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Pd/Al_2O_3-catalysed redox isomerisation of allyl alcohol: application in aldol condensation and oxidative heterocyclization reactions

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The application of Pd/Al_2O_3 catalyst in allyl alcohol isomerization and subsequent aldol-condensation and heterocyclization reactions is described. The activity of Pd/Al_2O_3 in these transformations is suggested to be due to the participation of the Lewis acidic sites of the support in the activation of the alcohol towards oxidative dehydrogenation by the metal and subsequent hydride transfer. The resulting enol(ate)/aldehyde could undergo further reactions promoted by the acid-base properties of the support. In the aldol condensation reactions of the isomerization product electron poor aromatic aldehydes and heteroaromatic aldehydes showed the highest activity, while aromatic aldehydes bearing electron donating substituents reacted after transformation to the corresponding *N*-tosyl imines. 1,2-disubstituted aromatics gave heterocyclic products in one-pot multistep reaction sequences.

Introduction

The transition metal catalysed redox isomerization of allylic alcohols to carbonyl compounds[1] (Figure 1a), has been widely studied not only because of its atom-economical nature[2] but also for its use in tandem isomerisation/C-C or C-heteroatom bond formation processes.[3]

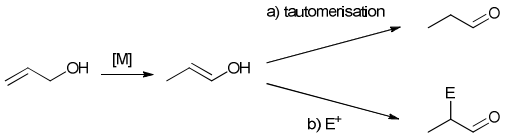

Figure 1 Transition metal catalysed redox isomerisation of allyl alcohol (M = Ru, Rh, Fe, Co, Ni, Mo, Ir, Pt, Os, etc.). The enolate intermediate could either tautomerise to the corresponding saturated carbonyl compound (a) or sequentially react with an electrophile (E^+) to form a new C-C or C-heteroatom bond.

The most extensively studied tandem reactions of allylic alcohols are those where these molecules are participating as the corresponding enols/enolates (aldol and Mannich reactions, electrophilic fluorinations, *etc*.) produced *via* transition-metal catalysed double bond isomerisation (Figure 1b). The majority of the catalysts developed for the isomerisation chemistry are transition metal complexes; particularly efficient are Ru and Rh complexes but other metals from the groups 8, 9 and 10 have been used successfully as well.[4]

Compared to transition metal complexes supported transition metals are rarely documented as catalysts for isomerisation[5-10] and essentially there is no example of combining heterogeneous transition metal catalysed isomerisation with C-C or C-heteroatom bond formation processes exists.[11] This is surprising in light of the current efforts of developing one-pot tandem reactions over heterogeneous catalysts as a means of environmentally benign organic synthetic methodology.[12-20] Strikingly, although Pd is one of the most synthetically useful catalytic transition metals,[21] it is underrepresented in these kinds of transformations of allylic alcohols.[11,22-33] Pd-catalysed isomerisation is mostly discussed as a competing reaction of the double bond hydrogenation process.[22-24,26,27,31,32] There seems to be two main reasons why Pd-catalysis is problematic in this context. In one hand, Pd(0) complexes favour to form π-allyl complexes with allyl alcohol[34,35] instead of the insertion into the O-H bond.[36] The other issue is related to the formation of a metal-hydride, which has been identified as key catalytic species in the isomerisation of allylic alcohols.[3,4,37] While in the case of metal complexes the hydride can be present in the form of hydride ligand in the pre-catalyst[38-40] or could form *in situ* upon oxidation of the allylic alcohol used,[1,41,42] for supported Pd[23,24,26,27] or alkylthiol stabilized Pd nanoparticles[28-30] a H_2 atmosphere is described to be necessary for the isomerisation to proceed. In fact, some authors state that in the absence of hydrogen no reaction occurred.[22,23,26] The presence of H_2, however, can be responsible for lowering the product selectivity due to the

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†Electronic Supplementary Information (ESI) available: The effect of other Pd-sources, control experiments with propionaldehyde and acrolein, synthesis and characterisation and NMR spectra of compounds presented in this article. DOI: 10.1039/x0xx00000x

