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Recyclable Solid Ruthenium Catalysts Supported on Metal Oxides for the Addition of Carboxylic Acids to Terminal Alkynes

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Abstract: Ceria-supported ruthenium catalysts (Ru/CeO_2) were found to be quite effective for the addition of various carboxylic acids to terminal alkynes, which gave the corresponding enol esters in moderate to high yields. The major products of the reaction were *E*-isomers of anti-Markovnikov adducts. Among the ceria-supported ruthenium catalysts examined, those prepared using ruthenium precursors with chloride ligands showed high activities. The zirconia-supported ruthenium catalyst (Ru/ZrO_2) showed activity comparable to that of the ceria-supported catalyst. These catalysts were recyclable without a significant loss of activity, and the leaching of ruthenium species into the liquid phase was negligible after cooling the reaction mixture, which indicates marked superiority of the present solid oxide catalysts to conventional homogeneous catalysts.

Keywords: alkynes; carboxylic acids; ceria; enol esters; ruthenium; solid catalysts

Introduction

Homogeneous catalysts play a significant role in organic syntheses, and can be used to achieve excellent yields and/or control the selectivity through the choice of suitable ligands and additives. However, they are often associated with practical and environmental disadvantages, such as the difficulty of the separation and recovery of the catalysts from the reaction mixture as well as their relatively low thermal and/or chemical stability. The use of heterogeneous catalysts, particularly solid oxide catalysts, is an attractive alternative to overcome these drawbacks.[1,2]

On the other hand, enol esters are important reactants and useful intermediates for many organic reactions because of their numerous industrial applications,[3–10] and the addition of carboxylic acids to alkynes has been shown to be an atom-economical route to enol esters.[11,12] Low-valent ruthenium complexes have been reported to act as excellent homogeneous catalysts for this reaction.[13–20] Whereas the activities of ruthenium complex catalysts immobilized onto phosphine-modified resin[21a] as well as related Pd[21b] and Au[21c] catalysts for analogous reactions have been reported, there have been no previous reports on the application of solid oxide-supported ruthenium catalysts.

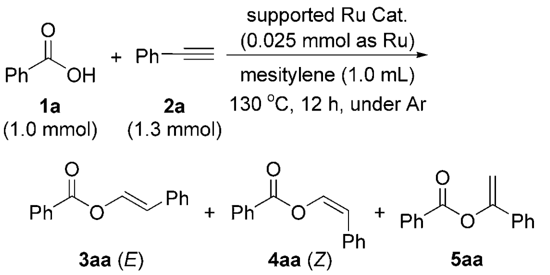
Ceria characteristically exhibits oxygen-storage capacity and strongly interacts with supported precious metal species,[22] and ceria-supported catalysts are used for various reactions.[23] Among them, Ru/CeO_2 is known to be quite effective as a catalyst for the liquid-phase oxidation of alcohols[24] and wet oxidative processes for the treatment of water pollution.[25] Very recently, we reported that Ru/CeO_2 acts as an effective heterogeneous catalyst for transfer-allylation from homoallyl alcohols to aldehydes,[26] the nitrogen-directed arylation of stable aromatic C−H bonds with aryl halides,[27a] and the addition of aromatic C−H bonds to vinylsilanes.[27b] These reactions take place *via* cleavage of a non-strained C−C or C−H bond. These results suggest that an Ru/CeO_2 catalyst may be a good alternative to homogeneous ruthenium catalysts.

We report here the first example for solid oxide-supported ruthenium catalysts that are effective for the synthesis of enol esters by the addition of carboxylic acids to terminal alkynes. Simple catalysts, Ru/CeO_2 and Ru/ZrO_2, showed excellent activities and could be used for the reactions of a variety of substrates. These catalysts were recyclable without a significant loss of activity, and the leaching of ruthenium species was not observed after cooling the reaction mixture. The effects of ruthenium precursors were examined and the catalysts were characterized by spectroscopic techniques.

