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Exploring Pd/Al_2O_3 Catalysed Redox Isomerisation of Allyl Alcohol as a Platform to Create Structural Diversity

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Abstract We report our results on exploiting the different reactivities present in the catalytic cycle of the Pd/Al_2O_3 catalyzed redox isomerization of allyl alcohol. We show that the reactivity of allyl alcohol derived acrolein and enol can be involved in further cascade reactions leading to a diverse set of products. While the oxidation product acrolein can react via Michael and oxa-Michael reactions, the isomerization product enol can be readily involved in aldol condensation processes. Salicylaldehydes, that are able to react on their electrophilic carbonyl and nucleophilic OH-groups with allyl alcohol derived enol and acrolein, respectively, are used to explore conditions where the structure of the product heterocycles can be controlled.

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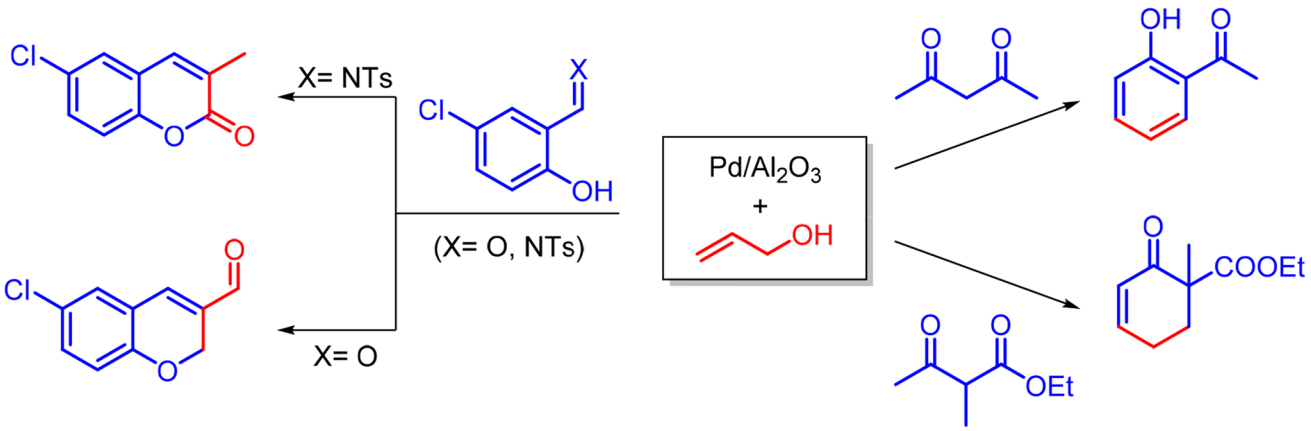
Graphical Abstract



Keywords Allyl alcohol · Isomerization · Pd/Al_2O_3 · Pt/Al_2O_3 · Michael addition · Heterocycles

1 Introduction

Major efforts in organic chemistry are directed towards synthesizing increasingly complex and diverse molecular structures in operationally simple and environmentally benign ways [1]. In this context several synthesis concepts have emerged in the last decades such as atom economical reactions [2], click chemistry [3] or one-pot strategies [4]. Especially attractive are the methodologies that realize those concepts under heterogeneous catalytic conditions [5–7]. Applying multi-site solid catalysts for one-pot sequential reactions is an emerging area of research with clearly foreseeable environmental and economic benefit [8, 9]. Solid catalysts represent environmentally more benign alternatives of many homogeneous systems as they can be recovered and reused several times that can ultimately reduce the energy need and the amount of waste produced during chemical processes.

Multi-site catalysts, due to their isolated catalytically active centres, are potentially able to produce different intermediates with distinct reactivities from a single starting material that could be exploited in different reactions. Such catalyst/reactant systems with tuneable reactivity profiles would be particularly interesting to develop one-pot multistep processes for producing diverse molecular structures [8].

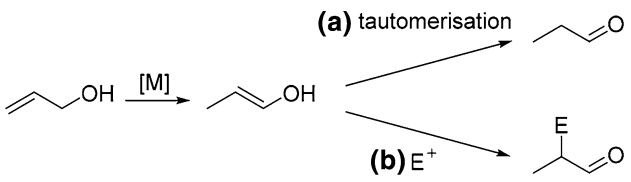


Fig. 1 Transition metal catalysed redox isomerisation of allyl alcohol (M = Ru, Rh, Fe, Co, Ni, Mo, Ir, Pd, Pt, Os, etc.). The enolate intermediate could either tautomerise to the corresponding saturated carbonyl compound (**a**) or sequentially react with an electrophile (**b**) to form a new C–C or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

To further develop this concept an interesting reaction is the transition metal-catalysed redox isomerisation of allylic alcohols to carbonyl compounds (Fig. 1a) [10–13]. This reaction has been widely studied because of its atom-economical nature, and also for its use in tandem isomerisation/C–C or C–heteroatom bond formation processes [14]. Regarding the tandem processes, allyl alcohol has been almost exclusively applied as an enolate equivalent (Fig. 1b).

