1. Introduction

The development of efficient heterogeneous catalysts is of particular research interest because of the potential to realize green functional group transformations\(^1\)\(^-\)\(^7\). The immobilization of catalytically active species onto (inert) solid supports and the attachment of active homogeneous catalysts through ionic or covalent bonds onto surface modified supports have been extensively investigated\(^1\)\(^-\)\(^7\). However, various drawbacks are frequently observed; for example, (i) the intrinsic catalytic performance of the parent active homogeneous catalyst is often decreased by immobilization or attachment, and/or (ii) leaching of the active species is sometimes observed. Therefore, the development of truly stable heterogeneous catalysts with at least comparable or preferably better catalytic performance than the corresponding homogeneous catalyst is very important. In addition, the development of effective new transformations possible only by using such heterogeneous catalysts will be very significant.

Our strategy to design highly active heterogeneous catalysts is to create monomerically (or at least highly) dispersed metal hydroxide species on appropriate supports. Combined action of the Lewis acid and Brønsted base sites on the same metal sites can activate various types of organic substrates; for example, alcohols → alkoxides, amines → amides, nitriles → \(\eta^2\)-amidates, and terminal alkynes → acetylides. In the presence of supported ruthenium hydroxide catalyst (Ru(OH)\(_x\)/Al\(_2\)O\(_3\)), oxidative dehydrogenation of alcohols and amines efficiently proceeds, forming the corresponding carbonyl compounds (aldehydes and ketones) and nitriles, respectively. Ru(OH)\(_x\)/Al\(_2\)O\(_3\) can also catalyze hydration of nitriles to primary amides, ammoxidation of primary alcohols to nitriles, and formal \(\alpha\)-oxygenation of primary amines to primary amides. In addition, oxidative alkyne homocoupling and 1,3-dipolar cycloaddition efficiently proceed in the presence of supported copper hydroxide catalysts (Cu(OH)\(_x\)/OMS-2 for homocoupling, Cu(OH)\(_x\)/TiO\(_2\) and Cu(OH)\(_x\)/Al\(_2\)O\(_3\) for cycloaddition; where OMS-2 is manganese oxide-based octahedral molecular sieve, KMn\(_8\)O\(_{16}\)). The catalytic processes for these transformations are heterogeneous, and the catalysts can be reused several times with maintained high catalytic activity.

Keywords
Supported metal hydroxide, Heterogeneous catalysis, Concerted activation, Lewis acid, Brønsted base, Green chemistry
nated activation of a nitrile by the Lewis acid and Brønsted base paired sites on the same metal site provided about a 10^10-fold rate acceleration compared with the common OH–-catalyzed nitrile hydration (Fig. 2). Therefore, we successfully achieved various green functional group transformations using these supported metal hydroxide catalysts.

The present review article summarizes our achievements with heterogeneously catalyzed green functional group transformations using supported metal hydroxide catalysts as follows: (i) oxidative dehydrogenation of alcohols and amines by Ru(OH)x/Al2O310), (ii) hydration of nitriles by Ru(OH)x/Al2O314), (iii) ammoxidation of primary alcohols by Ru(OH)x/Al2O315,16), (iv) formal α-oxygenation of primary amines by Ru(OH)x/Al2O317), (v) oxidative homocoupling of terminal alkynes by Cu(OH)x/OMS-218), and (vi) 1,3-dipolar cycloaddition of azides to terminal alkynes by Cu(OH)x/TiO219).

2. Oxidative Dehydrogenation of Alcohols and Amines by Ru(OH)x/Al2O3

Oxidative dehydrogenation of alcohols and amines are very important reactions because of the versatile use of the oxidation products, i.e., aldehydes, ketones, nitriles, and imines, as starting materials for important pharmaceuticals, agrochemicals, fragrances, and fine chemicals20,25). Numerous heterogeneous catalysts have been developed for oxidative dehydrogenation of alcohols and amines using O2 as the terminal oxidant22,23). The performance, applicabilities, and limitations of recently reported heterogeneous catalysts for aerobic oxidative dehydrogenation of alcohols have been comprehensively summarized22,23). Our10) and other research groups24,26 have focused on ruthenium hydroxide Ru(OH)x (hydrate oxide RuO2·nH2O) for the aerobic oxidative dehydrogenation of alcohols.