Results and Discussion

Ru/CeO_2 catalysts were prepared by the impregnation of $[RuCl_2(p\text{-cymene})]_2$ on cerium oxide followed by calcination at 400 °C. The reaction of benzoic acid **1a** with ethynylbenzene **2a** at 130 °C for 12 h in the presence of a catalytic amount of Ru/CeO_2 afforded adducts in an excellent total yield of 96% [Eq. (1), entry 1 in Table 1). The major product was the *E*-isomer of the anti-Markovnikov adducts (**3aa**), with 74% selectivity, and was obtained together with the *Z*-isomer **4aa** and a small amount of the Markovnikov adduct **5aa**. There was no sign of dimers or oligomers of **2a**. The reaction at 120 °C afforded the adducts in a lower total yield (entry 2). The reaction proceeded even in the open air, although the yields of the products were moderate (entry 3). The activity of the present solid catalyst is comparable to that of a homogeneous ruthenium carbonyl catalyst.[14a] Under the present conditions, the reaction catalyzed by $Ru_3(CO)_{12}$ afforded the enol esters in a total yield of 77% with 73% selectivity for **3aa** (entry 9). $[RuCl_2(p\text{-cymene})]_2$, the precursor of the supported Ru catalysts, showed a lower activity (entry 10), whereas several homogeneous ruthenium complex catalysts bearing phosphorus ligands[15–20,28] have been reported to show excellent activities at lower temperatures.

Table 1. Activity of ruthenium catalysts for the addition of benzoic acid **1a** to ethynylbenzene **2a**.



(1)

Entry	Catalyst[a]	Total yield [%][b]	Selectivity [%][c] **3aa**:**4aa**:**5aa**
1	Ru/CeO_2	96	74:21:5
2[d]	Ru/CeO_2	69	74:20:6
3[e]	Ru/CeO_2	46	65:33:2
4	Ru/ZrO_2	94	73:21:6
5	Ru/Al_2O_3	8	75:25:0
6	Ru/TiO_2	7	71:29:0
7	Ru/SiO_2	trace	–
8	Ru/MgO	trace	–
9	$Ru_3(CO)_{12}$[f]	77	73:19:8
10	$[RuCl_2(p\text{-cymene})]_2$[f]	54	52:43:5

[a] Supported Ru catalyst 125 mg.
[b] Total yield of **3aa**, **4aa**, and **5aa** determined by GLC.
[c] Molar ratio of isomers determined by GLC.
[d] At 120 °C.
[e] Reaction under the air atmosphere.
[f] Homogeneous catalyst.

The activity of the catalysts was significantly affected by the catalyst support (entries 4–8). The ZrO_2-supported catalyst showed activity comparable to that of the CeO_2-supported catalyst. The other ruthenium catalysts supported on Al_2O_3, TiO_2, SiO_2, and MgO were not effective. Note that a similar trend was observed in the transfer-allylation of homoallylic alcohols, the chelation-assisted direct arylation of aromatic C–H bonds, and the addition of C–H bonds to vinylsilanes.[26,27]

As shown in Table 2, the activity of Ru/CeO_2 catalysts was markedly affected by the ruthenium precursors used for their preparation. In general, catalysts prepared from precursors with chloride ligands showed high activities. However, the ruthenium precursors did not influence the selectivity. Among the precursors examined, $[RuCl_2(p\text{-cymene})]_2$ was found to be most suitable. The Ru/CeO_2 catalyst prepared from $Ru_3(CO)_{12}$ which has no chloride ligands showed low activity, but the addition of ammonium chloride (10 equivalents to Ru) to the reaction mixture gave a higher activity than the catalyst without NH_4Cl (entries 5 and 6). This result clearly indicates that the chloride species has a promoting effect. Catalysts prepared from $[RuCl_2(p\text{-cymene})]_2$ were used in the following study.

