Synthesis of *N*-Heterocycles via Oxidant-Free Dehydrocyclization of Alcohols Using Heterogeneous Catalysts

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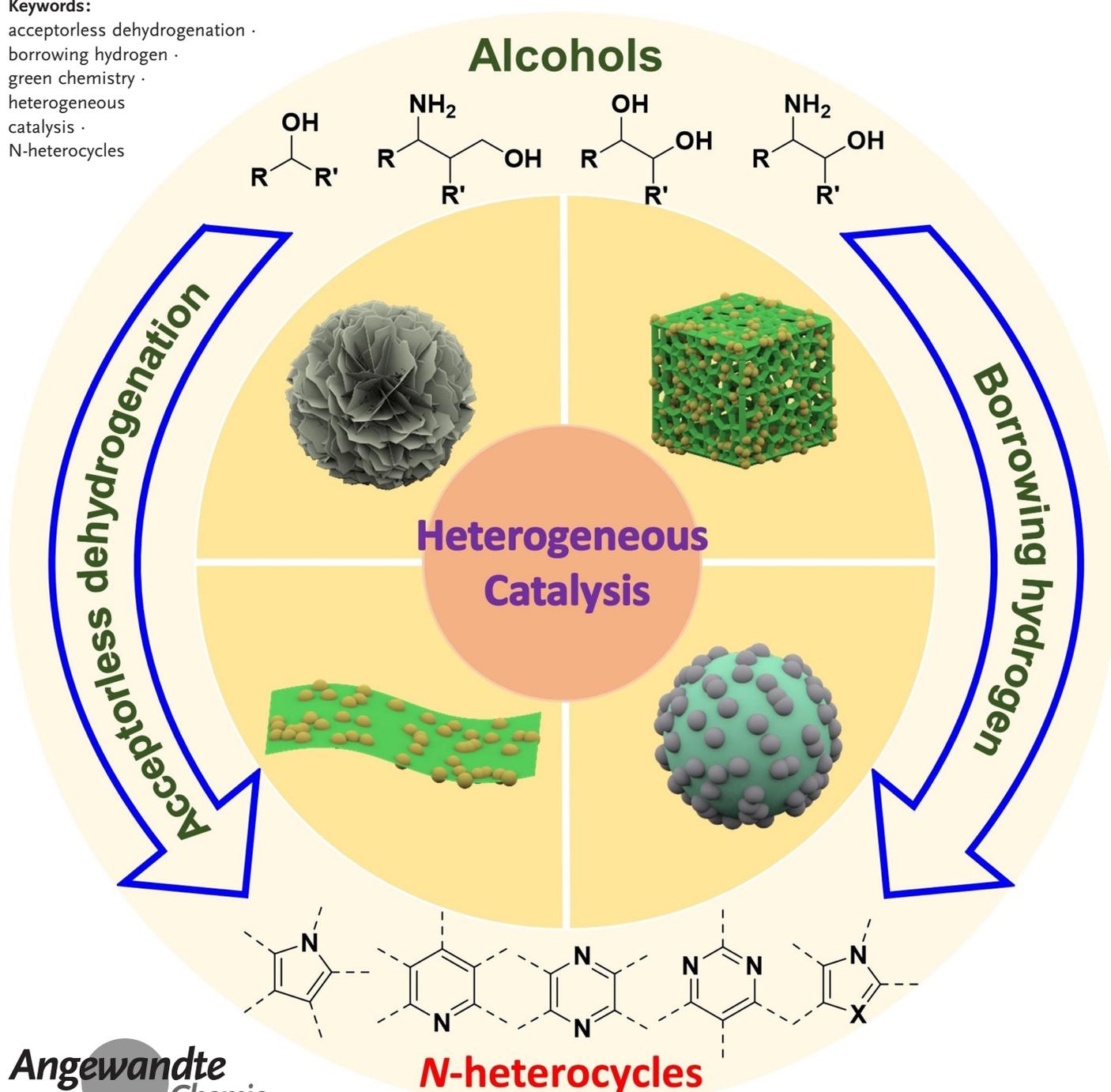
N-Heterocycles, such as pyrroles, pyrimidines, quinazolines, and quinoxalines, are important building blocks for organic chemistry and the fine-chemical industry. For their synthesis, catalytic borrowing hydrogen and acceptorless dehydrogenative coupling reactions of alcohols as sustainable reagents have received significant attention in recent years. To overcome the problems of product separation and catalyst reusability, several metal-based heterogeneous catalysts have been reported to achieve these transformations with good yields and selectivity. In this Minireview, we summarize recent developments using both noble and non-noble metal-based heterogeneous catalysts to synthesize N-heterocycles from alcohols and N-nucleophiles via acceptorless dehydrogenation or borrowing hydrogen methodologies. Furthermore, this Minireview introduces strategies for the preparation and functionalization of the corresponding heterogeneous catalysts, discusses the reaction mechanisms and the roles of metal electronic states, and the influence of support Lewis acid–base properties on these reactions.

1. Introduction

In the context of green chemistry and sustainable chemical transformations, dehydrocyclizations of alcohols for the construction of *N*-heterocycles via acceptorless dehydrogenations (AD) or borrowing hydrogen (BH) methodologies have attracted substantial attention due to their excellent redox economy and high atom-efficiency.[1] In general, in such transformations the alcohol substrate leads in situ to a reactive carbonyl compound by dehydrogenation, which subsequently reacts with an *N*-nucleophile to form the desired *N*-heterocycle in a straightforward manner (Figure 1a).[2]

N-Heterocycles are of continuing interest in organic chemistry for their diverse applications ranging from drugs to functional materials, and specific uses, for example, as ligands in catalysis.[3] The classical synthetic methods for their preparation usually suffer from specific reaction conditions, toxic reagents, and especially generation of (over)stoichiometric amounts of waste.[4] To overcome these problems, alcohols have been introduced as starting materials for the synthesis of *N*-heterocycles since many of them can be easily obtained from abundant biomass.[5]

The first report in this area applying heterogeneous materials dates back to 1982, when Mares and co-workers discovered that alcohols can be converted to aldehydes by Mo/Rh bimetallic catalysts producing only hydrogen as byproduct.[6] Notably, for such processes highly active catalysts and often high temperatures (> 140°C) are necessary owing to the high activation energy for the initial dehydrogenation of the respective alcohol.[7] Many homogeneous metal complexes based on Ir,[8] Ru,[9] Pt,[10] Co,[11] Ni,[12] Mn[13] Fe,[14] and other metals, have been elegantly developed for this transformation in the past decades. Unfortunately, most of these catalysts need expensive, sophisticated ligands and are more difficult to reuse, which also complicates separation of products. Thus, from the viewpoints of green chemistry and practical applications, the use of recyclable heterogeneous catalysts in these processes is advantageous.[15] Initially, for heterogeneous catalysts the use of noble metals dominated this area; however, more recently selected reports showcased the possibility to apply non-noble metal heterogeneous catalysts in such transformations (Figure 1b).

Notably, most reviews on BH or AD tandem transformations and multicomponent reactions of alcohols focus on applications of homogeneous catalysts.[2b,7,16] Only in 2018, Shimizu and co-workers presented the advancements in the development of AD reactions of alcohols with nucleophiles in the presence of noble metal-based heterogeneous materials.[17] In this Minireview, we present a more comprehensive summary of the recent advancements regarding the synthesis of *N*-heterocycles from alcohols promoted by heterogeneous catalysts via BH or AD strategies complementary to all the previous works. Our aim is to stimulate further research in this active field and inspire colleagues to explore new routes to *N*-heterocycles as well as to develop new materials for these interesting transformations.

2. General Considerations

2.1. Tentative Pathways

Domino transformations of alcohols under hydrogen borrowing or acceptorless dehydrogenation conditions provide a versatile toolbox for the synthesis of many organic

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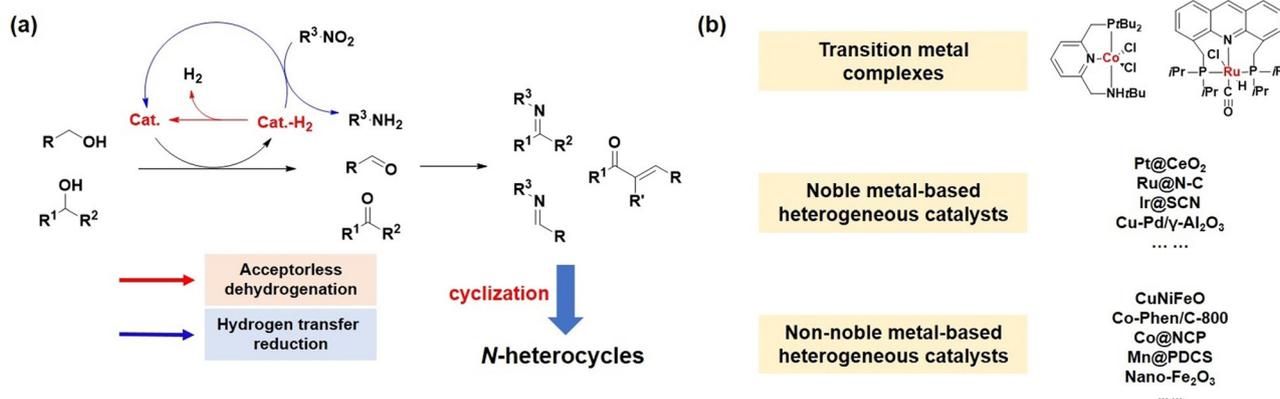https://doi.org/10.1002/anie.202104979.

