Heterogeneous Catalysis

Direct Olefination of Alcohols with Sulfones by Using Heterogeneous Platinum Catalysts

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Abstract: Carbon-supported Pt nanoparticles (Pt/C) were found to be effective heterogeneous catalysts for the direct Julia olefination of alcohols in the presence of sulfones and KOtBu under oxidant-free conditions. Primary alcohols, including aryl, aliphatic, allyl, and heterocyclic alcohols, underwent olefination with dimethyl sulfone and aryl alkyl sulfones to give terminal and internal olefins, respectively. Secondary alcohols underwent methylenation with dimethyl sulfone. Under 2.5 bar H₂, the same reaction system was effective for the transformation of alcohol OH groups to alkyl

Introduction

Olefins are important structural moieties in chemicals and synthetic intermediates; consequently, olefination is one of the most important steps in both small-scale organic synthesis and the production of chemicals in industry.^[1] Among various olefination protocols, the most convenient method is the olefination of carbonyl compounds with stabilized carbanions, such as Wittig reaction,^[2] Horner-Wittig reaction,^[3] Horner-Wadsworth-Emmons reaction,^[4] Peterson reaction,^[5] and Julia olefination.^[6] The olefination of alcohols is well established owing to the availability of a wide variety of substrates, and conventional methods use a two-step procedure: stoichiometric oxidation of the alcohol to give a carbonyl compound followed by olefination.^[7] To improve the atom efficiency of the olefination of alcohols, a few studies have reported the catalytic aero- $\mathsf{bic}^{^{[8a-e]}}$ and oxidant-free $^{^{[8f,g]}}$ oxidation of alcohols to carbonyl compounds followed by their Wittig-type olefination. Very recently, Milstein and co-workers^[9] reported the first example of the direct Julia olefination of aryl alcohols with sulfones through the acceptorless dehydrogenation of alcohols by using pincer PNP ruthenium complexes.^[10] Kang et al. have reported the direct Julia olefination of aryl alcohols (10 equiv)

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groups. Structural and mechanistic studies of the terminal olefination system suggested that Pt⁰ sites on the Pt metal particles are responsible for the rate-limiting dehydrogenation of alcohols and that KOtBu may deprotonate the sulfone reagent. The Pt/C catalyst was reusable after the olefination, and this method showed a higher turnover number (TON) and a wider substrate scope than previously reported methods, which demonstrates the high catalytic efficiency of the present method.

with phenyl methyl sulfone in the presence of NaH (2.5 equiv).^[11] Although the Julia olefination of alcohols is potentially attractive, the reported methods are only applicable to activated (benzyl, naphthyl) primary alcohols and are not effective for the olefination of primary aliphatic and secondary alcohols.^[9,11] The only example of a catalytic Julia olefination of primary alcohols^[9] suffers from a low turnover number (TON) and difficulties in catalyst/product separation and reuse of the homogeneous Ru catalyst. As a part of our continuing interest in the heterogeneous catalysis for bond formation reactions that are driven by the acceptorless dehydrogenation of alcohols,^[12] we report herein a heterogeneous catalytic system for the direct olefination of various primary and secondary alcohols with sulfones by using catalytic Pt nanoparticles loaded on carbon (Pt/C). To our knowledge, this is the first general heterogeneous Julia olefination of primary and secondary alcohols that includes aliphatic, aryl, and allyl alcohols.

Results and Discussion

Characterization of Pt/C

Figure 1 shows the temperature-programmed H₂-reduction (H₂-TPR) profile of an unreduced catalyst precursor, carbonloaded platinum oxide (PtOx/C). The H₂-TPR profile shows an H₂ consumption peak below 200 °C, which is assignable to the reduction of PtOx to metallic Pt. Figures 2A and B show the X-ray absorption near-edge structure (XANES) and the extended X-ray absorption fine structure (EXAFS) spectra, respectively, of the catalyst precursor PtOx/C, the reduced catalyst Pt/C at 300 °C, and a reference compound (Pt foil). Table 1 lists the distances and coordination numbers for Pt–O and Pt–Pt shells, which are estimated by the curve-fitting analysis of EXAFS. The

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Figure 1. H_2 -TPR profile of the precatalyst PtOx/C (unreduced precursor of Pt/C).



Figure 2. Pt $L_{\rm 3}\text{-}edge$ A) XANES spectra and B) EXAFS Fourier transforms of PtOx/C, Pt/C, and Pt foil.

| Table 1. Curve-fitting analysis of Pt L ₃ -edge EXAFS of Pt/C. | | | | | | | |
|---|---------------|-----------------------------------|---------------------------------------|----------------------------------|-------------------------|--|--|
| Sample | Shell | N ^[a] | R [Å] ^[b] | $\sigma [\text{\AA}]^{\rm [c]}$ | $R_{\rm f} [\%]^{[d]}$ | | |
| PtOx/C Pt/C Pt foil | O Pt Pt | 2.7 9.9 (12) ^[e] | 2.00 2.75 (2.76) ^[e] | 0.104 0.073 - | 1.6 1.1 - | | |
| [a] Coordination numbers. [b] Bond length. [c] Debye–Waller factor. [d] Re- | | | | | | | |

sidual factor. [e] Crystallographic data.

