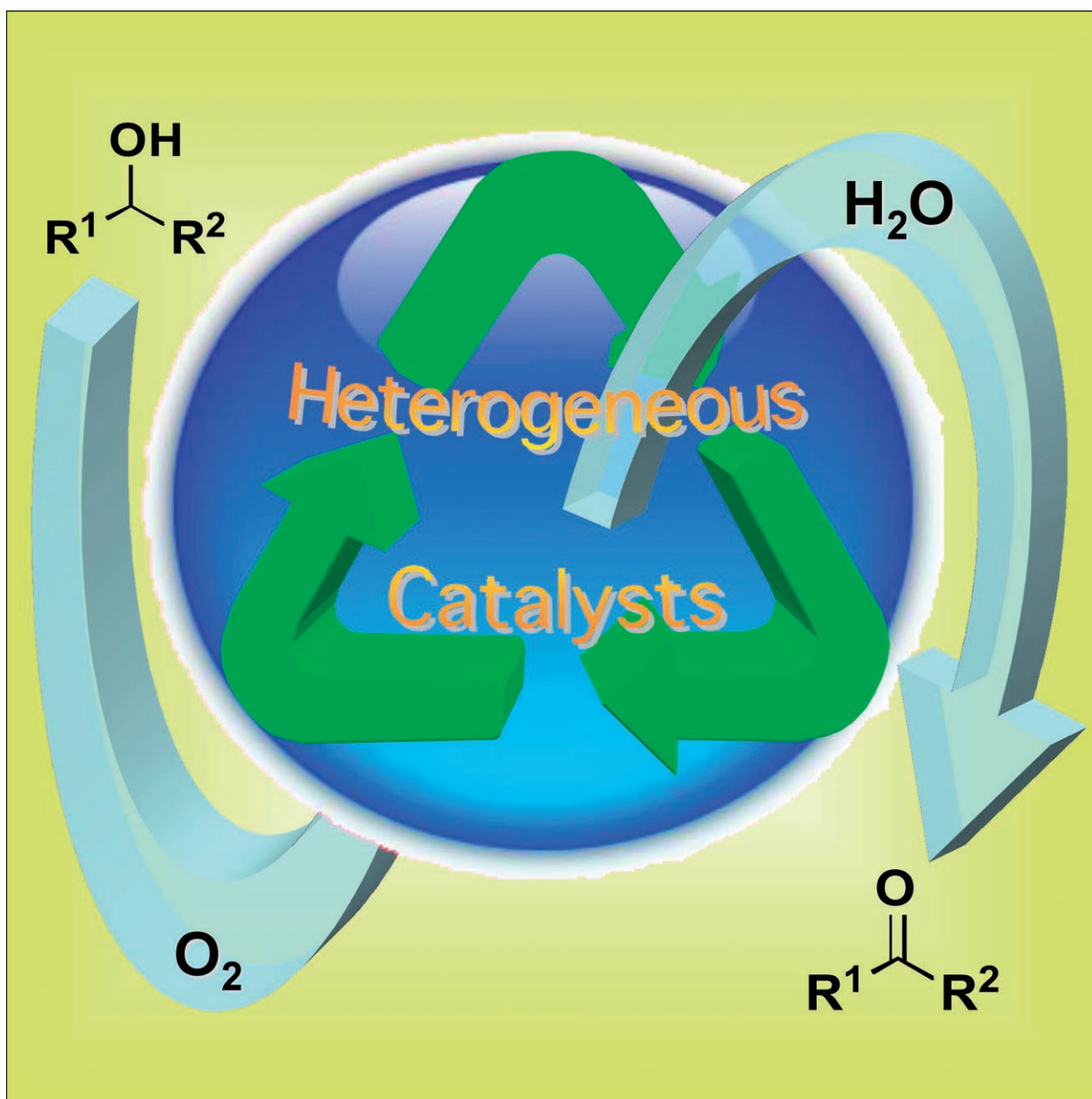# FOCUS REVIEWS

Recent Advances in Immobilized Metal Catalysts for Environmentally Benign Oxidation of Alcohols

Tsutomu Matsumoto, Masaharu Ueno, Naiwei Wang, and Shū Kobayashi[a]

Dedicated to Professor Teruaki Mukaiyama on the occasion of his 80th birthday

Abstract: One of the most significant organic transformations in catalyst technology is the selective oxidation of alcohols. The acceleration of catalyst discovery in this field contributes to the economic and environmental impact in the production of useful materials. Heterogeneous catalysts combined with environmentally benign oxidants, such as molecular oxygen and hydrogen peroxide, are major challenges of exploratory research in the oxidation of alcohols. A wide range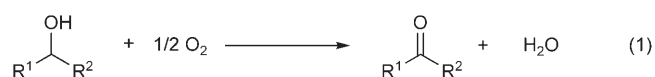 of recoverable catalysts has now emerged for these oxidation reactions. In this Focus Review, we present an overview of recent developments in immobilized metal catalysts and evaluate the potential of transition metals in the heterogeneously catalyzed oxidation of alcohols.

Keywords: heterogeneous catalysis · oxidation · dehydrogenation · alcohols

1. Introduction

Oxidation reactions are an essential process for organic synthesis and play an important role in giving the desired functionality to the intermediates of valuable compounds such as pharmaceuticals, agricultural chemicals, and fine chemicals.[1,2] Among various types of oxidative transformations, the oxidation of alcohols to carbonyl compounds occupies an important place in both laboratory and industry. However, a divide has opened between them in this area, according to a survey of synthetic methodology conducted by researchers in pharmaceutical companies.[3,4] The application of oxidation reactions in scaled-up synthesis for candidate drug molecules is very limited due to the use of heavy metals, thermal hazards, and moderate chemoselectivity for highly functionalized compounds in most oxidation reactions. If a technical solution for safety concerns is established, the research can be focused on the development of economically and environmentally friendly processes for the compounds to be launched. Therefore, much attention has been paid to develop catalytic reactions in place of classical oxidation methods with stoichiometric quantities of inorganic oxidants, which are highly toxic and environmentally polluting, and increasing environmental concerns have resulted in the use of "green oxidants" such as molecular oxygen or hydrogen peroxide to minimize chemical waste.[5-7] The use of molecular oxygen or hydrogen peroxide is favorable because they are inexpensive and water is the sole final by-product (Equations (1) and (2)). The sustainability of the selective oxidation of benzyl alcohol by using molecular oxygen, hydrogen peroxide, and other oxidants were recently ascertained.[8] Furthermore, dehydrogenation of alcohols under inert atmosphere [Eq. (3)] is another fascinating topic because the reactions can be conducted below the limits of explosion and flammability, which is a very important safety factor for large-scale syntheses.

$$\underset{R^1 \quad R^2}{\overset{OH}{\diagup}} + \ 1/2 \ O_2 \longrightarrow \underset{R^1 \quad R^2}{\overset{O}{\diagup}} + \ H_2O \qquad (1)$$

$$\underset{R^1 \quad R^2}{\overset{OH}{\diagup}} + \ H_2O_2 \longrightarrow \underset{R^1 \quad R^2}{\overset{O}{\diagup}} + \ 2\,H_2O \qquad (2)$$

$$\underset{R^1 \quad R^2}{\overset{OH}{\diagup}} \longrightarrow \underset{R^1 \quad R^2}{\overset{O}{\diagup}} + \ H_2 \qquad (3)$$

Although a large number of homogeneous metal-catalyzed systems for the oxidation of alcohols with molecular oxygen have been developed,[9-13] heterogeneous catalysts usually suffer from low catalytic activity relative to their homogeneous counterparts. Much effort has been made to overcome the difficulties involved because reduction of environmental loading due to easy separation and reuse of the catalysts could result. In early work in this field, supported palladium and platinum catalysts with metal promoters such as bismuth or lead were intensively investigated.[14] Furthermore, low-valent ruthenium species were known to be excellent catalysts for the dehydrogenation of alcohols.[15] Recent-

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ly, gold has been recognized as a promising metal for the aerobic oxidation of alcohols.[16,17] The transition metals described above have major uses in modern oxidation with heterogeneous catalysts for the aerobic oxidation of alcohols, and we will discuss their features in details.

Tsutomu Matsumoto was born in Kyoto, Japan. He received his MS in chemistry from Okayama University in 1992 and then joined Sumitomo Chemical Co., Ltd. He was a visiting scientist at North Carolina State University (1998–1999) working on software development for an automated chemistry workstation. He is currently a visiting scientist at The University of Tokyo, and his research involves the development of heterogeneous catalysts for oxidation reactions and their applications to microreactors.

Masaharu Ueno was born in 1974 in Tokyo, Japan. He received his PhD from Tokyo Univ. of Science in 2002 and was in the group of Prof. Kobayashi under a Research Fellowship for Young Scientists of the JSPS in 2002–2003. He was an Asst. Prof. at the Department of Applied Chemistry, The Univ. of Tokyo in 2003–2006. He then returned to the group of Prof. Kobayashi as an Asst. Prof. from 2006. His research interests involve organic reactions in microreactors, the development of metal-immobilized catalysts based on polymers, and organic reactions in water.
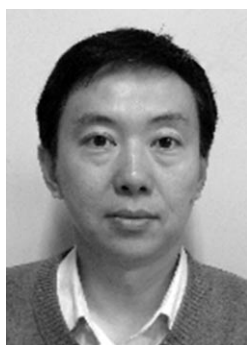
Naiwei Wang earned his PhD in the development of nitroxyl radical catalyzed selective oxidation of alcohols under the supervision of Prof. Xinmiao Liang from the Dalian Institute of Chemical Physics, Chinese Academy of Sciences in 2006. He subsequently joined the Kobayashi Highly Functionalized Reaction Environments Project in the Japan Science and Technology Agency (JST) as a postdoctoral researcher. His current research is focused on the development of catalytic oxidation methods and their application to microreactors.

Shū Kobayashi was born in Tokyo (1959) and received his PhD in 1988 under Prof. T. Mukaiyama, The Univ. of Tokyo. After 11 years at the Science Univ. of Tokyo, he moved to The Univ. of Tokyo (1998). His research involves the development of new synthetic methods and catalysts, organic reactions in water, solid-phase synthesis, total synthesis, and organometallic chemistry. He has received many awards, including the Springer Award in Organometallic Chemistry (1997), the IBM Science Award (2001), the JSPS Prize (2005), and an Arthur C. Cope Scholar Award (2006).

To enhance the productivity of chemical research and development, we should also be aware of the special features of each catalytic system with regard to activity and selectivity for transformation to their target compounds. Heterogeneous catalytic systems for the aerobic oxidation of alcohols were recently summarized.[13,18] Although some other types of recyclable catalytic systems such as liquid–liquid biphasic systems have been explored,[19-23] we mainly focus herein on the recent development of heterogeneous catalysts for the oxidation of alcohols with molecular oxygen or hydrogen peroxide and the dehydrogenation of alcohols under anaerobic conditions. Notably, this is not an inclusive review of the research in this field. The main purpose of this report is to provide an analysis of recent advances in the research into the heterogeneous catalytic oxidation of alcohols with molecular oxygen as well as the different nature of the catalysts to obtain the desired products in an efficient manner. To show the wide applicability of the catalytic systems, further oxidative transformation as well as alcohol oxidation is also covered. We hope that this report can result in design guidelines for next-generation catalysts and stimulate further research and development in this field.

2. Oxidation of Alcohols with Molecular Oxygen

2.1. Ruthenium-Based Catalysts

Of all the elements in the Periodic Table, ruthenium gives the widest range of oxidation states, from -2 to $+8$. Therefore, a large variety of oxidative transformations, including oxidation of alcohols, alkenes, amines, amides, β-lactams, phenols, and hydrocarbons, have been established.[15,24] Among the transition-metal catalysts that have potential for use in oxidation reactions, ruthenium displays excellent selectivity as well as wide substrate scope.

Pioneering work by Ley and co-workers dating back to 1997 involved the use of polymer-supported perruthenate (PSP), although this catalyst suffered from oxidative degradation of the polymer support.[25,26] Because of difficulties in recycling the catalyst, they investigated a mesoporous silicate (MCM-41) as an alternative support and found that it was effective for the immobilization of perruthenate. They also showed the reusability of the catalyst [Eq. (4)].[27]
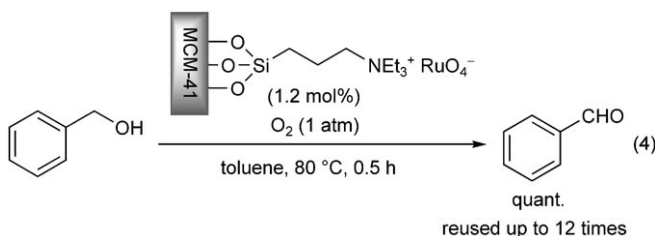

Organic–inorganic hybrid materials are recognized as a type of promising support that gives effective active sites for catalytic reactions.[28–32] A benefit of hybridization is that im-

proved synergistic properties of both the organic and inorganic materials can be achieved. Organically modified silicates (ORMOSIL) were investigated by Pagliaro and Ciriminna as an alternative support for tetra-n-propylammonium perruthenate (TPAP).[33,34] Sol–gel-encapsulated TPAP (SG-TPAP) was developed, and it was found that the surface hydrophobicity and the amount of water and methanol used were key to achieving high catalytic performance. The optimized catalyst showed higher activity than the unsupported TPAP, and it could be reused at least six times [Eq. (5)].