However, considering the proposed mechanisms of allylic alcohol isomerisation[1] there are at least three[2] intermediates where different reactivities could be extracted (Fig. 2). Acrolein (α,β-unsaturated carbonyls, generally) **A** with an electrophilic reactivity at the β-carbon, enolate **B** with a nucleophilic reactivity and aldehyde **C** with an electrophilic carbonyl carbon could be involved selectively in further reactions with properly chosen reagents.

Recently, we have expanded the scope of the available heterogeneous Pd-catalyzed allyl alcohol isomerization processes [16–20] and showed that reactivities **B** and **C** can be selectively exploited in combination with aldol condensation and oxidative heterocyclization reactions accessing a diverse set of structures with a single catalyst/reactant system (Fig. 3) [21]. Using simple Pd/Al_2O_3

[1] Note that the simplified mechanism presented here is based on recent mechanistic studies on Ru and Rh based catalysts and only aimed at showing the key intermediates whose reactivity could be exploited. For more mechanistic insights see refs. [10–13] and references therein.

[2] Note that allyl alcohol itself could be used for allylation also in Tsuji-Trost type reactions. For an overview see Muzart [15].

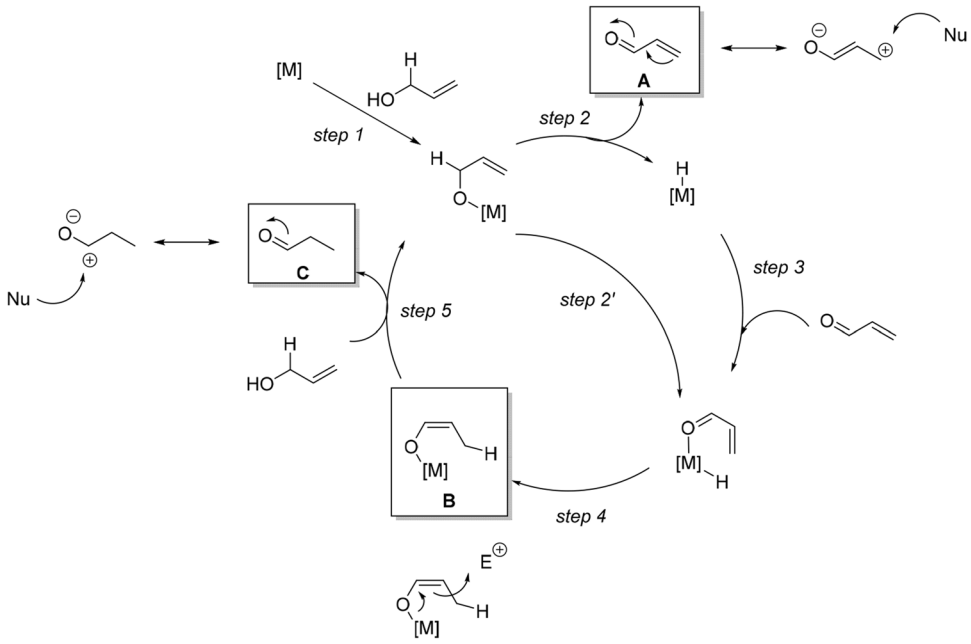


Fig. 2 Schematic representation of a plausible mechanism of the transition metal catalysed isomerisation of allyl alcohol. Structures **A, B** and **C** show possible reactivity profiles that could be individually exploited to create structurally divers products in a one-pot fashion using a single catalyst

catalyst in combination with allyl alcohol we were able to access α,β-unsaturated carbonyl compounds via an isomerisation/aldol condensation sequence and cyclic lactones via an isomerisation/aldol condensation/cyclic hemiacetal formation/oxidation sequence (Fig. 3 Reactivity **B**). While these reactions made use of the enolate reactivity derived from allyl alcohol, the carbonyl reactivity of the isomerisation product propionaldehyde could be exploited in the formation of a benzimidazole derivative (Fig. 3 Reactivity **C**). The initial step of this latter reaction is an imine formation between the aromatic amine and the carbonyl group of propanal.

Although using allyl alcohol as a carbonyl precursor in tandem reactions has scarcely been described, this reactivity is not independent from the enolate form as the two species are in equilibrium with each other. A more challenging task is to selectively exploit reactivity **A** involving the α,β-unsaturated compound acrolein. Acrolein forms in the first stage of the isomerisation process upon the oxidative dehydrogenation of ally alcohol and it is not in equilibrium with any of the following species in the cycle. Thus, any reaction involving acrolein has to take place before it gets reduced to the enolate form. Although the Pd-catalyzed oxidation chemistry of allylic alcohols have been investigated extensively, in most cases the isomerization pathway is not pronounced [22–33]. On the other hand it is a commonly observed side-reaction during the hydrogenation of the same type of compounds [16–19, 34–36]. In these cases isomerisation occurs only in the presence of hydrogen gas over heterogeneous Pd-catalysts, which is likely involved in the formation of Pd-H species necessary for the reduction step that leads to enolate formation.

Here we report our results on expanding the accessible structural diversity based on the heterogeneous catalytic redox isomerisation of allyl alcohol with a focus on the involvement of acrolein reactivity.