XANES spectrum of PtOx/C shows a large white line peak, which is characteristic of platinum oxides, and the EXAFS spectrum consists of a Pt-O contribution (2.7 Pt-O bonds at 2.00 Å). The latter indicates that the Pt species in PtOx/C is platinum oxide, which is consistent with the XANES results. The XANES spectrum of the reduced catalyst Pt/C is nearly identical to that of Pt foil, which is indicative of the metallic electronic state of Pt being present in the Pt/C catalyst. The EXAFS of the Pt/C catalyst consists of 9.9 Pt-Pt bonds with a length of 2.75 Å, which is close to the Pt–Pt distance of bulk Pt metal (2.76 Å). The Pt-Pt coordination number (9.9), which is lower than that of bulk Pt (12), is characteristic of small metal nanoparticles. Figure 3 shows a representative TEM image and the Pt particle size distribution histogram of Pt/C; the average diameter of Pt particles was 4.4 ± 1.1 nm. In summary, the unreduced precursor PtOx/C consists of carbon-supported platinum oxides, whereas the reduced catalyst Pt/C is made up of Pt metal nanoparticles, which are 4.4 nm in diameter, loaded on carbon.





Figure 3. Typical TEM image and Pt particle size distribution of Pt/C.

Optimization of catalysts and reaction conditions

We carried out a catalyst screening by using a series of supported Pt catalysts that had been pre-reduced in H₂ at 300 °C and contained 0.01 mmol (1 mol%) of Pt. These were tested in a model olefination reaction of benzyl alcohol (1.5 mmol) with dimethyl sulfone (1 mmol) and KOtBu (1.1 mmol) in refluxing toluene (1.5 mL) under N₂ for 10 h. Table 2 shows the conversion of dimethyl sulfone and the yield of styrene based on the sulfone with different catalysts. The reaction in the absence of the transition-metal catalyst (entry 1) or in the presence of platinum oxides loaded on carbon (PtO_x/C, entry 2) resulted in no yield of styrene, which indicates that neither KOtBu nor platinum oxides can catalyze the olefination reaction. The Pt/C catalyst, which was generated from the reduction of PtOx/C at

| Tab rene | le 2. Catalyst screening fo | or the olefination | of benzyl alcohol to sty- |
|-------------|---|---|-----------------------------|
| | Ph \sim OH + H ₃ C \sim CH ₃ 1.5 mmol 1.0 mmol | 1 mol% cat. 1.1 mmol KOt 1.5 mL toluene, ref - CH ₃ SO ₃ K | Bu Ph + H₂ lux, 10 h |
| | Catalyst | Conv. [%] | GC yield [%] ^[a] |
| 1 | - | - | - |
| 2 | PtO _x /C | 14 | - |
| 3 | Pt/C | 100 | 88 |
| 4 | Pt/C-air ^[b] | 76 | 65 |
| 5 | Pt/C _{KB} | 100 | 84 |
| 6 | Pt/C _{vx} | 95 | 81 |
| 7 | Pt/C _{SA} | 100 | 84 |
| 8 | Pt/Al ₂ O ₃ | 73 | 60 |
| 9 | Pt/CeO ₂ | 64 | 53 |
| 10 | Pt/MgO | 66 | 48 |
| 11 | Pt/ZrO ₂ | 64 | 47 |
| 12 | Pt/Nb ₂ O ₅ | 61 | 47 |
| 13 | Pt/TiO ₂ | 56 | 46 |
| 14 | Pt/SiO ₂ | 45 | 31 |
| 15 | Pt/HBEA | 41 | 29 |
| 16 | Rh/C | 74 | 63 |
| 17 | Ir/C | 73 | 61 |
| 18 | Ru/C | 67 | 59 |
| 19 | Pd/C | 58 | 48 |
| 20 | Re/C | 41 | 31 |
| 21 | Cu/C | 27 | 19 |
| 22 | Ni/C | 26 | 17 |
| 23 | Co/C | 20 | 16 |
| 24 | Pt(acac) ₂ | 44 | 35 |
| [a] Y | /ield of styrene is based o | n sulfone. [b] Pre | -reduced Pt/C catalyst was |

[a] Yield of styrene is based on sulfone. [b] Pre-reduced Pt/C catalyst was exposed to air at room temperature for 0.5 h.



300 °C, gave 88% yield of styrene (entry 3). Exposure of the reduced Pt/C catalyst to air at room temperature for 30 min resulted in a lower yield of 65% (entry 4), which could be due to the air oxidation of the surface Pt⁰ atoms. Hence, thereafter the metal-loaded catalysts were prepared by H₂ reduction (300 °C, entries 3-23) of the oxide precursor, and the olefination reactions were carried out without exposing the catalyst to air. The Pt/C catalyst prepared by using different carbon materials (Kishida chemical, entry 3; Ketjenblack EC-600 JD, entry 5; Vulcan-XC72, entry 6) and a commercial Pt catalyst from Sigma-Aldrich (Pt/C_{SA}, entry 7) showed similar yields of styrene (81-88%), which indicates that the activity does not markedly depend on the type of carbon or the catalyst preparation method. When the pre-reduced commercial Pt/C_{SA} was exposed to air, the yield was 63% (not shown). Hereafter, the Pt/C catalyst with the highest yield (entry 3) was used as the standard Pt/C catalyst.