The effects of ruthenium precursors on the surface composition of the fresh catalysts were examined by

Table 2. Effect of ruthenium precursors of Ru/CeO_2 catalysts.[a]

Entry	Precursor	Total yield [%][b]	Selectivity [%][c] **3aa**:**4aa**:**5aa**
1[d]	$[RuCl_2(p\text{-cymene})]_2$	96	74:21:5
2	$RuCl_3{\cdot}n\,H_2O$	91	73:22:5
3	$[RuCl_2(CO)_3]_2$	72	72:22:6
4	$Ru(acac)_3$	20	70:25:5
5	$Ru_3(CO)_{12}$	14	64:29:7
6	$Ru_3(CO)_{12}$[e]	43	65:26:9

[a] *Reaction conditions:* **1a** 1.0 mmol, **2a** 1.3 mmol, mesitylene 1.0 mL, 2.0 wt% Ru/CeO_2 catalyst (125 mg; 0.025 mmol as Ru), at 130 °C for 12 h.
[b] Total yield of **3aa**, **4aa**, and **5aa** determined by GLC.
[c] Molar ratio of isomers determined by GLC.
[d] Entry 1 in Table 1.
[e] NH_4Cl (10 equiv. to Ru) was added to the reaction mixture.

Table 3. XPS analysis of Ru (2.0 wt%)/CeO_2 catalysts prepared from various precursors.[a]

Precursors	C [%]	Ru [%]	Cl [%]	Ce [%]	O [%]	Ru $3d_{5/2}$ [eV]
$[RuCl_2(p\text{-cymene})]_2$	12.00	1.37	3.71	28.77	54.15	281.93
$RuCl_3 \cdot nH_2O$	17.39	1.21	3.70	26.34	51.36	281.63
$[RuCl_2(CO)_3]_2$	17.50	1.29	3.34	25.73	52.14	281.73
$Ru_3(CO)_{12}$	20.13	1.36	trace	24.80	53.71	281.61
$Ru(acac)_3$	17.50	1.34	trace	26.41	54.75	281.53

[a] Surface concentrations are shown as atomic%, measured at −100 °C.

XPS. As shown in Table 3, residual chloride species were observed on the surface of the catalysts prepared using Cl-containing ruthenium complexes, while there were no significant differences in the atomic ratios of the surface ruthenium species. The Ru $3d_{5/2}$ binding energies of these catalysts indicated the presence of surface Ru(IV) species,[29] but the electronic effects of Cl species were not distinctly recognized.

It is important to investigate whether the reaction actually proceeds on the surface of the solid catalyst.[30,31] To examine the contribution of ruthenium species in solution generated by the so-called "release and capture" manner, the effect of removal of the catalysts by hot filtration through a PTFE filter (pore size 0.47 μm) was examined. Figure 1 shows the time course of the reaction at 130 °C. Formation of the enol esters was greatly suppressed, but not completely stopped by removal of the solid catalyst. Distinct induction periods were not recognized. Note that ruthenium species was not detected in the cold filtrate after the reaction had proceeded at 130 °C for 12 h by ICP-AES. These results indicate that the reaction basically requires the presence of the solid catalyst. The ceria support might act as a macroligand that stabilizes and/or holds the catalytically active ruthenium species. However, the contribution of soluble ruthenium species or nano-sized ruthenium colloids, which were generated *via* "release and capture"[30,31] and passed through the filter, could not be completely ruled out. A further mechanistic study which includes observation of the catalytically active species is now in progress.