(5)

>99% conversion
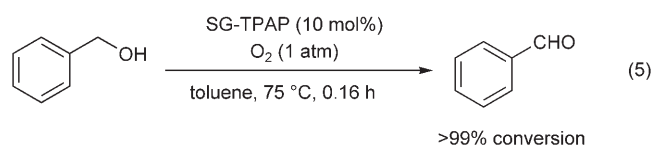
Although the original TPAP with molecular oxygen as a co-oxidant showed wide substrate scope that includes primary/secondary aliphatic alcohols,[35,36] no such examples that give aldehydes and ketones in good yield were included in the SG-TPAP oxidation. To broaden the application range of SG-TPAP, other reaction conditions were investigated, such as conditions of supercritical carbon dioxide (scCO$_2$) and the introduction of ionic liquids or a fluoroalkyl chain to the silica matrix of SG-TPAP.[37-40]

Kaneda and co-workers developed a monomeric ruthenium cation on the surface of hydroxyapatite (Ru/HAP), which gave efficient selectivity for various alcohols, including primary/secondary benzylic, primary/secondary aliphatic, primary/secondary allylic, and heterocyclic alcohols, although a higher loading of ruthenium (17 mol%) was needed for the reactions [Eq. (6)].[41]


(6)

R = C$_6$H$_5$, 80 °C, 3 h: >99% yield
R = n-heptyl, 60 °C, 16 h: 94% yield
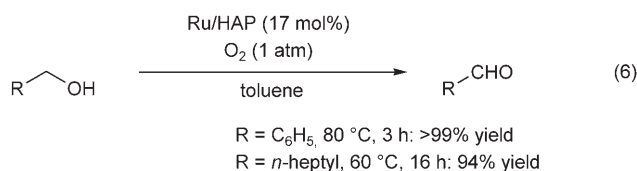
Examinations of the structure by X-ray absorption near-edge structure (XANES), k^3-weighted extended X-ray absorption fine structure (EXAFS), and other analytical techniques have been conducted to estimate the environment of Ru^{III} on HAP (Scheme 1). The substrate scope of Ru/HAP was found to be quite broad. Besides the aerobic oxidation of alcohols, the catalyst was applied to the aerobic oxidation of primary amines to nitriles[42] and organosilanes to silanols in the presence of water.[43]
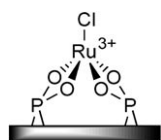

Scheme 1. The structure of Ru^{III}–hydroxyapatite (Ru/HAP).

Multicomponent systems capable of oxidizing alcohols by using inorganic supports such as Ru/CeO$_2$/CoO(OH)[44,45] and RuMn$_2$ species on hydrotalcite (HT) were also reported.[46] In the case of RuMn$_2$ on HT (RuMn$_2$/HT), the structure of the trimetallic RuMn$_2$ species on HT was reported to consist of Ru^{IV} and Mn^{IV} cations on the HT surface. In the absence of Ru species, Mn$_2$/HT did not show any activity at all. RuMn$_2$/HT was applied to the oxidation of benzylic and aromatic allylic alcohols. Benzyl alcohol was smoothly oxidized to benzaldehyde in the presence of RuMn$_2$/HT (3 mol%), and the catalyst was reused for a further three runs successfully [Eq. (7)].

(7)

1st 99%; 2nd 99%; 3rd 98%; 4th 99% yield
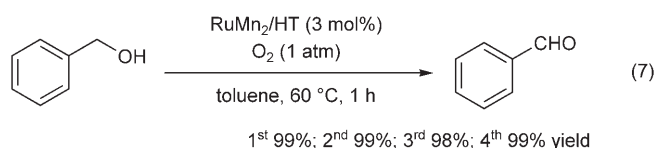
Baiker and co-workers reported that incorporation of a metal promoter into the HAP matrix before introduction of ruthenium dramatically improved the catalytic performance.[47] They described that the promoter ion, Co^{II} or Pb^{II}, occupies the "hidden" sites inside the narrow channels where the substrates are difficult to access. Consequently, the total amount of ruthenium was decreased by the pretreatment, and the ruthenium species that can be involved in the reaction was predominantly located on the surface. Compared with Ru/HAP, high turnover frequencies (TOF) by using RuCo/HAP (1.7 mol%) were obtained for various alcohols [Eq. (8)].
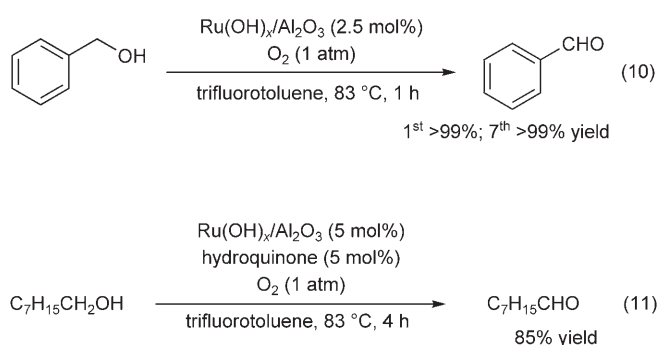

(8)

>99% yield, TOF: 78 h^{-1}
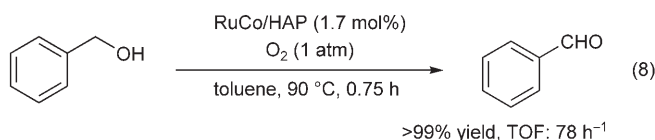
White and co-workers synthesized RuO$_2$ nanoclusters (1 nm) in the supercages of faujasite (FAU) zeolite (RuO$_2$/FAU), and they showed high activity and selectivity for various alcohols.[48] Although bulk RuO$_2$ showed low activity (16% yield), benzyl alcohol with RuO$_2$/FAU (7.8 mol%) was oxidized to benzaldehyde quantitatively under the same reaction conditions, and no decrease in yield was observed after the fifth run by using the recovered catalyst [Eq. (9)]. Another interesting feature of the zeolite-based catalysts derived from their uniform pore size is that they behave as a


(9)

>99% yield
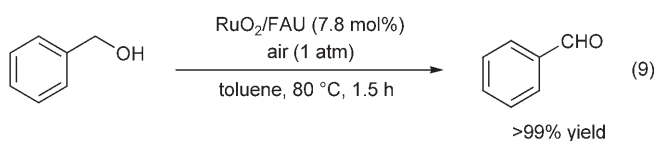
shape-selective catalyst. It was shown that a competitive reaction of benzyl alcohol over 9-hydroxyfluorene resulted in no formation of 9-fluorenone.

Ruthenium supported on alumina ($Ru(OH)_x/Al_2O_3$) was developed by Yamaguchi and Mizuno and demonstrated high catalytic activity and selectivity for both activated and non-activated alcohols.[49,50] Benzyl alcohol was converted into benzaldehyde in over 99% yield, and the subsequent six runs with the recovered catalyst gave quantitative yield of the aldehyde [Eq. (10)]. Furthermore, $Ru(OH)_x/Al_2O_3$ combined with the same equivalent of hydroquinone successfully catalyzed the oxidation of primary aliphatic alcohols to the corresponding aldehydes in good yields [Eq. (11)]. High TOF ($340\ h^{-1}$) in the oxidation of 1-phenylethanol was observed in the presence of $Ru(OH)_x/Al_2O_3$ (0.1 mol%) at 150°C under solvent-free conditions.

$$\text{(10)}$$

Ru(OH)$_x$/Al$_2$O$_3$ (2.5 mol%)
O$_2$ (1 atm)
trifluorotoluene, 83 °C, 1 h

1st >99%; 7th >99% yield

$$\text{(11)}$$

Ru(OH)$_x$/Al$_2$O$_3$ (5 mol%)
hydroquinone (5 mol%)
O$_2$ (1 atm)
trifluorotoluene, 83 °C, 4 h

$C_7H_{15}CH_2OH \longrightarrow C_7H_{15}CHO$

85% yield

It was assumed that the catalytic cycle initiated the ligand exchange between ruthenium hydroxide and an alcohol to give a ruthenium alcoholate, followed by hydride elimination to provide the corresponding oxidized compound and ruthenium hydride. The regeneration of ruthenium hydroxide completed the catalytic cycle by oxidation of the ruthenium hydride species (Scheme 2).
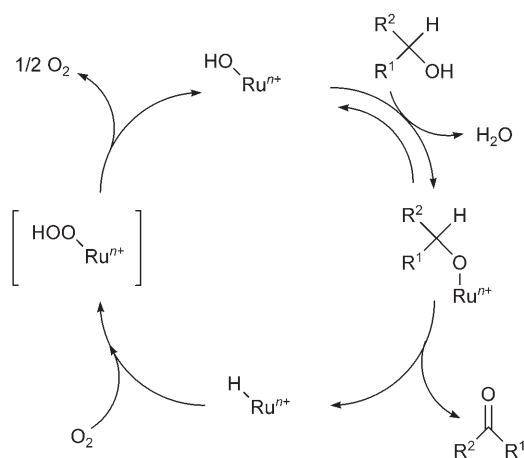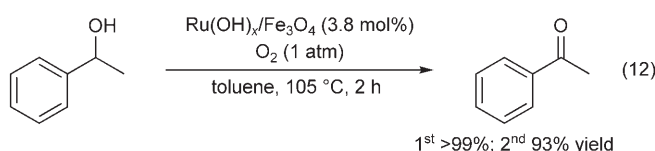
The catalyst has a wide applicability for other reaction systems besides the aerobic oxidation of alcohols. Aerobic oxidation of amines to nitriles or imines,[51] hydrogen-transfer reactions,[52] aerobic oxidative biaryl coupling in water,[53] hydration of nitriles,[54] and oxidation of alkyl arenes with molecular oxygen[55] were reported.

Ruthenium hydroxide species was also deposited onto the surface of TiO_2 nanotubes by Bavykin and co-workers.[56] The activity of the catalyst (Ru^{III}/TiO_2) was studied in the aerobic oxidation of alcohols in a continuous-flow multi-channel reactor. High TOF ($450\ h^{-1}$) in the oxidation of benzyl alcohol was obtained with high selectivity to benzaldehyde.

Recently, the use of superparamagnetic nanoparticles as a supporting material for immobilized metal catalysts was reported.[57-62] Separation is easily achieved by using an external permanent magnet to collect the immobilized catalyst on the wall of the reaction vessel. In 2006, Mizuno and co-workers synthesized a ruthenium hydroxide species on magnetite ($Ru(OH)_x/Fe_3O_4$).[63] The catalyst has wide substrate scope for the aerobic oxidation of alcohols, and the activities are comparable or a little lower than those of $Ru(OH)_x/Al_2O_3$, which were reported by the same group. 1-Phenylethanol was quantitatively oxidized to acetophenone, and catalyst separation from the reaction mixture was achieved with a permanent magnet as described above [Eq. (12)]. Treatment with aqueous NaOH was needed for the second run, and a recycling experiment under the same reaction conditions gave a slightly lower yield of acetophenone (93%). The catalyst was also found to be applicable to the aerobic oxidation of amines and the reduction of carbonyl compounds in the presence of a hydrogen donor.

$$\text{(12)}$$

Ru(OH)$_x$/Fe$_3$O$_4$ (3.8 mol%)
O$_2$ (1 atm)
toluene, 105 °C, 2 h

1st >99%; 2nd 93% yield

Scheme 2. Proposed catalytic cycle for $Ru(OH)_x/Al_2O_3$-catalyzed oxidation of alcohols.