As listed in entries 8–15, the metal-oxide-supported Pt catalysts showed lower yields of styrene (29–60%) than the Pt/C catalysts. Next, we tested a series of 5 wt% transition-metalloaded carbon catalysts (entries 16–23); the yield of styrene changed in the order of Pt > Rh > Ir > Ru > Pd > Re > Cu > Ni > Co. Platinum(II) acetylacetonate as a homogeneous Pt^{II} catalyst (entry 24) gave only 35% yield of styrene. In summary, the Pt/C catalyst (entry 3) was found to be the most effective catalyst for the model olefination of benzyl alcohol with dimethyl sulfone in the presence of KOtBu.

Next, we optimized the reaction conditions for the Pt/C-catalyzed model olefination reaction (Table 3). Initially, we studied the effect of the amount of KOtBu for the reaction of benzyl alcohol (1 mmol) with dimethyl sulfone (1 mmol). Styrene was not obtained in the absence of KOtBu (entry 1), which indicated that the base was indispensible for the success of the reaction. The yield increased with the amount of KOtBu up to 1.1 mmol (entries 2-4), above which it decreased (entries 5,6). In the presence of the optimal amount of KOtBu (1.1 mmol), we carried out the reaction with different amounts of dimethyl sulfone (1.0-2.0 mmol, entries 4,7-9), and we found that 1 mmol of dimethyl sulfone (entry 4) gave the highest yield of styrene based on benzyl alcohol. The reactions of dimethyl sulfone (1.0 mmol) with different amounts of benzyl alcohol (0.5-2.0 mmol, entries 4,10-13) showed that 1.5 mmol of benzyl alcohol (entry 12) resulted in the highest yield of styrene based on dimethyl sulfone. Comparison of the reactions in various solvents under reflux showed that toluene (entry 12) gave a higher yield than n-octane, n-nonane, and mesitylene (entries 14-16). Notably, the GC analysis of the reaction mixture after the reaction in toluene (entry 12) showed no peaks that were due to hydrogenation products of toluene (such as methylcyclohexane), which indicates that toluene does not act as a hydrogen acceptor in this system. The reaction with various basic additives (entries 12,17–23) showed that KOtBu (entry 12) was more effective than weak bases, such as K₂CO₃ and Cs₂CO₃ (entry 17,18), and strong nucleophilic bases, such as NaOH and KOH (entry 19,20). Organic bases, such as triethylamine and 1,8-diazabicyclo[5.4.0]undec-7-en (entry 22,23), gave 0 and 2% yield of styrene, respectively. The reactions under different at-

| Table 3.Optimizationalcohol to styrene. | ion of the | reaction conditions f | or ole | fination of ben | zyl |
|---|------------|-----------------------|--------|---------------------|-----|
| | 0、0 | 1 mol% Pt/C | | Ph + H ₂ | |

| | Ph ^{\sim} OH ⁺ H ₃ C ^{\sim} CH ₃ x mmol Base 1.5 ml solvent reflux 10 b | | | | | | |
|---------------|---|-------------------|---------------------------------------|-------------------------------------|---------------------------|-------------------|--|
| | | | 1.5 IIIE 8 | - CH ₃ SO ₃ K | 011 | | |
| | Alcohol [mmol] | Sulfone [mmol] | Base (x) | Solvent | Atmosphere | GC yield [%] | |
| 1 | 1.0 | 1.0 | - | toluene | N_2 | - | |
| 2 | 1.0 | 1.0 | KOtBu (0.5) | toluene | N ₂ | 28 | |
| 3 | 1.0 | 1.0 | KOtBu (1.0) | toluene | N ₂ | 53 | |
| 4 | 1.0 | 1.0 | KOtBu (1.1) | toluene | N ₂ | 68 | |
| 5 | 1.0 | 1.0 | KOtBu (1.25) | toluene | N ₂ | 61 | |
| 6 | 1.0 | 1.0 | KOtBu (2.0) | toluene | N ₂ | 47 | |
| 7 | 1.0 | 1.25 | KOtBu (1.1) | toluene | N ₂ | 59 ^[a] | |
| 8 | 1.0 | 1.5 | KOtBu (1.1) | toluene | N ₂ | 47 ^[a] | |
| 9 | 1.0 | 2.0 | KOtBu (1.1) | toluene | N ₂ | 35 ^[a] | |
| 10 | 0.5 | 1.0 | KOtBu (1.1) | toluene | N ₂ | 29 | |
| 11 | 1.25 | 1.0 | KOtBu (1.1) | toluene | N ₂ | 75 | |
| 12 | 1.5 | 1.0 | KOtBu (1.1) | toluene | N ₂ | 88 | |
| 13 | 2.0 | 1.0 | KOtBu (1.1) | toluene | N ₂ | 82 | |
| 14 | 1.5 | 1.0 | KOtBu (1.1) | <i>n</i> -octane | N ₂ | 54 | |
| 15 | 1.5 | 1.0 | KOtBu (1.1) | <i>n</i> -nonane | N ₂ | 57 | |
| 16 | 1.5 | 1.0 | KOtBu (1.1) | mesitylene | N ₂ | 65 | |
| 17 | 1.5 | 1.0 | K ₂ CO ₃ (1.1) | toluene | N ₂ | 11 | |
| 18 | 1.5 | 1.0 | Cs ₂ CO ₃ (1.1) | toluene | N ₂ | 29 | |
| 19 | 1.5 | 1.0 | NaOH (1.1) | toluene | N ₂ | 45 | |
| 20 | 1.5 | 1.0 | KOH (1.1) | toluene | N ₂ | 59 | |
| 21 | 1.5 | 1.0 | NaOCH ₃ (1.1) | toluene | N ₂ | 34 | |
| 22 | 1.5 | 1.0 | Et ₃ N (1.1) | toluene | N ₂ | - | |
| 23 | 1.5 | 1.0 | DBU (1.1) | toluene | N ₂ | 2 | |
| 24 | 1.5 | 1.0 | KOtBu (1.1) | toluene | O ₂ | 86 | |
| 25 | 1.5 | 1.0 | KOtBu (1.1) | toluene | N_2 flow ^[b] | 88 | |
| 26 | 1.5 | 1.0 | KOtBu (1.1) | toluene | H ₂ | 60 ^[c] | |
| [a] \ 20 c | [a] Yield of styrene is based on benzyl alcohol. [b] N_2 flow rate was $20 \text{ cm}^3 \text{min}^{-1}$ [c] Ethylbenzene (0.25 mmol) was observed | | | | | | |