2 Experimental

2.1 General Remarks

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 and 5% Pt/Al_2O_3 were Engelhard 40,692 and Engelhard 4759 type, respectively. Catalysts were used without any pre-treatment,[3] or otherwise noted. Reactions were performed without the exclusion of air, or otherwise noted. 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.

[3] Our earlier results (see ref. [21]) showed that reductive pretreatment of the catalyst results in a decreased activity, hence we used the as-received catalysts throughout the present study.

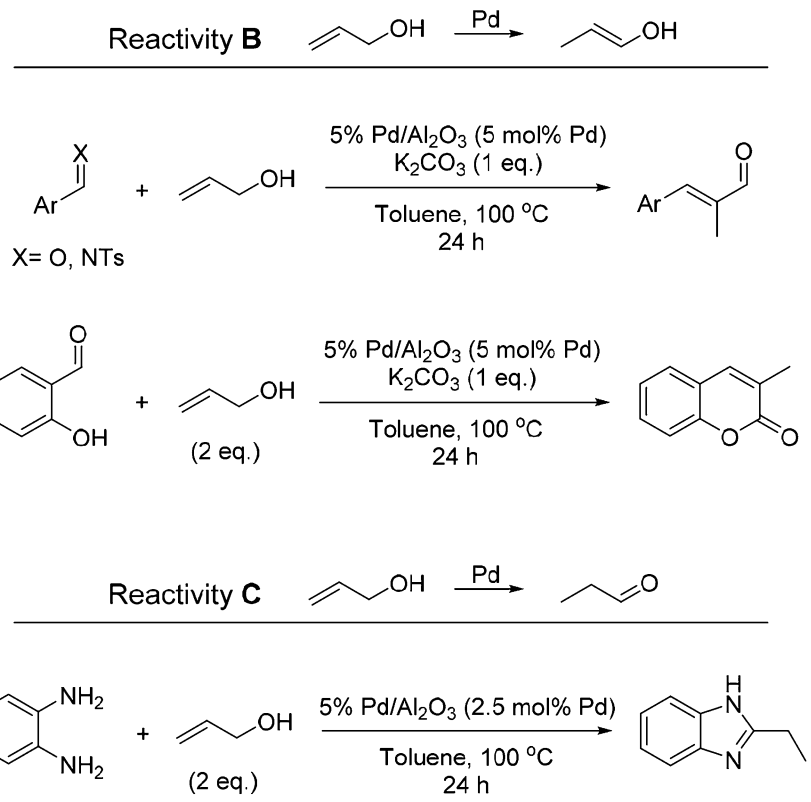


Fig. 3 Examples of the use of enol-type reactivity (**B**) and carbonyl-type reactivity (**C**) for the synthesis of different products based on the Pd/allyl alcohol catalyst/reactant system

2.2 Instrumentation

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AVANCE DRX 400 or a Varian 500 spectrometer. All spectra were recorded at 25 °C. The residual solvent peaks were used as the internal reference ($CDCl_3$: $\delta_H = 7.26$ ppm, $\delta_C = 77.16$ ppm). ^{1}H NMR spectra are reported as follows: chemical shift δ in ppm relative to TMS ($\delta = 0$ ppm), multiplicity, coupling constant (J in Hz), number of protons. The resonance multiplicity is described as s (singlet), d (doublet), t (triplet), q (quartet), combinations thereof, or m (multiplet). Broad signals are described with br. (broad). ^{13}C NMR spectra are reported as follows: chemical shift δ in ppm relative to TMS ($\delta = 0$ ppm) (number of carbons if greater than 1). Mass spectra (MS) of the products were recorded on an Agilent 6980N-5973 GC-MSD.

Imaging of the Pt/Al_2O_3 and the Pd/Al_2O_3 catalysts was performed by a FEI TECNAI G^2 20 X-Twin high-resolution transmission electron microscope (equipped with electron diffraction) operating at an accelerating voltage of 200 kV. The samples were drop-casted onto carbon film coated copper grids from ethanol suspension.

The surface reactions were followed by FTIR spectroscopy on a Bruker Vertex 70 FTIR spectrometer with MIR light source. In-situ reactions were performed in a Specac HPHT reaction chamber with ZnSe windows. The cell was upgraded with temperature controller, reflectance mode kit and gas flushing accessory. The surface reactions on different catalysts were followed in diffuse reflectance (DRIFT) mode, with 512 scans and 2 cm^{-1} resolution.

2.3 Allyl Alcohol Oxidation/Isomerization Over Pd/Al_2O_3 and Pt/Al_2O_3 in the Gas Phase

Catalytic transformation of allyl-alcohol to acrolein and propanal was performed in a continuous flow reactor system at 80 °C, where N_2:O_2 with a 9:1 ratio and a total flow rate of 100 ml min^{-1} at 1 bar were bubbled through a saturator filled with allyl alcohol at 23 °C. The reaction products were analyzed with an Agilent 4890 gas chromatograph equipped with PORAPAK 1/2Q + PORAPAK 1/2S packed and Equity-1 capillary column. The sampling loop of the GC was 225 µl. The conversion of the allyl-alcohol was calculated taking into account the amount of reactant consumed. In a typical catalytic test, 5 mg of the catalyst were mixed with 1 g of inert Stöber silica and pretreated for 30 min in Ar with a flow rate of 10 ml min^{-1} at 80 °C before the reaction. The conversion were <14% during the catalytic tests. Calculation of the metallic active sites was based on the average size of the nanoparticles assuming that every surface atom is active in the reactions.