The Ru/CeO_2 catalyst could be used with a variety of substrates. The results of the reaction of various carboxylic acids **1b–i** with **2a** at 130 °C for 12 h are shown in Eq. (2) and Table 4. The reaction with aromatic carboxylic acids with both electron-donating and electron-withdrawing substituents (**1b–e**) proceeded smoothly to afford adducts in moderate to high yields. A bulky substrate (**1f**) and carboxylic

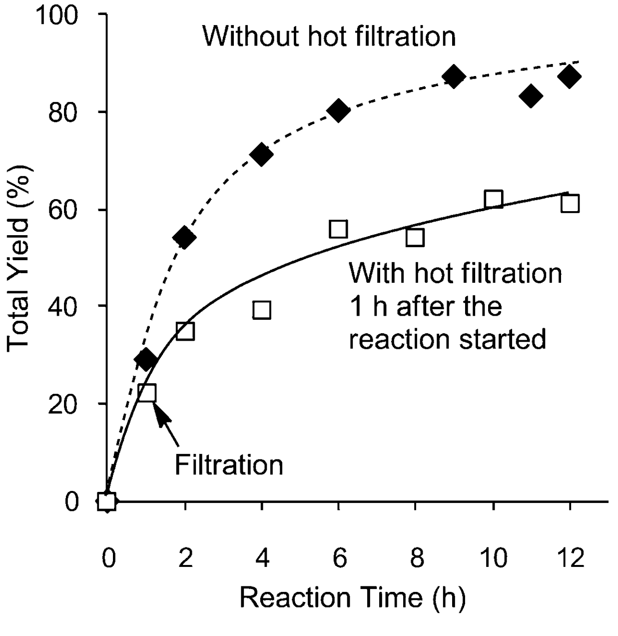
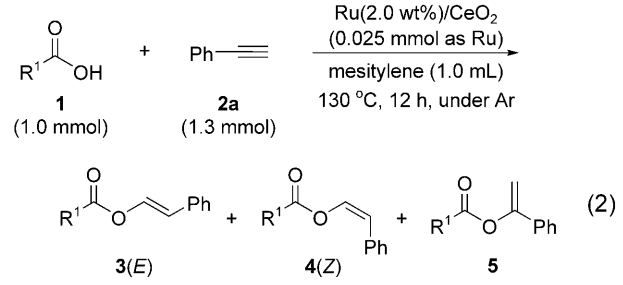


Figure 1. Effects of catalyst removal by hot filtration on the reaction of **1a** with **2a** at 130 °C. The reaction conditions were identical to those for entry 1 in Table 1.

Table 4. Scope of substrates (carboxylic acids).[a]



(2)

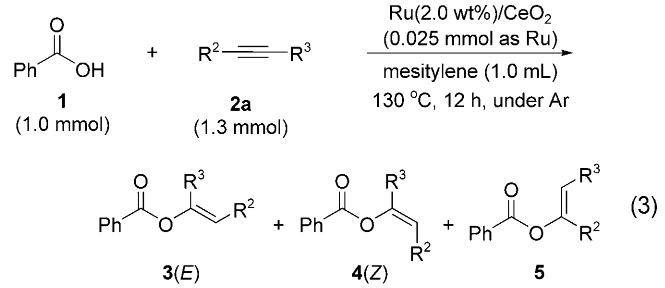
Entry	1	R^1	Total yield [%][b]	Selectivity [%][c] **3**(*E*):**4**(*Z*):**5**
1	**1b**	$4\text{-}CH_3C_6H_4$	58	79:17:4
2	**1c**	$3\text{-}CH_3OC_6H_4$	90	76:18:6
3	**1d**	$3\text{-}NO_2C_6H_4$	87	48:34:18
4	**1e**	$4\text{-}CF_3C_6H_4$	82	66:24:10
5	**1f**	$2,4,6\text{-}(CH_3)_3C_6H_2$	92	71:27:2
6	**1g**	2-thienyl	81	56:38:6
7	**1h**	3-furyl	76	72:22:6
8	**1i**	$n\text{-}C_7H_{15}$	40	75:21:4

[a] Ru/CeO_2 catalyst 125 mg.

[b] Isolated yield.

[c] Molar ratio of isomers determined by ^1H NMR.

