 mA with the step size of 0.02°. The BET surface area and pore volume were measured by N$_2$ physisorption using a Micromeritics 3Flex (Micromeritics Instrument Corp., Norcross, GA, USA) after degassing at 200 °C for 2 h. ICP-MS analysis was performed in an iCAP RQ spectrometer (Thermo Fisher Scientific, Waltham, MA, USA) to measure actual Cu content. XPS analysis was performed with a K-alpha plus spectrometer (Thermo Fisher Scientific, Waltham, MA, USA) with a monochromatic Al K$_\alpha$ source of 1486.6 eV. All of the spectra were obtained with a pass energy of 50 eV and a step size of 0.1 eV, followed by calibration based on the standard C 1s binding energy of 284.6 eV. The Raman spectrometer DXR-3xi (Thermo Fisher Scientific, Waltham, MA, USA) was used with 532 nm laser excitation generated by a diode-pumped solid state laser with a sample power of 1 mW. Raman spectra were obtained in the range 50–3400 cm$^{-1}$ with a resolution of 2 cm$^{-1}$. Transmission electron microscopy (TEM) images were taken in a JEM-ARM200F microscope (JEOL USA, Inc., Peabody, MA, USA) operated at 200 kV after a sample in ethanol was dropped onto a 300-mesh copper grid and dried at 60 °C under vacuum overnight.

Figure 12. Catalytic performance of 5 wt % Cu/Pr$_2$Zr$_2$O$_7$ in the cross-coupling of the ABE mixture. Reaction conditions: 20 g reactant with the acetone/butanol/ethanol mole ratio of 2.3:3.7:1, catalyst 2 g, 240 °C, and 24 h.
To measure Cu surface area and Cu dispersion, N\textsubscript{2}O reactive frontal chromatography experiments were performed using a BELCAT-B coupled with a mass detector (BEL Japan, Inc., Toyonaka, Japan). After reduction of a sample (ca. 50 mg) at 250 °C for 2 h with 10% H\textsubscript{2}/Ar (30 cm\textsuperscript{3} min\textsuperscript{-1}) and cooling to 40 °C under He, 1% N\textsubscript{2}O/He (5 cm\textsuperscript{3} min\textsuperscript{-1}) was introduced and the released nitrogen (m/z = 28) was measured by a mass detector. The calculation was based on the reaction stoichiometry of Cu to oxygen (Cu/O = 2), and the copper surface density of 1.46 × 10\textsuperscript{19} Cu atoms m\textsuperscript{-2}. CO\textsubscript{2}-TPD experiments were performed using a BELCAT-B instrument in line with a mass detector. For the calcined samples (50 mg), pretreatment was conducted at 250 °C for 2 h with a flow of 10% H\textsubscript{2}/He (50 cm\textsuperscript{3} min\textsuperscript{-1}) to yield metallic copper particles, and cooled to 35 °C under He. After 5% CO\textsubscript{2} in H\textsubscript{2} was supplied at 35 °C for 30 min and purged for 2 h with He, CO\textsubscript{2} desorption in He flow (30 cm\textsuperscript{3} min\textsuperscript{-1}) was recorded while the sample was heated to 850 °C at a rate of 10 °C min\textsuperscript{-1}. For support samples, all the steps were identically performed, except the pretreatment at 250 °C for 2 h in He flow. TPR experiments were conducted in an Autochem 2910 instrument (Micromeritics Instrument Corp., Norcross, GA, USA). After pretreatment at 400 °C (for Cu catalysts) or 600 °C (for supports) for 3 h in 10% O\textsubscript{2}/He, the temperature increased to 850 °C at a rate of 5 °C min\textsuperscript{-1} in a 10% H\textsubscript{2}/Ar flow of 50 cm\textsuperscript{3} min\textsuperscript{-1}.