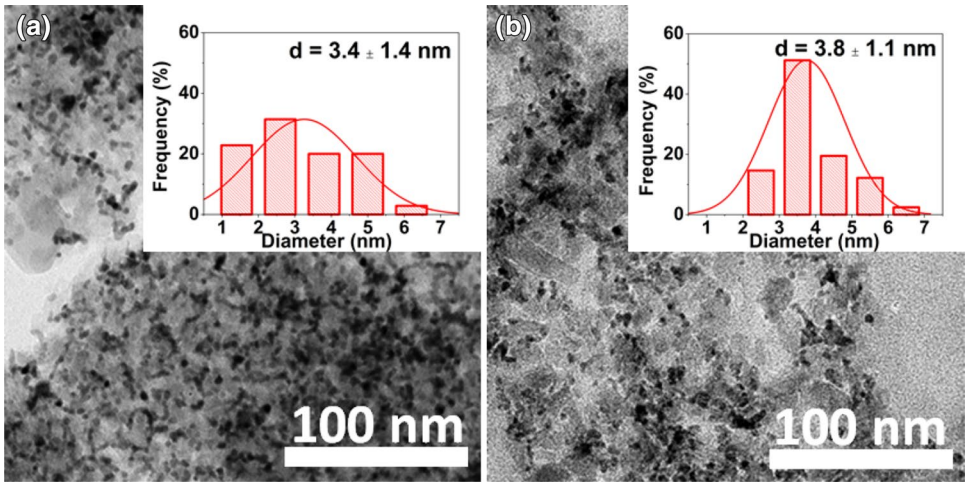


Fig. 4 TEM images of 5% Pt/Al_2O_3 (**a**) and 5% Pd/Al_2O_3 (**b**) catalysts

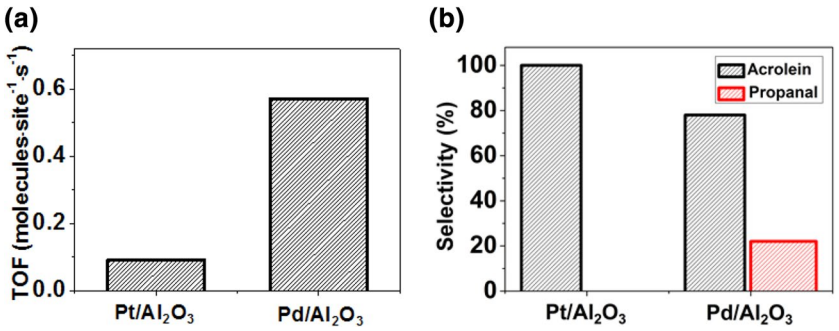


Fig. 5 Activity (**a**) (steady state conditions) and selectivity (**b**) of allyl alcohol transformations over 5% Pt/Al_2O_3 and 5% Pd/Al_2O_3 catalysts in the gas phase at 80 °C

2.4 In-Situ Infrared Spectroscopic Study

In a typical procedure, 5 mg of the catalyst (Pt/Al_2O_3; Pd/Al_2O_3; Al_2O_3) was deposited by pressuring to thin layers onto the 12 mm diameter, highly reflective aluminium foil surfaces. Catalysts were deposited in order to perform Diffuse Reflectance Infrared Fourier Transform (DRIFT) measurements in a High Temperature-High Pressure (HTHP) cell. For the static state reactions, the HTHP cell was first purged by N_2 to avoid contaminants and water. The actual catalyst compositions were backgrounded under N_2 atmosphere. The allyl alcohol reactant was injected to the chamber as saturated vapour by N_2 flow through a gas saturator at RT. After 5 min of the allyl alcohol saturation, the chamber was closed and heated to the reaction temperature (80 °C). After 24 h, the chamber was purged for 15 min with pure N_2 in order to determine the adsorbed species on the surface of the catalysts.

2.5 Synthesis and Characterization

The detailed synthetic procedures and characterization of compounds described in this article can be found in the Supporting Information.

2.5.1 General Procedure for the Solution Phase Cascade Reactions

The ketone, ketoester, aldehyde or *N*-tosyl imine (0.5 mmol), 5% Pd/Al_2O_3 or Pt/Al_2O_3 (5 mol% metal), 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.

3 Results and Discussions

3.1 Gas-Phase Transformation and In-Situ FTIR Study

Initially, we investigated the capacity of the applied Pd/Al_2O_3 catalyst to transform allyl alcohol into the oxidation product acrolein and isomerisation product propanal. This was expected to give information on the conversion and selectivity values that can be obtained during the transformation. As a control catalyst, we used Pt/Al_2O_3 which was expected to be active primarily in the oxidation of allyl alcohol to acrolein [37].