mospheres are compared in entries 12 and 24–26. The reaction under 1 atm O_2 gave a similar yield of styrene compared to the reaction in N_2 (86%, entry 24 vs. 12), which suggests that O_2 does not act as a hydrogen acceptor in this system. The reaction under 1 atm of flowing N_2 gave the same yield as that of the closed system under N_2 (88%, entry 25 vs. 12). This implies that removal of the H_2 gas that is produced by the reaction does not improve the yield of styrene, which is possibly due to the low pressure of H_2 produced in the standard closed system under N_2 . The reaction under 1 atm H_2 (entry 26) gave 60% yield of styrene with 25% yield of ethyl benzene as a hydrogenated product.

Figure 4 shows the concentration/time plot of the reactive components under the standard conditions. It was found that the reaction time of 10 h was sufficient to obtain the highest yield of styrene (88%) based on dimethyl sulfone. The byproducts that were observed by GC analysis after 10 h were identified as α -methylstyrene (0.02 mmol) and diphenyl butene (0.03 mmol), but ethyl benzene was not observed. A further increase in the reaction time resulted in the gradual hydrogenation of styrene to give ethylbenzene (results not shown). In conclusion, the optimized conditions for the Pt-catalyzed olefination are as follows: dimethyl sulfone (1.0 mmol), benzyl alco-

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Figure 4. Amount of (∇) benzyl alcohol, (+) dimethyl sulfone, (\odot) styrene, (\triangle) benzaldehyde, (∇) α -methylstyrene, and (\bullet) ethylbenzene versus reaction time. Conditions: benzyl (1.5 mmol) alcohol, dimethyl sulfone (1 mmol), Pt/C (1 mol%), KOtBu (1.1 mmol).

hol (1.5 equiv), KOtBu (1.1 equiv), and Pt/C (1 mol%) in toluene under N_2 heated at reflux for 10 h.

To further support that the present reaction is an acceptorless dehydrogenative reaction, we analyzed the gas-phase products by mass spectrometry in the early stage of the reaction. The results, which are depicted in Equation (1), show that the amount of benzyl alcohol that is converted (0.42 mmol) is close to the amount of H_2 that is produced in the gas phase (0.40 mmol) as well as the total amount of the liquid-phase products (0.41 mmol), which can be produced by the dehydrogenation of benzyl alcohol. This confirms that the reaction is an acceptorless dehydrogenative reaction.



Pt/C-catalyzed direct olefination of alcohols with sulfones

Under the optimized reaction conditions, we studied the catalytic properties of the Pt/C-catalyzed olefination method. Figure 5 shows the results of the catalyst recycle tests for the standard reaction. After each cycle, acetone (3 mL) was added to the mixture and the catalyst was separated by centrifugation, washing with water (3 mL) and acetone (6 mL), drying at 100 °C for 3 h, and H₂ reduction at 300 °C for 0.5 h. The fresh reaction mixture with KOtBu (1.1 mmol) was then added to the reactor with the recovered Pt/C catalyst. The recovered catalyst was reused four times without a marked loss of the yield. After the first cycle, ICP-AES analysis of the reaction mixture after the removal of the Pt/C catalyst showed that the content of Pt in the solution was below the detection limit (10 ppb). These results demonstrate that Pt/C is a reusable heterogeneous catalyst under this reaction protocol.



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Figure 5. Catalyst reuse for the olefination of benzyl alcohol by dimethyl sulfone with Pt/C for 10 h. Conditions: see Table 3, entry 12.

Next, we studied the substrate scope of this catalytic olefination method. Initially, we tested the terminal olefination of primary alcohols with dimethyl sulfone (Table 4). As the previous catalytic method for this reaction was effective only for aryl alcohol substrate,^[9] we tested the olefination of various primary alcohols, which included aryl, aliphatic, and heterocyclic alcohols. Benzyl alcohols with different electron-donating and -withdrawing para substituents (methyl, methoxy, tert-butyl, fluoro, chloro, CF₃-, phenyl) were successfully methylated to give the corresponding vinylbenzene derivatives in good to high isolated yields (77-94%, entries 1-8) based on the sulfone. Disubstituted benzyl alcohol, 3,4-dimethoxybenzyl alcohol (entry 9), was successfully transformed to 1,2-dimethoxy-4vinylbenzene in 91% yield. Naphthyl alcohols (1- and 2-naphthylmethanol) were converted to give the corresponding vinyl naphthalene products in high yields (entries 11 and 10, respectively). Heteroaromatic alcohols with furanyl, thienyl, pyridinyl, and benzo[1,3]dioxonyl groups were also tolerated, and the corresponding olefins were obtained in 78, 75, 84, and 89% yield, respectively (entries 12-15). Aliphatic (entries 16,17) and allylic primary alcohols (entries 18,19) also underwent the olefination to give the corresponding vinyl and conjugated allyl derivatives in moderate to good yields. This is the first direct catalytic method for the terminal Julia olefination of a wide range of primary alcohols (aryl, aliphatic, allyl, and heterocyclic alcohols).