More recently, Kaneda and co-workers developed magnetic γ-Fe_2O_3 containing ruthenium hydroxyapatite (Ru/HAP-γ-Fe_2O_3), which was found to be an effective catalyst for the oxidation of alcohols under atmospheric pressure of molecular oxygen.[64] γ-Fe_2O_3 nanocrystallites were dispersed in the HAP matrix, and a monomeric ruthenium cation exists on the outer surface uniformly. The oxidation state of ruthenium on HAP-γ-Fe_2O_3 was revealed to be +4, which is different from that of Ru/HAP (Ru^{III}). The activity of Ru/HAP-γ-Fe_2O_3 was dramatically improved over Ru/HAP, and the former was found to be applicable to various alcohols, including primary/secondary benzylic, primary/secondary aliphatic, primary allylic, and heterocyclic alcohols. The oxidation of benzyl alcohol with Ru/HAP-γ-Fe_2O_3 (0.5 mol%) was achieved to give benzaldehyde in 98% yield [Eq. (13)]. In contrast to the previously reported HAP-supported catalysts Ru/HAP (TOF: $2\ h^{-1}$) and RuCo/HAP (TOF: $78\ h^{-1}$),

Ru/HAP-γ-Fe$_2$O$_3$ showed a higher catalytic performance (TOF: 196 h^{-1}). Furthermore, 1-dodecanol was oxidized to the corresponding carboxylic acid selectively without any additives [Eq. (14)]. The oxidation of several alcohols was also conducted at room temperature. The oxidation of benzyl alcohol in the presence of Ru/HAP-γ-Fe$_2$O$_3$ (1.25 mol%) proceeded smoothly to afford benzaldehyde in 98% yield after 24 h.

$$\text{(13)}$$

98% yield, TOF: 196 h^{-1}

$$\text{(14)}$$

98% yield, TOF: 11 h^{-1}
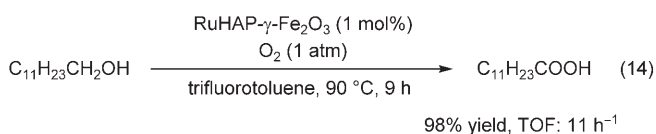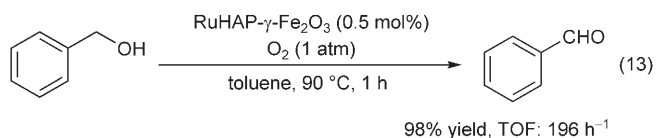
In contrast to the many reports of inorganic supports, only a few polymer-supported catalysts for the aerobic oxidation of alcohols are known. Kobayashi and co-workers developed a polymer-incarcerated ruthenium catalyst (PI Ru) capable of oxidizing alcohols, based on the technique of microencapsulation and cross-linking.[65] The novel immobilization technique for metal catalysts, the polymer-incarcerated (PI) method, is described in detail later (see Scheme 5 and [Eq. (37)] for the preparation of polymer-incarcerated gold (PI Au)). PI Ru was prepared from a polystyrene-based copolymer (Scheme 3) with ruthenium chloride hydrate as the

x/y/z = 84:12:4
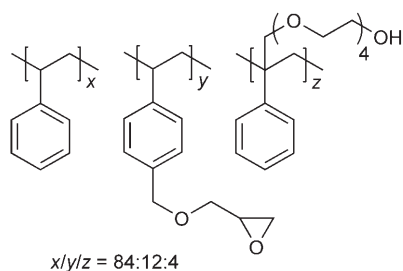
Scheme 3. Structure of copolymer for encapsulating ruthenium species.

metal source. The catalyst thus obtained showed wide applicability to various alcohols with high reusability of the catalyst in the presence of 2,2,6,6-tetramethylpiperidine N-oxyl (TEMPO).

4-Methoxybenzyl alcohol was oxidized in the presence of 5 mol% of PI Ru and 15 mol% of TEMPO to afford the corresponding aldehyde in 98% yield [Eq. (15)]. The recovered catalyst could be reused without any further treatment. It was found that no decrease in yield was observed even after repeated use (10 times), although a slightly longer re-

$$\text{(15)}$$

1st 98%; 10th 97% yield
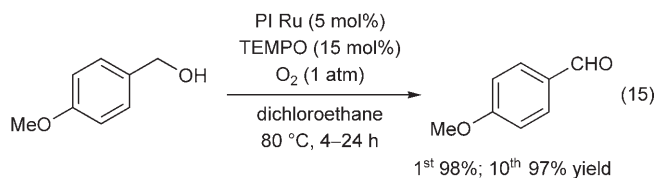
action time was needed to obtain full conversion of the alcohol.

An organic–inorganic hybrid copolymer was also designed as a novel support material for ruthenium [Eq. (16)]. A reusable heterogeneous ruthenium catalyst, organic–inorganic hybrid ruthenium (HB Ru), was prepared from dichloro-tris(triphenylphosphanyl)ruthenium [RuCl$_2$(PPh$_3$)$_3$] as the metal source and the copolymer shown in [Eq. (16)], which has a trimethoxysilyl functionality for the heterogenization of the catalyst. A sol–gel process was employed to initiate hydrolysis by adding aqueous NaOH followed by polycondensation (cross-linking) to afford HB Ru.[66]

$$\text{(16)}$$
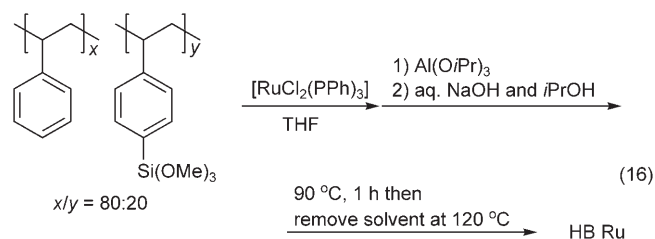
The oxidation of various alcohols proceeded smoothly to give the corresponding aldehydes and ketones under atmospheric pressure of molecular oxygen or air. 4-Methylbenzyl alcohol with HB Ru (5 mol%) was oxidized to p-tolualdehyde in 97% yield without any additives [Eq. (17)]. After treatment with aqueous K$_2$CO$_3$, the catalyst was reused at least five times without loss of activity.

$$\text{(17)}$$

1st 97%; 5th 95% yield
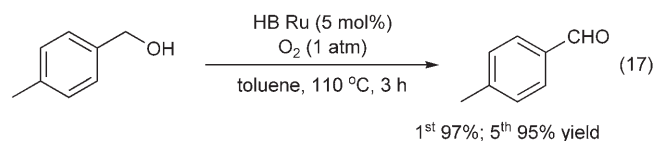
2.2. Palladium-Based Catalysts

Besides the aerobic oxidation of alcohols, palladium catalyzes many oxidative transformations, including epoxidation of alkenes, oxidation of terminal alkenes to ketones, aldehydes, and other Wacker-type reactions, oxidation of alkanes, hydroxylation of benzenes, and oxidative coupling reactions.[67] Finely divided palladium such as Pd/C is a well-known catalyst for hydrogenation and dehydrogenation reactions as well as petroleum cracking.

Hydrotalcite, a type of the basic clay mineral, is a suitable support for palladium complexes. Uemura and co-workers reported the oxidation of alcohols to aldehydes and ketones catalyzed by Pd^{II} on hydrotalcite (Pd/HT) by using atmospheric pressure of molecular oxygen or air [Eq. (18)].[68–70] They compared two catalytic systems, Pd/HT and their previous catalytic system, homogeneous $Pd(OAc)_2$/pyridine/ MS3A (3-Å molecular sieves), and found that the Pd/HT system has higher activity. They confirmed that the reaction pathway is the same and that hydrotalcite has a role in decomposing the hydrogen peroxide generated. In the oxidation of alcohols with a catalytic amount of $Pd(OAc)_2$/pyridine without MS3A, a ratio of the amount of oxygen uptake to the yield of the corresponding aldehyde of about 1:1 was observed, whereas a roughly 1:2 ratio was observed when the reaction was carried out in the presence of Pd/HT. Pd/HT was reused at least three times, although a gradual decrease in catalytic activity was observed.


$$(18)$$
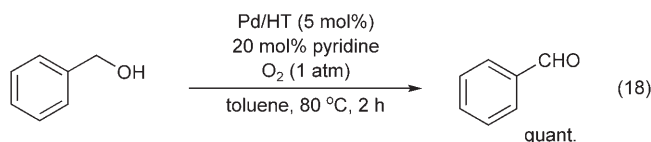
Kaneda and co-workers reported hydroxyapatite-supported palladium nanoclusters (Pd/HAP-0) prepared from stoichiometric HAP with $[PdCl_2(PhCN)_2]$ as a metal source.[71,72] The atomic ratio of Pd to Cl was found to be 1:2 by X-ray photoelectron spectroscopy (XPS) and energy-dispersive X-ray (EDX) analysis, and the Pd K-edge XANES spectra of Pd/HAP-0 revealed that the palladium species are in the divalent state. Fresh Pd/HAP-0 had an induction period of about 10 min, and it was pointed out that the monomeric Pd^{II} species were converted into Pd^0 nanoparticles during the induction period. According to transmission electron microscopy (TEM), the mean diameter of palladium nanoclusters was about 3.8 nm with a narrow size distribution. The oxidation of a wide variety of alcohols was exemplified by the oxidation of 1-phenylethanol with Pd/HAP-0 (0.2 mol %) in trifluorotoluene at 90 °C, which gave acetophenone quantitatively, and high TOF (9800 h^{-1}) was obtained in the presence of Pd/HAP-0 (4×10^{-4} mol %) at 160 °C for 24 h without organic solvent [Eq. (19)]. They also demonstrated the aerobic oxidation of alcohols catalyzed by Pd/HAP-0 in water [Eq. (20)].
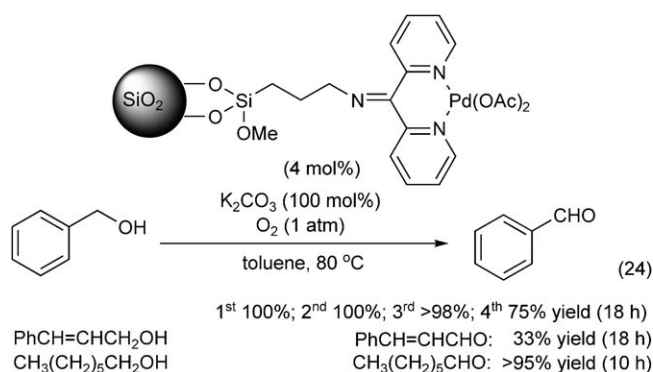

$$(19)$$
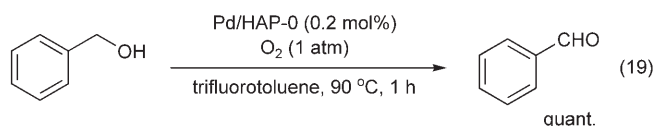
Uozumi and Nakao reported an amphiphilic resin dispersion of palladium nanoparticles (ARP-Pd), which was pre-


$$(20)$$
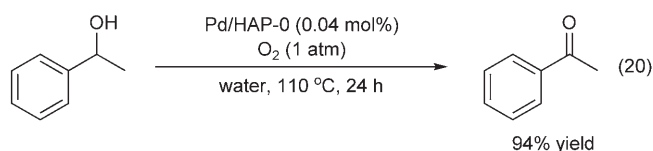
pared by reduction of a polystyrene–poly(ethylene glycol) (PS-PEG) resin-supported Pd^{II} complex [Eq. (21)].[73] The mean diameter of palladium clusters was 9.1 nm with a narrow size distribution, and the catalytic activity of ARP-Pd was examined for various alcohols in water ([Eq. (22)] and [Eq. (23)]). The aqueous filtrate after the removal of the ARP-Pd showed no catalytic activity, which means that leaching of palladium did not occur during the reaction. Oxidation of benzylic alcohols and a secondary allylic alcohol proceeded smoothly in the presence of ARP-Pd (1–5 mol %) in water heated at reflux. Although 20 mol % of the ARP-Pd was needed in the case of aliphatic alcohols, the activity of the recovered catalyst did not decrease after fourth run. In the case of primary aliphatic alcohols, the corresponding carboxylic acids were obtained in excellent yield in the presence of K_2CO_3.

$$(21)$$

$$(22)$$

$$(23)$$
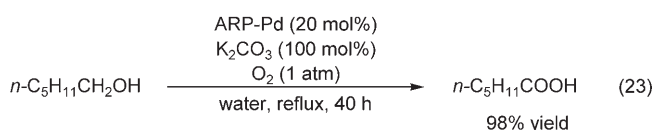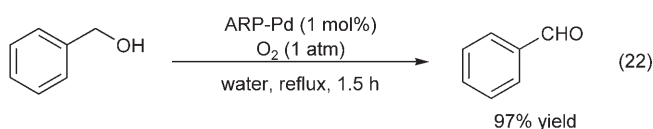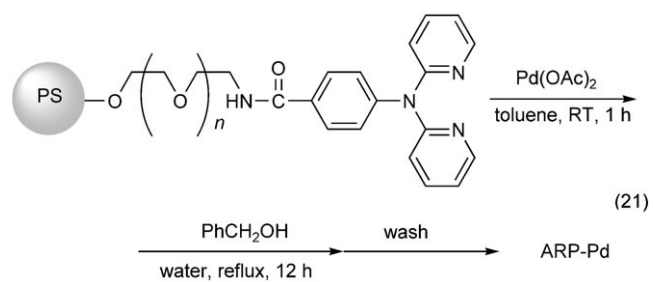
A bipyridyl Pd^{II} complex was immobilized onto a silica surface. Karimi et al. prepared a silica-supported catalyst from $Pd(OAc)_2$ and aminopropyl-functionalized silica (AMPS).[74] Benzyl alcohol was oxidized to benzaldehyde quantitatively in the presence of 4 mol % of the catalyst and K_2CO_3 (100 mol %) under atmospheric pressure of molecular oxygen [Eq. (24)]. A decrease in activity with the recovered catalyst was observed at the fourth run, and addition of K_2CO_3 was found to be essential because of the formation of palladium black.