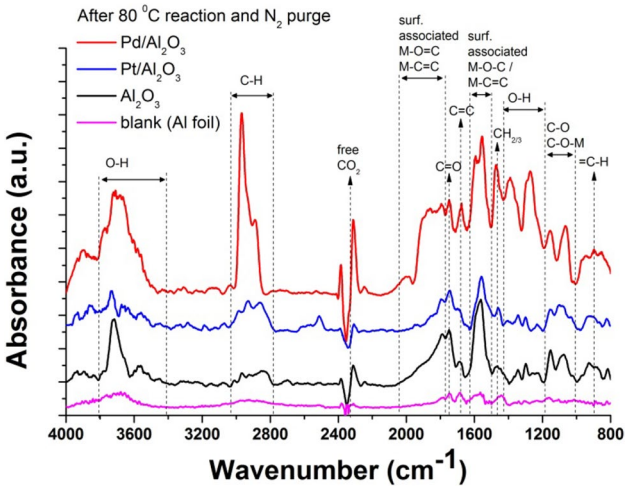


Fig. 6 In-situ IR spectra of the surface of the Pt/Al_2O_3 and Pd/Al_2O_3 after 24 h allyl alcohol exposure at 80 °C

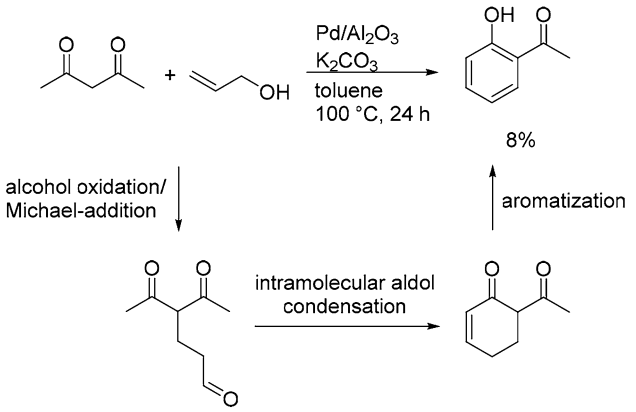


Fig. 7 Transformation of acetylacetone to 2-acetylphenol with acrolein generated from allyl alcohol. The sequence, apart from the oxidation of allyl alcohol, involves a Michael addition, an intramolecular aldol-condensation and an aromatization step

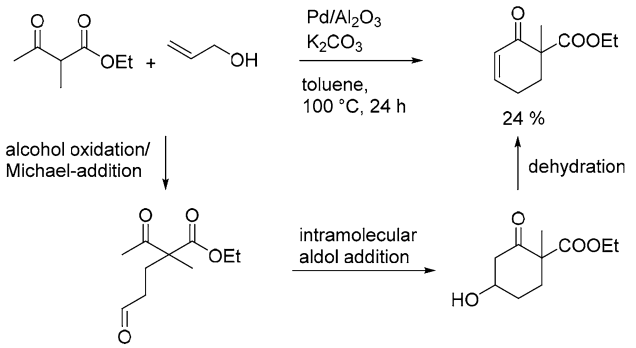


Fig. 8 Transformation of ethyl 2-methylacetoacetate to a cyclohexenone derivative with acrolein generated from allyl alcolhol. The sequence, apart from the oxidation of allyl alcohol, involves a Michael addition, and an intramolecular aldol-condensation step

In the case of both 5% Pt/Al_2O_3 and 5% Pd/Al_2O_3 catalysts, the metal components were present as nanoparticles highly dispersed on the surface of the Al_2O_3 support (Fig. 4). The average diameter of the catalyst particles was 3.4 ± 1.4 and 3.8 ± 1.1 nm for Pt/Al_2O_3 and Pd/Al_2O_3, respectively.

We tested the activity of both catalysts in the transformation of allyl alcohol in a flow mode gas reactor at 80 °C.

The catalytic activity of Pd and Pt on Al_2O_3 was markedly different (Fig. 5). While with Pd/Al_2O_3 an overall Turnover frequency of 0.57 molecules site^{-1} s^{-1} was obtained, Pt/Al_2O_3 was poorly active delivering only 0.09 molecules site^{-1} s^{-1} (Fig. 5a). Not only had the activity showed differences, but also the obtained selectivities (Fig. 5b). As expected, the Pt containing catalyst was active only in the oxidation step and only acrolein was detected in the product mixture. On the other hand, over Pd/Al_2O_3 both the oxidation product acrolein and isomerisation product propanal was formed with 78 and 22% selectivity, respectively. These results are in line with our previous findings on the activity of these catalyst in the reaction of allyl alcohol with substituted benzaldehydes leading to α,β-unsaturated carbonyls via reactivity B [21].

The results point out that under Pd catalysis both the oxidation and the isomerisation processes are operating. Moreover, the presence of considerable amount of acrolein suggests that its reduction to the enol is not so fast that would prevent the possibility of its involvement in other reactions (e.g. Michael addition). It has to be noted, that the gas-phase measurements cannot be directly paralleled to the results obtained in solution phase reactions where a complex multicomponent mixture is surrounding the catalyst, however, they give the basis for further exploring solution phase cascade reactions.