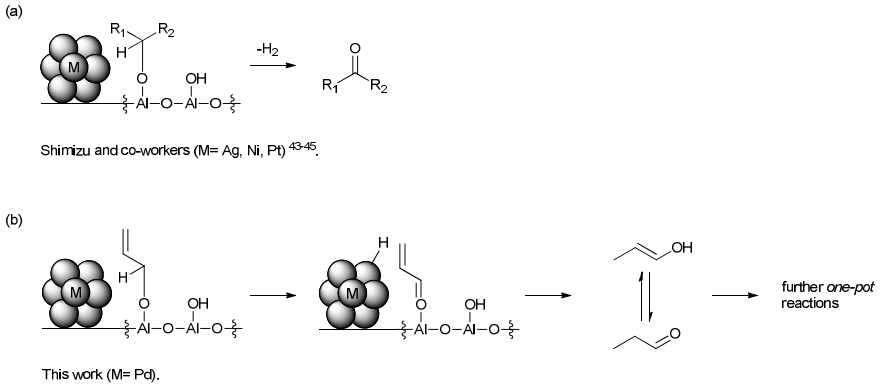


Figure 1 (a) Cooperative oxidative dehydrogenation of alcohols over Al_2O_3-supported transition metals; (b) Isomerisation of allyl alcohol to the corresponding enol(ate) over Pd/Al_2O_3.

competing hydrogenation process leading to the corresponding saturated alcohol and could potentially interfere with additional catalytic steps. Therefore, extensive optimization is necessary for maximising the selectivity of the required isomerisation product.

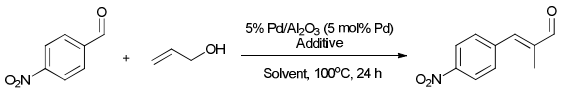
Building on the design of Shimizu and co-workers using Al_2O_3-supported transition metals for cooperative oxidative dehydrogenation of alkyl and cycloalkyl alcohols[43-45] (Fig. 2. a) we envisioned that the M-H species forming during the process could participate in a conjugate reduction of oxidised allyl alcohol (acrolein) that would lead to enol(ate) formation (Fig. 2. b). Thus, the isomerisation of allyl alcohol could be realised on supported transition metal catalyst and the resulting enol(ate) could be involved in further one-pot reactions.

Here we report the Pd/Al_2O_3-catalysed isomerisation of allyl alcohol and the subsequent one-pot transformation of the isomerisation products in aldol condensation and heterocyclization reactions without added H_2 gas. We suggest that the synergistic activation of the alcohol reactant by the Lewis-acidic sites of the Al_2O_3 support and the Pd metal is key for the reactions to occur.

Results and discussion

The optimization of the reaction conditions to isomerise allyl alcohol to the corresponding enol(ate) over Pd/Al_2O_3 and involve it in aldol chemistry with 4-nitrobenzaldehyde are shown in Table 1. In line with our expectations, Pd/Al_2O_3 alone proved to be an active catalyst for both the isomerisation and the condensation steps. Other Pd-based catalysts (Pd(II) salts, $Pd/CaCO_3$, $Pd/BaSO_4$, Pd/SiO_2, Pd/C, Pd/CeO_2) failed to catalyse the reaction or delivered minor amount of condensation product (for more details and control experiments, see sections S2 and S3 of the ESI). The isolated yields could be further increased with the addition of 1 eq K_2CO_3 (Table 1, entry 2), however, increasing the amount of the carbonate did not considerably affect the yield.