Figure 1. a) The construction of *N*-heterocycles from alcohols through AD or BH processes; b) selected catalysts for this transformation.

chemicals. In this context, the corresponding transformations to *N*-heterocycles are especially interesting due to the importance of the resulting products. Notably, the underlying reaction network is highly complex and involves many competing reaction steps. In the presence of a catalyst and often co-catalysts, these materials will influence not only one specific reaction step, but many of them. Thus, the detailed understanding of the catalyst function in the overall transformation is very difficult. Nevertheless, herein we try to understand the plausible reasons for the observed catalytic

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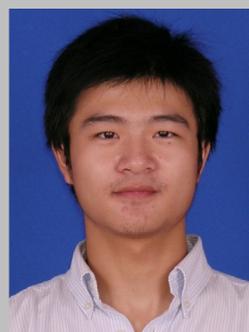
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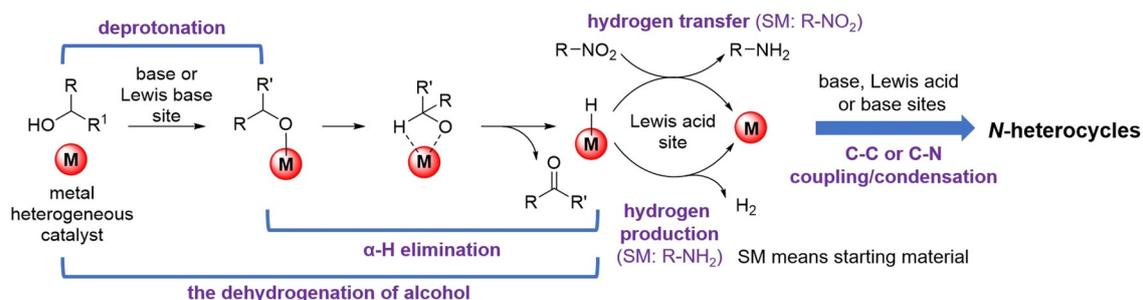
Figure 2. Tentative pathways for the tandem transformations of alcohols to *N*-heterocycles via BH or ADC processes.

activities in many cases. In general, all these transformations include the following elementary reaction steps: a) dehydrogenation of the alcohol substrate (deprotonation and α-H elimination), b) hydrogen transfer (e.g., SM is nitroarenes) or hydrogen generation (SM is amines) from the catalytic center, and c) C–C or C–N coupling/condensation steps (Figure 2). Typically, for borrowing hydrogen reactions, the α-H elimination is the rate-determining step.[18] For acceptorless dehydrogenations, α-H elimination or hydrogen generation often are rate-determining.[19]

All the elementary reaction steps are influenced by different properties of the heterogeneous catalyst material: In general, for the deprotonation of alcohols (the first step), base or Lewis basic sites are necessary. The following α-H elimination depends on the metal–hydrogen (M–H) bond energy or adsorption energies of H atoms on the metal surface. Hydrogen transfer and hydrogen production require low M–H bond energies, meanwhile Lewis acidic sites can enhance these steps.[20] In addition, the often-required additional base and/or Lewis acid–base sites on the support can promote subsequent C–C or C–N coupling/condensation steps.[21]

2.2. Electronic Effects of Transition Metals

Noble metals such as Pt, Ir, Ru, and Pd have higher electronegativity and higher proportion of d orbitals and electrons than their non-noble congeners (e.g., Co, Cu, Mn). As a consequence, they have higher adsorption energies of H atoms and moderate M–H bond energies, which is beneficial for α-H elimination of alcohols, hydrogen transfer, and hydrogen production. According to the Sabatier principle, the adsorption and catalyst interaction should be neither too strong nor too weak to achieve best catalytic performance.[22] Therefore, in general, noble metal-based heterogeneous catalysts have much better catalytic performance than the corresponding non-noble metal-based catalysts. At this point, it is noteworthy that the charge state of the metal can be regulated through electronic metal–support interactions,[23] which is directly related to the d-band center, thereby adjusting the adsorption energies of H atoms and M–H bond energies.[24]

In this context, heteroatom-doped carbon materials seem to be a kind of ideal support for non-noble metals since their d-band center can also be tuned by heteroatom dopants to enhance their catalytic performance.[25] For example, the DOS (density of states) plot of CoP/NCNHP (*N*-doped carbon nanotube hollow polyhedron supported CoP) shows that the electronic states of the Co d-orbital around the Fermi level can be enhanced by the electronic interaction between CoP and the *N*-doped NCNHP support (Figure 3).[24b] So far, only few reports mention that heteroatom doping will change the metal electronic state, thereby promoting such reaction.[25] Furthermore, at present there is no literature that relates the catalytic activity of metal heterogeneous catalysts in this transformation to the metal d-band center.
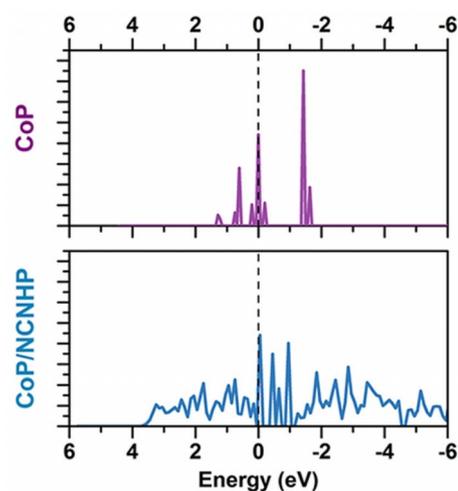

Figure 3. Calculated DOS curves of CoP and CoP/NCNHP. Reproduced with permission from ref. [24b]. Copyright 2018 American Chemical Society.

Alloying different metals is another strategy for tuning the metal d-band center.[26] For example, different PtM alloys have different d-band centers, and are predicted to possess different O adsorption energies (Figure 4).[27] Although some works have adopted alloy metal catalysts to achieve these reactions, no reasonable explanation for their activity has been presented, yet.[28–31] In these cases, we assume that the change of metal d-band center may be the main reason for the superior performance of certain alloy metal catalysts compared to others.

According to the above results, it can be concluded that the electronic state (d-band center) of the metal surface has a crucial influence on the reaction. Hence, the precise
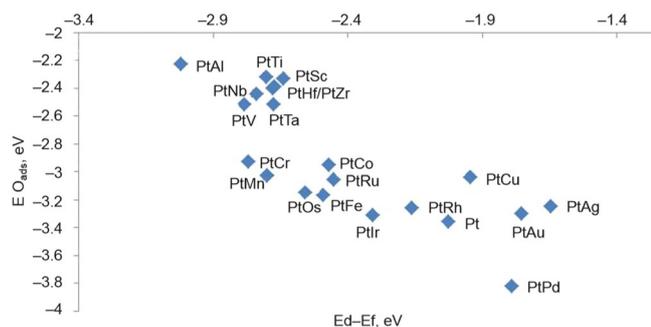
Figure 4. Correlation of d-band center and O adsorption energy for Pt-M-Pt alloys. Modified with permission from ref. [27]. Copyright 2015 Johnson Matthey Plc.

adjustment of the electronic state of the surface metal species by changing the coordination environment of the metal centers, e.g., electronic metal–support interaction, alloying, heteroatom doping, can significantly influence its catalytic performance in the reaction.

2.3. The Lewis Acid–Base Nature of Supports

The Lewis acid–base nature of the support is also crucial for the success of numerous tandem or domino reactions. Metal oxides[32–38] and heteroatom-doped carbons[25] as the supports usually have acid–base pair sites, which are sufficient to promote the dehydrogenation of alcohols and C–C/C–N coupling without the need for additional base in these transformations. Compared with basic or relatively acidic supports, amphoteric supports usually have higher catalytic activity, which can be attributed to the coexistence of acidic and basic sites on the support surface.

As an example, the domino reaction of 2-aminobenzyl-amine and 1-octanol to form quinazolines indicates that the reaction yield is proportional to the O 1s binding energy of the support, verifying that the support basicity is beneficial to the catalytic performance (Figure 5).[32] However, MgO with strong basic sites only provided a moderate yield of **3a**, which can be attributed to its lack of acid sites.