As shown in Table 5, the method was also effective for the direct olefination of secondary alcohols, including benzylic and aliphatic derivatives. 1-Phenyl-ethanol with methyl and methoxy substituents at the *p*-position, 1-naphthyl-ethanol, cyclo-propyl-phenyl-methanol, diphenyl-methanol, and 2-octanol were converted to the corresponding 2,2-disubstituted alkenes with good to high yields (68–94%, entries 1–7). This is the first direct method for the transformation of OH groups into methylidene groups by Julia olefination.

Next we studied the internal olefination of primary alcohols with phenyl ethyl sulfone (Table 6, entries 1–12) and phenyl benzyl sulfone (entries 13–30) under the standard reaction conditions. Benzyl alcohol, *p*-substituted benzyl alcohols with methyl, methoxy, *tert*-butyl, chloro, and phenyl groups, 3,4-methoxybenzyl alcohol, and 2-naphthyl alcohol were transformed into the corresponding propenyl benzene derivatives in 71–83% yields (entries 1–8). The internal olefination of het-

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Table 4. Pt/C-catalyzed terminal olefination of primary alcohols.

| | | R (1.5 mr | CH + C H ₃ C nol 1.0 | S CH ₃ 1.1 mm mmol - CH | nl% Pt/C nol KOtBu pluene, refl H ₃ SO ₃ K | → R → + H ₂ | | | |
|-----------|--|------------------|---------------------------------------|---------------------------------------|---|---|------------------------------|--------------|--------------------------|
| | Alcohol | Olefin | <i>t</i> [h] | Yield [%] ^[a] | | Alcohol | Olefin | <i>t</i> [h] | Yield [%] ^[a] |
| 1 | ОН | | 10 | 88 ^(b) | 11 | OH | | 15 | 94 |
| 2 | ОН | | 10 | 86 | 12 | ОТОН | o j | 12 | 78 ^[b] |
| 3 | МеО | MeO | 12 | 82 | 13 | S ОН | S S | 12 | 75 ^[b] |
| 4 | ОН | | 12 | 79 | 14 | ОН | | 12 | 84 |
| 5 | F OH | F | 10 | 81 ^[b] | 15 | ОПОН | | 12 | 89 |
| 6 | СІ | CI | 10 | 79 ^[b] | 16 | <i>п</i> -С ₇ Н ₁₅ ОН | n-C7H15 | 15 | 56 ^[b] |
| 7 | F ₃ C OH | F ₃ C | 8 | 77 ^[b] | 17 | ОН | $\bigcirc \bigcirc \bigcirc$ | 15 | 74 ^[b] |
| 8 | Рһ | Ph | 12 | 94 | 18 | ОН | | 15 | 69 ^[b] |
| 9 | МеО | MeO | 15 | 91 | 19 | ОН | | 15 | 79 ^[c] |
| 10 | ОН | | 15 | 96 | | | | | |
| [a] Yield | [a] Yields of isolated products based on sulfone. [b] GC yield. [c] $E/Z = 94$:6 (determined by ¹ H NMR analysis). | | | | | | | | |

eroaromatic alcohols with phenyl ethyl sulfone gave the corresponding 2-propenyl-derivatives in high yields (78–81%, entries 9–11). Cinnamyl alcohol was converted into penta-1,3-dienyl-benzene and isolated in 83% yield and an E/Z ratio of 82:18 (entry 12). The reaction of *n*-octanol with phenyl ethyl sulfone gave 17% yield of the corresponding olefin (result not shown).

The reaction of various primary alcohols with benzyl phenyl sulfone (entries 13-30) also resulted in the highly E-selective formation of styryl derivatives. Benzyl alcohols were selectively converted to give the corresponding E-stilbenes with high isolated yields (83-93%, entries 13-20). Naphthyl alcohols (entries 21,22) and heteroaromatic alcohols with furanyl, thienyl, pyridinyl, and benzo[1,3]dioxonyl groups (entries 23-26) were also converted to the corresponding styryl derivatives in good to high yields (84-94%). The internal olefination of cinnamyl alcohol gave trans, trans-1,4-diphenyl-1,3-butadiene in 92% yield with high stereoselectivity. The olefination of aliphatic alcohols with benzyl phenyl sulfone was also successful (entries 28-30). For most of the reactions in Table 6 (entries 1-28), we have reported E/Z ratios in a range of 86:14 to 99:1, which indicates that the present internal olefination method is highly E selective. Exceptionally, the reaction of *n*-octanol resulted in the highly Z-selective formation of the styryl derivative (entry 29). Overall, the results in Table 6 demonstrate that this is a general internal olefination method for primary alcohols with sulfones, which includes the first example of the internal olefination of aliphatic alcohols.

