Effects of Organic Modifiers on a Palladium Catalyst in the Competitive Hydrogenation of 1-Octene Versus Octanal: An Evaluation of Solid Catalysts with an Ionic Liquid Layer

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The competitive hydrogenation between 1-octene and octanal has been investigated with a ≈ 5 % palladium on alumina catalyst prepared in situ with the following organic modifiers: pyridine, 1-methylimidazole, 1,3-dimethylimidazole methylsulfate, 1,3-dimethylimidazole bis(trifluoromethylsulfonyl)imide and methyltri-*sec*-butylphosphonium methylsulfate. The results of these investigations indicate that the ionic liquid modifiers have significant and specific effects on catalytic performance, for example, certain systems can completely suppress octanal conversion. In addition, analytical techniques reveal that the matrix and quantity of organic species on the used catalysts are different if different ionic liquids are used as modifiers. Surface studies also reveal that the modifiers have a noticeable effect on the crystallite size and chemisorption properties of the catalysts.

Introduction

Competitive hydrogenation between inter-molecular functional groups is a relatively unexplored area compared to intra-molecular versions. As a result of current methods in the industrial production of hydrocarbons, downstream industrial feedstocks may contain several species of unsaturated molecules.[1] For example, in the hydroformylation of alkenes by homogeneous Rh catalysts, the product may contain unreacted alkenes with aldehydes.[1c] Further chemical manipulations of such product streams often require the removal of one or more minor constituents to prevent either undesired side reactions or catalyst poisoning.[1c, 2] Hydrogenation by heterogeneous catalysts is often used to remove catalyst poisons such as alkynes and dienes.[2] As a result, a catalyst that is selective for the hydrogenation of one or related components versus others in a multi-component feed is desirable.

Heterogeneous catalyst modification by either inorganic or organic modifiers has been used to either increase the intrinsic activity of a catalyst or its selectivity. For example, cinchonidine has been used to promote asymmetric catalytic hydrogenations[3] and site modification by CO has been used to enhance reaction selectivity.[4] Pyridine has found use as a modifier of heterogeneous catalysts.[5] Indeed, N-containing organic compounds have found widespread use as organic modifiers of traditional heterogeneous catalysts.[6]

The additions of other metals are also seen as modifiers of traditional mono-metallic catalysts. They form multi-metallic catalysts with enhanced selectivity and increase catalyst stability for a variety of reasons, both electronic and morphological.[6–7]

As a result, a potential plethora of catalytic performance modifications exist with both inorganic and organic modifiers. Investigations with ionic liquids in continuous-flow processes have focused traditionally on supported ionic-liquid-phase (SILP) catalysis, whereby a homogeneous catalyst is dissolved in an ionic liquid, which is itself supported on common porous and non-porous heterogeneous supports such as alumina and other metal oxides.[8] These reactions are performed typically under gas-phase conditions.

Recently, a new concept with ionic liquids and heterogeneous catalysis has emerged. The solid catalyst with ionic liquid layer (SCILL) is effective to alter the selectivity and intrinsic activity of a number of different reactions, which include competitive hydrogenation between two different substrates.[9] In particular, the selective hydrogenation of citral to citronellal with Pd-based catalysts[10] has been investigated, with improved selectivities towards citronellal.[11]

The SCILL catalysts described to date have shown that the ionic liquid layers remain intact on the catalyst in both batch and trickle-bed conditions. However, it is still unknown to what relative extent transport effects (if any) and crystallite modification effects contribute to the SCILL catalyst behaviour. Diffusion effects have been claimed to have no effect,[9d] however, the idea that diffusion effects do not play any role has been challenged.[9a, c] In addition, no relation or comparison has been made with traditional organic catalyst modifiers such as pyridine.