As shown in Figure 6, for the dehydrogenation reactions of cyclododecanol and 2-octanol, volcano-type relationships between the reaction rate and the support electronegativity have been observed.[39] In general, the supports with only Lewis acidic or basic sites displayed lower activity than amphoteric supports. These results confirm again that both acidic and basic sites on the support surface have a positive influence on the dehydrogenation of alcohols. In agreement with these observations, also plots of the catalyst activity (in terms of turnover frequency, TOF) of the C–N coupling reaction of alcohols and ammonia showed that supports with amphoteric nature have better catalytic performance than pure basic or acidic supports (Figure 7).[20] In this specific reaction, the Lewis basic sites of γ-Al$_2$O$_3$ promoted the dehydrogenation of alcohol, and the acidity of γ-Al$_2$O$_3$ is assumed to accelerate the hydrogen transfer process. Again,
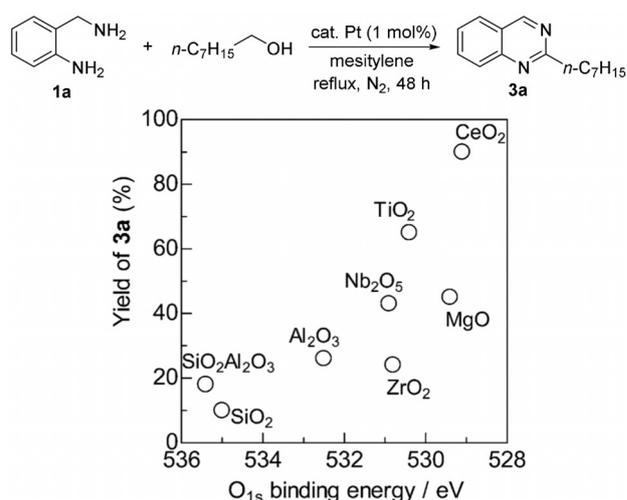
Figure 5. The relationship between the yield of **3a** and the O1s binding energy of the support. Reproduced with permission from ref. [32]. Copyright 2014 Royal Society of Chemistry.
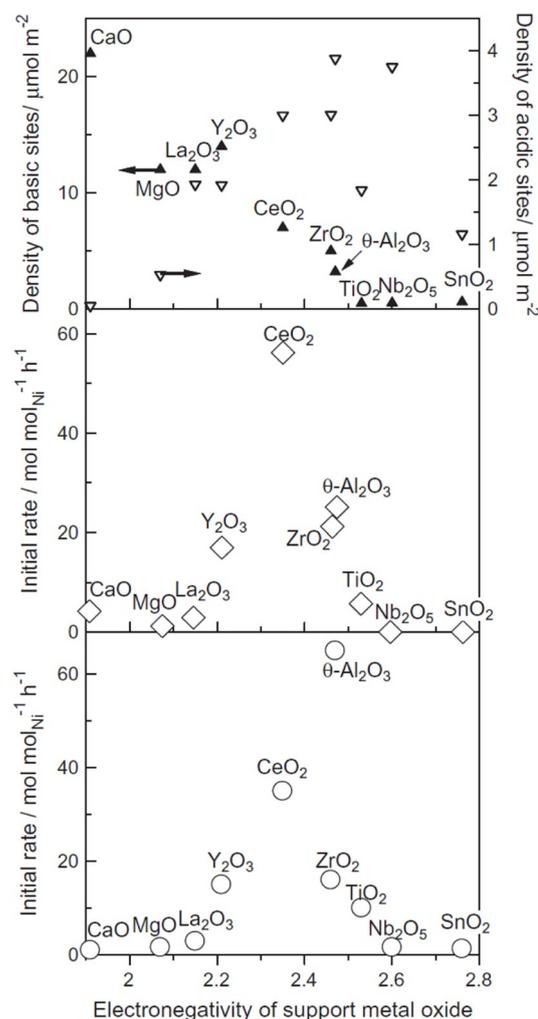
Figure 6. The surface densities of basic (▲) and acidic (▽) sites of different metal oxides and the relationship between the electronegativity of the support and the reaction rate (the dehydrogenation reactions of cyclododecanol (○) and 2-octanol (◇)). Reproduced with permission from ref. [39]. Copyright 2013 Elsevier.
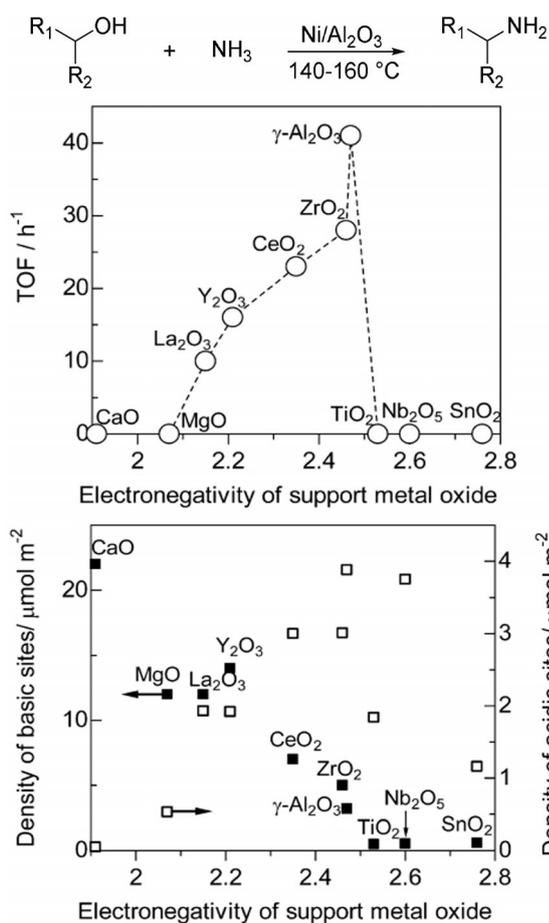
Figure 7. The relationship between TOF (○) or the surface densities of basic (■) and acidic (□) sites with the electronegativity of support. Reproduced with permission from ref. [20]. Copyright 2012 American Chemical Society.

these results confirm the importance of both acidic and basic sites on the support surface for various BH processes.

3. Noble Metal-Based Heterogeneous Catalysts

Noble metal-based heterogeneous catalysts, such as Pt, Ir, Ru, Pd on various supports are known for their superior catalytic activity for the dehydrogenation of alcohols and the reverse hydrogenation processes.[9–11] Hence, not surprisingly, such materials can be efficiently employed in both AD and BH processes and have been also applied in the dehydrocyclization of alcohols to form *N*-heterocycles.

3.1. Pt-Based Heterogeneous catalysts

In recent years, Shimizu's group have developed several Pt-based heterogeneous catalysts for the formation of different *N*-heterocycles. As an example, HBEA zeolite-supported Pt nanoparticles (NPs) (Pt/HBEA) were applied for the preparation of quinazolinones through the acceptorless dehydrogenative coupling (ADC) and cyclization reaction

of *o*-aminobenzamide and alcohols in 2014 (Scheme 1).[40] This catalytic system allowed the conversion of various aliphatic alcohols, including linear and branched alcohols, giving good to excellent yields (78–95%) of the corresponding quinazolinones. Additionally, the authors found that metallic Pt^0 species on the Pt NPs surface constitute the active catalyst species and their re-oxidation decreased the overall activity of the catalyst. Notably, hot filtration experiments and ICP measurements suggest that the Pt leaching of this catalyst is negligible.
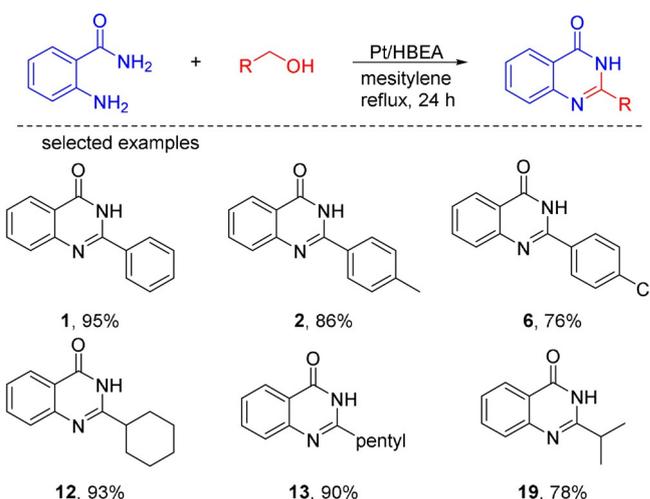

Scheme 1. The synthesis of quinazolinones from *o*-aminobenzamide and alcohols via ADC strategy.