Table 5. Scope of substrates (alkynes).[a]



Entry	2	R^2	R^3	Total yield [%][b]	Selectivity [%][c] **3**(*E*):**4**(*Z*):**5**
1	**2b**	4-$CH_3C_6H_4$	H	83	67:23:10
2	**2c**	4-$CH_3OC_6H_4$	H	72	44:17:39
3	**2d**	3-thienyl	H	78	59:17:24
4	**2e**	2-pyridyl	H	24	43:0:57
5	**2f**	$(CH_3)_3Si$	H	trace	–
6	**2g**	*n*-C_3H_7	*n*-C_3H_7	0	–
7	**2h**	Ph	Ph	0	–

[a] Ru/CeO_2 catalyst 125 mg.

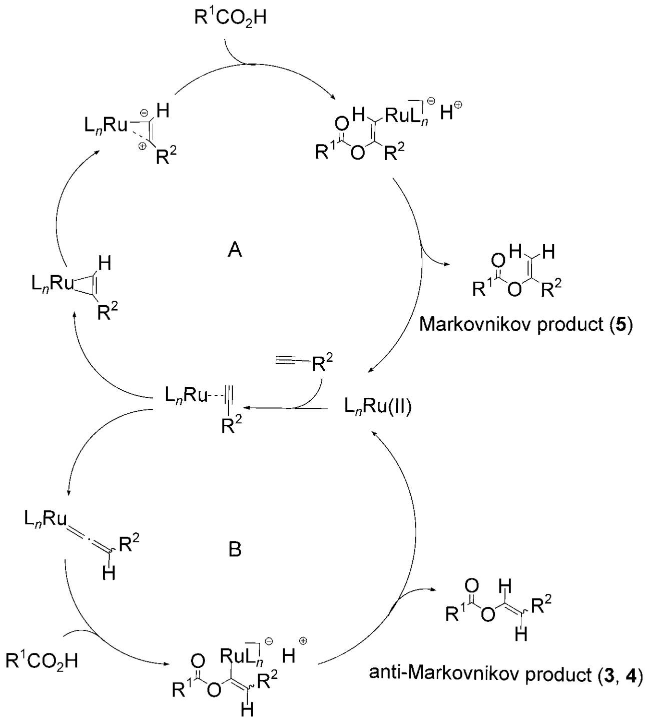
[b] Isolated yield.

[c] Molar ratio of isomers determined by ^{1}H NMR.

acids with thiophene and furan rings (**1g** and **1h**) were also applicable. The reaction with an aliphatic carboxylic acid (**1i**) also gave the desired adduct in a moderate yield. In all of the cases examined, the major products were *E*-isomers of anti-Markovnikov adducts (**3**).

The reactions with **1a** and various alkynes were examined [Eq. (3)]. As shown in Table 5, the reactions of terminal alkynes with phenyl groups (**2b** and **2c**) and that with a thiophene ring (**2d**) afforded the adducts in high yields, while the reaction with 2-ethynylpyridine (**2e**) resulted in a low yield of enol esters. The selectivity greatly depended on the alkynes. High selectivity of a Markovnikov adduct (**5**) was observed with an alkyne bearing a pyridyl group (**2e**). On the other hand, the reactions of a terminal alkyne with a trimethylsilyl substituent (**2f**) and internal alkynes (**2g** and **2h**) did not proceed under the present conditions.

To date, several mechanisms have been proposed for homogeneously catalyzed reactions (Scheme 1).[11,20b] One plausible mechanism involves the formation of vinylidene intermediates (*cycle B*),[18b,19b] while another probable cycle is likely to start with the coordination of an alkyne to a ruthenium species, followed by the addition of a carboxylate nucleophile to the η^2-coordinated alkyne (*cycle A*).[18b] We examined the reaction of **1a** with $Ph{-}C{\equiv}C{-}D$ (**2a**-*d*$_1$), and the deuterium shifting from the terminal to the 2-position was found to be predominant, which supported the formation of the ruthenium vinylidene species as an intermediate (*cycle B*). In entry 4 of Table 5 (the reaction of **1a** with **2e**), the strong coordination of a pyridyl group to a ruthenium center would promote the formation of a η^2-alkyne intermediate, which leads to a Markovnikov product through *cycle A*.



