

Direct conversion of alcohols to long-chain hydrocarbons via tandem dehydrogenation-decarbonylative olefination

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Design of active and selective supported catalysts is critical for developing new tandem processes for upgrading biomass-derived alcohols. Hydrogen-free upgrading alcohols to liquid hydrocarbons is desirable for producing drop-in fuel substitutes, but direct and atom-economical processes are yet to be reported. Here we report a novel alcohol upgrading and deoxygenation cascade that meets these criteria. This hydrogen-free cascade is catalyzed by multifunctional Pd catalysts, whose supports feature a range of acid-base properties: primarily basic MgO, acidic Al₂O₃ and Mg-Al hydrotalcite (HT) with a combination of Lewis acidic and basic sites. The impact of support selection on selectivity offers insights into the design principles for next-generation catalysts for this process and related transformations.

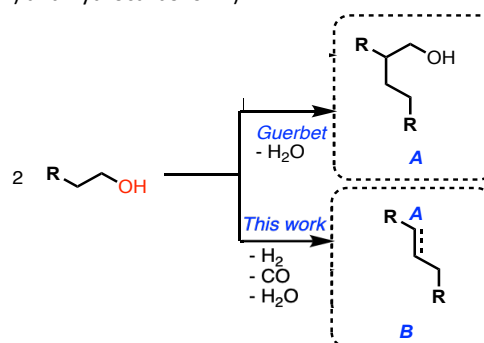
The ability to produce liquid hydrocarbon fuels from renewable biomass is a highly attractive strategy for producing drop-in fuel substitutes with high energy density¹ and for existing petrochemical processes. As renewable sources of alcohols become increasingly abundant,² interest in their catalytic conversion to energy-dense hydrocarbons is also growing,³ but is yet to be realized in an efficient manner. Practical processes for such transformations should be energy-efficient, use low-cost, robust, heterogeneous catalysts, and be tolerant to aqueous, dilute alcohol feedstreams, such as those often derived from fermentation processes. Achieving these objectives requires the design of active and selective supported catalysts tailored for new tandem processes based on the upgrading of biomass-derived alcohols. Current approaches to upgrading alcohols primarily rely on the Guerbet condensation, wherein alcohols are coupled to produce longer-chain, branched primary alcohols through a sequence of dehydrogenation, aldol condensation and hydrogenation reactions (Scheme 1, Reaction A).⁴⁻¹⁵

The Guerbet reaction can be catalysed by supported noble metal catalysts, metal oxides and mixed metal oxides (MMOs). The latter may be derived by calcination of layered double hydroxides (LDHs), and their selectivity tuned through altering the composition and morphology.^{4, 5, 9-11, 14, 15} However, to our knowledge there are no reports of alcohol coupling processes able to upgrade primary alcohols to

alkanes or alkenes (Scheme 1, Reaction B), as described here. Effecting the requisite tandem transformations in a one-pot reaction (to minimize reactor complexity and cost) necessitates multifunctional catalysts possessing catalytic sites effective for dehydrogenation, aldol condensation and decarbonylation. Optimizing the formulation and operation of multifunctional catalysts is generally challenging, since it hinges on controlling the activity and selectivity of several interdependent steps. In turn, this requires control over the size, location and structure of catalytically active species, and mechanistic insight into corresponding structure-activity relationships, including the role of supports.¹⁶ Efforts by our group and others to develop Pd catalysts on tunable supports for organic synthesis and biomass valorisation have identified strong interactions with support matrices that regulate metal speciation and resulting reactivity.^{17-23,24}

MgO and Al₂O₃ supported metal catalysts are well-known to present different acid-base properties:²⁵⁻²⁸ Saad et al. reported Pt-supported MgO displays strong basicity, whereas Pt-Al₂O₃ displays strong acidity.²⁴ Similar observations were made by Groppo et al. for Pd analogues.²⁹ Hydrotalcites (HTs) are a sub-set of LDHs with general formula $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}(A^{n-})_{x/n}.mH_2O$, where M^{2+} and M^{3+} are Mg²⁺ and Al³⁺ or compatible alkali earth and transition metal cations.³⁰ Although LDH materials similar to the present HT exhibit basic properties approaching those of MgO,³¹ the tunable nature of such materials means that both O²⁻ and Al³⁺ respective Lewis base and acid centres are accessible.^{32, 33}

Scheme 1: Upgrading of primary alcohols to longer chain alcohols (A) and hydrocarbons *B).



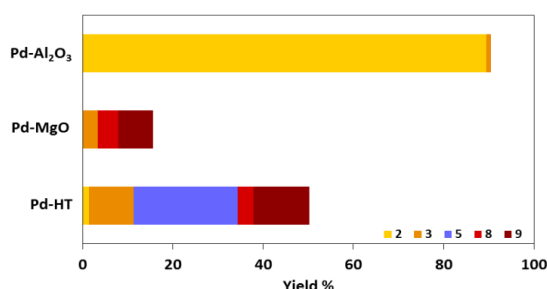


Figure 2. Product yield and selectivity for *n*-heptanol coupling over supported Pd catalysts. Conditions: 0.2 mol % Pd, 180 °C, 48 h, in air.