Easily prepared Ru(OH)x/Al2O3 has the potential to act as an efficient heterogeneous catalyst for oxidative dehydrogenation of various structurally diverse alcohols and primary amines using O2 or air (1 atm) as the terminal oxidant (Fig. 3). The reaction hardly proceeds in the absence of catalysts or in the presence of only supports, unsupported ruthenium hydroxide species Ru(OH)x, or anhydrous RuO2. A simple physical mixture of Ru(OH)x, and Al2O3 had no catalytic activity. We also prepared a supported ruthenium chloride catalyst (RuClx/Al2O3). Oxidative dehydrogenation of benzyl alcohol hardly proceeded with RuClx/Al2O3 under the conditions described in Fig. 3. RuClx/Al2O3 supported catalyst was then treated with an aqueous solution of NaOH (0.1 M) at room temperature.
Oxidative dehydrogenation of benzyl alcohol with the treated catalyst under the same conditions showed high catalytic activity of the base-treated RuCl/Al$_2$O$_3$ and resulted in a quantitative yield of benzaldehyde. These results suggest that highly dispersed ruthenium hydroxide species are important for the oxidative dehydrogenation of alcohols.

Aerobic oxidative dehydrogenation of various types of structurally diverse alcohols efficiently proceeded in the presence of Ru(OH)/Al$_2$O$_3$, forming the corresponding aldehydes and ketones (Fig. 3). Oxidative dehydrogenation of benzylic alcohols with electron-donating or electron-withdrawing substituents at each position of the benzene rings also efficiently proceeded to form the corresponding benzaldehydes. Allylic alcohols were converted to the corresponding α,β-unsaturated carbonyl compounds without hydrogenation of the double bonds. This catalytic system could also be applied to the conversion of aliphatic and heteroaromatic alcohols. Furthermore, various types of structurally diverse primary amines including benzylic, allylic, and aliphatic amines could be converted into the corresponding nitriles (Fig. 3). In addition, secondary amines such as N-phenylaniline and dibenzylamine could be converted into the corresponding imines (Fig. 3). These oxidative dehydrogenation reactions completely stopped after removing the Ru(OH)/Al$_2$O$_3$ catalyst by hot filtration. X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and X-ray absorption fine structure (XAFS) analyses confirmed that the state of the ruthenium species in Ru(OH)/Al$_2$O$_3$, e.g., the degree of polymerization and oxidation state, hardly changed after these reactions. Moreover, Ru(OH)/Al$_2$O$_3$ could be reused several times with maintained high catalytic performance for these reactions.

The addition of radical scavengers such as 2,6-di-tert-butyl-4-methylphenol and hydroquinone did not affect the reaction rates and product selectivities, suggesting that radical intermediates were not formed during these oxidative dehydrogenation reactions. Competitive oxidative dehydrogenation of benzyl alcohol and 1-phenylethanol with Ru(OH)/Al$_2$O$_3$ showed that the dehydrogenation of benzyl alcohol proceeded ca. 10 times faster than that of 1-phenylethanol. This faster oxidation of benzyl alcohol even in the presence of more reactive 1-phenylethanol suggests the formation of alkoxide species$^{27)} _{29)}$. The competitive dehydrogenation of $p$-substituted benzyl alcohols had a Hammett $\rho$ value of $-0.46$. This negative Hammett $\rho$ value can be interpreted in terms of the formation of a carbenium ion-type transition state through hydride abstraction, in which electron-donating substituents stabilize the carbenium ion-type transition state$^{30)}$. On the basis of these results, a possible reaction mechanism for Ru(OH)/Al$_2$O$_3$-catalyzed oxidative dehydrogenation of alcohols is proposed (Fig. 4). The oxidative dehydrogenation of primary and secondary amines also proceeds through the same pathway as that for alcohols; that is, amide formation followed by β-elimination. This experimentally proposed reaction mechanism was further theoretically investigated by density functional theory (DFT) calculations using model catalysts “Ru(OH)$(\text{OH}_2)_2$” (Fig. 5) and “RuCl$(\text{OH}_2)_2$” for Ru(OH)/Al$_2$O$_3$ and RuCl/Al$_2$O$_3$, respectively$^{31)}$. Using 2-butanol as the model substrate, the calculated activation energy for alkoxide formation (step 1 in