Table 1 Optimisation of Pd/Al_2O_3 catalysed allyl alcohol isomerisation/aldol condensation sequence.[a]



Entry	Solvent	Additive	Yield (%)[b]
1	toluene	-	38
2	toluene	K_2CO_3 (1 eq)	45
3	toluene	K_2CO_3 (2 eq)	40
4[c]	toluene	K_2CO_3 (1 eq)	44
5[d]	toluene	K_2CO_3 (1 eq)	28
7	toluene	$MgSO_4$ (1 eq)	35
8	toluene	4Å mol. sieves	29
9	toluene	NaOAc (1 eq)	25
10	toluene	KO*t*Bu (1 eq)	mixture
11	toluene	Et_3N (1 eq)	15
12	H_2O	K_2CO_3 (1 eq)	<5
13	1,4-dioxane	K_2CO_3 (1 eq)	19
14	DMSO	K_2CO_3 (1 eq)	<5
15	DMF	K_2CO_3 (1 eq)	<5
16[e]	toluene	K_2CO_3 (1 eq)	26

[a] Reaction conditions: 0.5 mmol 4-nitrobenzaldehyde, 1 mmol allyl alcohol, 1 mL toluene, 5 mol% Pd of a given source, additive, 100°C, 24 h. [b] Isolated yield of the aldol condensation product. [c] The reaction was performed under N_2 atmosphere. [d] The reaction was performed at 50°C. [e] The catalyst was pre-treated: 90 min in H_2 flow (30 mL/min) at 200°C then 30 min at He flow (30 mL) at rt.

In order to test the role of the K_2CO_3 additive, weather it is a base or a drying agent to eliminate the water forms during the condensation step, we performed the reaction in the presence

of $MgSO_4$ and 4Å molecular sieves (Table 1, entries 7, 8). As the results with these additives are similar to those obtained without any additive, we conclude that K_2CO_3 is rather has a role as a base. It could participate in the alcohol deprotonation and in the aldol condensation step complementing the effect of the support material. It has to be noted, that using Al_2O_3 alone did not lead to product formation, furthermore under Pd/Al_2O_3 catalysis we detected the formation of some 2-methyl-2-pentenal from the self-aldol condensation of propanal as a side-product. We also tested other bases (1 eq) in combination with Pd/Al_2O_3 (Table 1, entries 9-11). Using NaOAc gave a decreased yield of 25%, while in the case of KOtBu a complex mixture of products were formed. Et_3N was not beneficial either as only 15% isolated yield was obtained in this case.

Using more polar solvents gave generally lower yields compared to toluene (Table 1, entries 12-15). Moreover, in such solvents we observed the formation (up to 10%) of the decarbonylated product nitrobenzene and also benzaldehyde upon loss of the NO_2-group. The formation of inactive carbonyl complexes could contribute to catalyst deactivation under such conditions.

Performing the reaction without the exclusion of air or under N_2 atmosphere did not significantly affect the outcome (Table 1, entry 2 vs 4), however, reductive pre-treatment (H_2, 200°C) of the catalyst led to decreased yield (Table 1, entry 16). This result is in agreement with previous findings on the nature of active sites in heterogeneous Pd-catalysed selective oxidation of allylic alcohols. It has been shown that the presence of higher oxidation state surface environments is necessary for the oxidative dehydrogenation to proceed efficiently.[46-48] Particularly, the Pd-O-Al surface structures[47] at the perimeter of the metal particles likely have an important role in the activation of the allyl alcohol towards isomerisation that could be destroyed during the reductive pre-treatment. The formation of such metal-support contacts has been observed for Pt-based catalysts[49,50] and suggested for Pd/Al_2O_3 as well.[47,51]

As a comparison we tested 5% Pt/Al_2O_3 (Engelhard 4759) also, however, over this catalyst no condensation product was isolated. Instead, apart from unreacted aldehyde, we detected the formation of (4-nitrophenyl)methanol, the reduced derivative of 4-nitrobenzaldehyde as the only product, which is likely the result of a transfer-hydrogenation reaction, allyl alcohol being the hydrogen source. The different reactivity of the Pt and Pd systems could be based on the different stability of the forming M-H species[36] that is involved in the next step of the catalytic cycle. Pt-H being more stable, reacts only with the carbonyl carbon of the aromatic aldehyde that carries more positive charge relative to the β-carbon of acrolein.

The influence of allyl alcohol excess in the reaction of 4-nitrobenzaldehyde and allyl alcohol was studied in order to increase the isolated yield of the aldol condensation product (Fig. 3.). However, we found that the alcohol has a poisoning effect as increasing its amount led to decreased yields.