Finally, we studied the TON of the present system for gramscale reactions by using 10.0 mmol of dimethyl sulfone, 15.0 mmol of alcohol, 11.0 mmol of KOtBu, and 0.02 mol% of Pt/C catalyst in 10 mL of toluene for 90 h. The reactions with benzyl alcohol, 4-biphenylmethanol, and diphenylmethanol gave 79, 76, and 85% yields of the corresponding olefin based on the sulfone [Eq. (2)–(4)], and the TONs of these reactions were 3950, 3800, and 4520, respectively. These TON values are more than 150 times higher than that of the previously reported catalyst (TON of 25) for the olefination of benzyl alcohol with dimethyl sulfone.^[9]



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Kinetic study

Regarding the mechanism of this reaction, Milstein et al.^[9] reported that the Julia olefination of benzaldehyde and dimethyl sulfone with a homogeneous catalyst gave a much lower yield of styrene than the reaction of benzyl alcohol and dimethyl sulfone. They speculated that a metal-coordinated aldehyde rather than a free aldehyde was an intermediate in the reaction, which then reacted with the sulfone species to yield a β hydroxy sulfone intermediate.^[9] Our test reactions also suggest that "free" benzaldehyde is not an intermediate in the production of styrene; the Pt/C-catalyzed reaction of benzaldehyde (1.0 mmol) and dimethyl sulfone (1.0 mmol) with of KOtBu (1.1 mmol) in toluene (1.5 mL) under standard conditions gave 0.13 mmol of styrene. However, as an α -C–H/ α -C–D kinetic isotopic effect (KIE) was observed for the reaction of dimethyl sulfone and benzyl alcohol (or α -deutero benzyl alcohol), we can infer that the dehydrogenation of the benzyl alcohol is involved in the kinetically important steps of the catalytic Julia olefination (Figure 6). Furthermore, the moderate $k_{\rm H}/k_{\rm D}$ value of 2.2 indicates that the dissociation of the α -C–H bond of benzyl alcohol is a moderately slow step.



Figure 6. Kinetic isotopic effect (KIE) in the olefination of benzyl alcohol (1.5 mmol) with dimethyl sulfone (1 mmol), Pt/C (1 mol%), and KOtBu (1.1 mmol) in refluxing toluene. The KIE ($k_{\rm H}/k_{\rm D}$) estimated from the zero-order rate constants (the slope of the lines) are shown.



Figure 7. Formation rate of styrene as a function of the concentration of A) benzyl alcohol (0.30 to 1.11 m), B) dimethyl sulfone (0.58 to 1.11 m), and C) KOtBu (0.30 to 1.11 m). Conditions: benzyl alcohol (1.0 m), dimethyl sulfone (0.66 m), and KOtBu (0.73 m).

Figure 7 shows the effects of the initial concentration of benzyl alcohol (A), dimethyl sulfone (B), and KOtBu (C) on the formation rates of styrene. The double logarithmic plots all show linear relationships, and the slope of the line corresponds to the reaction order (n). The rate increased with the concentration of benzyl alcohol and KOtBu, and the reaction orders were +1.2 and +1.5, respectively. Conversely, a negative slope (n = -0.6) was observed when the concentration of dimethyl sulfone was increased. These results suggest that the alcohol and KOtBu are involved in kinetically important steps, which is consistent with the KIE result, whereas dimethyl sulfone is not involved in a rate-limiting step. Scheme 1 shows a possible reaction pathway for the Pt-catalyzed olefination method. The Pt/C catalyst is responsible for the dehydrogenation of the alcohol to afford an aldehyde, which is the rate-limiting step. The reaction order with respect to KOtBu is +1.5 (Figure 7), which indicates that KOtBu is involved in a kinetically important step. In accordance with the mechanism proposed in the literature for the acceptorless dehydrogenation of alcohols,^[10] the base may deprotonate alcohols and facilitate their dehydrogenation. By considering the previously reported results that a strong base can deprotonate a sulfone to give a sulfone salt^[13] combined with our observation that the weak bases (such as K₂CO₃) give lower yields of styrene than KOtBu (Table 3), we propose that KOtBu deprotonates the sulfone to give a sulfone salt. The aldehyde on the catalyst reacts with the sulfone salt to yield the olefin possibly via a β -hydroxy sulfone intermediate.

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| Table 6. | Pt/C-catalyzed | internal | olefination | of primary | / alcohols. |
|----------|----------------|----------|-------------|------------|-------------|
|----------|----------------|----------|-------------|------------|-------------|

| $E/Z^{[c]}$ |
|-------------|
| 99:1 |
| 99:1 |
| 99:1 |
| 99:1 |
| 99:1 |
| 99:1 |
| 99:1 |
| 99:1 |
| 98:2 |
| 97:3 |
| 98:2 |
| 99:1 |
| 92:8 |
| 18:82 |
| - |
| |

Scheme 1. A proposed pathway for the Pt-catalyzed olefination of benzyl alcohol with dimethyl sulfone.