Later, the same group developed CeO_2-supported Pt nanoparticles (Pt/CeO_2), which enabled the synthesis of quinazolines from 2-aminobenzylamine with primary alcohols via an acceptorless dehydrogenative process (Scheme 2).[40] However, comparably high temperatures (170 °C) must be applied here. A plausible mechanism is shown in Scheme 2b: Here, CeO_2 with its strong basicity promotes the condensation of 2-aminobenzylamine with aldehydes, which are produced by the Pt-catalyzed dehydrogenation of alcohols, to afford intermediates **2**. Subsequently, the catalyst mediates the dehydrogenation of **2** to the thermodynamically more stable quinazoline products.[40]

In 2015, Shimizu and co-workers disclosed that Pt on TiO_2 could achieve the acceptorless dehydrogenative synthesis of 2-substituted benzothiazoles or benzimidazoles from alcohols under base-free conditions (Scheme 3a).[33] Notably, their catalyst system has a higher turnover number (TON) than most of the known homogeneous catalysts and the reaction is carried out under neutral conditions. However, the scope of the alcohols is limited so far, and the yields of the desired products can be improved. In the same year, they also reported that Pt/Nb_2O_5 and Pt/HBEA acted as more effective heterogeneous catalysts for the synthesis of indoles via acceptorless dehydrogenative cyclization of 2-(2-aminophenyl)ethanol (Scheme 3b).[34] In this case, the Pt/Nb_2O_5 material can be reused at least three times without significant loss of activity, while the reusability of Pt/HBEA was
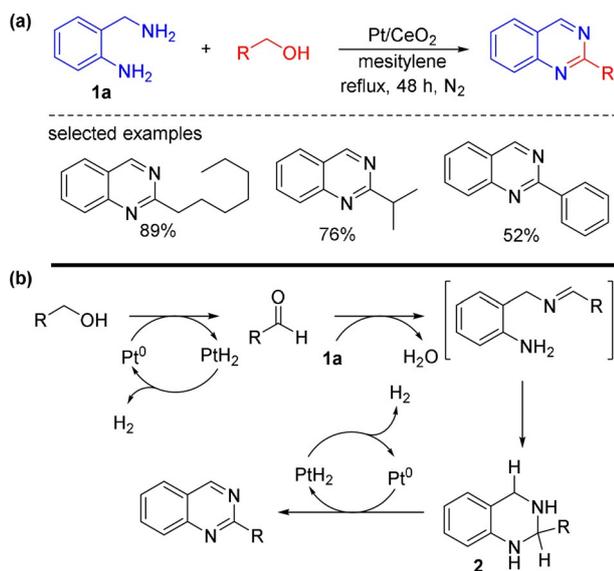
Scheme 2. a) The reaction of 2-aminobenzylamine and primary alcohols for the synthesis of quinazolines via the AD process; b) a tentative pathway for this transformation in the presence of Pt/CeO$_2$.
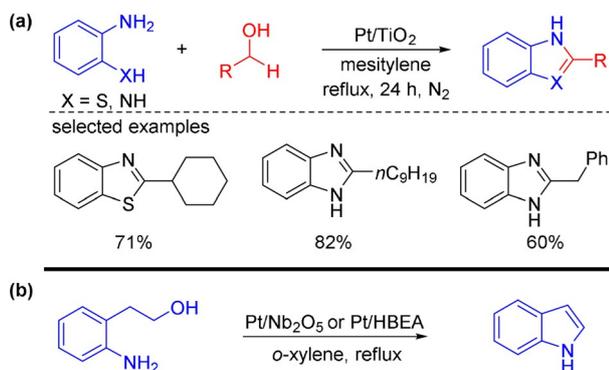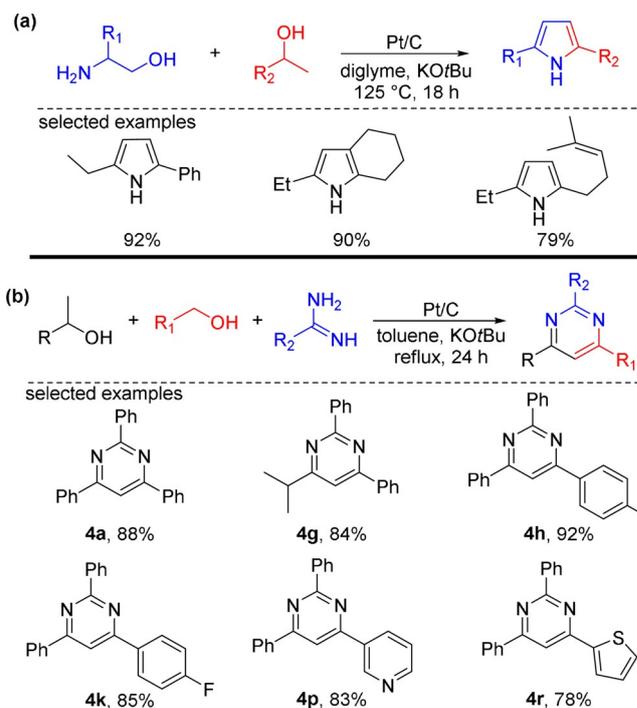

Scheme 3. The synthesis of N-heterocyclic aromatics over Pt-based heterogeneous catalysts.

unsatisfactory. In more detail, ICP analysis showed that there is only 3.4 ppm Pt in the solution after complete reaction. In addition, the authors demonstrated that 2-nitroaryl alcohols can be selectively converted to the corresponding indoles under 1 atm of molecular hydrogen.

In 2016, Shimizu and co-workers prepared Pt/C catalysts by a facile impregnation method. The optimal catalyst system displays outstanding performance for the AD synthesis of 2,5-disubstituted pyrroles from 1,2-aminoalcohols and secondary alcohols in the presence of KO*t*Bu as base (Scheme 4a).[41] In this reaction, various metals and supports were tested, and Pt/C showed the best performance. Additionally, no significant reduction in the catalytic activity of this heterogeneous catalyst was found after four runs. In this case, ICP analysis also showed that the leaching of Pt is negligible after the first cycle.

More recently, the same group found that Pt/C was also effective for the synthesis of 2,4,6-trisubstituted pyrimidines by the one-pot reaction of alcohols and amidines in the presence of KO*t*Bu as a strong base (Scheme 4b).[42] In this

Scheme 4. Acceptorless dehydrogenative synthesis of N-heterocycles catalyzed by Pt/C.

study, it was found that M–H bond energies are critical to the activity of the catalyst. Metals with low H adsorption energy do not efficiently promote the alcohol dehydrogenation step, while high H-adsorption energies of metal are detrimental to the H$_2$ production. The catalyst can be reused at least five times with a slight decrease of activity. Apparently, the increase in particles size is responsible for the decrease of catalytic activity after every run. The presented plausible mechanism involves a Pt-catalyzed dehydrogenation of the alcohols and subsequent base-promoted condensation, followed by cyclization and finally dehydrogenation.

In 2018, Ballesteros-Garrido and co-workers described the synthesis of different indoles from anilines and ethylene glycol in the presence of Pt/Al$_2$O$_3$ and ZnO at 175 °C (Scheme 5).[35] Interestingly, the reaction does not proceed well in the absence of ZnO. Under optimized conditions, the condensation of various anilines with ethylene glycol afforded the corresponding indoles in moderate to good yields. However, only anilines with donor substituents can be converted to the corresponding indoles with good yields.
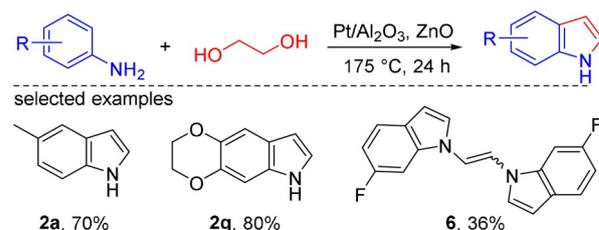
Scheme 5. The synthesis of indoles from anilines and ethylene glycol.

3.2. Ir-Based Heterogeneous Catalysts

Kempe and co-workers demonstrated an elegant tandem transformation of secondary alcohols and 1,2-amino alcohols to give pyrroles under mild conditions (Scheme 6).[43] In this work, the Ir precatalyst is synthesized by crosslinking commercially available polysilazane HTT1800 and the molecular Ir complex in THF. After removal of the solvent, the sample is pyrolyzed under N_2 atmosphere at 1100 °C (Fig-
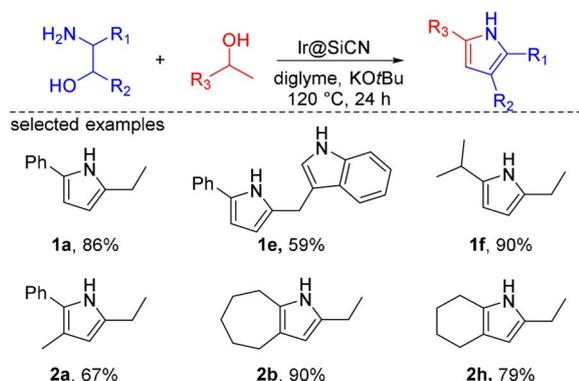

Scheme 6. The synthesis of pyrroles over Ir@SiCN.

ure 8). The resulting heterogeneous catalyst Ir@SiCN showed excellent reusability and catalytic activity, while other commercial Ir catalysts suffered from activity loss after recycling in the second run. Upon optimization of the alcohol and base concentrations, the yields of products can be increased up to 96%. In addition, various aliphatic or aromatic secondary alcohols can be smoothly converted to the corresponding pyrroles; however, the scope of the amino alcohols is somewhat limited.