3.3. Activity Tests for the Cross-Coupling of Acetone with Butanol

The reaction was performed in a stainless steel autoclave reactor (100 cm\textsuperscript{3}) charged with the prepared Cu catalyst of 1.0 g, acetone of 97 mmol, and butanol of 194 mmol. After N\textsubscript{2} purging five times, the reactor was heated to a certain temperature and maintained for a desired period under N\textsubscript{2}, where the reactor pressure reached 25 bar. Similarly, the ABE mixture was used for the coupling reaction using acetone (51 mmol), butanol (81 mmol), and ethanol (22 mmol). After the reaction run was complete, the reactor was cooled to room temperature in order to condense the species that can exist as vapor phase under reaction conditions. The product mixture was separated from the catalyst via a syringe filter and then mixed with cyclohexane and analyzed with a YL6100 gas chromatograph (Younglin Instrument, Anyang, Korea) equipped with an HP-INNOWAX column (50 m × 0.2 mm × 0.4 µm) and a flame ionization detector. The conversion of acetone was calculated by subtracting the initial mole of acetone by the mole of acetone remaining after the reaction.

4. Conclusions

We demonstrated the potential of fluorite-type praseodymia–zirconia (i.e., Pr\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7}) support in the Cu-catalyzed conversion of the acetone–butanol mixture and, furthermore, the acetone–butanol–ethanol mixture. A solid solution of the two metal oxide components was achieved by co-precipitation, which could lead to two effects: (1) stabilizing the structure of the less stable PrO\textsubscript{1.83} by the more stable m-ZrO\textsubscript{2} and (2) reducing the basicity of the more basic PrO\textsubscript{1.83}. The latter was supported by the result that the selectivity of the di-coupling products was lower with Cu/Pr\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7} than with Cu/PrO\textsubscript{1.83}, and their activity difference was not significant. The former was consistent with the measured stability of Cu/Pr\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7} showing little structural change under the tested conditions. Thus, Cu/Pr\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7} was tolerant to water of up to 5 wt % relative to the substrate, and recyclable when calcination and H\textsubscript{2} reduction were accompanied. Consequently, the Pr\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7} solid solution coupled with Cu metal can be used for efficient production of fuel precursors such as branched ketones and alcohols by the coupling of acetone with linear aliphatic saturated alcohols.

Supplementary Materials: The following is available online at: https://www.mdpi.com/article/10.3390/catal12101279/s1, Table S1: Conversion of butanol measured under different reaction conditions, where the reactant was 20 g with the butanol/acetone mole ratio of 2 and the catalyst used was 1 g. Figure S1: N\textsubscript{2} physisorption results of Cu/m-ZrO\textsubscript{2}, Cu/PrO\textsubscript{1.83}, and Cu/Pr\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7} listed in Table 1: (a) BET isotherms and (b) pore size distribution curves. Figure S2: XRD patterns of the reduced Cu/Pr\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7} of 1, 3, and 5 wt % Cu. The diffraction peak of Cu (111) is represented by
the square symbol. Figure S3: TEM images, Cu EDS mapping images, and line scanning results (obtained by tracking the orange line in the first image): (a) 1Cu/Pr2Zr2O7, (b) 3Cu/Pr2Zr2O7, and (c) 5Cu/Pr2Zr2O7.


Funding: This work was financially supported by the program titled “Technology Development Program to Solve Climate Changes” of the National Research Foundation of Korea under the Ministry of Science, ICT & Future Planning, Republic of Korea (NRF-2020M1A2A2080856), and by the Basic Science Research Program through the National Research Foundation of Korea under the Ministry of Education, Republic of Korea (NRF-2016R1A6A1A03013422).

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

References

1. Liberato, V.; Benevenuti, C.; Coelho, F.; Botelho, A.; Amaral, P.; Pereira, N., Jr.; Ferreira, T. Clostridium sp. as bio-catalyst for fuels and chemicals production in a biorefinery context. Catalysts 2019, 9, 962. [CrossRef]
11. Kim, M.; Park, J.; Kannapu, H.P.R.; Suh, Y.-W. Cross-aldol condensation of acetone and n-butanol into aliphatic ketones over supported Cu catalysts on ceria-zirconia. Catalysts 2017, 7, 249. [CrossRef]