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**Fig. 3** Ru(OH)/Al$_2$O$_3$-catalyzed Oxidative Dehydrogenation of Alcohols and Amines$^{10)} _{13)}$

**Fig. 4** Possible Reaction Mechanism for the Ru(OH)/Al$_2$O$_3$-catalyzed Oxidative Dehydrogenation of Alcohols$^{10)} _{13)}$
Fig. 4 was 27.7 \text{kJ mol}^{-1} with \text{Ru(OH)}_3(\text{OH}_2)_3 and 123.2 \text{kJ mol}^{-1} with \text{RuCl}_3(\text{OH}_2)_3. Therefore, alkoxide formation with \text{Ru(OH)}_x/\text{Al}_2\text{O}_3 would proceed much more easily than with \text{RuCl}_x/\text{Al}_2\text{O}_3. This calculation result is consistent with the above-mentioned experimental results using \text{Ru(OH)}_x/\text{Al}_2\text{O}_3 and \text{RuCl}_x/\text{Al}_2\text{O}_3. The activation energy for β-elimination (step 2 in Fig. 4) was calculated to be 77.2 \text{kJ mol}^{-1} (Fig. 5). Therefore, step 2 is included in the rate-determining step for the present oxidative dehydrogenation. The kinetic isotope effects also support this conclusion\textsuperscript{10).}

The activation energies for the reverse reactions of β-elimination (hydride readdition) and alkoxide formation were calculated to be 38.5 \text{kJ mol}^{-1} and 19.8 \text{kJ mol}^{-1}, respectively (Fig. 5). Therefore, racemization of 2-butanol can readily proceed in the absence of \text{O}_2. Indeed, racemization of various optically active secondary alcohols efficiently proceeded in the presence of \text{Ru(OH)}_x/\text{Al}_2\text{O}_3 under "anaerobic" conditions (Fig. 6)\textsuperscript{32,33)}.

For the reaction of the hydride species with \text{O}_2 (step 3 in Fig. 4), the coordination of the electron-donating ligands (in particular, an alcohol molecule and \text{H}_2\text{O}) to form the six-coordinated ruthenium monohydride (Ru-H) species is the key to promote \text{O}_2 insertion into the hydride species\textsuperscript{31}. Electron donation from these ligands to the hydride species can weaken the Ru-H bond, resulting in lower activation energy for the \text{O}_2 insertion step. Then, the hydroxide (or alkoxide) species is regenerated with the formation of \text{H}_2\text{O}.

3. Hydration of Nitriles by \text{Ru(OH)}_x/\text{Al}_2\text{O}_3

Amides are one of the most important compounds in modern chemistry as well as biology, and are widely utilized as raw materials for engineering plastics, fragrance intensifiers, anti-block reagents, color pigments for inks, detergents, lubricants, and starting materials for peptide and protein synthesis\textsuperscript{34,35).} Aminolysis of activated carboxylic acid derivatives, e.g., acid chlorides and acid anhydrides, with amines is still widely utilized for synthesis of amides\textsuperscript{36,37).} However, aminolysis requires stoichiometric reagents, e.g., \text{SOCl}_2, for the pre-activation of carboxylic acids. In addition, at least equimolar amounts of byproducts are formed not only during the aminolysis but also the pre-activation step; a typical procedure for the synthesis of nicotinamide is shown in Fig. 7\textsuperscript{36,37).} Thus, the development of green catalytic procedures for the synthesis of amides from readily available and inexpensive starting materials is a very important subject\textsuperscript{38).} Currently, benzonitrile or its substitutes and acrylonitrile are industrially produced by ammoxidation using \text{O}_2 as the oxidant and \text{NH}_3 as the nitrogen source. Thus, nitrile hydration is a reliable procedure from both environmental and economical viewpoints for the synthesis of benzanide derivatives and acrylamide.