In 2011, Cao and co-workers developed TiO_2-supported Ir nanoclusters for the borrowing hydrogen synthesis of quinolines from nitroarenes and alkyl alcohols (Scheme 7).[36] In this transformation, the combination of TiO_2 with mild surface acidity and iridium clusters with smaller particle size provides higher intrinsic activity for direct quinoline synthesis. In general, nitrobenzenes with electron-donating groups afforded higher yields than ones with electron-withdrawing groups. Regarding metal leaching, ICP analysis confirmed that no significant amount of Ir is present in the solution after hot filtration.
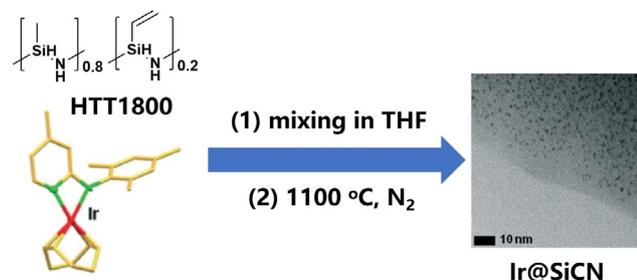

Figure 8. Procedure for the synthesis of Ir@SiCN. Reproduced with permission from ref. [43]. Copyright 2014 Royal Society of Chemistry.
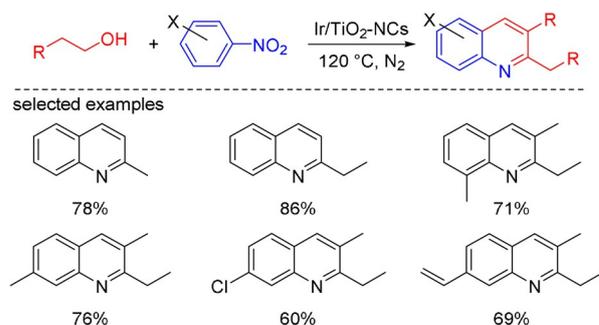
**Scheme 7.** The borrowing hydrogen synthesis of quinolones over Ir/TiO₂-NCs.

Additionally, the reaction rate of *ortho*-methylnitrobenzene is lower than that of *meta* and *para* analogues, which indicates that the steric effect may inhibit the annulation process in the reaction. Furthermore, Wada and co-workers found that Ir/TiO₂ exhibited excellent performance for the acceptorless dehydrogenative synthesis of benzimidazoles (Scheme 8a).[37] In this case, the catalyst is prepared by impregnation, drying, calcination, and H_2 reduction. Compared with other metal–support combinations, Ir/TiO₂ displayed the best result for the synthesis of benzimidazoles at 120 °C. The catalyst is also effective for the synthesis of indole from 2-(2-aminophenyl)ethanol at lower temperature (100 °C) (Scheme 8b).[38] Comparing the different forms of titania, the Ir catalyst supported on rutile showed better selectivity that supported on anatase. This phenomenon is explained by the fact that the Ir nanoparticles supported on rutile are smaller and better reduced than those on anastase. ICP analysis revealed that the leaching of Ir species after the catalytic is very little.
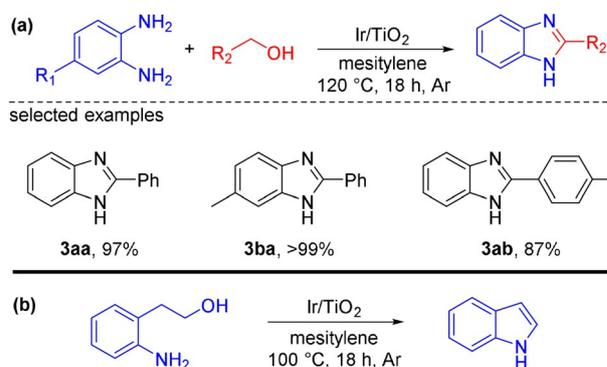
Scheme 8. The synthesis of *N*-heterocycles over Ir/TiO₂.

3.3. Ru-Based Heterogeneous Catalysts

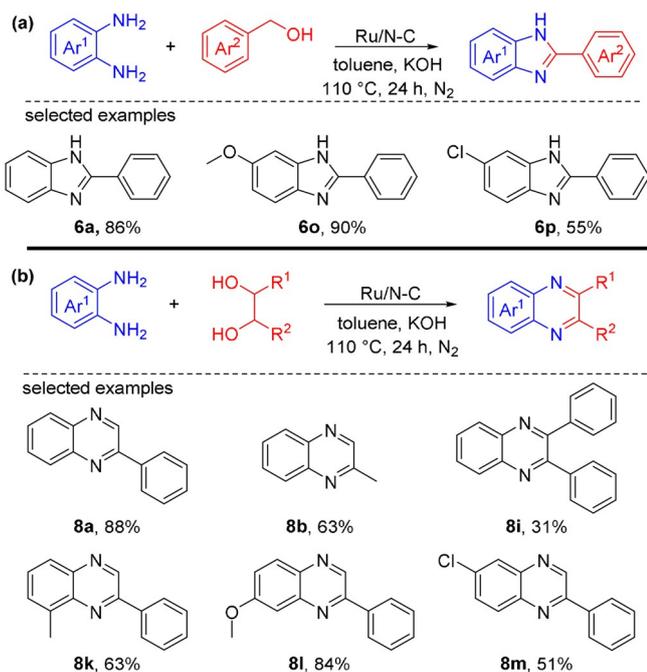The Wada group also explored Ru-based catalysts for related reactions. More specifically, they developed a simple Ru/CeO₂ catalyst that active for the acceptorless dehydrogenative cyclization of 2-(2-aminophenyl)ethanol (Scheme 9).[44] Here, the catalyst preparation included impregnation, drying, and calcination steps. The activity depended mainly on the nature of support and the calcination temperature. Ru/CeO₂
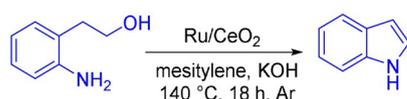
Scheme 9. The synthesis of indole over Ru/CeO$_2$.

calcined at 200 °C showed the highest activity and afforded up to 99 % yield of indole. Ru^{IV}=O species on the catalyst surface are assumed to be converted to the active sites at the beginning of the transformation.

Ru nanoparticles supported on *N*-doped carbon (Ru/N-C) were applied for the synthesis of benzimidazoles and quinoxalines by Lang and co-workers (Scheme 10).[45] This specific catalyst is synthesized by calcination of a mixture of *cis*-Ru(phen)$_2$Cl$_2$ and carbon powder (Figure 9).[45] It is assumed that the nitrogen doping stabilizes Ru NPs. However, an excess of N sites on the support can also reduce the catalyst activity because it may block the active catalytic sites, too. In the case of diamines with electron-rich groups, good to excellent yields of the desired products are afforded (**6o**, **8l**), while only moderate yields are provided when diamines with electron-withdrawing groups are used as the substrates (**6p**, **8m**). Interestingly, the catalyst also showed significant stability; thus, after five cycles, the ICP analysis indicated that 93 % Ru is retained on the surface.
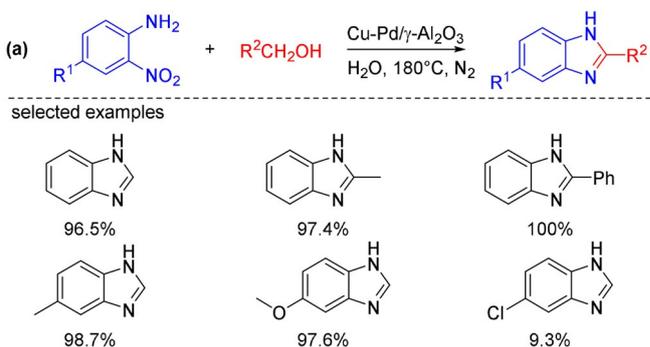

Figure 9. Procedure for the synthesis of Ru/M-C: a) TEM image, b) HRTEM image, c) HAADF-STEM image, and d) STEM-EDS elemental mappings of Ru/N-C. Reproduced from with permission from ref.[45]. Copyright 2018 Wiley-VCH.

phenylenediamine and aldehyde. Subsequently, the Lewis acid sites of γ-Al$_2$O$_3$ mediate the coupling step to give the desired benzimidazoles (Scheme 11a).[28] Later, the same group found that the addition of Mg to this catalyst could improve its catalytic performance (Scheme 11b).[29] The reason is that the added Mg can neutralize the acid sites of γ-Al$_2$O$_3$ and enhance the basicity of the catalyst, thereby accelerating the dehydrogenation of alcohol. Some structurally more complex benzimidazole derivatives, such as bisbenzimidazole, were also synthesized using Cu-Pd/(Mg)γ-Al$_2$O$_3$ as the catalyst. However, a relatively high temperature of 180 °C is necessary for both systems.