We investigated the transformation pathways of allyl alcohol over the Pd- and Pt-based catalyst by in-situ DRIFT spectroscopy to get more insight into the processes occur on the catalyst surfaces. Generally, the results reflect the more rich chemistry occur on the surface of Pd/Al_2O_3 compared to Pt/Al_2O_3, similarly to that observed in the gas phase reactions.

Figure 6 shows the assumed adsorbed species in dependence of catalyst composition. Due to intensive purging of the reaction chamber only adsorbed species appeared on the spectra. Minimal deposition of allyl alcohol appeared on the reference aluminium foil, with hardly shifted broad peaks compared to its gas phase spectrum (see SI). Spectra for Al_2O_3 and Pt/Al_2O_3 samples show similar absorption patterns, indicating the same type of surface associated bonding of the allyl-alcohol intermediates. In contrast, Pd/Al_2O_3 showed differently shifted, broader and even

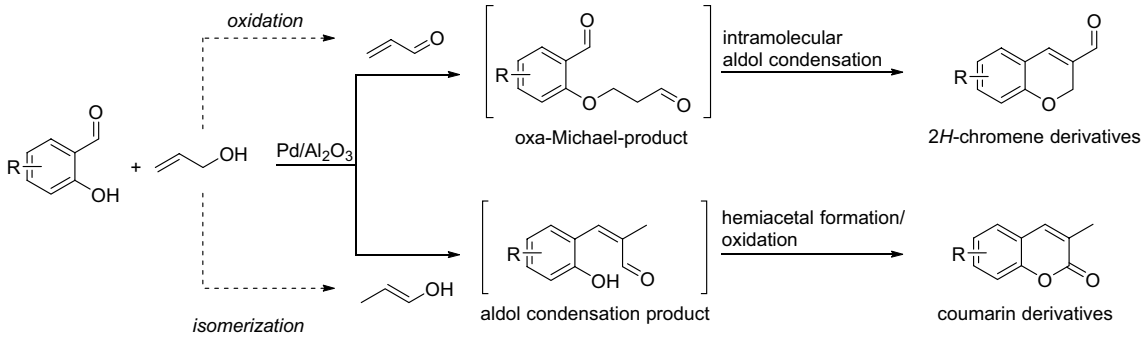


Fig. 9 Salicylaldehydes are able to react on their electrophilic carbonyl and nucleophilic –OH groups with allyl alcohol derived enol and acrolein, respectively. Exploiting the different reactivites could be a handle to control the product structure

splitted peaks, presumably influenced by surface association bonding.

The peaks in the 3800–3400 and 1400–1200 cm^{-1} regions indicate the additional Al–OH groups and allyl alcohol OH groups on the catalyst surfaces. In the case of the Pd/Al_2O_3 catalyst, peaks are more intense and broader, indicating multiple ways of association of the allyl alcohol. In addition, the associated M–O and M–C bonds related 2050–1770 cm^{-1} region shows a blue shift compared to the Pt/Al_2O_3 and Al_2O_3 samples indicating the presence of favourable surface adsorbed propanal as well as the allyl alcohol associated on multiple points on Pd/Al_2O_3 due to the high affinity of the carbon–carbon double bond to the metallic Pd. In the case of the Pd-based catalyst, C=C stretching at 1630 cm^{-1} showing the stable presence of acrolein or enol form on the surface. We suggest that the occurred selectivity differences of Pd/Al_2O_3 and Pt/Al_2O_3 can be related to association affinity difference of carbon double bond to Pd and Pt on alumina support. High selectivity of Pt/Al_2O_3 towards acrolein seems to be related to low affinity of carbon double bond to the Pt metal. In the case of Pd/Al_2O_3 catalyst, the surface intermediated enol form are more stable resulted in the high amount of propanal in the gas phase reaction products.

3.2 Solution Phase Cascade Reactions

Initially, we tested carbon nucleophiles under the previously established reaction conditions [21] to exploit acrolein reactivity by means of a Michael addition.

Acetylacetone could be converted to 2-acetylphenol (Fig. 7), a common motif in bioactive compounds [38], although the conversion of the starting material was poor. This reaction is suggested to proceed through a Robinson annulation/aromatization sequence, where the metal component of the catalyst has a role in the allyl alcohol oxidation and the last aromatization step, while the Al_2O_3 promotes the Michael step and the intramolecular aldol condensation reaction. The amount of the allyl alcohol was not affecting the reaction as both 1 and 2 equiv. gave the same results. Performing the reaction under identical conditions but using acrolein directly, led to a somewhat increased yield of 17%. This suggests that in the acetylacetone/allyl alcohol reaction mixture other reaction pathways are also operational, such as the transfer hydrogenation of the diketone with the alcohol as the hydrogen source. This would decrease the concentration of the active nucleophile and ultimately reduce the yield. It is noted, that using Pt/Al_2O_3 catalyst or without Pd/Al_2O_3 the reaction did not result in product formation.