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In the hope that Pd SCILL catalysts may have different effects on the hydrogenation performance with respect to industrially important alkenes and aldehydes in competitive modes, a series of ionic-liquid-modified Pd on alumina catalysts ($\approx 5\%$ w/w) were used in the competitive hydrogenation between 1-octene and octanal (1:1 v/v, 2% each in hexane) under continuous-flow conditions. A comparison with the effects of some traditional organic modifiers, such as pyridine and 1-methylimidazole, are also included in this study. The following compounds were used as modifiers in the in situ preparation of these catalysts: pyridine, 1-methylimidazole, 1,3-dimethylimidazole methylsulfate ([MMIM][MeOSO$_3$]), 1,3-dimethylimidazole bis(trifluoromethylsulfonyl)imide ([MMIM][NTf$_2$]) and methyltri-sec-butylphosphonium methylsulfate ([MePsec-Bu$_3$][MeOSO$_3$]). The structures of these modifiers are shown in Figure 1.
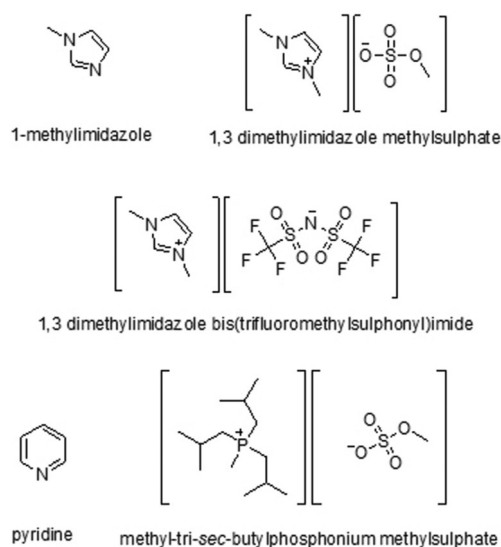

Figure 1. Structures for the different organic molecules used to modify the 5% Pd on alumina catalyst.

Results and Discussion

Hydrogenation of 1-octene and octanal over a 5% Pd on alumina catalyst

To determine the effects of the modifiers in question on the competitive hydrogenation between 1-octene and octanal, the performance of the uncoated (no ionic liquid) catalyst at different iso-conversion points was first established. For the purpose of this discussion, iso-conversion is defined as the constant conversion attained once steady state has been achieved in a continuous-flow reaction.[9a] Typical reaction profiles at 40% conversion of octanal and 1-octene are shown in Figure 2. By-products include diols and acetyls amongst others. The increase in octanal and 1-octene content over time, until steady state is reached, is because of a decrease in the ability of the catalyst to convert the respective substrates (initial catalyst deactivation).

To avoid confusion, the unreacted mixture, before passing over the catalyst bed, is seen to contain 100% 1-octene and
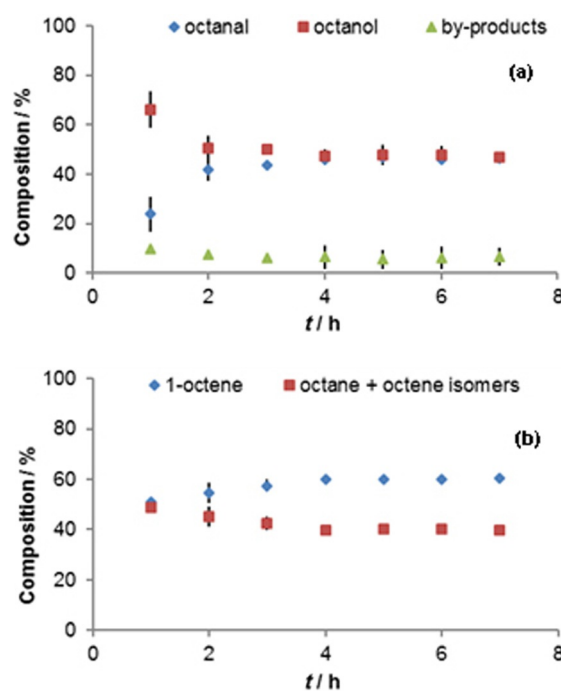

Figure 2. A typical reaction profile for the hydrogenation of a) octanal to octanol and b) 1-octene to octane with the uncoated catalyst ($T = 130\,°C$, $P = 50$ bar, GHSV = 319.49 h^{-1} and LHSV 24.02 h^{-1}).

100% octanal. However, for a meaningful comparison we would like to focus on the conversion (obtained at steady state with a minimum time of 7 h on stream) versus liquid hourly space velocity (LHSV) plots (Figure 3 a). Furthermore, in general terms, intrinsic reactivity is defined as the rate at which a catalytic cycle turns over on an active site, which is expressed in terms of a logarithmic function that is proportional to the number of active sites present on the catalyst.[12] The intrinsic activity is defined as the LHSV required to bring about a 50% conversion.[12]

The conversion data for the uncoated catalyst are shown in Figure 3 a. It is evident that the LHSV versus conversion follows a logarithmic trend. The ranges of the octanal and 1-octene conversions do not overlap (LHSV values at which both 1-octene and octanal convert) and the catalyst is more active towards 1-octene conversion than octanal conversion. This is in agreement with the knowledge that Pd is known as an effective catalyst for C–C bond hydrogenation.