3.5. Au-Based Heterogeneous Catalysts

In 2015 Wang and co-workers introduced an efficient and selective protocol for the synthesis of 2,4-disubstituted quinazolines starting from *o*-nitroacetophenones and alcohols using NH$_3$·H$_2$O as the N source in the presence of Au/TiO$_2$

Scheme 10. The synthesis of *N*-heterocycles over Ru/N-C.

3.4. Pd-Based Heterogeneous Catalysts

In 2016, Li and co-workers developed a multifunctional Cu-Pd/γ-Al$_2$O$_3$ catalyst for the direct synthesis of benzimidazoles from *o*-nitroaniline and alcohols. In this protocol, it is proposed that both Pd and Cu promote the dehydrogenation of the alcohol and the hydrogenation of *o*-nitroaniline to *o*-

Scheme 11. The synthesis of benzimidazoles from *o*-nitroaniline and alcohols.

(Scheme 12).[46] This methodology has a good tolerance to air and water. In addition, it presents a broad substrate scope and offers an interesting approach to the formation of multiple C–N bonds. For selected examples, the Au/TiO$_2$ could be recovered by simple phase separation and reused at least eight times without loss of activity.
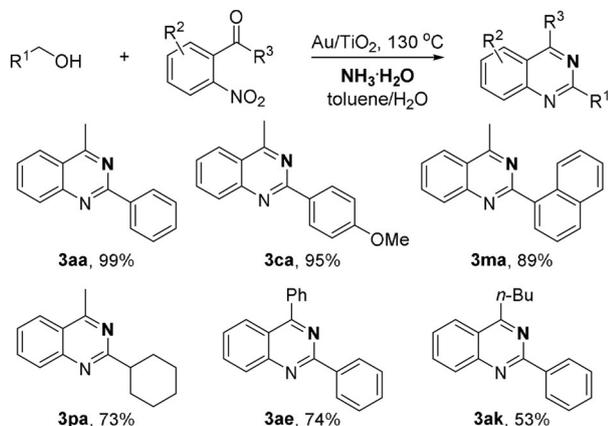
Scheme 12. The synthesis of quinazolines utilizing Au/TiO$_2$.

4. Non-noble Metal-Based Heterogeneous Catalysts

Although various noble metal-based heterogeneous catalysts exhibit excellent performance in these reactions (vide supra), the higher cost and availability of these metals limit their applications, especially considering industrial processes. Therefore, the development of heterogeneous non-noble metal-based catalysts is of significant interest to many researchers in recent years.

In this context, He and co-workers prepared NiAl-LDO-supported Ni (Ni-NiAl-LDO) materials for the borrowing hydrogen synthesis of 1,2,3,4-tetrahydroquinoline (THQ) under base-free conditions (Scheme 13).[30] The precursor NiAl-LDHs (Layered Double Hydroxide) is prepared by the static homogeneous coprecipitation method to afford Ni-NiAl-LDO (Figure 10).[30] Reducing the size of Ni nanoparticles or the activating the surface of Ni nanoparticles with an appropriate amount of O$_2$ can improve the catalytic activity due to Ni^0/Ni$^{\delta+}$ synergistic catalysis. Furthermore, the acid–base amphoteric sites on the surface of Ni-NiAl-LDO are beneficial for C–C and C–N coupling and condensation reactions. Various aliphatic alcohols and 2-aminobenzyl alcohols are converted to the corresponding products in good yields.

Another interesting and innovative non-noble metal catalyst for this class of transformations was introduced by Bhanage and co-workers. Specifically, they developed a magnetically separable CuNiFeO catalyst for the domino transformation of 2-aminobenzyl alcohols with secondary alcohols to give quinolines in the presence of KO^{t}Bu (Scheme 14a).[31] The catalyst was prepared by the sol–gel method. Appropriate amounts of metal salt and citric acid are dissolved in distilled water to generate a gel. The black powder prepared
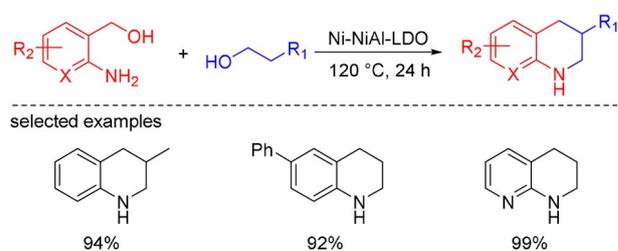
Scheme 13. The synthesis of tetrahydroquinolines catalyzed by Ni-NiAl-LDO.
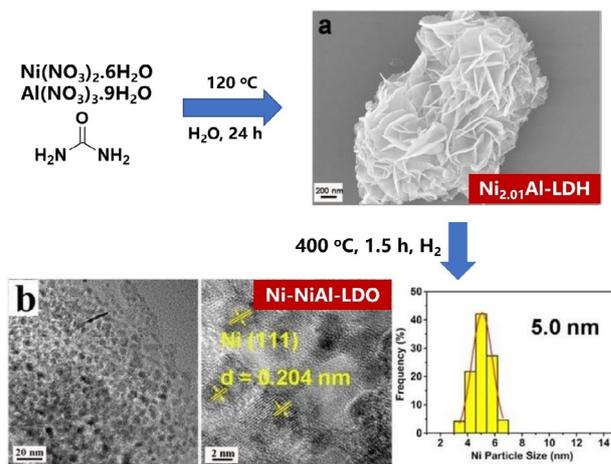
Figure 10. Procedure for the synthesis of Ni-NiAl-LDO: a) SEM images of NiAl-LDHs; b) TEM image, HRTEM image, and size distribution of Ni-NiAl-LDO. Reproduced with permission from ref. [30]. Copyright 2019 American Chemical Society.

by the autocombustion of this resulting gel was ground, calcined, and reduced to give the magnetic CuNiFeO material (Figure 11).[31]

Various alcohols including acyclic, cyclic, and heteroatom-containing substrates, can be converted into the respective products. Furthermore, this catalyst is also effective for the conversion of 2-aminobenzyl alcohols with alcohols to quinolines under similar conditions. The catalyst can be recycled up to five times without any significant change in catalytic
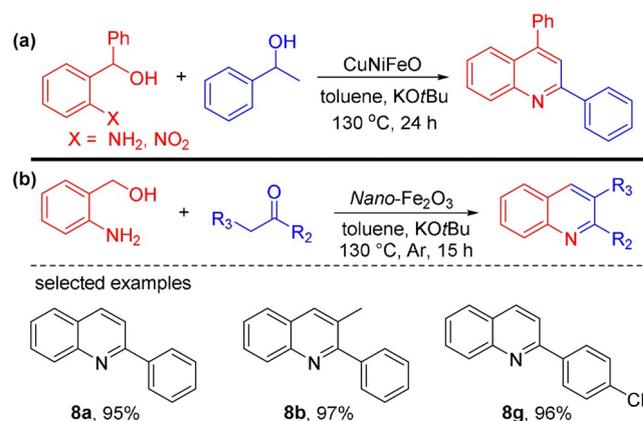
Scheme 14. The synthesis of quinolines over heterogeneous CuNiFeO.

Figure 11. Synthesis of CuNiFeO.

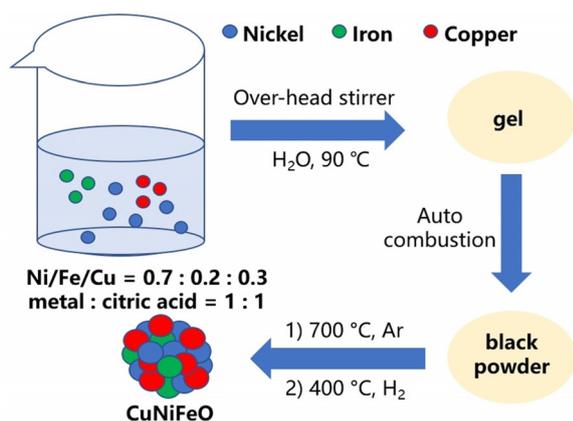activity. After the reaction, no traces of metal were observed in the reaction mixture, which indicates negligible leaching of metal species from the catalyst surface.