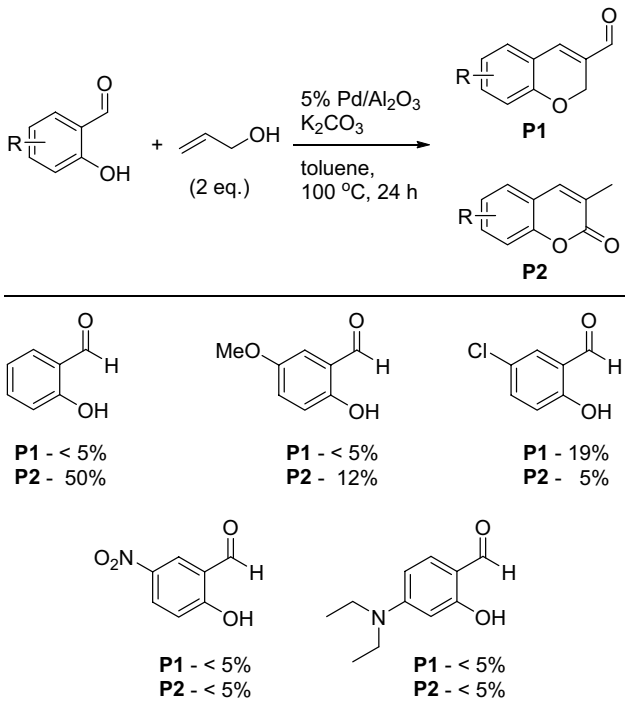


Fig. 10 Reactivity of salicylaldehydes towards allyl alcohol derived acrolein and enol

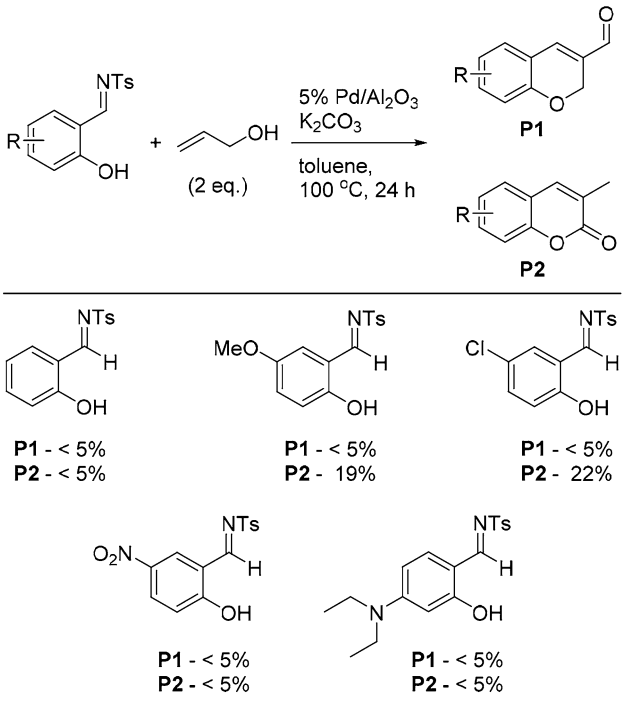


Fig. 11 Reactivity of *N*-tosylimine derivatives of salicylaldehydes towards allyl alcohol derived acrolein and enol

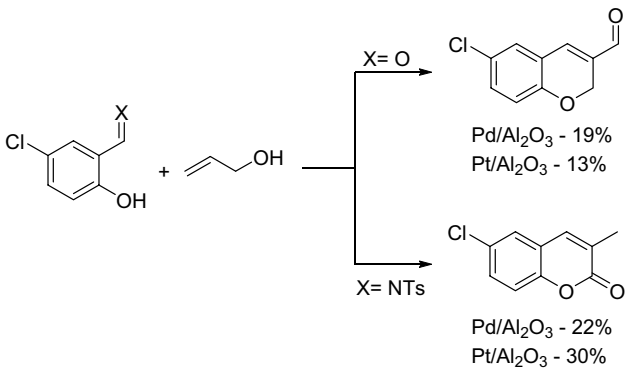


Fig. 12 Switching the reactivity of 5-cholorsalicylaldehyde towards allyl alcohol derived acrolein and enol by *N*-tosylimine formation

Interestingly, a somewhat weaker nucleophile, ethyl 2-methylacetoacetate, was converted more efficiently (Fig. 8). This substrate is of interest as no aromatization is possible in this case and the transformation leads to the formation of 2-cyclohexenone ring structure containing an all-carbon quaternary centre. Similarly to the previous case, product formation was not observed when the reaction was performed without the presence of metal catalyst.

Heteroatom nucleophiles such as phenol and thiophenol, did not participate in conjugate addition with acrolein under the reaction conditions. In case of phenol no conversion was obtained, while from thiophenol the corresponding disulphide was formed selectively.

Salicylaldehydes, comprising both electrophilic carbonyl function and nucleophilic phenolic OH-group, are especially interesting as they are potentially able to undergo reaction with both the elecrophilic acrolein and nucleophilic enolate derived from allyl alcohol (Fig. 9). Reaction of salicylaldehydes with acrolein would lead to 2*H*-chromene derivatives through an oxa-Michael addition/aldol condensation sequence. Reaction with the enol would give coumarin derivatives via an aldol condensation/hemiacetal formation/oxidation pathway. Both 2*H*-chromene and coumarin derivatives are common motifs in natural products. The ambident reactivity character of salicylaldehydes has scarcely been considered in controlling product structure through controlling reactivity pattern [39–42].