Scheme 1. Proposed catalytic mechanisms for the addition of carboxylic acids to terminal alkynes. *Cycle A:* Markovnikov addition; *Cycle B:* anti-Markovnikov addition.

One major advantage of heterogeneous catalysts is their reusability. Therefore, the changes in the activity

Table 6. Activities of fresh and reused Ru/CeO_2 catalysts.[a]

Treatment of recovered catalyst	Catalyst	Total yield [%][b]	Selectivity [%][c] **3aa**:**4aa**:**5aa**
Washing + drying + calcination	Fresh[d]	96	74:21:5
	2nd use	93	75:20:5
	3rd use	72	72:21:7
	4th use	71	72:23:5
	4th use[e]	82	73:22:5
Washing + drying	2nd use	79	72:23:5
	3rd use	43	70:23:7
	4th use	28	71:22:7

[a] *Reaction conditions:* **1a** 1.0 mmol, **2a** 1.3 mmol, mesitylene 1.0 mL, Ru/CeO_2 catalyst 0.025 mmol as Ru (loading level 2.0 wt%) prepared from $[RuCl_2(p\text{-cymene})]_2$, at 130 °C for 12 h.
[b] Total yield of **3aa**, **4aa**, and **5aa** determined by GLC.
[c] Molar ratio of isomers determined by GLC.
[d] Entry 1 in Table 1.
[e] Prolonged run for 18 h.

of Ru/CeO_2 catalyst over the course of repeated uses were examined, as shown in Table 6. After the first run, which gave the adducts in 96% yield, the catalyst was recovered from the reaction mixture by centrifugation followed by washing three times with diethyl ether (10 mL) at room temperature, and then calcined at 400 °C for 30 min in air. The recovered Ru/CeO_2 catalyst gave the adducts in 93% yield in the 2nd use, although the yields decreased to some extent in the 3rd and 4th uses. Reuse of the catalyst without calcination resulted in a significant decrease in catalytic activity. The severe deposition of organic species on the surface would suppress the activity of the catalyst (see below). In addition, re-deposited ruthenium species after cooling *via* release and capture cycles would be less or no longer active, which could be one reason for the poor reusability of the catalysts.

To examine the properties of the Ru/CeO_2 catalyst before and after the reaction, H_2 temperature-programmed reduction (TPR) measurements were performed, as shown in Figure 2. In the profile of the fresh catalyst, two peaks appeared at a low-temperature range, one at *ca.* 50 °C and one at 75 °C. The reduction of ruthenium species on other supports such as titania occurred at a temperature higher than 200 °C, and a temperature higher than 100 °C was required for the reduction of bulk RuO_2.[26,32] These results indicate that the surface ruthenium species on ceria is easily reduced. The used catalyst after the calcination showed a profile similar to that of the fresh catalyst, suggesting that the original surface ruthenium species are regenerated by calcination of the used catalyst. Note that characterization of the fresh catalysts was performed by nitrogen gas adsorption and XRD, and the results are summarized in Supporting Information.

The surface states of the Ru/CeO_2 catalyst before and after the reaction were also examined by XPS, diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), and TG. According to the XPS results shown in Table 7, a large part of the surface of the used catalyst was covered by carbonaceous materials, probably because of the deposition of benzoate species on the surface during the catalytic run, as suggested by DRIFTS (see Supporting Information). TG analysis of the catalyst after the first use showed *ca.* 4 wt% weight decrease due to the combustion of organic species adsorbed on the surface. Unfortunately, severe overlapping with C 1*s* peaks disturbed the precise measurement of the Ru $3d_{5/2}$ binding energy of the used catalyst. Most of the carbonaceous species was removed by calcination at 400 °C for 30 min in air. The surface atomic ratio of Cl greatly decreased after the 1st use, indicating that some of the chloride species were leached from the surface during the catalytic run. A slight decrease in the surface ruthenium