As mentioned in Section 1, nitrile hydration can be promoted by the coordinated activation of nitriles by the Lewis acid and Brønsted base paired sites (Fig. 2)\textsuperscript{39).} Inspired by this pioneering work, we prepared various types of supported metal hydroxide catalysts for nitrile hydration. Fortunately, we found that nitrile hydration
efficiently proceeded in water in the presence of several metal hydroxide catalysts; in particular, Ru(OH)$_x$/Al$_2$O$_3$ showed high catalytic activity and selectivity$^{14)}$. The potential of the Ru(OH)$_x$/Al$_2$O$_3$-catalyst system for the synthesis of various types of structurally diverse nitriles is summarized in Fig. 8. Benzonitriles were hydrated to the corresponding benzamides with little change in the reaction rates caused by the electronic variation due to substituents on the benzene rings. In addition, Ru(OH)$_x$/Al$_2$O$_3$ successively catalyzed the hydration of heteroaromatic nitriles. Less reactive aliphatic nitriles could also be selectively hydrated to the corresponding aliphatic primary amides without formation of carboxylic acids.

After the hydration of benzonitrile was completed, Ru(OH)$_x$/Al$_2$O$_3$ could readily be separated from the reaction mixture by simple hot filtration, and no ruthenium was detected in the filtrate (Fig. 9). The crystals could easily be retrieved from the water solvent by simple decantation. Thus, the present hydration process was totally free of organic solvent even in the workup process. The observed catalysis reaction was truly heterogeneous in nature. In addition, the retrieved catalyst could be reused at least twice for the hydration of benzonitrile.

Recently, we found that hydration of various types of nitriles efficiently proceeded in the presence of amorphous MnO$_2$ (with relatively large BET surface area, 304 m$^2$ g$^{-1}$) using only 2 equiv. (or less) of water with respect to the nitrile$^{39)}$. Such MnO$_2$-catalyzed nitrile hydration efficiently proceeded even without any solvents$^{39)}$.

4. Ammoxidation of Primary Alcohols by Ru(OH)$_x$/Al$_2$O$_3$

Nitriles are an important class of chemicals that are widely used as starting materials for various important pharmaceuticals, agrochemicals, and fine chemicals$^{40)}$–$^{43)}$. The SN2 substitution of alkylhalides, the Sandmeyer reaction, and the Wittig reaction are the most commonly utilized procedures for laboratory scale nitrile synthesis$^{40)}$–$^{43)}$. Oxidative dehydrogenation of primary amines is a good candidate, as mentioned in Section 2. Ammoxidation is an attractive procedure for green nitrile synthesis.

Ru(OH)$_x$/Al$_2$O$_3$ showed high catalytic performance for ammoxidation of primary alcohols to nitriles using a THF (or 1,4-dioxane) solution of NH$_3$ in the presence of air as the oxidant (Fig. 10)$^{15),16)}$. Ammoxidation of benzylic alcohols, which contain electron-donating as well as electron-withdrawing substituents, efficiently proceeded, giving the corresponding substituted benzonitriles. Aromatic allylic alcohols were converted to the corresponding unsaturated nitriles without hydration, isomerization, or hydration of the double bonds. Heteroaromatic alcohols were also converted into the corresponding heteroaromatic nitriles. Although the present system was applicable to the ammoxidation of benzylic, aromatic allylic, and heteroaromatic alcohols, the reaction of simple aliphatic alcohols was unfortunately unsuccessful; for example, 1-octanol gave only 4 % yield of n-octanenitrile under the conditions described in Fig. 10. This is a limitation of the present Ru(OH)$_x$/Al$_2$O$_3$-catalyzed ammoxidation method.

The reaction profiles for the ammoxidation of benzyl alcohol showed that benzaldehyde was initially produced followed by the formation of benzonitrile. Moreover, Ru(OH)$_x$/Al$_2$O$_3$ showed high catalytic performance for the transformation of various types of
aldehydes to the corresponding nitriles under the conditions described in Fig. 10\(^{(15,16)}\). In particular, aliphatic aldehydes could be converted into the corresponding aliphatic nitriles\(^{(15,16)}\).