Previously, we found that unsubstituted salicylaldehyde undergo reaction with the enol derived from allyl alcohol yielding the corresponding coumarin (Fig. 3).

We tested salicylaldehydes with different substituents, both electron donor and acceptor types, to explore their reactivity towards the species derived from allyl alcohol (Fig. 10).

We found that within the examined series of salicylaldehydes the substituents had a major role in determining the reactivity. Salicylaldehyde with no substituent yielded the corresponding coumarin (**P2**) and also provided the highest yield among the compounds. Introduction of the donor methoxy substituent, although the yield was comparably lower, still resulted in the coumarin derivative as the major product. This tendency was reversed when a Cl-substituent was present in the molecule. Unlike in the case of salicylaldehyde and 5-methoxysalicylaldehyde, the formation of the 2*H*-chromene derivative (**P1**) was preferred in the reaction. This implies that while in the first two cases the electrophilic carbonyl group was the reactive function, in the case of the Cl-substituted salicylaldehyde the oxa-Michael reaction/aldol condensation was the preferred pathway. When strong acceptor ($–NO_2$) or strong donor ($–NEt_2$) group was present, essentially no desired product could be isolated. These starting materials led to a complex (polymeric) product mixture. The lack of metal catalyst in the reaction mixture resulted in no product formation.

As an attempt to improve the results we converted the aldehydes to the corresponding *N*-tosylimines (Fig. 11). We expected that this transformation will shift the reactivity towards the aldol chemistry on the carbonyl group.

The transformation did not affect the reactivity of the nitro- and diethylamino-substituted starting materials. However, in line with the expectations, for 5-methoxy and 5-chlorosalicylaldehyde it improved the yield of the coumarin product (**P2**). This also means that in the case of 5-chlorosalicylaldehyde the derivatization is switching the

initial reactivity of the compound from primarily nucleophilic to primarily electrophilic (Fig. 12).

Unexpectedly, Pt/Al_2O_3 was also found to be active in the transformation of 5-cholorsalicylaldehyde delivering comparable results to that obtained with Pd/Al_2O_3 regarding both yields and the product selectivity. This is in contrast to the previously discussed reactions, where the Pt-based catalyst showed no activity. We do not have a firm explanation to this change in catalytic activity, however, the formation of acylplatinum species [43, 44] of some sort could be involved leading to soluble Pt-complexes. Homogeneous Pt-complexes have been described to have activity in ally alcohol isomerisation processes [45].

We conducted control experiments in order to get further insights into the latter process. Isomerization of allyl alcohol in toluene in the presence of Pt/Al_2O_3 catalyst gave similar results to that obtained in the gas-phase measurements regarding catalyst activity. When the reaction mixture contained only allyl alcohol and the catalyst in toluene after 4 h at 100 °C about 98% of the allyl alcohol remained untouched and only about 1% of each product (acrolein and propanal) could be detected. The addition of K_2CO_3 did not improve considerably the conversion of allyl alcohol (about 3% conversion to 1:1 mixture of the products). These results point towards the involvement of 5-chlorosalicylaldehyde in the catalytic process when Pt is the catalytic metal. In comparison, under the same conditions the transformation of allyl alcohol over Pd/Al_2O_3 catalyst was complete in 4 h to propanal. When K_2CO_3 was added to the reaction mixture the formation of 2-methyl-2-pentenal, the self aldol condensation product of pentanal was also detected by GC-MS supporting the role of the base in the aldol chemistry following the isomerization step.

When 5-Chlorosalicylaldehyde was submitted to the reaction conditions (see Sect. 2.5) using Pt/Al_2O_3 as catalyst, after 12 h GC-MS analysis showed the starting aldehyde and the chromene derivative in about 1:1 ratio and trace amount of the coumarin product. (Note that this does not mean 50% conversion to the desired product as unidentified polymeric side products could not be measured.) After 12 h the solid material was filtered and the filtrate was heated for an additional 12 h. The results after the 24 h reaction time were practically unchanged.

4 Conclusions

In summary, we have shown that allyl alcohol can not only be considered as an enolate (or carbonyl) equivalent but it is possible to use it to generate acrolein, which can be involved in further cascade reaction with appropriately chosen reactants. Carbon nucleophiles (acetylacetone, ethyl 2-methylacetoacetate) did undergo Michael addition/aldol condensation sequences with allyl alcohol derived acrolein leading to industrially relevant molecular building blocks. Salicilyladehydes could be involved in reactions both on the electrophilic carbonyl and on the nucleophilic phenolic –OH sites. Their reactivity, however, was strongly influence by the nature of substituents. Transforming the salicylaldehydes to the corresponding *N*-tosyl imine derivatives resulted in switching initial reactivity in case of 5-chlorosalicylaldehyde from primarily nucleophilic to primarily electrophilic.

The possibility to exploit the different reactivities involved in the catalytic allyl alcohol isomerization cycle by using heterogeneous transition metal catalyst gives new perspectives for this chemistry in a greener and sustainable context.

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