$$(24)$$

$$1^{st} \ 100\%; \ 2^{nd} \ 100\%; \ 3^{rd} \ >98\%; \ 4^{th} \ 75\% \ \text{yield (18 h)}$$

PhCH=CHCH$_2$OH   PhCH=CHCHO: 33% yield (18 h)
CH$_3$(CH$_2$)$_5$CH$_2$OH   CH$_3$(CH$_2$)$_5$CHO: >95% yield (10 h)

A comparison of the relative reactivity of primary and secondary alcohols was also made. Although benzyl alcohol reacted faster than 1-phenylethanol in separate experiments, the oxidation of a 1:1 mixture of benzyl alcohol and 1-phenylethanol under the conditions shown in [Eq. (25)] gave no conversion of benzyl alcohol and quantitative yield of acetophenone.

$$(25)$$
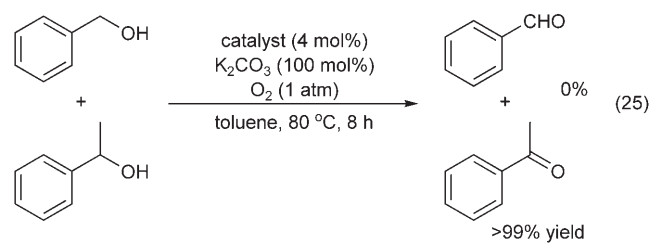
A supported bipyridyl Pd^{II} catalyst was also developed by changing the structure of the silica backbone to highly ordered mesoporous silica SBA-15.[75] The catalyst (Pd/SBA-15) thus obtained was applied to the oxidation of various alcohols in the presence of K$_2$CO$_3$ (100 mol%) under atmospheric pressure of molecular oxygen or air [Eq. (26)]. Benzylalcohol was converted into benzaldehyde quantitatively, and primary and secondary allylic alcohols reacted successfully to afford the corresponding aldehydes and ketones. Primary aliphatic alcohols were oxidized to the corresponding
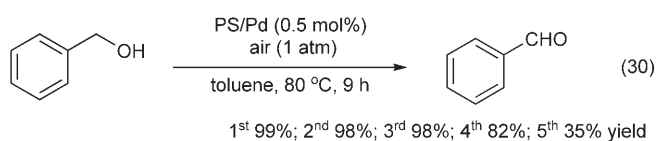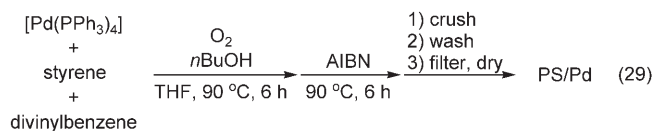

$$(26)$$

$$1^{st} \ >99\% \ (3.5 \ h); \ 5^{th} \ >99\% \ (7.0 \ h)$$
$$12^{th} \ >99\% \ \text{yield (7.4 h)}$$

PhCH=CHCH$_2$OH   PhCH=CHCHO: 98% yield (5 h)
CH$_3$(CH$_2$)$_5$CH$_2$OH   CH$_3$(CH$_2$)$_5$CO$_2$(CH$_2$)$_6$CH$_3$:   >99% yield (24 h)
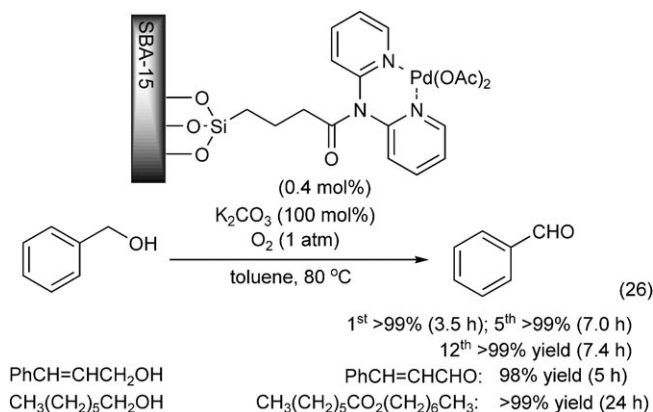
esters selectivity. No decrease in yield with the recovered catalyst was observed at all even after the reaction was repeated 12 times, although a slightly longer reaction time was needed to obtain full conversion of the alcohol.

Park and co-workers reported aluminum hydroxide supported palladium nanoparticles (Pd/AlO(OH)) prepared from [Pd(PPh$_3$)$_4$], tetra(ethylene glycol), 1-butanol, and aluminum tri-*sec*-butoxide [Eq. (27)].[76] The catalyst displayed dual catalytic activity for both alkene hydrogenation and aerobic oxidation of alcohols. Successful hydrogenation of cholesterol followed by aerobic oxidation to give cholestan-3-one was demonstrated in a one-pot manner [Eq. (28)]. The excellent recycling ability of the catalyst was also revealed. The hydrogenation of cholesterol and the oxidation of 1-phenylethanol were repeated 10 times independently without loss of activity. Aromatic and aliphatic primary 1,4-diols were transferred to the corresponding β-lactones quantitatively. However, Pd/AlO(OH) did not catalyze the oxidation of primary aliphatic alcohols such as 1-octanol.

$$(27)$$

$$(28)$$

99% yield
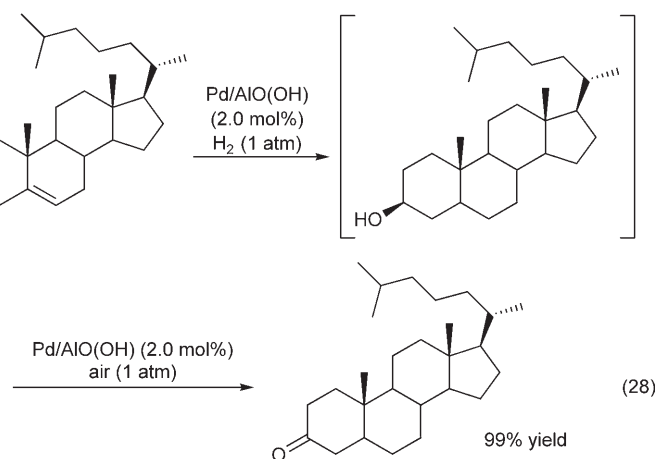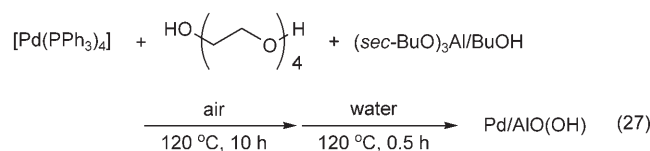
The palladium nanoparticles were also successfully developed onto a polystyrene-based polymer (PS/Pd) [Eq. (29)] (AIBN = 2,2′-azobisisobutyronitrile).[77] Not only aerobic oxidation of alcohols but also hydrogenation of alkynes and alkenes, Suzuki–Miyaura, Heck–Mizoroki, Sonogashira, and allylation reactions proceeded smoothly. In the case of the oxidation of benzyl alcohol, benzaldehyde was obtained quantitatively by using PS/Pd (5 mol%) in toluene [Eq. (30)]. Four subsequent runs with the recovered catalyst resulted in deactivation of the catalyst. PS/Pd was found to be inapplicable for the oxidation of secondary alcohols (1-phenylethanol: 6%; 2-octanol: trace) and an aliphatic primary alcohol (1-octanol: trace).

[Pd(PPh$_3$)$_4$]
+
styrene
+
divinylbenzene

$\xrightarrow[\text{THF, 90 °C, 6 h}]{\substack{O_2 \\ n\text{BuOH}}}$ $\xrightarrow[\text{90 °C, 6 h}]{\text{AIBN}}$ $\xrightarrow{\substack{\text{1) crush} \\ \text{2) wash} \\ \text{3) filter, dry}}$ PS/Pd   (29)

Benzyl alcohol $\xrightarrow[\text{toluene, 80 °C, 9 h}]{\substack{\text{PS/Pd (0.5 mol\%)} \\ \text{air (1 atm)}}}$ CHO   (30)

1st 99%; 2nd 98%; 3rd 98%; 4th 82%; 5th 35% yield

Pillai and Sahle-Demessie developed a palladium catalyst on magnesium oxide (Pd/MgO) and compared its catalytic activity with that of Pd on other support materials such as HT, Al$_2$O$_3$, SiO$_2$, and zeolite-β.[78] The scope of oxidation of alcohols was studied by using Pd/MgO (0.94 mol%) in trifluorotoluene at 70–80 °C. 1-Phenylethanol was oxidized to acetophenone quantitatively in trifluorotoluene after 8 h. The catalyst was recovered by simple filtration and reused six times without loss of activity.

Wang and co-workers demonstrated that the preparation method of palladium catalyst on aluminum oxide was important for high catalytic performance.[79] The activity of Pd/Al$_2$O$_3$ catalyst prepared by an adsorption method (Pd/Al$_2$O$_3$-ads) was higher than that prepared by an impregnation method. Benzyl alcohol was successfully oxidized to benzaldehyde (93% yield) in the presence of Pd/Al$_2$O$_3$-ads (0.006 mol%) under solvent-free conditions, although toluene was obtained as a by-product. This catalyst retained its activity even after six runs [Eq. (31)].

Benzyl alcohol $\xrightarrow[\text{no solvent, 88 °C, 8 h}]{\substack{\text{Pd/Al}_2\text{O}_3\text{-ads (0.006 mol\%)} \\ O_2 \text{ (1 atm)}}}$ CHO   (31)

93% yield, TOF: 1950 h^{-1}
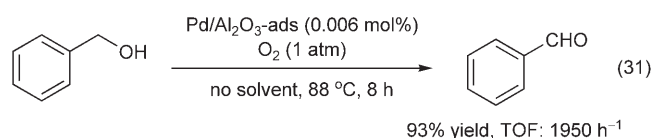
Recently, Schüth and co-workers prepared subnanometer palladium clusters in the carbon walls of ordered mesoporous carbon (Pd-OMC) (Scheme 4).[80] The catalytic activity of Pd-OMC was tested by using several alcohols in scCO$_2$. Selective oxidation of cinnamyl alcohol to cinnamaldehyde
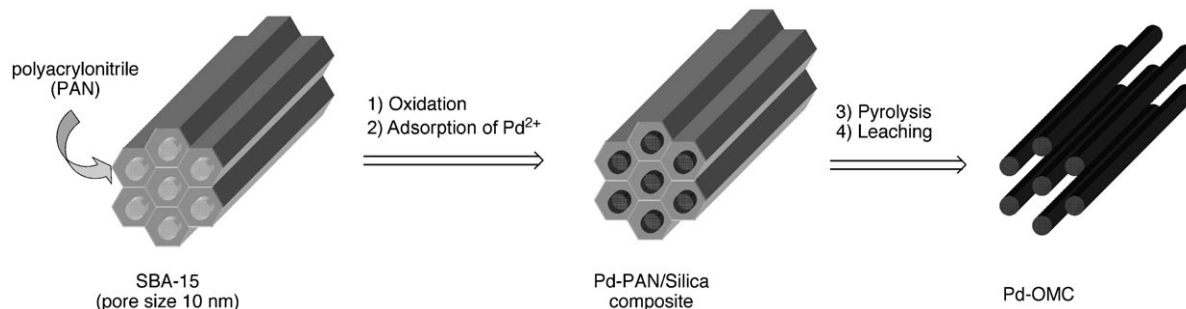
was achieved, but the conversion reached a plateau, presumably due to chemical poisoning.