The conversion data for the pyridine-modified catalyst are shown in Figure 3 b. Pyridine is a known catalyst modifier,[5] and it is noticeable that the modification by pyridine results in the formation of a slightly more intrinsically active catalyst (intrinsic activity defined as the LHSV required to bring about a 50% conversion; Table 1)[12] in the conversion of both 1-octene and octanal. Additionally, there seems to be a slight increase in the intrinsic reactivity of the catalyst (defined as the gradient or slope of the logarithmic function;[12] Table 1) for both 1-octene and octanal conversion, which implies an improvement on the speciation/numbers or efficiency of the catalyst sites responsible for the conversions.
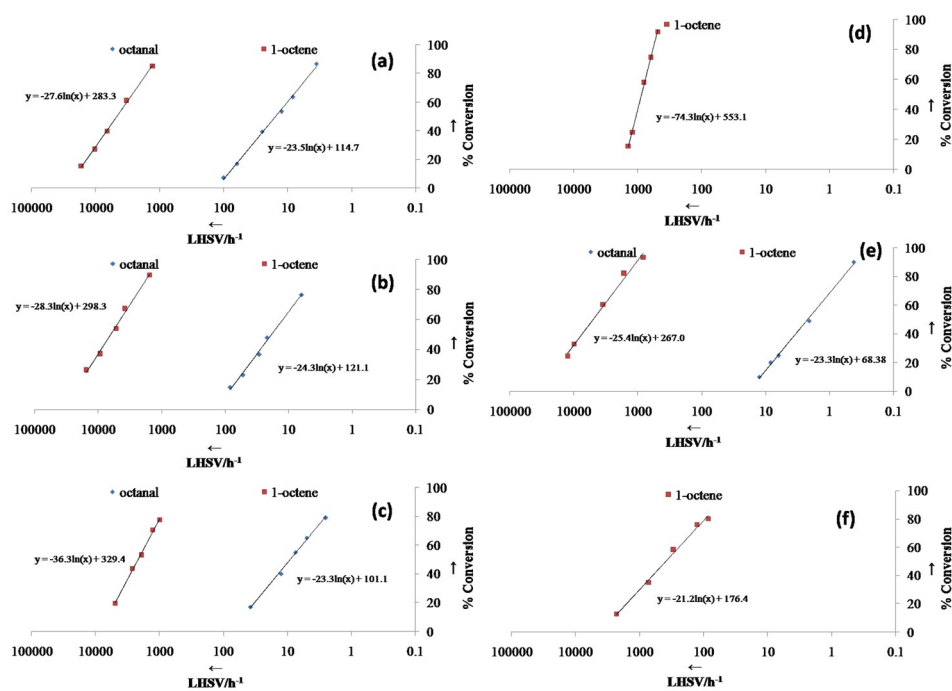
Figure 3. Iso-conversion points of both 1-octene and octanal plotted to the LHSV values required to obtain them with the a) uncoated, b) pyridine-modified, c) 1-methylimidazole-modified, d) [MMIM][MeOSO$_3$]-modified, e) [MMIM][NTf$_2$]-modified and f) [MePsec-Bu$_3$][MeOSO$_3$]-modified catalyst ($T=130\,^\circ$C and $P=50$ bar).

Table 1. Chemical and physical properties of Pd/γ-Al$_2$O$_3$ catalysts.

Coating	1-Octene conversion		Octanal conversion	
	Reactivity[a] [% h]	Activity[b] (LHSV, [h^{-1}])	Reactivity[a] [% h]	Activity[b] (LHSV, [h^{-1}])
uncoated	−27.6	4688	−23.5	16
pyridine	−28.3	6463	−24.3	19
1-methylimidazole	−36.3	2201	−23.3	9
[MMIM][MeOSO$_3$]	−74.3	872	≈0	≈0
[MMIM][NTf$_2$]	−25.4	5132	−23.3	2
[MePsec-Bu$_3$][MeOSO$_3$]	−21.2	388	≈0	≈0

[a] Defined as the gradient of the logarithmic function.[12] [b] Defined as the LHSV (defined as the volume of liquid flow through a constant volume of catalyst in an hour) required to bring about a 50 % conversion. Values listed as ≈0 are below the detection limit ($T=130\,^\circ$C and $P=50$ bar).[12]

and contain nitrogen in their ring systems (Figure 1), and π bonding is known to have effects,[13g] however, they exhibit different effects as catalyst modifiers. This may be related to the basicity of the organic modifiers (pyridine p$K_b=8.78$[14] and 1-methylimidazole p$K_b=6.95$),[3b] which may have an effect on the metal crystallite formation or surface support properties. However, 1-methylimidazole is a known precursor for many different ionic liquids, some of which noticeably modify the intrinsic activity and selectivity of catalysts used in several different hydrogenation reactions.[9]