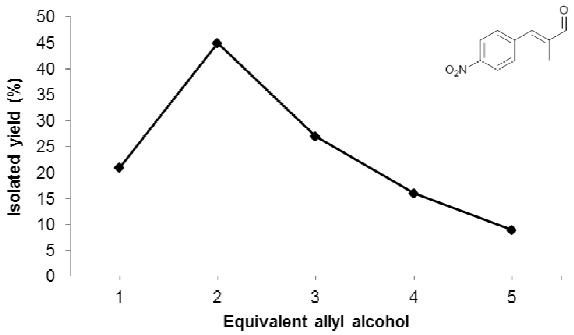
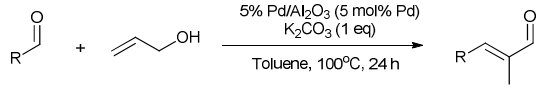
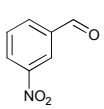
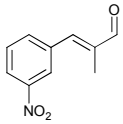
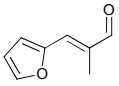
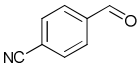
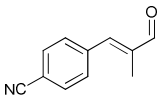
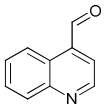
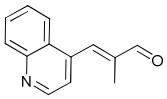
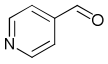
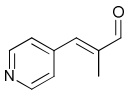
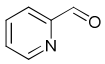
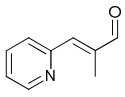
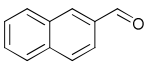
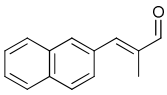
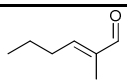


Figure 2 Effect of allyl alcohol excess on the reaction of 4-nitrobenzaldehyde with allyl alcohol. (Reaction conditions: 0.5 mmol aldehyde, 1 mL toluene, 5 mol% Pd (source: 5 % Pd/Al_2O_3), 0.5 mmol K_2CO_3, 100°C, 24 h.)

Table 2 Reactivity of different aldehydes in the Pd/Al_2O_3 catalysed isomerisation/aldol condensation sequence.[a]



Entry	Aldehyde	Product	Yield (%)[b]
1			20
2			67 (45)[c]
3			58
4[d]			50
5[d]			54
6[d]			26
7			8

8			traces

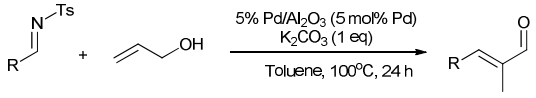
[a] Reaction conditions: 0.5 mmol aldehyde, 1 mmol allyl alcohol, 1 mL toluene, 5 mol% Pd (source: 5 % Pd/Al_2O_3), 0.5 mmol K_2CO_3, 100°C, 24 h. [b] Isolated yield of the aldol condensation product. [c] Isolated yield without K_2CO_3 additive. [d] Reaction time was 48 h.

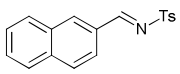
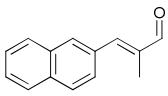
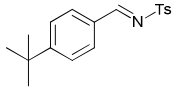
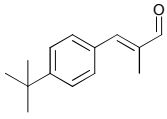
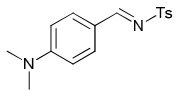
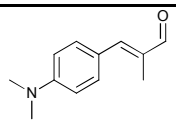
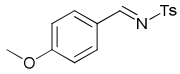
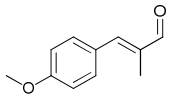
A possible reason for such an effect is the competitive interaction of allyl alcohol (or the isomerisation product propionaldehyde) with the Lewis acidic sites of the support that hinders the activation of the aromatic aldehyde towards the aldol condensation step. Similar effect of reactant excess in Lewis acidic zeolite catalysed aldol condensation has been recently reported.[52]

Other aldehyde substrates were also tested under the $Pd/Al_2O_3/K_2CO_3$ conditions. In the case of aromatic aldehydes with electron withdrawing groups and heteroaromatic aldehydes we obtained the aldol condensation products in moderate to good yields (Table 2). However, aliphatic aldehydes and aromatic aldehydes bearing electron donating groups did not undergo reaction. Products from such aldehydes would be desirable as those are precursors to flavour and fragrance compounds (such as lilial or canthoxal that contain 4-tert-butylphenyl and 4-methoxyphenyl groups, respectively; Table 3, entries 2 and 4).