The present ammoxidation reaction possibly proceeds through three sequential reactions of (i) aerobic oxidative dehydrogenation of the alcohol to aldehyde, (ii) dehydrative condensation of the aldehyde and NH\(_3\) to aldimine, and (iii) aerobic oxidative dehydrogenation of the aldimine to form the corresponding nitrile as the final product. The observed catalysis was intrinsically heterogeneous, and the catalyst could be reused several times.

5. **Formal \(\alpha\)-Oxygenation of Primary Amines by Ru(OH)\(_x\)/Al\(_2\)O\(_3\)**

As mentioned in Section 3, nitrile hydration is one of the most reliable procedures for the synthesis of benzamide derivatives and acrylamide. On the other hand, other nitriles have generally been synthesized by expensive non-green procedures\(^{(40)}\)–\(^{(43)}\), so that nitrile hydration is not the best choice. \(\alpha\)-Oxygenation of primary amines would be one of the most useful synthetic procedures for primary amines. However, in general, oxygenation of the \(\alpha\)-position of primary amines is very difficult, although in-situ generation of strong oxidant RuO\(_4\) from RuO\(_2\)+\(\cdot\)H\(_2\)O and NaIO\(_4\) has been utilized with protection of the amino groups, for example (Fig. 11)\(^{(44)}\). As mentioned in Sections 2 and 3, Ru(OH)\(_x\)/Al\(_2\)O\(_3\) acts as an efficient heterogeneous catalyst for oxidative dehydrogenation of primary amines to nitriles as well as hydration of nitriles to primary amines. Therefore, sequential one-pot performance of these two reactions would represent “formal” \(\alpha\)-oxygenation of primary amines to primary amides.

Fortunately, in the presence of Ru(OH)\(_x\)/Al\(_2\)O\(_3\), various primary amines are efficiently converted into the corresponding primary amides in water using air as the only oxidant\(^{(17)}\). The potential of the Ru(OH)\(_x\)/Al\(_2\)O\(_3\)-catalyzed formal \(\alpha\)-oxygenation of primary amines to primary amides is summarized in Fig. 12. The \(\alpha\)-oxygenation of benzylamine derivatives efficiently proceeded to form the corresponding benzamide derivatives. Nicotinamide could be obtained from 3-picolylnamine. In addition, non-activated linear, branched, and cyclic aliphatic amines could be converted into the corresponding aliphatic primary amides. Catalysis of this transformation was heterogeneous, and Ru(OH)\(_x\)/Al\(_2\)O\(_3\) could be reused without significant loss of catalytic performance.

Quite recently, we found that manganese oxide-based octahedral molecular sieve (OMS-2, KMn\(_8\)O\(_{16}\), Fig. 13)\(^{(55)}\)–\(^{(57)}\) could act as an efficient reusable heterogeneous catalyst for formal \(\alpha\)-oxygenation of primary amines to primary amides (Fig. 13)\(^{(48)}\). In addition, amidation of primary alcohols\(^{(49)}\)–\(^{(50)}\) and alkylarenes\(^{(51)}\) using NH\(_3\) as the nitrogen source also efficiently proceeded in the presence of OMS-2.
6. Oxidative Homocoupling of Terminal Alkynes by Cu(OH)\(_x\)/OMS-2

Diyne derivatives are key structural elements for natural product synthesis, polymer chemistry, and supramolecular chemistry\(^{52}\). Oxidative homocoupling of terminal alkynes is one of the most widely utilized procedures for the synthesis of symmetrical diynes\(^{52}\). We found that supported copper hydroxide species on TiO\(_2\) (Cu(OH)\(_x\)/TiO\(_2\), with mean Cu oxidation state of \(\uparrow\uparrow\)\(^{2}\)) could catalyze the aerobic oxidative homocoupling of terminal alkynes\(^{53}\). Various types of terminal alkynes could be converted into the corresponding diynes. However, the Cu(OH)\(_x\)/TiO\(_2\)-catalyzed system had the serious problem of formation of inactive (polymeric) copper(I) acetylide species (Fig. 14, right) during the homocoupling, probably due to the slow reoxidation of Cu(I) species with O\(_2\). As a result, severe deactivation of the Cu(OH)\(_x\)/TiO\(_2\) catalyst was observed.