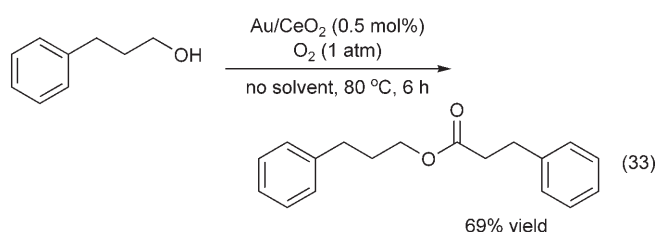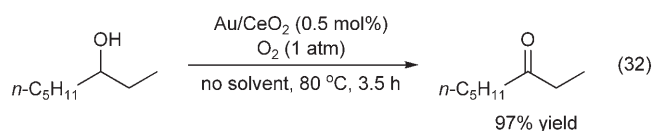## 2.3. Gold and Bimetallic Systems

Although bulk gold was for a long time regarded as a poorly active metal, the surprisingly high activity of gold nanoparticles as low-temperature CO oxidation catalysts[81] has initiated intensive research into the use of gold nanoparticles for aerobic oxidation reactions.[82]

In 1998, Prati and Rossi reported in their seminal studies that gold nanoparticles on carbon are very effective catalysts for the selective liquid-phase oxidation of diols.[83] Contrary to palladium and platinum catalysts, which are effective under acidic as well basic conditions, the presence of a base is indispensable when gold catalyst is used. This is attributed to the inactivity of gold in the hydride abstraction from an alcohol. Compared with Pd/C and Pt/C catalysts, Au/C catalysts showed the best stability in recycling tests, whereby neither deactivation nor metal leaching was observed. Subsequently, it was shown that smaller gold particles on metal oxides (Al$_2$O$_3$ and TiO$_2$) displayed higher reactivity than larger ones, whereas Au/C showed an opposite trend until a mean dimension of 7.5 nm was reached.[84] Generally, it is mostly considered that small particles give high activity. However, XPS analysis revealed that the activity in the case of Au/C depends not only on the size of the gold particles but also on their surface concentration. When activated carbon is used as a support, small gold particles can take up positions difficult to access by substrates.[85]

Au/C catalyst is also effective for a range of other alcohols besides diols.[86–88] Hutchings and co-workers reported that glycerol was successfully oxidized to glyceric acid with complete selectivity by using 1% Au/C catalyst under mild reaction conditions in water (60 °C, 3 h).[86] Prati and Porta found that a progressive decrease in activity and a simultaneous an increase in selectivity toward sodium glycerate was observed in the selective oxidation of glycerol when the metal-particle size was tuned from 2 to 16 nm.[87] Au/C also showed good activity in oxidizing aldehydes to the corresponding carboxylic acids in water, and, contrary to Pt/C, no deactivation of the catalyst upon recycling was observed.[88]

Recently, Corma and co-workers prepared gold nanoparticles supported on nanocrystalline ceria (Au/CeO$_2$) for se-

Scheme 4. Schematic illustration of the synthetic produce for Pd-OMC.

lective aerobic oxidation of alcohols.[89,90] In the absence of solvent and base, benzylic alcohols and aliphatic secondary alcohols were oxidized to the corresponding aldehydes or ketones, and aliphatic primary alcohols were converted into the corresponding alkyl esters ([Eq. (32)] and [Eq. (33)]). In the presence of base, primary alcohols were converted into the corresponding carboxylic acids. The key point concerning the excellent activity of Au/CeO_2 was ascribed to the presence of surface oxygen vacancy that arises from the nanometer size of ceria and the presence of positive gold species in a cluster that contains many Au^0 atoms.

$$n\text{-}C_5H_{11}\text{-CH(OH)-CH}_2\text{CH}_3 \xrightarrow[\text{no solvent, 80 °C, 3.5 h}]{\substack{Au/CeO_2\ (0.5\ \text{mol\%}) \\ O_2\ (1\ \text{atm})}} n\text{-}C_5H_{11}\text{-CO-CH}_2\text{CH}_3 \quad (32)$$

97% yield

$$\xrightarrow[\text{no solvent, 80 °C, 6 h}]{\substack{Au/CeO_2\ (0.5\ \text{mol\%}) \\ O_2\ (1\ \text{atm})}} \quad (33)$$

69% yield

Au/CeO_2 was also applied to the selective oxidation of al-lylic alcohols.[91] Compared with palladium-based catalysts, Au/CeO_2 showed higher chemoselectivity for the oxidation of allylic alcohols. The most likely reason for the high selectivity of gold catalysts is due to the different stability and steady-state concentration of metal hydrides (Pd–H and Au–H), which can promote C=C reduction and isomerization [Eq. (34)]. Under the reaction conditions applied, Au–H species is easily oxidized by dioxygen during the catalytic cycle and has a lower activity for both undesired pathways than Pd–H species.
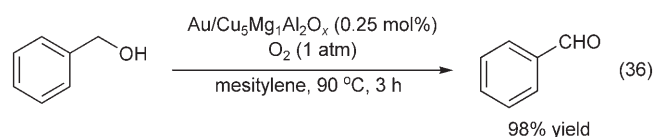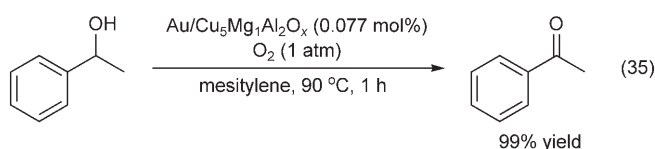
$$\xrightarrow[\substack{\text{supported Pd} \\ O_2,\ 120\ °C}]{\text{supported Au}} \quad (34)$$

polymeric material
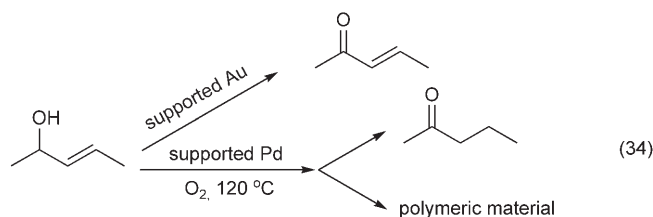
Further studies showed that gold supported on a mesoporous CeO_2 matrix catalyzes the aerobic oxidation of aldehydes and is more effective than other reported catalysts such as Pt/C/Bi catalysts.[92]

Titania was also used as a support for gold nanoparticles. Hutchings and co-workers demonstrated several gold catalysts on metal oxides prepared by coprecipitation and im-

pregnation procedures.[93] Although the activity of Au/TiO_2 was lower than that of Au/CeO_2, their further investigation of the catalyst preparation by a sol-immobilization technique resulted in high activity.[94] Whilst high TOF ($31900\ h^{-1}$) was observed in the oxidation of benzyl alcohol under pressurized conditions (10 bar) at 160 °C without solvent, selectivity toward benzaldehyde was low (55%).

Recently, Zheng and Stucky reported that a trace amount of metal carbonate, acetate, or borate (0.1 mol%) significantly improved the activity of Au/TiO_2 under solvent-free conditions.[95] However, the selectivity of benzyl alcohol to benzaldehyde was not efficient. The addition of NaOH or NEt_3 instead of the promoters above did not lead to any promotional effect. Christensen and co-workers reported Au/TiO_2-catalyzed reactions in which methyl esters were produced in high yields by the oxidation of primary alcohols in methanol with sodium methoxide.[96] Aliphatic, benzylic, and allylic alcohols as well as an alcohol with an amine functionality were oxidized to the corresponding methyl esters in good to excellent yields.

Haider and Baiker reported that gold clusters on ternary (CuMgAl) mixed oxides ($Au/Cu_5Mg_1Al_2O_x$) could catalyze the aerobic oxidation of alcohols ([Eq. (35)] and [Eq. (36)]).[97] For most of the alcohols, full conversion was achieved with high selectivity, except for primary aliphatic alcohols. 1-Phenylethanol was oxidized to acetophenone in 99% yield (TOF: $1290\ h^{-1}$), and benzyl alcohol was selectively converted into benzaldehyde in 98% yield (TOF: $130\ h^{-1}$). On the other hand, gold catalysts on binary mixed oxides $Au/Mg_3Al_1O_x$ and $Au/Cu_3Al_1O_x$ showed lower catalytic activities.

$$\xrightarrow[\text{mesitylene, 90 °C, 1 h}]{\substack{Au/Cu_5Mg_1Al_2O_x\ (0.077\ \text{mol\%}) \\ O_2\ (1\ \text{atm})}} \quad (35)$$

99% yield

$$\xrightarrow[\text{mesitylene, 90 °C, 3 h}]{\substack{Au/Cu_5Mg_1Al_2O_x\ (0.25\ \text{mol\%}) \\ O_2\ (1\ \text{atm})}} \quad (36)$$

98% yield

Chemists have paid much attention to screening various metal oxides as a support material for gold catalysts while largely ignoring the inherent advantages of polymer supports. Although organic polymers were known to stabilize gold nanoclusters, only a few examples were reported for the aerobic oxidation of alcohols. Gold nanoclusters stabilized by poly(N-vinyl-2-pyrrolidone) showed high catalytic activity for aerobic oxidation of alcohols, whereas growth of the gold clusters emerged during recycling experiments and resulted in a decrease in catalytic activity.[98,99] However, polymer compounds are still attractive because they work as

quasi-homogeneous catalysts and provide a large contact area to organic substrates.

Prati and co-workers prepared cross-linked copolymers of *N,N*-dimethylacrylamide (DMAA), 2-(methylthio)ethyl methacrylate (MTEMA), and *N,N′*-methylenebisacrylamide to immobilize gold nanoclusters inside the polymer frameworks.[100] The activity and selectivity of the catalyst (Au/MTEMA-DMAA) were studied in the oxidation of 1-butanol. Au/MTEMA-DMAA showed higher selectivity toward 1-butanal than the palladium counterpart (Pd/MTEMA-DMAA), Pd/C, Au/C, and Au-Pd/C, but the selectivity was moderate.

Recently, Kobayashi and co-workers developed a polymer-incarcerated gold catalyst (PI Au) for the selective oxidation of alcohols at room temperature and atmospheric pressure of molecular oxygen or air [Eq. (37)].[101]

$$x/y/z = 28{:}34{:}38 \tag{37}$$
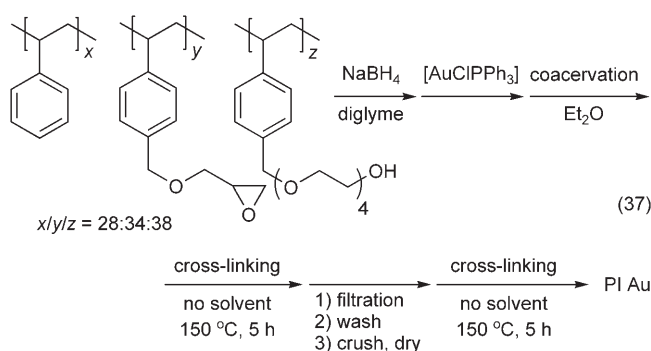
In the polymer-incarcerated (PI) method,[102–112] a copolymer that contains alcohol and epoxide moieties for cross-linking acted not only as a nanoparticle stabilizer but also as a solid support (Scheme 5).

Control experiments showed that gold nanoclusters were stabilized by the π electrons from the benzene rings of polystyrene after the reduction of chlorotriphenylphosphine gold ([AuClPPh$_3$]) by sodium borohydride (NaBH$_4$). Small gold nanoclusters (≈1 nm) were observed by TEM analysis, and no contamination by phosphorus was observed. Aromatic and aliphatic secondary alcohols were oxidized to the corresponding ketones in excellent yields, and primary aromatic and allylic alcohols were converted into the corresponding aldehydes in good yields. PI Au catalyzed heteroatom-containing (such as S and N) alcohols, which are well known to coordinate strongly to gold nanoparticles, to afford the desired ketones in high yields without metal leaching; the catalyst could be reused at least 10 times without loss of activity [Eq. (38)]. PI Au also showed high TOFs of average 20000 h^{-1} at 160 °C under solvent- and base-free conditions.
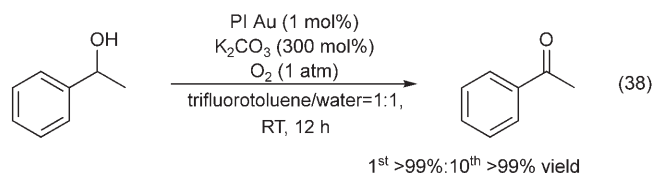
Another advantage of the PI method is that it can be applied to triphasic (gas–liquid–solid) reactions by using a microchannel reactor and a capillary column.[113–115] The epoxide moiety of a copolymer works as a functional group to make a chemical bond on the wall of the microchannel. Notably, the immobilized catalyst showed high catalytic activity due to its extremely large specific interfacial area per unit volume.