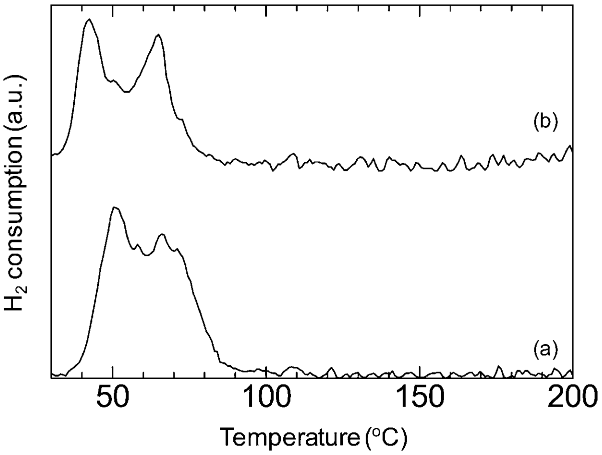


Figure 2. H_2 TPR profiles of (**a**) fresh and (**b**) used Ru (2.0 wt%)/CeO_2 catalyst prepared from $[RuCl_2(p\text{-cymene})]_2$. The used catalyst was calcined in air at 400 °C for 30 min.

Table 7. XPS analysis of the Ru (2.0 wt%)/CeO_2 catalyst prepared from $[RuCl_2(p\text{-cymene})]_2$.[a]

Remarks	C [%]	Ru [%]	Cl [%]	Ce [%]	O [%]	Ru $3d_{5/2}$ [eV]
fresh catalyst	12.00	1.37	3.71	28.77	54.15	281.93
after 1st use	40.62	1.02	1.90	15.81	40.65	–
after 1st use, calcined	12.35	1.10	2.84	24.12	59.60	281.23

[a] Surface concentrations are shown as atomic%, measured at −100 °C.

ratio of the used catalyst after calcination can be attributed to the sintering of ruthenium species during the regeneration procedure, since the leaching of ruthenium species was not observed after cold filtration of the catalyst (see above).

Figure 3 shows DRIFT spectra of the Ru/CeO_2 catalyst in the range of 800 to 1100 cm^{-1} before and after the catalytic run (entry 1 of Table 1). The spectrum of the fresh catalyst showed a distinct band at 984 cm^{-1} that could be assigned to a ruthenium oxo (Ru=O) species.[32] Although such a distinct peak was not recognized for Ru/ZrO_2, the formation of similar ruthenium-oxygen species has also been proposed for the zirconia-supported catalyst.[33] There were no signs of oxo species for ruthenium catalysts supported on Al_2O_3, TiO_2, SiO_2, or MgO. The characteristic band at 984 cm^{-1} of Ru/CeO_2 disappeared after the reaction [Figure 3 (**c**)], suggesting that the ruthenium oxo species were transformed to other catalytically active species during the reaction. The band at 980 cm^{-1} reappeared in the spectrum of the used catalyst after calcination, indicating that ruthenium oxo species were regenerated [Figure 3 (**d**)].