To overcome such deactivation, the reoxidation rate of the reduced copper species should be increased. A “biomimetic oxidation strategy” has been developed using electron-transfer mediators (ETMs) to lower the activation energies between reduced catalysts and oxidants\(^{54}\). Based on this biomimetic oxidation strategy, we utilized OMS-2 as the support as well as the ETM for the copper hydroxide species for the following reasons (Fig. 15): OMS-2 has (i) thermodynamically suitable redox potential for reoxidation of Cu(I) using O\(_2\), (ii) high electron-conduction property, (iii) oxygen reduction ability, and (iv) relatively large (external) surface area\(^{45}\)~\(^{47}\).

As we expected, Cu(OH)\(_x\)/OMS-2 had high catalytic performance for the homocoupling of terminal alkynes (Fig. 16)\(^{18}\). In sharp contrast to Cu(OH)\(_x\)/TiO\(_2\)\(^{53}\), little deactivation of Cu(OH)\(_x\)/OMS-2 was observed, and Cu(OH)\(_x\)/OMS-2 could be reused for the homocoupling of phenylacetylene at least thirteen times without appreciable loss of its high catalytic activity\(^{18}\).

To investigate the mechanisms of OMS-2 in detail, control experiments were performed with the following findings. Treatment of Cu(OH)\(_x\)/TiO\(_2\) (Cu: 10 \(\mu\)mol) with phenylacetylene under an Ar atmosphere converted an almost equimolar amount of phenylacetylene with respect to the copper species into the corresponding diyne. On the other hand, similar treatment of Cu(OH)\(_x\)/OMS-2 (Cu: 10 \(\mu\)mol) ca. 20 times larger amount of phenylacetylene than the copper species in Cu(OH)\(_x\)/OMS-2, clearly showing that reoxidation of the reduced Cu(I) species occurs even under Ar atmosphere in the presence of OMS-2. In addition, XPS analysis confirmed that the oxidation state of the copper species in Cu(OH)\(_x\)/OMS-2 was still \(\uparrow\uparrow\)\(^{2}\) even after the 13th reuse. Therefore, the reduced manganese species in OMS-2 is possibly reoxidized by O\(_2\) under catalytic turnover conditions\(^{45}\)~\(^{47}\).

Various types of terminal alkynes could be converted into the corresponding diynes using Cu(OH)\(_x\)/OMS-2 (Fig. 16). Phenylacetylenes with electron-donating as well as electron-withdrawing substituents at various positions were efficiently converted to the corresponding 1,4-diphenyl-1,3-butadiyne derivatives. Heteroaromatic, enyne, and silylacetylene derivatives were converted into the corresponding diynes. Homocoupling efficiently proceeded even for less reactive aliphatic alkynes. Homocoupling of propargylic alcohol and amine was also successful.
1,3-Dipolar cycloaddition of azides to terminal alkynes because the active Cu(I) species are formed efficiently proceeded to form the corresponding 1,4-disubstituted-1,2,3-triazole derivatives in the presence of Cu(OH)x/TiO2 (Fig. 17)59,60. The Cu(OH)x/TiO2-catalyzed 1,3-dipolar cycloaddition of various combinations of organic azides (including aromatic and aliphatic ones) and terminal alkynes (including aromatic, aliphatic, and double bond-containing ones) exclusively proceeded in the presence of Cu(OH)x/TiO2 to form the corresponding 1,4-disubstituted-1,2,3-triazole derivatives in a completely regioselective manner, as shown in Fig. 1759. Cu(OH)x/OMS-2 did not catalyze the 1,3-dipolar cycloaddition. However, 1,3-dipolar cycloaddition of azomethine imines to terminal alkynes efficiently proceeded to form the corresponding N,N-bicyclic pyrazolidinone derivatives in the presence of Cu(OH)x/Al2O3 (Fig. 18)57.