Bimetallic catalysis has always been a subject of exciting investigation for aerobic oxidation reactions because new electronic and steric features can be produced from different combinations of metals. As the resistance of gold to poisoning derives both from (by-)products and overoxidation, gold bimetallic catalysts prepared by several methods on different supports have also been studied for the aerobic oxidation of alcohols. Prati and co-workers studied the effect of gold with palladium or platinum supported on carbon for the selective oxidation of polyols (glycerol and sorbitol) and various primary alcohols under mild reaction conditions (<60 °C and <4 atm).[116–121] Bimetallic catalysts were by far more active than monometallic ones and also showed prolonged catalyst lifetimes for the selective oxidation of polyols.[116, 117] To correlate the activity with the structure of bimetallic catalysts, single-phase Pd-Au supported on activated carbon was prepared and characterized by TEM analysis, and subsequent tests showed that the single-phase Pd-Au catalyst exhibited higher activity in the selective oxidation of glycerol than the monometallic Pd/C and Au/C or the mixed-phase Pd-Au catalyst.[118] Therefore, the high activity
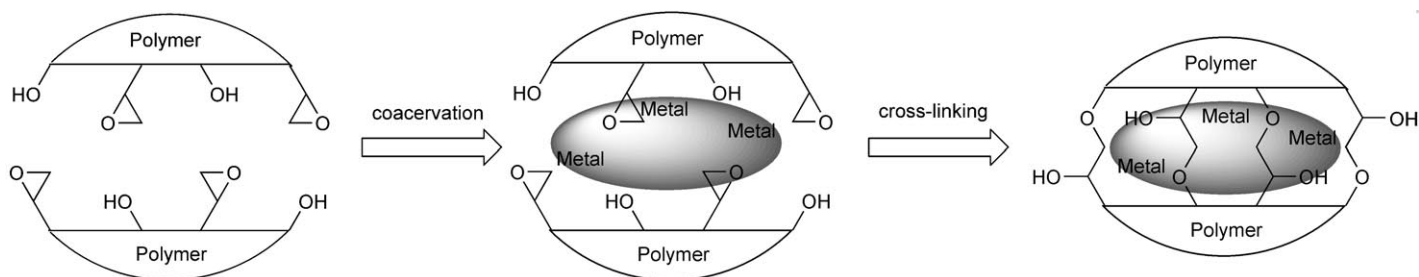
Scheme 5. Polymer-incarcerated (PI) method.

of bimetallic catalysts is undoubtedly attributed to the synergistic effect of alloying. The effect of the Au/Pd atomic ratio in the selective oxidation of glycerol was further investigated. The strong synergistic effect was found to be maximized for the composition Au$_{90}$-Pd$_{10}$, and gold-rich catalysts thus obtained showed increased durability relative to palladium-rich catalysts.[119] Furthermore, the catalytic activity of single-phase Au/Pd decreased slightly (about 10%) after reuse of 10 times for the oxidation of glycerol, and partial leaching of palladium metal was observed.[120] On the other hand, bimetallic catalysts (Au/Pd and Au/Pt) showed different synergistic effects in the selective oxidation of various primary alcohols: Au/Pd was positive, whereas Au/Pt was negative. When water was used as a solvent instead of toluene, the activities of both Au/Pd and Au/Pt were improved, with some change in selectivity as well.[121]

Hutchings and co-workers demonstrated that Au-Pd/TiO$_2$ catalysts gave the highest TOF (269000 h^{-1}) for the solvent-free oxidation of 1-phenylethanol [Eq. (39)].[122] Scanning transmission electron microscopy (STEM) and XPS results showed that the Au-Pd nanocrystals were made up of an Au-rich core with a Pd-rich shell. It was claimed that gold was thought as an electronic promoter on the basis of the results. Further study showed that Au-Pd/TiO$_2$ is most active when the weight ratio of Au to Pd is 1:1.[123]


(39)

TOF: 269 000 h^{-1}
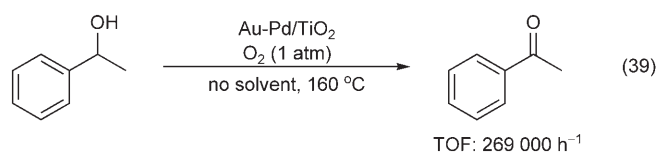
2.4. Other Metals

Although supported platinum catalysts have been investigated more than half a century ago, deactivation of platinum catalysts due to the blocking of active sites by chemical poisoning and the corrosion of the surface active sites was known to be problematic for its efficient reuse.[14] Griffin and co-workers studied the efficiency of various mono- and bimetallic Pt and Ru catalysts for the oxidation of alcohols by using high-throughput screening (HTS) techniques.[124] The selective oxidation of 1-octanol to 1-octanoic acid in water was demonstrated by using 5% Pt and 1% Bi/C under pressurized conditions (3 atm), and the catalyst could be reused three times without significant loss of activity.

Uozumi and co-workers extended their ARP method to the immobilization of platinum nanoparticles.[125] ARP-Pt was prepared from PS-PEG amino resin and the Zeise salt (K[PtCl$_3$(CH$_2$CH$_2$)]) as a metal source, and the platinum nanoparticles obtained after reduction by benzyl alcohol had a mean diameter of 5.9 nm with a very narrow size distribution [Eq. (40)]. The oxidation of various alcohols with ARP-Pt was examined in water ([Eq. (41)] and [Eq. (42)]). Not only activated alcohols such as benzylic and allylic alcohols but also nonactivated alicyclic and aliphatic alcohols

were transformed into the corresponding carboxylic acids and ketones under relatively mild conditions. In comparison with ARP-Pd as shown previously, ARP-Pt showed high catalytic activity for the oxidation of aliphatic secondary alcohols, and an organic-solvent-free workup procedure to extract the desired products by using scCO$_2$ was demonstrated.

(40)

(41)

99% yield

(42)

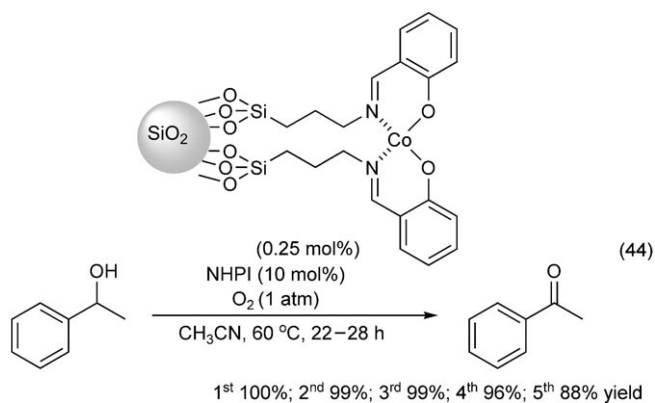1st 82%; 2nd 81%; 3rd 84%; 4th 92%; 5th 90% yield
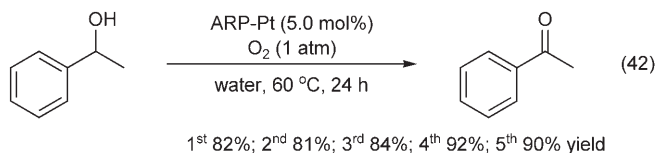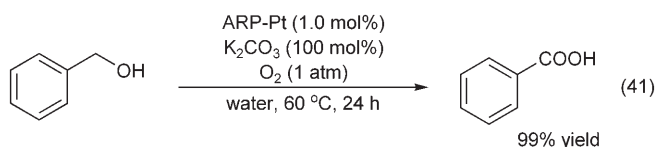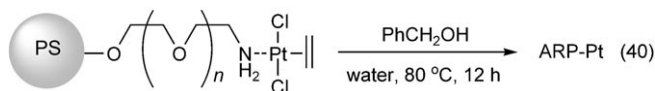
Recently, Besson and co-workers reported a study of the selective oxidation of alcohols to aldehydes or carboxylic acids by using Pt/C in dioxane/water co-solvent systems.[126, 127] The choice of solvents was important in determining the selectivity of the oxidized compounds [Eq. (43)].

(43)

Solvent	t	Conversion [%]	Selectivity
dioxane	7 h	>99%	>99% (aldehyde)
dioxane/water=1:1	<16 h	>99%	>99% (acid)
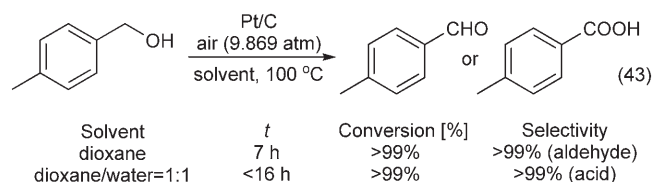
Rajabi and Karimi reported the aerobic oxidation of alcohols catalyzed by a combination of *N*-hydroxyphthalimide (NHPI) and silica-supported Co^{II} complex [Eq. (44)].[128] Primary alcohols were oxidized to the corresponding carboxylic acids in the presence of heterogeneous Co^{II} complex (0.25 mol%) and NHPI (10 mol%), although the selectivity toward carboxylic acids was not perfect. The catalyst was recovered and reused at least five times without significant loss of activity.

The first example of a recyclable molybdenum catalyst, polyaniline-supported MoO$_2$(acac)$_2$ (acac = acetylacetonate), was reported by Punniyamurthy and co-workers in 2004 [Eq. (45)].[129] The catalyst showed wide substrate scope, including primary aliphatic and heterocyclic alcohols. Interestingly, this heterogeneous catalytic system displayed higher

$$(44)$$

(0.25 mol%)
NHPI (10 mol%)
O_2 (1 atm)
CH_3CN, 60 °C, 22–28 h

1st 100%; 2nd 99%; 3rd 99%; 4th 96%; 5th 88% yield

activity than its homogeneous counterpart, $MoO_2(acac)_2$. The catalyst could be filtered and recycled three times without loss of activity.

$$(45)$$

(3 mol%)
O_2 (1 atm)
toluene, 100 °C

1st 96%; 2nd 95%; 3rd 94% yield
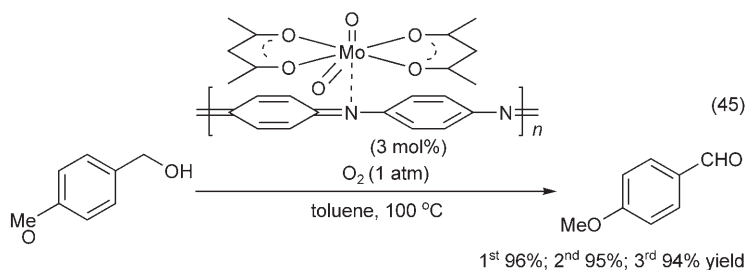
Polyoxometalates, including transition-metal ions, have been received as potential redox catalysts. Recently, Wang and co-workers reported a recyclable polyoxometalate catalyst ($Na_{6.3}Fe_{0.9}(AlMo_{11}O_{39})\cdot 2H_2O$) from sodium molybdate and aluminum nitrate nonahydrate.[130] Benzyl alcohol with 0.5 mol% of the catalyst was oxidized to benzaldehyde in 96% yield, and the catalyst could be reused at least three times successfully [Eq. (46)].


$Na_{6.3}Fe_{0.9}[AlMo_{11}O_{39}]\cdot 2H_2O$ (0.5 mol%)
air (1 atm)
toluene, 80 °C, 1 h

$$(46)$$

1st 96%; 2nd 95%; 3rd 96% yield
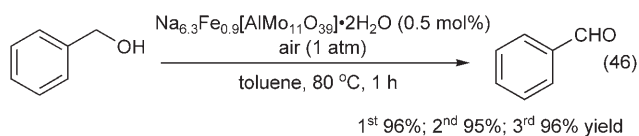
## 3. Oxidation of Alcohols under Anaerobic Conditions

The catalytic oxidation of alcohols with molecular oxygen or air is clearly superior to conventional stoichiometric inorganic oxidants with respect to atom economy and cost of the oxidizing agent.[8] The oxidative dehydrogenation of alcohols in the presence of dioxygen as a hydrogen acceptor is an effective method because only water is formed as the single final by-product. However, large-scale production has sometimes brought up the seriousness of the safety concerns

if the reaction is carried out in a flammable solvent under aerobic conditions. Transfer dehydrogenation of alcohols in the presence of a hydrogen acceptor such as alkenes or ketones under inert atmosphere would be considered an alternative method. Recently, several catalytic systems on solid support under anaerobic conditions for the conversion of alcohols into carbonyl compounds were reported.