Another iron-based catalyst was reported by Kayambu and co-workers, who used commercially available nano-Fe_2O_3 for the synthesis of quinolines from 2-aminobenzyl alcohols and methyl ketones (Scheme 14b).[47] Here, a range of substrates reacted smoothly, providing the desired quinolines with excellent yields.

In addition, Kundu and co-workers reported the homogeneous catalyst NiBr$_2$/phen to be effective for the synthesis of quinoxalines from 1,2-diaminobenzene and diols (Scheme 15a).[48] Interestingly, they found that insoluble NiO$_x$ nanoparticles formed during the reaction which showed outstanding catalytic activity for this transformation. PXRD, XPS, and TEM results revealed the presence of NiO$_x$ nanoparticles.

The same group reported also a heterogeneous cobalt catalyst Co-Phen/C-800, which displayed superior reactivity for the coupling between diamines and diols (Scheme 15b).[49] For the preparation of the active catalyst, Co(OAc)$_2$ is mixed with phenanthroline to form the corresponding cobalt complex, which is then supported on carbon black. Subsequently, this prepared precursor is pyrolyzed at 800°C under N$_2$ to generate Co-Phen/C-800. In the presence of this system, the reaction of diamines with diols affords the corresponding quinoxaline moieties. Unfortunately, no desired quinolines are produced when *o*-phenylenediamine derivatives with electron-withdrawing groups are employed. The recyclability of this catalyst was tested for up to eight cycles, and it does not lose its activity significantly. The yield of 2-methylquinoxaline dropped when acid-treated Co-phen/C-800 was used, indicating both CoN$_x$ and CoO$_x$ play vital roles in this reaction.

Some of us introduced another Co-based heterogeneous catalyst: N,P-codoped porous-carbon-supported Co NPs (Co@NCP) for borrowing hydrogen synthesis of quinoxalines via the reaction of *o*-nitroanilines and diols (Scheme 15c).[25] At first, (NH$_4$)$_2$HPO$_4$ NPs are precipitated by an antisolvent method. The in situ growth of MOF shell on (NH$_4$)$_2$HPO$_4$ NPs can be achieved by directly mixing of Co^{2+}, Zn^{2+}, and 2-MeIm (2-methylimidazole). The resulting NPs, referred to as BMZIFs-NPs, are further carbonized under certain conditions to afford the catalyst Co@NCP (Figure 12).[25] The
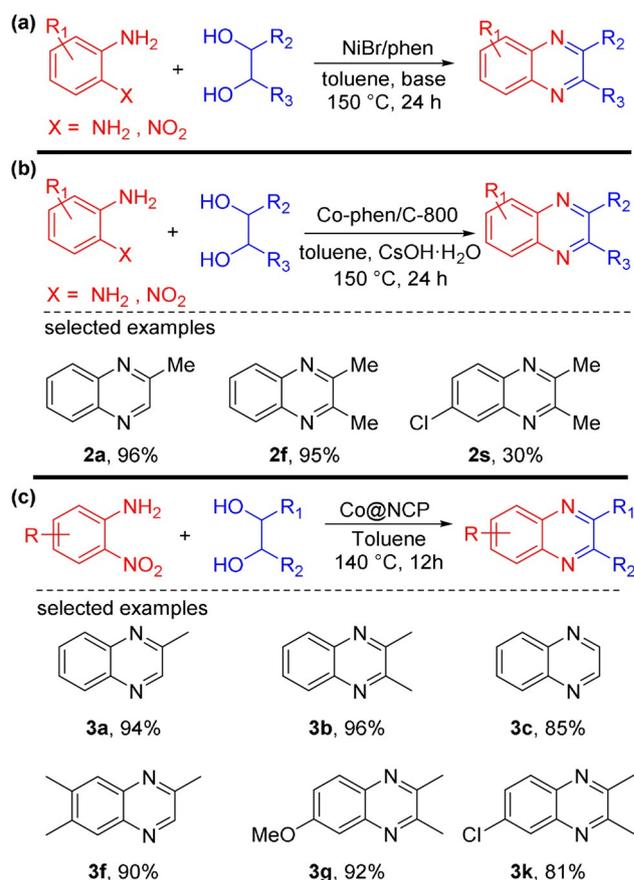

Scheme 15. The synthesis of quinoxalines from *o*-nitroanilines and vicinal diols.

superior performance of this latter material is attributed to its large surface area, high pore volume, high density and strongly basic sites, and the electronic effects of P doping on Co sites. Moreover, the metal content in Co@NCP hardly changed after six cycles due to the strong anchoring effects of N and P atoms. However, when this catalyst system was applied, electron-withdrawing substituents on *o*-nitroaniline substrates have a negative effect on the heterocycle synthesis.

In related work, Wang and co-workers reported the direct conversion of *o*-phenylenediamine and alcohols to give 1-benzyl-2-aryl-1*H*-benzo[*d*]imidazole catalyzed by [Cu-(binap)I]$_2$@HT in water at relatively low temperature (90°C) (Scheme 16a).[50] The catalyst precursor [Cu(binap)I]$_2$ prepared from BINAP and CuI was supported on hydrotalcite (Figure 13). In this reaction, various aromatic alcohols could be converted to the corresponding benzimidazoles in mediocre yields. The amount of Cu leaching after five
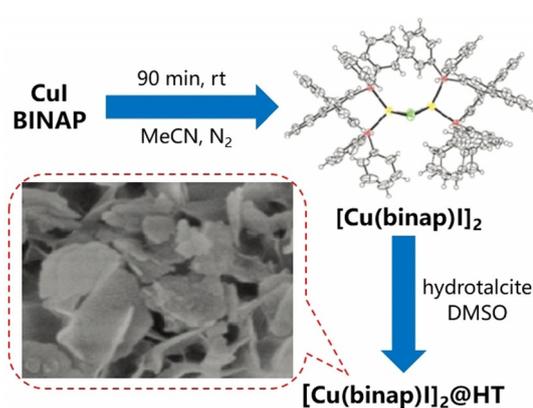

Figure 12. Procedure for the synthesis of Co@NCP. Reproduced with permission from ref. [25]. Copyright 2020 Wiley-VCH.
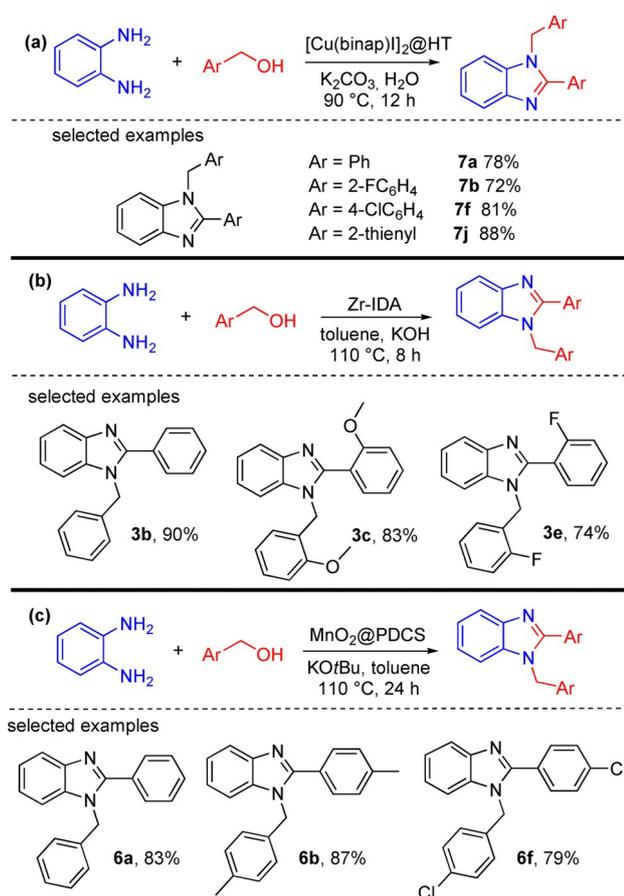
Scheme 16. The synthesis of benzimidazole over heterogeneous non-noble catalysts.

Figure 13. Procedure for the synthesis of [Cu(binap)I]$_2$@HT. Modified with permission from ref. [49]. Copyright 2018 Royal Society of Chemistry.

produces hydrogen, nor whether the reaction is protected by inert gas.