Fig. 17 Cu(OH)x/TiO2-catalyzed 1,3-Dipolar Cycloaddition of Azides to Terminal Alkynes

Reaction conditions: Cu(OH)x/TiO2 (2.5 mol%), azide (0.5 mmol), terminal alkyne (0.5 mmol), toluene (1.5 mL), 60 °C, Ar (1 atm).

Fig. 18 Cu(OH)x/Al2O3-catalyzed 1,3-Dipolar Cycloaddition of Azomethine Imines to Terminal Alkynes

Reaction conditions: Cu(OH)x/Al2O3 (1.5 mol%), azomethine (0.5 mmol), terminal alkyne (0.55 mmol), toluene (2 mL), 40 °C, Ar (1 atm).

7. 1,3-Dipolar Cycloaddition of Azides to Terminal Alkenes by Cu(OH)x/TiO2

As mentioned in Section 6, the copper species in Cu(OH)x/TiO2 were readily reduced to Cu(I) in the presence of terminal alkynes. This is a serious disadvantage for oxidation reactions but an advantage for 1,3-dipolar cycloaddition of azides to terminal alkynes because the active Cu(I) species are formed in-situ without additional reducing agents. As we expected, the 1,3-dipolar cycloaddition of various combinations of organic azides (including aromatic and aliphatic ones) and terminal alkynes (including aromatic, aliphatic, and double bond-containing ones) exclusively proceeded in the presence of Cu(OH)x/TiO2 to form the corresponding 1,4-disubstituted-1,2,3-triazole derivatives in a completely regioselective manner, as shown in Fig. 1759.

8. Conclusion

This review article summarized our research into efficient heterogeneously catalyzed green functional group transformations using supported metal hydroxide catalysts. Besides the above-mentioned transformations, we have successfully developed several functional group transformations using hydroxide-based heterogeneous catalysts; for example, oxygenation and aromatization of alkylarenes, oxidative homocoupling of 2-naphthols and substituted phenols, N-alkylation of amines and NH3 using alcohols as the alklylation reagents, self-condensation of primary amines to secondary amines, rearrangement of aldoximes to primary amides, and dehydration of aldoximes to nitriles. Our hydroxide-based strategy demonstrated here has high generality and applications especially in the fields of catalytic chemistry and synthetic organic chemistry.

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要 旨

danjūjinshūsuikaibutsu o kikin toshita enkōtaiyōgenjūhīkenhōkaiko no tame no gōkenō tōkōzukaihuku hakogaku

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我々は、金属水酸化物が同一金属上に、Lewis 酸と Brønsted 塩基を併せもつという性質に着目し、金属水酸化物を基盤とした固体触媒開発を行った。担持金属水酸化物触媒は、アルコール、アミン、ニトリル、末端アルキンなどの様々な基質を Lewis 酸と Brønsted 塩基の協奏作用により効率よく活性化できることを明らかにした。担持水酸化ルテニウム触媒（Ru(OH)x/Al2O3）は、分子状酸素を酸化剤としたアルコールやアミンの酸化的脱水素反応に極めて高い活性を示すことを明らかにした。本 Ru(OH)x/Al2O3 は酸化反応だけでなく、水素移行型還元反応やニトリルの水和反応に対しても高活性を示した。また、Ru(OH)x/Al2O3 を用いた第1級アルコールのアノモ酸化、第1級アミンの形式の α-酸素添加反応などの酸化的官能基変換の開発にも成功した。さらに我々は、本触媒設計概念がルテニウム以外の種々の遷移金属類にも適用可能で一般性が高いことを示し、これらの同一金属上に存在する金属由来の Lewis 酸と水酸基由来の Brønsted 塩基の協奏的効果を利用した種々の高効率官能基変換反応、たとえば担持水酸化鉄触媒を用いたアルキンの酸化カップリング反応やアジドと末端アルキンの1,3-双極子付加環化などの開発にも成功した。