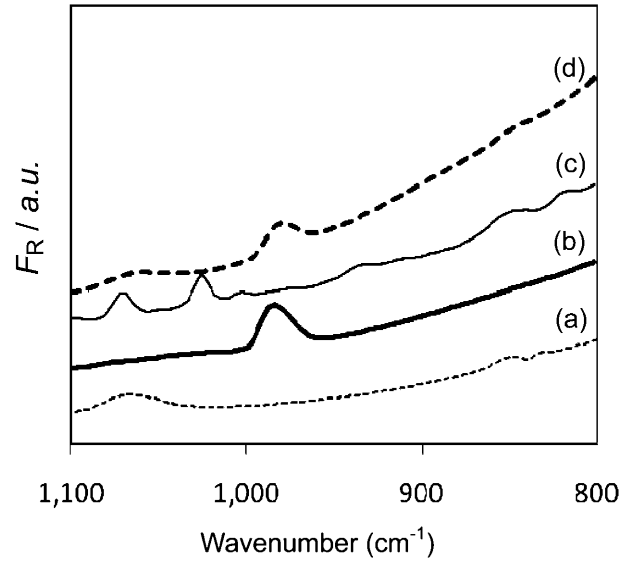


Figure 3. DRIFT spectra of (**a**) CeO_2, (**b**) fresh Ru/CeO_2 catalyst prepared from $[RuCl_2(p\text{-cymene})]_2$, (**c**) used catalyst, and (**d**) used catalyst after calcination.

As demonstrated above, the catalytic activity of Ru/CeO_2 gradually decreased during repeated uses. In the present case, the gradual loss of surface chloride species shown in the XPS study would not be a major reason: The addition of NH_4Cl (1 to 4 equivalents to Ru species) did not improve the activity of recycled catalysts, although the addition of NH_4Cl significantly promoted the reaction by the catalysts prepared using chlorine-free Ru sources (see Table 2, entries 5 and 6). The slight sintering of ruthenium species as recognized by the XPS study may have contributed to this result.

The combined results of the spectroscopic study suggest the formation of well-dispersed Ru(IV) oxo species on the surface of the fresh Ru/CeO_2 catalyst. A previous XANES study showed the formation of five-coordinate Ru(IV) species on the surface of Ru/CeO_2 prepared by a similar method.[32] Based on the results of DRIFTS and an H_2-TPR study, these oxo species are thought to be transformed to reduced active ruthenium species during the catalytic runs. The absence of distinct induction periods (see Figure 1) suggests that the generation of active species might occur at the very initial stage of the reaction. Although the nature of the true catalytically active species is not yet clear, the absence of leaching of ruthenium species after the reaction and the recyclability of the catalyst indicate that the present oxide-supported catalysts are promising alternatives to conventional homogeneous catalysts.

Conclusions

Solid oxide-supported ruthenium catalysts that are effective for the addition of a variety of carboxylic acids to terminal alkynes have been developed for the first time: Ru/CeO_2 and Ru/ZrO_2 showed excellent activities. A variety of carboxylic acids and terminal alkynes could be used with this catalyst. The present Ru/CeO_2 catalyst was recyclable, and the leaching of ruthenium species was not observed after cooling the reaction mixture. These features are quite attractive and advantageous from synthetic, industrial, and environmental points of view. Further studies to improve the regio- and stereoselectivities of the recyclable solid ruthenium catalysts are currently in progress.

Experimental Section

Preparation of the Ru/CeO_2 Catalysts

Supported catalysts were prepared by the impregnation method through the use of various supports and ruthenium complexes. A typical procedure is as follows: 1.0 g of CeO_2 was added to a solution of $[RuCl_2(p\text{-cymene})]_2$ (62 mg, 0.10 mmol, 20 mg as Ru) in 10 mL of methanol at 50 °C. After impregnation, the resulting light yellow powder was calcined in air at 400 °C for 30 min to afford Ru (2.0 wt%)/CeO_2 as a dark brown powder.

General Procedure for the Addition of Carboxylic Acids to Terminal Alkynes

All of the reactions were performed by the use of hot stirrers equipped with cooling blocks for refluxing the solution. A typical reaction procedure is as follows: A mixture of carboxylic acid (1.0 mmol) and terminal alkyne (1.3 mmol) in mesitylene (1.0 mL) was placed in a 20-mL glass Schlenk tube with a balloon under an Ar atmosphere together with 125 mg of the Ru (2.0 wt%)/CeO_2 catalyst (0.025 mmol as Ru). The reaction mixture was stirred at 130 °C for 12 h, and then cooled rapidly in an ice bath. The products were identified by GC-MS, ^{1}H and ^{13}C NMR, and quantified by ^{1}H NMR and GLC analyses using biphenyl as an internal standard.

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