We transformed the aromatic aldehydes with electron donating groups to the corresponding *N*-tosyl imines in order to activate them towards reaction with the enolate. This transformation was proved to be successful in terms of reactivity, however, it also raised some difficulties. The eliminated sulphonamide participated in side reactions, such as reaction with the product aldehyde that made the purification tedious in some cases.

Table 3 Reactivity of *N*-tosyl imine derivatives of electron rich aromatic aldehydes in the Pd/Al_2O_3 catalysed isomerisation/aldol condensation sequence.[a]



Entry	*N*-tosyl imine	Product	Yield (%)[b]
1			25
2			59
3			32
4			50

[a] Reaction conditions: 0.5 mmol *N*-tosyl imine, 1 mmol allyl alcohol, 1 mL toluene, 5 mol% Pd (source: 5 % Pd/Al_2O_3), 0.5 mmol K_2CO_3, 100°C, 24 h. [b] Isolated yield of the aldol condensation product.

We also examined the reusability of the catalyst in the reaction of 4-cyanobenzaldehyde with allyl alcohol (Table 4). After a reaction was performed we filtered the catalyst, washed with EtOAc and Et_2O, dried and used in the next reaction. The catalyst remained active in four consecutive reactions, although the activity decreased considerably. This could be due to the formation of polymeric side products that could not be washed off the surface of the catalyst. We also tested the potential contribution of dissolved active catalyst. We found no increment in the conversion after filtering the catalyst at 3 h reaction time from the reaction mixture and heated the solution further until the 24 h reaction time was complete (see also ESI).

Table 4 Catalyst recycling study in the reaction of 4-cyanobenzaldehyde with allyl alcohol over Pd/Al_2O_3 catalyst.[a]

Entry	Cycle	Time (h)	Yield (%)[b]
1	1	24	58
2	2	24	38
3	3	24	35
4	4	48	12

[a] Reaction conditions: 0.5 mmol aldehyde, 1 mmol allyl alcohol, 1 mL toluene, 5 mol% Pd (source: 5 % Pd/Al_2O_3), 0.5 mmol K_2CO_3, 100°C. [b] Isolated yield of the aldol condensation product.

To further increase the structural diversity accessible with the allyl alcohol/supported Pd system we examined 1,2-disubstituted aromatics under the reaction conditions. We speculated that after the first, aldol condensation (or imine formation) step ring-closing reactions might be feasible to obtain heterocycles. We studied the reaction of salicylaldehyde and ortho-substituted anilines with allyl alcohol.

As we envisioned, ring closing occurred in the reaction of salicylaldehyde, however, the reaction did not stop in the lactol stage, but proceeded further with an oxidation step that delivered 3-methylcoumarine as the overall product (Fig. 4.). We also compared the activity of Pd/C and Pd/Al_2O_3 catalyst in this reaction. Similarly as in the aldol chemistry the Pd/Al_2O_3 system outperformed Pd/C.

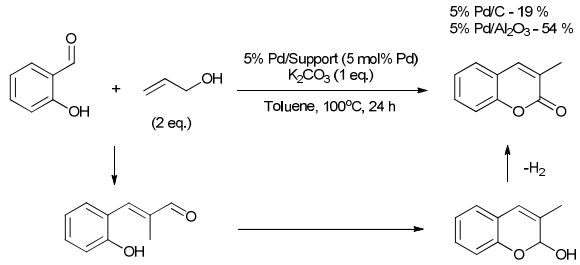


Figure 3 Supported Pd-catalysed one-pot isomerisation/aldol condensation/lactol formation/dehydrogenation cascade reaction of allyl alcohol with salicyladehyde.