Hayashi and co-workers found that Pd/C under ethylene atmosphere catalyzed the dehydrogenation of aromatic and allylic alcohols.[131] 1-Phenylethanol was converted into acetophenone (78% yield) in the presence of Pd/C (2.3 mol%) at 50 °C after 2 days [Eq. (47)].
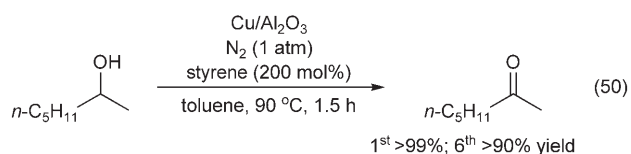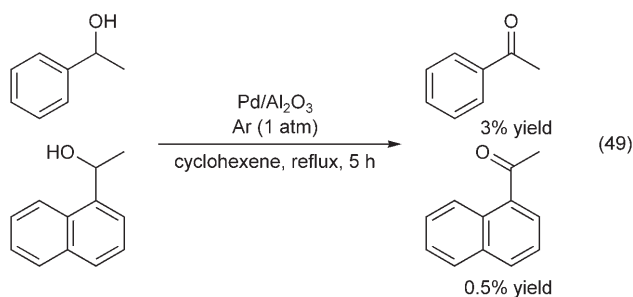

Pd/C (2.3 mol%)
ethylene (1 atm)
CH_3CN, 50 °C, 48 h

78% yield

$$(47)$$
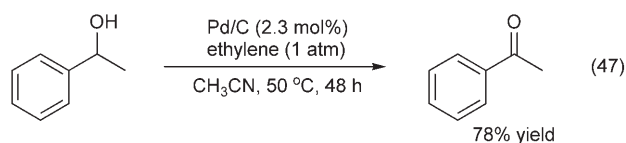
Baiker and co-workers reported Pd/Al_2O_3 for the transfer dehydrogenation of secondary aromatic alcohols.[132] Several hydrogen acceptors were investigated, and cyclohexene showed the best performance. Other olefins such as cyclopentene or styrene for the oxidation of 1-phenylethanol over Pd/Al_2O_3 did not work at all. 1-Phenylethanol with Pd/Al_2O_3 (0.57 mol%) in cyclohexene was successfully converted into acetophenone in 92% [Eq. (48)].

Pd/Al_2O_3 (0.57 mol%)
Ar (1 atm)
cyclohexene, reflux, 3 h

92% yield

$$(48)$$
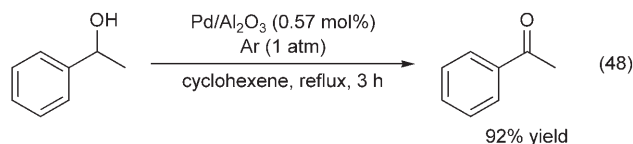
Dehydrogenation of α-methyl-1-naphthalenemethanol was very slow; it afforded less than 1% yield of the corresponding ketone. A competitive reaction of α-methyl-1-naphthalenemethanol and 1-phenylethanol was conducted [Eq. (49)]. An astonishing decrease in the reaction rate of 1-phenylethanol was observed, and this, the formation of only 3% acetophenone in contrast to the yield shown in [Eq. (48)], was thought to be caused by the strong adsorption of 1-acetonaphthone on the palladium surface.

In 2005, Ravasio and co-workers revealed that Cu/Al_2O_3 catalyzed the dehydrogenation of secondary aliphatic alcohols in the presence of styrene as a hydrogen acceptor.[133] Primary aliphatic alcohols were not transferred to the corresponding carbonyl compounds, nor did they give any other product in this catalytic system. Both complete conversion and selectivity were achieved for the dehydrogenation of 3-octanol with Cu/Al_2O_3 and styrene (200 mol%) as a hydrogen acceptor [Eq. (50)]. The catalyst could be reused six times without significant loss of activity.

$$\text{(49)}$$

$$\text{(50)}$$

phatic alcohol was the exception. 1-Phenylethanol was converted into acetophenone quantitatively in the presence of Ru/AlO(OH) (3 mol%) under argon atmosphere. The reusability of the catalyst was tested until the 10th run, and it was found that neither a decrease in activity nor leaching of ruthenium was observed [Eq. (53)]. The valance state of the immobilized ruthenium species was suggested to be mainly Ru^0, according to EDX and XPS analysis.


$$\text{(52)}$$

$$\text{(53)}$$

An acceptor-free dehydrogenation was demonstrated by two types of ruthenium-based catalysts by Park and co-workers. In 2004, a heterogeneous version of the Shvo-type ruthenium catalyst was designed for the dehydrogenation of alcohols without any hydrogen acceptors.[134] Two terminal hydroxy groups were introduced into the Shvo complex (Scheme 6) and treated with tetramethyl orthosilicate to form the solid catalyst.
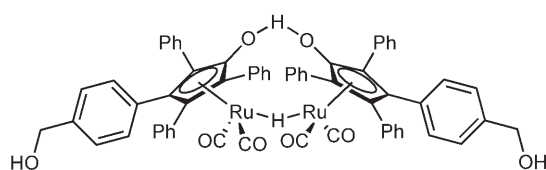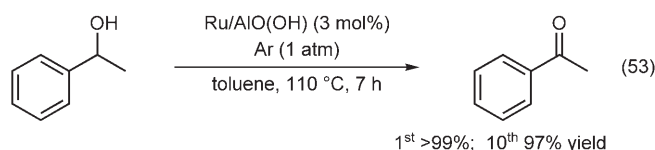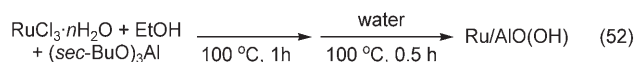

Scheme 6. The Shvo complex with terminal hydroxy groups.

The catalyst thus obtained ([Ru]-SiO$_2$) was applied to the dehydrogenation of alcohols. Acetophenone was obtained in 97% yield in the presence of [Ru]-SiO$_2$ (4.4 mol%) in toluene heated at reflux under argon atmosphere. The catalyst could be reused, although the catalytic activity gradually decreased [Eq. (51)].


$$\text{(51)}$$
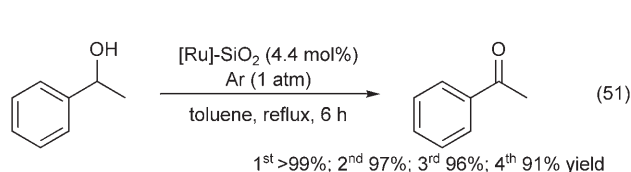
Another ruthenium-based solid catalyst was also developed from the easily accessible reagents RuCl$_3$·nH$_2$O, EtOH, and (sec-BuO)$_3$Al [Eq. (52)].[135] The catalyst (Ru/AlO(OH)) gave high activity and selectivity for various alcohols under both aerobic and anaerobic conditions, although the primary ali-

Dehydrogenation of alcohols with Ru(OH)$_x$/Al$_2$O$_3$ both in the presence of acetone as a hydrogen acceptor[136] and in the absence of hydrogen acceptor[137] was reported by Karvembu et al. In the latter catalytic system, 1-phenylethanol with Ru(OH)$_x$/Al$_2$O$_3$ (4 mol%) in toluene was converted into acetophenone in 77% yield, and Ru(OH)$_x$/Al$_2$O$_3$ retained its activity until the fourth run.

Recently, Kaneda and co-workers developed an efficient catalytic system for the oxidant-free dehydrogenation of alcohols by using silver nanoparticles on hydrotalcite (Ag/HT), which was the first silver catalyst for the dehydrogenation of alcohols under anaerobic conditions.[138] Ag/HT showed high catalytic performance except for primary aliphatic alcohols. 1-Phenylethanol with Ag/HT (0.0045 mol%) was converted into acetophenone quantitatively in p-xylene, and Ag/HT could be recovered and reused for another four runs without loss of activity [Eq. (54)]. When styrene was added as a hydrogen acceptor for the dehydrogenation of 1-phenylethanol, no transfer of hydrogen to styrene was observed at all, and only molecular hydrogen was released [Eq. (55)].

$$\text{(54)}$$

$$\text{(55)}$$
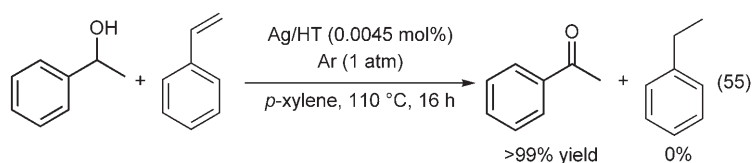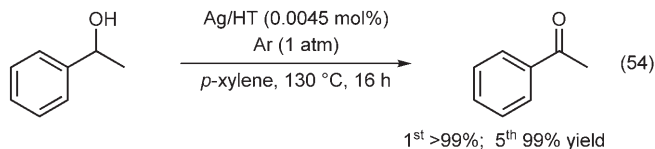
4. Oxidation of Alcohols with Hydrogen Peroxide

As well as dioxygen, hydrogen peroxide (H_2O_2) is an attractive oxidant because it produces water as the only by-product and is relatively cheap. One of the problems frequently encountered in metal-catalyzed oxidations with H_2O_2 is the concomitant decomposition of H_2O_2, which makes the use of a large excess of H_2O_2 necessary to obtain full conversion of substrates. A large number of applications of H_2O_2 to the oxidative transformations of organic compounds, in particular, metal-catalyzed epoxidations, have been recently reviewed.[6, 139, 140] Recent studies of the oxidation of alcohols with solid catalysts with H_2O_2, such as Fe^{III}/montmorillonite-K10,[141] TPAP-doped OMROSIL,[142] Ti/SiO_2,[143] polymer-supported methyltrioxorhenium (MTO),[144] tetraaza[14]annulene Cu^{II}/zeolite-Y,[145] hexaazacyclotetradecanel Cu^{II}/zeolite-Y,[146] and microporous copper and ruthenium complexes,[147] were reported.

Kumar and co-workers developed the supported polyoxometalates phosphomolybdic acid/vanadium–aluminum mixed oxide (PMA/VAMO) for the oxidation of alcohols with H_2O_2.[148] Primary benzylic alcohols were successfully oxidized in the presence of PMA/VAMO and a phase-transfer catalyst to the corresponding aldehydes in good to excellent yields. 4-Methoxybenzyl alcohol was oxidized to 4-methoxybenzaldehyde in 98% yield [Eq. (56)]. After the catalyst was filtered, washed, and heated at 250 °C, it was reused, although the activity was gradually decreased.

$$\text{PMA/VMAO} \quad 50\% \text{ aq. } H_2O_2 \quad n\text{-}C_{16}H_{33}N^+Me_3Br^- \text{ (7 mol\%)} \quad \text{toluene, } 65\,°C, 2\,h$$

(56)

98% yield, TOF: 88 h^{-1}
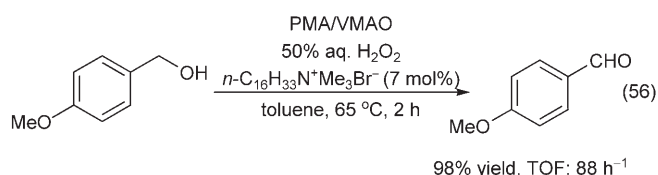
Sato and co-workers found an efficient catalytic system for the oxidation of allylic alcohols with H_2O_2.[149] Cinnamyl alcohol was oxidized to cinnamaldehyde with 5% H_2O_2 in the presence of Pt black (1 mol%) without any organic solvents. The purification of the product by distillation after filtration produced analytically pure cinnamaldehyde in 94% yield [Eq. (57)]. The recovered catalyst could be reused at least seven times without loss of activity.

$$\text{Pt Black (1 mol\%)} \quad 5\% \text{ aq. } H_2O_2 \text{ (110 mol\%)} \quad 90\,°C, 3\,h$$

(57)

94% yield
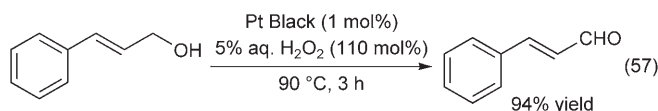
Hou and co-workers prepared the three metal coordination polymers $\{[Fe(fcz)_2Cl_2]\cdot 2CH_3OH\}_n$, $\{[Cu(fcz)_2(H_2O)]\cdot SO_4\cdot DMF\cdot 2CH_3OH\cdot 2H_2O\}_n$, and $\{[Cu(fcz)_2Cl_2]\cdot 2CH_3OH\}_n$ (fcz = 1-(2,4-difluorophenyl)-1,1-bis[(1H-1,2,4-triazol-1-yl)methyl]ethanol).[150] Their catalytic activities were investigated with benzyl alcohol as a test substrate. Benzyl alcohol was converted into benzaldehyde in 87% yield at 40 °C after 4 h in the presence of $\{[Fe(fcz)_2Cl_2]\cdot 2CH_3OH\}_n$ (0.22 mol%) with H_2O_2 as an oxidant. $\{[Fe(fcz)_2Cl_2]\cdot 2CH_3OH\}_n$ gave the best result among the three catalysts, and the catalyst was reused three times without significant loss of activity (1st run: 87%; 2nd run: 85%; 3rd run: 81%).