Finally, as a last example, Wang and co-workers prepared a novel α-MnO$_2$@PDCS catalyst in 2019, which displayed excellent performance for the synthesis of 1-benzyl-2-aryl-1*H*-benzo[d]imidazole via borrowing hydrogen reactions (Scheme 16c).[52] The support consists of poly 2,4-dichlorostyrene microspheres (PDCS), which were prepared by an AIBN-initiated polymerization of 2,4-dichlorostyrene. Then, a mixture of PDCS, KMnO$_4$, and MnSO$_4$ is stirred in water. The obtained solid is crystallized, and after centrifugation and drying, the catalyst α-MnO$_2$@PDCS is obtained (Figure 15a). Compared with other modified supports, PDCS provided the best results (Figure 15b,c).[51]

5. Summary and Outlook

This Minireview focuses on the actual synthesis of *N*-heterocycles from alcohols via the AD or BH methodologies applying various types of heterogeneous catalysts. In general, such methodologies constitute ideal examples of modern, state-of-the-art organic synthesis. Nevertheless, this is a rela-

recycling cycles is 2.83% and P leaching is 0.35%, showing that the leaching of [Cu(binap)I]$_2$@HT is comparably low. However, regarding the substrate scope of alcohols, only benzyl alcohol participated in the reaction. In 2020, the same group prepared a zirconium(IV) coordination polymer (Zr-IDA) by coordination of 1-(carboxymethyl)-1*H*-indazole-5-carboxylic acid (H$_2$IDA) and ZrCl$_4$ (Scheme 16b).[51] H$_2$IDA is synthesized from the reaction of 1*H*-indazole-5-carboxylate, methyl 2-bromoacetate, and anhydrous potassium carbonate in MeCN. After ZrCl$_4$ and H$_2$IDA were dissolved in DMF/HOAc, the resulting solid is separated by filtration, washed with DMF and EtOH, and heated at 80 °C for 5 h to afford Zr-IDA (Figure 14). This heterogeneous catalyst displayed high catalytic activity in the synthesis of 1,2-disubstituted benzimidazole derivatives from *o*-phenylenediamines and aromatic alcohols at 110 °C. In this transformation, the capture of the intermediate bisimine indicates that the synthesis of 1,2-disubstituted benzimidazole catalyzed by Zr-IDA is different from that using Cu or Ru as the catalyst. When the reaction mixture was stirred after removal of the catalyst, only low conversion of substrate was observed. As a result, the authors concluded that the leaching of the zirconium species into the liquid phase was negligible. At present, it is uncertain whether oxygen participates in the reaction, because it was not determined whether the reaction
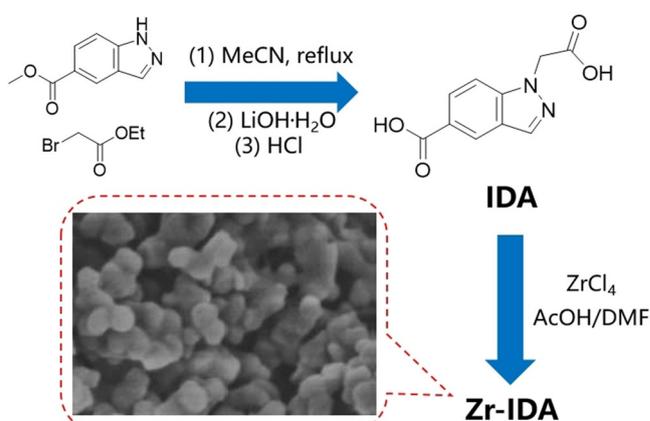

Figure 14. Procedure for the synthesis of Zr-IDA. Reproduced with permission from ref. [50]. Copyright 2020 Wiley-VCH.
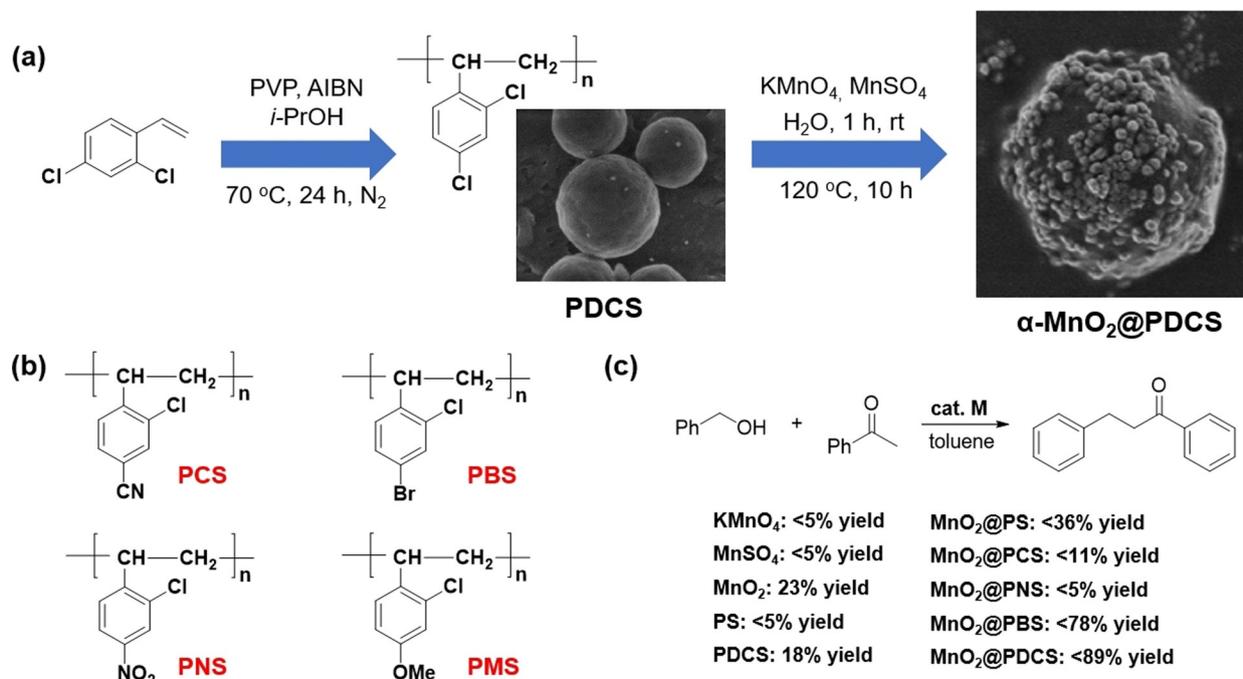
Figure 15. (a) The procedure for the synthesis of α-MnO$_2$@PDCS, (b) several modified supports, and (c) the catalyst exploration experiments. Reproduced with permission from ref. [51]. Copyright 2019 Royal Society of Chemistry.

tively young research field, which has evolved in only the past two decades. In general, noble metal-based heterogeneous catalysts prevail in this area due to their enhanced catalytic activity and stability compared to their non-noble metal congeners. However, the latter materials offer advantages with respect to cost and toxicity.

It should be noted that heterogeneous noble metal catalysts display much better dehydrogenation ability for many primary alkyl alcohols, which is often the rate-determining step of the overall reaction sequence (see Figure 2). Nevertheless, in recent years also Co- and Ni-based heterogeneous catalysts with comparable activities have been developed for the oxidant-free dehydrogenation of some primary alkyl alcohols. Ideally, one would like to use Fe- and Mn-based heterogeneous catalysts for such transformations; however, at present, these latter systems can only activate benzyl alcohols, which are easier to react due to the stabilization of the corresponding benzylic intermediates.

For many of the heterogeneous catalysts, recycling experiments have been performed, showing a decrease of activity after several cycles. In general, the reduced catalytic performance is not due to the leaching of metal species but results from changes in the physical and chemical properties of the metal species, such as particle size, surface electronic state, and number of exposed active sites.

The advantages of these transformations are obvious: 1) use of abundant and readily available raw materials; 2) no need for stoichiometric oxidants, which also limits by-product formation; 3) the possibility to use recyclable catalysts simplified product purification; 4) high step- and atom-economy of the overall transformation. Nevertheless, a closer look at the various protocols reveals that this chemistry still

suffers from limitations, which need to be addressed in the coming years. For example, most of the shown reactions require high temperature (>100 °C is the norm) and often additional stoichiometric amounts of base are required. Furthermore, expensive, and scarce noble metal-based catalysts still dominate in this field, as their non-noble congeners show low activity, especially for the dehydrogenation of primary aliphatic alcohols. Form a synthetic point of view, the scope of substrates is still limited, and interesting functional groups are not tolerated or have not yet been explored.

Consequently, new and improved heterogeneous materials have to be developed for the synthesis of *N*-heterocycles from alcohols. Ideally, such processes should operate under milder conditions for a broader scope of substrates. To achieve this, more rational structure–activity relationships (SAR) for the (heterogeneous) catalyst must be developed. Indeed, such insight will be key for the design of more effective and sustainable heterogeneous catalysts for these transformations. Clearly, both the mechanism of these reactions and the structure of heterogeneous materials are highly complex, which makes it extremely challenging to establish a connection between them. Nevertheless, we believe this is a worthwhile task and we suggest the following strategy for a more rational design of such catalysts: First, the rate-determining steps of the overall reaction as well as the main active sites of the catalyst have to be identified and confirmed. Based on that information, relations between reactivity and certain structural parameters can be established, which then can be used to optimize the structure of the main active sites. In this context, one should not only focus on the specific metal nanoparticles or individual metal sites but also consider the importance of the support and its specific

Conflict of Interest

The authors declare no conflict of interest.

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