The conversion data for [MMIM][MeOSO$_3$], an ionic liquid based on 1-methylimidazole, are shown in Figure 3d. There is a dramatic change in the intrinsic activity and reactivity in the conversion of 1-octene compared to that of the uncoated catalyst. There is a decrease in intrinsic activity and an increase in intrinsic reactivity as evidenced by the slope of the trend line. With regards to 1-octanal hydrogenation, the ionic liquid completely inhibits the reaction, at least within the limits of the reactor capabilities. This shows that the ionic liquid discriminates strongly between 1-octene and octanal hydrogenation and increases the selectivity of the catalyst to 1-octene conversion and increases its intrinsic reactivity (Figure 3d).[12]

To investigate the effect that a change in the anion would have on the intrinsic activity and reactivity of 1-octene and octanal conversion, [MMIM][NTf$_2$] was used as a modifier, and the results are shown in Figure 3e. There is a slight increase in the intrinsic activity of 1-octene conversion with a decrease in the intrinsic reactivity compared to that of the uncoated catalyst. There is also a strong effect on the octanal conversion. Although there is no outright inactivity compared to the [MMIM][MeOSO$_3$]-modified catalyst, there is a large decrease in the intrinsic activity compared to the uncoated catalyst, the pyridine-modified catalyst and the 1-methylimidazole-modified catalyst.

The effects of coating the catalyst with the ionic liquid [MePsec-Bu$_3$][MeOSO$_3$] are shown in Figure 3f. There is a significant change to both the intrinsic activity and reactivity of 1-octene conversion, and both the intrinsic reactivity and activity of the reaction decrease the most out of all the modified catalysts. As with the [MMIM][MeOSO$_3$]-modified catalyst, the [MePsec-Bu$_3$][MeOSO$_3$]-modified catalyst was inactive in the conversion of octanal.

The results of the conversion of 1-octene and octanal show that the ionic-liquid-modified catalysts have a very significant

The conversion data for the Pd catalyst coated with 1-methylimidazole are shown in Figure 3c. There is a larger effect on the intrinsic activity and reactivity of both 1-octene and octanal conversion compared to the reaction over the pyridine-modified catalyst. However, the effect is different from the pyridine modification. The intrinsic reactivity of 1-octene conversion is greater (larger gradient) but the intrinsic activity has diminished (lower LHSV) compared to both the uncoated and pyridine-modified catalysts. With regards to octanal conversion, the intrinsic reactivity is similar to that of the uncoated catalyst but the intrinsic activity is decreased. Structurally (with regard to the geometric arrangement of atoms), 1-methylimidazole is in respects similar to pyridine as they are both sp^2 hybridised

effect on the intrinsic reactivity and activity of the reaction (Table 1). Especially, the selectivity of the product obtained from the conversion of a particular reactant is an important aspect that ionic-liquid-modified catalysts have been shown to alter in a number of related hydrogenation reactions. The product selectivity of the hydrogenation reactions versus their corresponding iso-conversion level for both 1-octene and octanal are summarised in Tables 2 and 3.

Table 2. Iso-conversion of 1-octene versus the mol fraction of converted 1-octene to octane over the range of iso-conversion points with the modified catalysts ($T = 130\,°C$ and $P = 50$ bar).

Coating	% Conversion/selectivity to octane [mol fraction]				
uncoated	10:0.60	30:0.71	40:0.67	60:0.73	80:0.76
pyridine	27:0.57	40:0.56	50:0.55	65:0.53	75:0.58
1-methylimidazole	20:0.53	45:0.58	50:0.60	70:0.65	78:0.69
[MMIM][MeOSO$_3$]	10:0.30	25:0.41	50:0.43	75:0.53	90:0.69
[MMIM][NTf$_2$]	25:0.50	33:0.46	60:0.57	80:0.66	93:0.75
[MePsec-Bu$_3$][MeOSO$_3$]	10:0.47	35:0.44	60:0.47	75:0.43	80:0.45

Table 3. Iso-conversion of octanal versus the mol fraction of converted octanal to octanol over the range of iso-conversion points with the differently modified catalysts ($T = 130\,°C$ and $P = 50$ bar).