A comparable reaction with Pd-HT affords negligible quantity of the ether (**3**); instead, we observe near complete selectivity for products arising from initial alcohol dehydrogenation (Scheme 2): 46% selectivity for Guerbet alcohol (**5**), 7% for 6-*E*-tridecene (**8**), 22% for tridecane (**9**) and 22% ester **3** (with 50% alcohol conversion). Pd-HT is thus significantly more efficient at facilitating the initial alcohol dehydrogenation than Pd-Al₂O₃, likely due to the higher concentration of Pd metal sites.¹³ Product selectivity is dictated by the subsequent fate of heptanal: reaction with the parent alcohol and dehydrogenation forms the ester **3**, whereas aldol condensation affords (**7**) which in turn unlocks access to saturated oxygenates (**4**, **5**) or alkenes/alkanes **8/9**. The molar ratio of ester **3** to the observed aldol reaction products (**5**, **8** and **9**) of 1:3.6 evidences that the strong basic sites in the HT support promote aldol condensation.¹⁵ In contrast, the lack of basic sites and weak acidic sites on Al₂O₃ promote ether formation (**3**) by either dehydration or ketal hydrogenolysis, as previously reported by Marecot et al.⁴¹

Since downstream hydrogenation is dependent on the rate of the upstream dehydrogenation,⁷ the selectivity for **5** versus hydrocarbons (**8** and **9**), (~2:1 for Pd-HT) reflects the relative rates of re-hydrogenation versus decarbonylation of the reactively-formed aldol product **7**. High selectivity to hydrocarbons requires faster decarbonylation, which in turn will depend on the Pd speciation.^{19, 40}

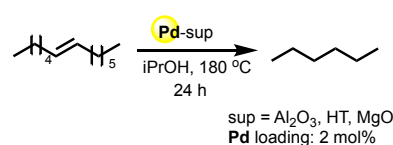
Compared to the other catalysts, Pd-MgO was significantly less active for heptanol conversion (16%), but exhibited the highest selectivity for hydrocarbons **8** (29%) and **9** (50%), alongside ester **3**. These observations suggest that Pd-MgO possesses few or weak Lewis acid sites and limited Pd metal sites, accounting for slow dehydrogenation and no dehydration, and favoring decarbonylation over re-hydrogenation of the aldol condensate **7**. We anticipate that optimizing the Pd loading and particle size (both strong influencers of palladium speciation)⁴¹ could significantly increase dehydrogenation activity, and hence heptanol conversion and the hydrocarbon yield.

Further mechanistic insight was obtained by investigating the three catalysts for the decarbonylative coupling of heptanal via stepwise aldol condensation and decarbonylation (Figure

S3). All three catalysts showed high activity and selectivity for the desired alkene **8** in 8 h at 180 °C, with yields of **8** of 97% (Pd-Al₂O₃), 92% (Pd-MgO) and 85% (Pd-HT), the latter reflecting incomplete decarbonylation of the aldol condensate **7**. The lower olefin yield afforded by Pd-HT relative to Pd-MgO suggests the former is a less efficient decarbonylation catalyst of the two. This is consistent with the selectivity observed for the alcohol reaction: Pd-HT affords ~3:2 ratio of Guerbet alcohol (**5**) to hydrocarbons **8** and **9**, while Pd-MgO affords no alcohol **5**. Thus, driving selectivity for the hydrocarbons requires optimizing catalytic efficiency of decarbonylation. The experiment also suggests that the rate-determining step in hydrocarbon formation catalysed by Pd-MgO is dehydrogenation of the parent alcohol.

To rationalize the ratio of alkene **8** versus alkane **9**, and thus the ability of the catalyst to facilitate transfer hydrogenation (TH) of alkenes to alkanes, we compared the efficiency of the three catalysts for the TH of 6-*E*-tridecene (**8** in Scheme 2) using 2-propanol as hydrogen donor (Scheme 3). Pd-MgO afforded ~4-fold lower yield of alkane than Pd-HT (15% vs 62%), consistent with the lower fraction of **9:8** afforded by Pd-MgO in the heptanol reaction (1:1.7 for and 1:3.4 with Pd-MgO and Pd-HT respectively, Figure 2). This trend is also consistent with the faster heptanol conversion observed for Pd-HT compared to Pd-MgO. Interestingly, Pd-Al₂O₃ affords 51% yield of **9**, suggesting it too is an efficient TH catalyst. However, as previously discussed, Pd-Al₂O₃ favors formation of ether **2**, and hence does not form alkene (Figure 2). In a similar experiment with aldol product **7**, we find Pd-HT is ~2-fold more active than Pd-MgO for formation of alcohol **5**. Thus, the selectivity of Pd-MgO for **8** and **9** over **5** is the result of its faster decarbonylation and slower TH relative to that of Pd-HT.

Scheme 3. Transfer hydrogenation of tridec-6-ene using 2-propanol.



Conclusion

Pd supported on both basic and acidic supports (MgO and hydrotalcite, HT) are promising heterogeneous catalysts for a novel alcohol upgrading route to long-chain hydrocarbons proceeding via tandem dehydrogenation, aldol condensation and decarbonylation. Initial results with heptanol show that the support acid-base properties influence Pd speciation, and catalytic activity for each reaction steps. Pd-MgO exhibits highest selectivity to alkene and alkane products, but lowest conversion, whereas Pd-HT offers high conversion but lower selectivity for hydrocarbons, as it is less active for decarbonylation. Pd-Al₂O₃ affords only ethers, likely due to faster ketal hydrogenolysis than aldol condensation. Optimum hydrocarbon formation requires synergy between

Pd metal and support acidic/basic sites, as well as optimization of the four sequential catalytic steps required for the transformation. Further investigations into the design of more active and selective multifunctional catalysts for this attractive alcohol coupling pathway are underway.

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