One-pot synthesis of C-C bond formation by olefination

Only a few studies have reported the direct catalytic conversion of alcohol hydroxyl groups into alkyl groups. Lebel et al. reported a tandem oxidation/Wittig olefination of alcohols followed by hydrogenation of the C=C bond under pressured H_2 .^[14b] Williams et al.^[14b] developed the borrowing-hydrogentype C–C bond formation by dehydrogenation/Wittig olefination of alcohols followed by hydrogenation of the C=C bond of the olefins by borrowed hydrogen. Milstein et al. developed the direct conversion of a hydroxyl group into a methyl group by a Julia-type olefination of alcohols with dimethyl sulfone followed by hydrogenation of the C=C bond of the olefin under pressured H_2 .^[9] Knowing that our heterogeneous catalytic system is effective for the Julia-type olefination of alcohols and the Pt/C catalyst can generally hydrogenate olefins to give

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| Table 7. Pt/C-catalyzed direct conversion of alcohol hydroxyl groups into alkyl groups. | | | | | | |
|---|--|---|--|--------------------------|--|--|
| | $R^{1} OH + R^{2}S$ 1.5 mmol 1.0 mm | D + H ₂ R ³ 1. _{nol} 2.5 bar 1 | 1 mol% Pt/C 1 mmol KO/Bu .5 mL toluene reflux, 24 h - R ² SO ₃ K | [∧] R³ | | |
| | Alcohol | Sulfone | Alkane | Yield [%] ^[a] | | |
| 1 | ОН | 0、0 H₃C ^{´S´} CH₃ | | 73 | | |
| 2 | МеО | 0,_0 H₃C ^{∽S[∽]CH₃} | MeO | 81 | | |
| 3 | Ph | 0,_0 H₃C ^{´S´} CH₃ | Ph | 79 | | |
| 4 | MeO OH OMe | О, О Н₃С́ ^{Ѕ́} СН₃ | MeO OMe | 76 | | |
| 5 | ОН | ОО H ₃ C СН ₃ | | 77 | | |
| 6 | OH | ОО H ₃ C S CH ₃ | | 72 | | |
| 7 | ОН | 0_0 Ph ⁻ S ⁻ _CH ₃ | | 66 | | |
| 8 ^[b] | ОН | O O Ph [∕] S Ph | Ph | 80 | | |
| [a] GC | yields based on sulfo | one. [b] 36 h. | | | | |

alkanes under pressured H₂, we tried the direct alkylation of alcohols by using our standard olefination conditions under pressured H₂ (Table 7). We carried out the Pt/C-catalyzed reaction of benzyl alcohol (1.5 mmol), dimethyl sulfone (1 mmol) and KOtBu (1.1 mmol) in toluene under H₂ (2.5 bar) heating at reflux for 24 h. GC and GC-MS analyses of the mixture showed 73% yield of ethylbenzene, 2% yield of 1-isopropyl-benzene, and 17% yield of ethylcyclohexane. Under the same conditions, hydroxyl groups of substituted benzyl alcohols, 2-naphthylmethanol, and nicotinyl alcohol were also converted to methyl groups with good yields of the products (76-81%, entries 2-6). The method was also effective for the conversion of alcohol hydroxyl groups into ethyl and benzyl moieties: the reactions of benzyl alcohol with phenyl ethyl sulfone and phenyl benzyl sulfone under H₂ gave propylbenzene and 1,2-diphenylethane in 66 and 80% yield, respectively (entries 7,8).

Conclusion

We have developed the first heterogeneous and reusable catalytic method for the terminal and internal olefination of primary alcohols and methylenation of secondary alcohols by using sulfone reagents, catalytic carbon-supported Pt nanoparticles, and KOtBu under N₂. Additionally, the alcohol hydroxyl groups can be selectively converted into alkyl groups by hydrogenation of the C=C bond under 2.5 bar H₂. Compared with a previous catalytic method for the Julia olefination of alcohols, our method has the following advantages: 1) easy catalyst/product separation, 2) catalyst reusability, 3) high TON, and

4) wide substrate scope, which includes primary and secondary alcohols with aryl, alkyl, allyl, or heterocyclic substituents.

Experimental Section

General

Commercially available organic and inorganic compounds (from Tokyo Chemical Industry, Wako Pure Chemical Industries, Kishida Chemical, or Mitsuwa Chemicals) were used without further purification. Benzyl- α , α -d₂ alcohol (BzCD₂OH) with 99.5 atom % D was purchased from Aldrich. The GC (Shimadzu GC-14B) and GCMS (Shimadzu GCMS-QP2010) analyses were carried out with Ultra ALLOY capillary column UA⁺-1 (Frontier Laboratories Ltd.) by using nitrogen or He as the carrier gas. ¹H and ¹³C NMR spectra were recorded at ambient temperature on a JEOL-ECX 600 spectrometer operating at 600.17 and 150.92 MHz, respectively, with tetramethyl-silane as an internal standard.

Catalyst preparation

The standard carbon support (296 m²g⁻¹, Kishida Chemical) and other carbon materials (C_{KB} = Ketjenblack EC-600 JD, Lion, 1310 m²g⁻¹; C_{VX} = carbon black, Vulcan XC72, 210 m²g⁻¹) were commercially supplied. γ -Al₂O₃ was prepared by calcination of γ -AlOOH (Catapal B Alumina purchased from Sasol) at 900 °C for 3 h. CeO₂ (JRC-CEO3, 81 m²g⁻¹), MgO (JRC-MGO-3), TiO₂ (JRC-TIO-4), and H⁺-type BEA zeolite (HBEA, SiO₂/Al₂O₃ = 25 ± 5, JRC-Z-HB25) were supplied by Catalysis Society of Japan. ZrO₂ was prepared by hydrolysis of zirconium oxynitrate 2-hydrate by an aqueous NH₄OH solution, followed by filtration, washing with distilled water, drying at 100 °C for 12 h, and calcination at 500 °C for 3 h. Nb₂O₅ was prepared by calcination of Nb₂O₅·n H₂O (supplied by CBMM) at 500 °C for 3 h. SiO₂ (Q-10, 300 m²g⁻¹) was supplied from Fuji Silysia Chemical Ltd.