We considered o-phenylenediamine as an interesting substrate, as in this case not the nucleophilic enolate but the electrophilic carbonyl reactivity was necessary for any reaction to occur (Fig. 5). However, when the reaction was performed under basic (K_2CO_3, 1 eq.) conditions a mixture of products were formed, with the diimine as the main component. Nevertheless, we detected 2-ethylbenzimidazole in the product mixture that already suggested a second oxidation step during the process. Importantly, without added base the benzimidazole derivative was isolated as the main product. Interestingly, Pd/C was also active in this transformation, likely due to the basicity of the aniline nitrogen that was comparably beneficial as K_2CO_3 in the aldol condensation reactions. Using 3 eq of alcohol resulted in 6% increment of the isolated yield with Pd/Al_2O_3 catalyst.

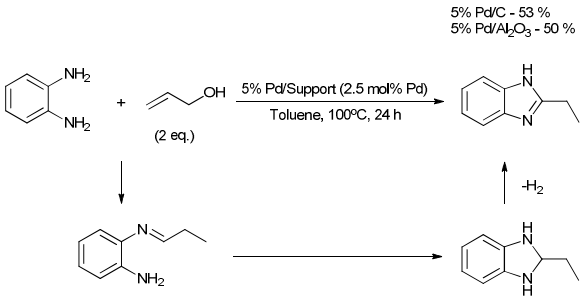


Figure 4 Supported Pd-catalysed one-pot isomerisation/imine formation/ring closing/dehydrogenation cascade reaction of allyl alcohol with *o*-phenylenediamine.

The reactivity of 2-aminothiophenol and 2-aminophenol was also tested under the reaction conditions. In the former case the oxidative formation of the corresponding disulphide was faster than the isomerization/imine formation/ring closing sequence and we isolated the disulphide in high yield (Fig. 6.). It is noted that the allyl alcohol is not necessary for this transformation, as we obtained the same result when the reaction was repeated without the alcohol.

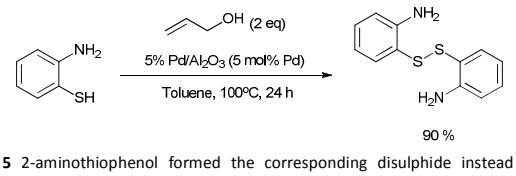


Figure 5 2-aminothiophenol formed the corresponding disulphide instead of the benzothiazole derivative under the reaction conditions.

Similarly as for *o*-phenylenediamine, the added base decreased the selectivity somewhat. The reaction of 2-aminophenol resulted in the formation of a complex mixture with only traces of the expected benzoxazole derivative. The mixture also contained the imine and minor amount of *O*- and *N*-allylation products.

For the occurrence of both the aldol condensation reactions and ring formations described above the isomerisation of allyl alcohol is prerequisite. As all the reactions studied took place more efficiently when Pd/Al_2O_3 was used as a catalyst, we propose a metal/support cooperativity that operates under the reaction conditions (Fig. 7). Such cooperativity has been described in heterogeneous alcohol oxidation chemistry[43-45,53,54] but unprecedented in isomerisation reactions.

We propose that the key for the isomerisation to occur is the coordination of the alcohol to a Lewis-acidic Al-site adjacent to Pd-particles (Fig. 7, step 1), which is positioning and activating the alcohol towards the oxidative dehydrogenation step catalysed by the metal. This process is further supported by the affinity of the double bond to the Pd. After the dehydrogenation takes place and the metal hydride forms, the product acrolein either stays coordinated to the support (step 2b) or decoordinates (step 2) and coordinates again in a next step (step 3). In any case, a hydride transfer follows that yields the enolate (step 4) that tautomerises to the corresponding saturated aldehyde (step 5). We performed control experiments with allyl acetate and acrolein to show that both the O-H proton and the α-proton adjacent to the OH group are necessary to be present for the isomerisation. In fact, the use of these reagents did not lead to product formation in the reaction with 4-nitrobenzaldehyde. (For further control experiments, see section S3 of the ESI.) The participation of the Lewis-acidic Al-sites is also supported by the poor results when bases that are able to block these centres (KOtBu, Et_3N) were used. On the other hand, the role of framework oxygens in Al_2O_3 as basic sites[45,52] was tested with the addition of CH_3COOH to the reaction mixture. Upon addition of 25 mol% acid resulted in a decrease in the isolated yield (25% with acid *vs*. 38% without any additive) of the condensation product. These together suggest the importance of both acidic and basic sites of the support material in the overall transformation.