5. Comparative Examination of Metal-Immobilized Catalysts for the Aerobic Oxidation of Alcohols

As described above, it is evident that the three principal transition metals, palladium, ruthenium, and gold, play a central role for the aerobic oxidation of alcohols nowadays. Although it is worthwhile to evaluate these metals, it is difficult to rank them according to their catalytic performance because reaction conditions such as catalyst loading, solvent, concentration, and temperature vary, and the expected efficacy also depends on the situation. For example, the application of a given reaction to the synthesis of analogues, which is a technique in the field of combinatorial chemistry, often requires a fixed set of reaction conditions to examine a number of reactions at a time. In this context, wide substrate scope should be the first priority for the catalyst. On the other hand, for the production of a certain compound to be launched, substrate scope is not essential. Both high catalytic activity and selectivity toward the target compound as well as cost and safety would be the important factors. Here we summarize selected examples that have a high potential for the selective production of oxidized compounds to give a better understanding of the features of each immobilized metal catalyst (Table 1).

Generally, ruthenium-based catalysts have wide substrate scope, although their TOF values are not so excellent. Among the catalysts shown in Table 1, $Ru(OH)_x/Al_2O_3$ showed the widest substrate scope: primary and secondary alcohols as well as benzylic, aliphatic, and allylic ones added up to 33 substrates. Furthermore, $Ru(OH)_x/Al_2O_3$ is applicable to other transformations such as oxidation of amines (13 substrates), hydrogen-transfer reactions (29 substrates), oxidative biaryl coupling in water (10 substrates), hydration of nitriles (12 substrates), and oxidation of alkyl arenes (12 substrates) under atmospheric pressure of molecular oxygen. A TOF of 340 h^{-1} was reached in the oxidation of 1-phenylethanol in the presence of $Ru(OH)_x/Al_2O_3$ (0.1 mol%) at 150 °C under solvent-free conditions and a TOF of 40 h^{-1} was attained in the presence of $Ru(OH)_x/Al_2O_3$ (2.5 mol%) at 83 °C in trifluorotoluene as the solvent. Ru/HAP-γ-Fe_2O_3 (0.5 mol%) afforded a TOF of 91 h^{-1} in toluene at 90 °C for the same substrate. These two ruthenium-containing catalysts, $Ru(OH)_x/Al_2O_3$ and Ru/HAP-γ-Fe_2O_3, have different selectivities toward primary aliphatic alcohols. 1-Octanol with $Ru(OH)_x/Al_2O_3$ was converted into 1-octanal in the presence of hydroquinone as an additive, whereas 1-dodecanol with Ru/HAP-γ-Fe_2O_3 was oxidized to 1-dodecanoic acid without any additives. In both cases, com-

Table 1. Comparison of selective oxidation methods with immobilized metal catalysts.

Entry	Metal	Catalyst (loading [mol%])	Substrate	Conditions	Yield [%]	Substrate scope[a]	Reuse (no. of times)	TOF [h^{-1}] (solvent-free conditions)	Reference
1	Ru	Ru/HAP (17)	benzyl alcohol	$C_6H_5CH_3$, 80°C, 3 h, O_2, 1 atm	>99	A, B, C, D, E, F, K	4		[41]–[43]
2	Ru	RuCo/HAP (1.7)	benzyl alcohol	$C_6H_5CH_3$, 90°C, 0.75 h, O_2, 1 atm	>99	A, B, C, D, E	–[b]		[47]
3	Ru	RuO$_2$/FAU (7.8)	benzyl alcohol	$C_6H_5CH_3$, 80°C, 1.5 h, air, 1 atm	>99	A, C, D, E, F	5		[48]
4	Ru	Ru(OH)x/Al$_2$O$_3$ (2.5)	benzyl alcohol	$C_6H_5CF_3$, 83°C, 1 h, O_2, 1 atm	>99	A, B, C, D, E, F, K	7	340 (1-phenylethanol, 150°C)	[49]–[55]
5	Ru	Ru(OH)x/Fe$_3$O$_4$ (3.8)	1-phenylethanol	$C_6H_5CH_3$, 105°C, 2 h, O_2, 1 atm	>99	A, B, D, E, K	2		[63]
6	Ru	Ru/HAP-γ-Fe$_2$O$_3$ (0.50)	benzyl alcohol	$C_6H_5CH_3$, 90°C, 1 h, O_2, 1 atm	98	A, B, D, E, I	2		[64]
7	Ru	PI Ru (5.0) TEMPO (15)	4-methoxylben-zyl alcohol	$(CH_2Cl)_2$, 80°C, 3 h, O_2, 1 atm	98	A, B, C, D, E	10		[65]
8	Ru	HB Ru (5.0)	4-methylbenzyl alcohol	$C_6H_5CH_3$, 110°C, 2 h, O_2, 1 atm	97	A, B, D, E	5		[66]
9	Ru	Ru/AlO(OH) (3.0)	1-phenylethanol	$C_6H_5CH_3$, 110°C, 7 h, Ar, 1 atm	>99	A, B, D, E, F	10		[135]
10	Pd	Pd/HT (5.0) Pyridine (20)	benzyl alcohol	$C_6H_5CH_3$, 80°C, 2 h, O_2, 1 atm	>99	A, B, C, D, E, F	3		[68]–[70]
11	Pd	Pd/HAP (0.20)	benzyl alcohol	$C_6H_5CF_3$, 90°C, 1 h, O_2, 1 atm	99	A, B, D, E, F	3	9800 (1-phenylethanol, 160°C)	[71], [72]
12	Pd	ARP-Pd (20)	cyclooctanol	H_2O, reflux, 20 h, O_2, 1 atm	88	A, B, D, F, I	4		[73]
13	Pt	ARP-Pt (5.0)	1-phenylethanol	H_2O, 60°C, 24 h, O_2, 1 atm	82	B, D, F, G, H, I	5		[125]
14	Pd	Pd/SBA-15 (0.40) K$_2$CO$_3$ (100)	benzyl alcohol	$C_6H_5CH_3$, 80°C, 3.5 h, O_2, 1 atm	>99	A, B, D, E, F, J	12		[75]
15	Pd	Pd/AlO(OH) (0.20)	1-phenylethanol	$C_6H_5CF_3$, 80°C, 2 h, O_2, 1 atm	>99	A, B, D, K	10	560 (1-phenylethanol, 150°C)	[76]
16	Pd	Pd/Al$_2$O$_3$-ads (0.0062)	benzyl alcohol	neat, 88°C, 8 h, O_2, 1 atm	93	A, C, D	6	1950 (benzyl alcohol, 88°C)	[79]
17	Au	Au/CeO$_2$ (0.50)	3-octanol	neat, 80°C, 3.5 h, O_2, 1 atm	97	A, B, D, E, F, G, H, I, J,	4	12500 (1-phenylethanol, 160°C)	[89], [90]
18	Au	PI Au (1.0) K$_2$CO$_3$ (300)	1-phenylethanol	$C_6H_5CF_3$/H_2O, RT, 5 h O_2, 1 atm	>99	A, B, D, E	10	20000 (1-phenylethanol, 160°C)	[101]
19	Au	Au/Cu$_5$Mg$_1$Al$_2$O$_x$ (0.077)	1-phenylethanol	$C_6H_3(CH_3)_3$, 90°C, 1 h O_2, 1 atm	>99	A, B, D, E	–[b]	11700 (1-phenylethanol, 160°C)	[97]
20	Ag	Ag/HT (0.0045)	1-phenylethanol	$C_6H_4(CH_3)_2$, 130°C, 16 h Ar, 1 atm	>99	A, B, D, E	5		[138]

[a] Letters represent tested transformations into oxidized compounds that afforded more than 50% yield. A = primary benzylic alcohols to aldehydes, B = secondary benzylic alcohols to ketones, C = primary aliphatic alcohols to aldehydes, D = secondary aliphatic alcohols to ketones, E = primary allylic alcohols to aldehydes, F = secondary allylic alcohols to ketones, G = primary benzylic alcohols to carboxylic acids, H = primary allylic alcohols to carboxylic acids, I = primary aliphatic alcohols to carboxylic acids, J = primary aliphatic alcohols to esters, K = other oxidative transformations instead of alcohols under aerobic conditions. [b] Not mentioned.

plete selectivity was established. Ru/AlO(OH) is applicable to both aerobic and anaerobic conditions, and the latter was examined without hydrogen acceptor under argon atmosphere. Although several catalysts prepared from palladium or gold sources are superior to those prepared from ruthenium sources with regard to TOF, immobilized ruthenium catalysts would give a better choice given that high selectivity of the oxidized compound and wide substrate generality are indispensable at the present moment.

Palladium-based catalysts often show higher activity than ruthenium-based ones. Pd/Al$_2$O$_3$-ads prepared by an adsorption method gave a TOF of 1950 h^{-1} in the oxidation of benzyl alcohol at 88°C without solvent. Pd/HAP (4× 10^{-4} mol%) showed a TOF of 9800 h^{-1} in the solvent-free

oxidation of 1-phenylethanol at 160°C, and Pd/HAP (0.2 mol%) gave a TOF of 490 h^{-1} in trifluorotoluene at 90°C. Pd/HAP can also be applied to the oxidation of alcohols in water. Among other characteristics, the use of water has the advantage of decreasing the safety concerns when the reactions are conducted under aerobic conditions with flammable liquids. ARP-Pd and ARP-Pt prepared from amphiphilic polystyrene–poly(ethylene glycol) resin can catalyze the oxidation of alcohols in water. These catalysts provide highly concentrated reaction environments for organic substrates in aqueous media due to the amphiphilic nature of the support material. These catalysts have different selectivities in the oxidation of benzyl alcohol, that is, ARP-Pd affords benzaldehyde but ARP-Pt gives benzoic acid. Pd/

AlO(OH) also gave high activity for the oxidation of 1-phenylethanol in water, and, notably, dual catalytic performance of both hydrogenation and oxidation was attained. One-pot transformation of cholesterol to cholestan-3-one was achieved. Pd/SBA-15 showed high activity for various substrates and excellent reusability of the catalyst, but the oxidation of 2-substituted benzylic alcohols with Pd/SBA-15 was not successful. Steric hindrance by the quasi-two-dimensional surface of the nanoparticles was claimed to cause the low activity for these substrates, associated with the oxidation of 2-hydroxybenzyl alcohol catalyzed by gold nanoclusters on poly(N-vinyl-2-pyrrolidone) (PVP).

Recently, gold nanoparticles have emerged as viable catalysts for the aerobic oxidation of alcohols, which give high TOFs compared with ruthenium- and palladium-based catalysts, although an inorganic base and water are sometimes needed. Au/CeO$_2$ catalyzed various alcohols to the corresponding aldehydes, ketones, acids, and esters. Although it is difficult to obtain excellent selectivity in some cases, it is remarkable that a TOF of 12 500 h^{-1} was reached in the oxidation of 1-phenylethanol under solvent- and base-free conditions. The gold nanoparticles formed on Au/CeO$_2$ were claimed to interact with the ceria surface, which stabilized the positive oxidation states of gold by creating Ce^{III} and oxygen-deficient sites in the ceria. PI Au showed high TOF (20 000 h^{-1}) and excellent reusability of the catalyst. Various alcohols were converted into the corresponding carbonyl compounds at room temperature in excellent yield. The polystyrene-based catalyst PI Au gives an opportunity to perform the smooth oxidation of alcohols at ambient temperature. This indicates that weak interactions of the gold clusters with the benzene rings of polystyrene-based polymers play a crucial role in enhancing catalytic activities of gold-catalyzed reactions. The bimetallic catalyst Au-Pd/TiO$_2$ afforded the highest TOF (269 000 h^{-1}), and the selectivity of benzyl alcohols to benzaldehyde was up to 96 %. As mentioned above, the catalytic activities of gold-based catalysts are superior to those of other immobilized metal catalysts. Although silver-based catalysts seldom appear the oxidation of alcohols, Ag/HT showed interesting properties for the dehydrogenation of alcohols under anaerobic conditions. Neither the isomerization nor the hydrogenation product was observed for the oxidant-free dehydrogenation of cinnamyl alcohol; only cinnamaldehyde was obtained quantitatively. Ag/HT is also applicable to the aerobic oxidation of alcohols. On the other hand, these gold- and silver-based catalysts often do not give good activity and selectivity in the oxidation of primary alcohols to aldehydes.

6. Conclusions and Perspectives

The environmentally benign conversion of alcohols into carbonyl compounds by using solid catalysts described herein can contribute to the sustainable development of chemistry. Although much progress has been made in this field, there is plenty of room for further development. Lower catalyst loading under ambient temperature, prolongation of catalyst lifetimes, and operation under safe reaction conditions are challenging topics for reaching the ultimate green processes. Interdisciplinary studies based on new technology for the stabilization of nanoparticles, the creation of mesoporous materials with large surface areas, and characterization techniques for solid catalysts would accelerate research in this area and allow chemists to design a number of catalysts with various interesting properties.

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