The precursor of Pt/C was prepared by an impregnation method. A mixture of carbon and an aqueous HNO₃ solution of Pt(NH₃)₂(NO₃)₂ was concentrated at 50 °C followed by drying at 90 °C for 12 h. Before each catalytic experiment, the Pt/C catalyst with Pt loading of 5 wt% was prepared by pre-reduction of the precursor in a pyrex tube under a flow of H₂ (20 cm³min⁻¹) at 300 °C for 0.5 h. Other supported Pt catalysts with Pt loading of 5 wt% were also prepared by the same method. M/C (M=Rh, Ir, Ru, Pd, Re, Cu, Ni, Co) catalysts with metal loading of 5 wt% were prepared by the similar manner as for Pt/C by using an aqueous HNO₃ solution of Rh(NO₃)₃ or Pd(NH₃)₂(NO₃)₂ or an aqueous solution of metal nitrates (for Ni, Cu, Co), IrCl₃·nH₂O, RuCl₃, or NH₄ReO₄. A commercial Pt-loaded carbon catalyst (Pt/C_{SA}, Pt=5 wt%) was purchased from Sigma–Aldrich.

Characterization

Temperature-programmed reduction under H₂ (H₂-TPR) was carried out with BELCAT (MicrotracBEL). Unreduced precursor of PtOx/C (20 mg) was mounted in a quartz tube, and the sample was heated with a temperature ramp-rate of 10 °C min⁻¹ in a flow of 5% H₂/Ar (20 cm³min⁻¹). The effluent gas was passed through a trap containing 4Å MS to remove water, then through the thermal conductivity detector. The amount of H₂ consumed during the experiment was detected by a thermal conductivity detector.

The number of surface metal atoms in the Pt/C catalyst, reduced under H_2 at 300 °C for 0.5 h, was estimated from the CO uptake of the samples at room temperature by using the pulse-adsorption of

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CO in a flow of He by BELCAT (MicrotracBEL). The average Pt particle size was calculated from the CO uptake, which was based on the assumption that CO was adsorbed on the surface of spherical Pt particles at CO/(surface Pt atom) = 1:1 stoichiometry. Transmission electron microscopy (TEM) measurements were carried out by using a JEOL JEM-2100F TEM operated at 200 kV. X-ray diffraction (XRD) patterns of the powdered catalysts were recorded with a Rigaku MiniFlex II/AP diffractometer with Cu_{Kα} radiation.

Pt L₃-edge X-ray absorption near-edge structures (XANES) and extended X-ray absorption fine structure (EXAFS) were measured in a transmittance mode at the BL01B1 with an Si(111) double-crystal monochromator in SPring-8 operated at 8 GeV (Proposal No. 2015B1246). The Pt/C catalyst was pre-reduced under a flow of H₂ (20 cm³ min⁻¹) for 0.5 h at 300 °C, cooled to room temperature under the flow of H₂, and sealed in cells made of polyethylene under N₂ ready for EXAFS spectroscopy at room temperature. The spectra of Pt foil and unreduced catalyst precursor (PtOx/C) were recorded without the pre-reduction treatment. The EXAFS analysis was performed by using the REX version 2.5 program (RIGAKU). The parameters for Pt–O and Pt–Pt shells were provided by the FEFF6.

Typical procedure of catalytic reactions

Pt/C (39 mg, 1 mol% with respect to the sulfone), pre-reduced from PtOx/C at 300°C in a sealed glass tube with a septum inlet, was cooled to room temperature under H₂, and toluene (1.5 mL) was injected. The septum was tentatively removed under air, the alcohol (1.5 mmol), sulfone (1.0 mmol), KOtBu (1.1 mmol), n-dodecane (0.25 mmol), and a magnetic stirrer bar were added to the tube, and the tube was filled with N_2 through the septum inlet. The resulting mixture was magnetically stirred whilst heating at reflux. For the standard reaction of benzyl alcohol and dimethyl sulfone in the catalyst screening (Table 2), condition optimization (Table 3), kinetic studies, and control reactions the conversion of the dimethyl sulfone and yields of the products (based on sulfone) were determined by GC analysis by using *n*-dodecane as an internal standard and by adopting the GC sensitivity that was estimated with the isolated or commercial products. For the catalytic experiments shown in Tables 4-6, the products were isolated by column chromatography with silica gel 60 (spherical, 63-210 µm, Kanto Chemical Co. Ltd.) by using hexane as the eluting solvent, and the yields of the isolated olefin (based on sulfone) were determined. The products were identified by ¹H and ¹³C NMR spectroscopy and by using a GC-MS that was equipped with the same column as the GC spectrometer. Analysis of the gas-phase product (H₂) in Equation (1) was carried out by a mass spectrometer (BELMASS).

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