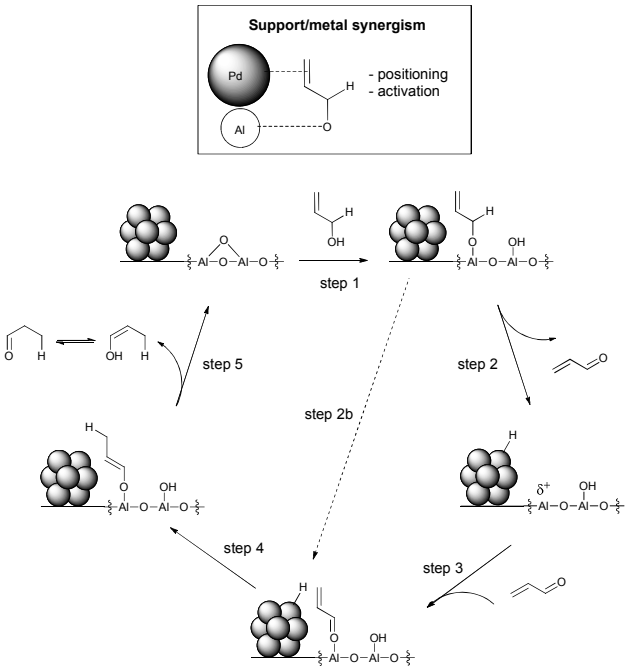


Figure 6 Proposed mechanism for the isomerisation of allyl alcohol over Pd/Al_2O_3 involving support/metal synergism.

Conclusions

Alumina supported Pd was found to be an active catalyst in allyl alcohol isomerization which transformation was combined with aldol condensation and heterocyclic ring formation reactions one-pot. The activation of the alcohol by the alumina towards oxidative dehydrogenation by the metal and the subsequent hydride-transfer resulted in the overall isomerization reaction without the need of added H_2 gas. The acid-base properties of the support material also allowed for subsequent aldol condensation and imine formation reactions one-pot, yielding α,β-unsaturated aldehydes and heterocyclic compounds, thus, providing considerable structural diversity accessible using a simple catalyst/reactant system. The described reaction sequences open up new possibilities in the Pd-catalysed chemistry of allyl alcohols and could be integrated into more complex one-pot reactions in the future.

Experimental

Commercial reagents, solvents and catalysts (Aldrich, Alfa Aesar, Fluka, VWR) were purchased as reagent–grade and used without further purification. 5% Pd/Al_2O_3 was Engelhard 40692 type. Pd/CeO_2 was prepared according to a literature procedure.[55] Catalysts were used without any pre-treatment or otherwise noticed. Reactions were performed in a screw cap vial without the exclusion of air or otherwise noticed. Solvents for extraction or column chromatography were of technical quality. Organic solutions were concentrated by rotary evaporation at 25-40 °C. Thin layer chromatography was carried out on SiO_2–layered aluminium plates (60778-25EA, Fluka). Flash column chromatography was performed using SiO_2–60 (230–400 mesh ASTM, 0.040–0.063 mm from Merck) at 25 °C. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AVANCE DRX 400 spectrometer. Mass spectra (MS) of the products were recorded on an Agilent 6890N-5973 GC-MSD. For further details on the synthesis and characterization of the products presented in this article, see ESI.

General procedure for the isomerization/aldol condensation sequence: The aldehyde or *N*-tosyl imine (0.5 mmol), 5% Pd/Al_2O_3 (5 mol% Pd, 53 mg), K_2CO_3 (0.5 mmol) were suspended in toluene (1 mL) and subsequently allyl alcohol was added (1 mmol). The mixture was heated at 100°C for 24 h then filtered. The residue was washed several times with EtOAc. The organic phase was concentrated and purified by flash column chromatography.

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