Coating	% Conversion/selectivity to octanol [mol fraction]				
uncoated	7:1.0	17:0.89	39:0.86	54:0.89	87:0.87
pyridine	13:0.94	23:0.97	37:0.92	47:0.98	86:0.94
1-methylimidazole	16:0.71	36:0.91	46:0.92	75:0.94	82:0.92
[MMIM][MeOSO$_3$]	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0
[MMIM][NTf$_2$]	9:1.0	19:1.0	26:0.90	49:0.87	91:0.89
[MePsec-Bu$_3$][MeOSO$_3$]	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0

This selectivity versus iso-conversion of 1-octene hydrogenation for the uncoated (no ionic liquid) catalyst reveals that as the conversion increases, there is an increase in the selectivity towards octane. This can potentially be explained by an increase in residence time of the unsaturated alkene with the catalyst to result in a relative increase in alkene saturation. The selectivity versus iso-conversion of octanal reveals that as the iso-conversion increases there is a decrease in the selectivity towards octanol. This is understandable as alumina is known to catalyse side reactions with oxygen-containing groups (that is, aldol condensation) by its basic and acidic sites.[15] It stands to reason that a decrease in LHSV and an increase in the concentration of octanol will result in an increase in byproduct formation.

The pyridine-modified catalyst provides a lower but constant level of selectivity to octane versus iso-conversion. This implies that the pyridine has modified the catalyst in a manner to decrease the relative rate of H$_2$ addition to the unsaturated C—C bond. Interestingly, the selectivity to octanol is also relatively constant but at a much higher average level compared to that of the uncoated catalyst. It is known that acidic sites on alumina are in part responsible for byproduct formation,[15a] so it is to be expected that the basicity of pyridine reduces the number of these acidic sites.[6, 15a]

The 1-methylimidazole-modified catalyst exhibits a similar trend to the uncoated catalyst with regard to the product selectivity versus iso-conversion of 1-octene, except the product selectivity to octane is lower. This suggests that the modification effect on the catalyst is different from that of pyridine but that it still has a depressive effect on the relative rate of unsaturated C—C bond hydrogenation. The trend in selectivity versus the iso-conversion of octanal is, however, different from that of the uncoated catalyst and is similar to that of the pyridine-modified catalyst. The potential reasons for this are similar to those for the pyridine-modified catalyst.

The [MMIM][MeOSO$_3$]-modified catalyst also shows a trend in selectivity versus iso-conversion of 1-octene similar to the uncoated catalyst. However, the general level is far lower than that of the uncoated catalyst (as much as half the selectivity at lower conversion levels), the pyridine-modified catalyst and the 1-methylimidazole-modified catalyst. Furthermore, the catalyst is inactive in the hydrogenation of octanal.

The [MMIM][NTf$_2$]-modified catalyst reveals a trend that is also similar to that of the uncoated catalyst with regards to 1-octene hydrogenation (increasing selectivity with increasing iso-conversion). As with the [MMIM][MeOSO$_3$]-coated catalyst, the general selectivity to octane is lower than that of the uncoated catalyst but not to the same extent. However, in contrast to the [MMIM][MeOSO$_3$]-modified catalyst, this catalyst was active in octanal hydrogenation and its selectivity to octanol decreases with increasing levels of iso-conversion. Although the selectivity at lower levels of iso-conversion is higher than that of the uncoated catalyst, it decreases after 39% conversion. This implies that there may be an effective concentration level after which byproduct formation starts to occur.

The [MePsec-Bu$_3$][MeOSO$_3$]-modified ionic liquid shows a constant and reduced level of selectivity, compared to the uncoated catalyst, with increasing levels of iso-conversion of 1-octene. This trend is similar to that of the pyridine-modified catalyst, albeit at a lower level of selectivity to octane, and in addition to this, the catalyst is inactive in the hydrogenation of octanal to octanol.

Catalyst characterisation

To reveal some of the reasons as to why these organic modifiers can have such dramatically different effects on the uncoated Pd catalyst, a series of surface and analytical experiments were conducted. These included BET surface area analysis between the used and freshly prepared catalysts, diffuse reflectance infrared transmittance spectroscopy (DRIFTS), inductively coupled plasma optical emission spectroscopy (ICP-OES), thermogravimetric analysis with differential scanning calorimetry (TGA-DSC), high-resolution transmission electron microscopy (HRTEM), scanning transmission electron microscopy (STEM)

Table 4. BET surface area, pore volume, pore width and sulfur content analysis of the freshly prepared and used catalysts.

Coating	Surface area [m²g⁻¹]	Pore volume [cm³g⁻¹]	Pore width [Å]	S content [wt%]
uncoated fresh	190	0.62	131	–
uncoated used	142	0.39	110	–
pyridine fresh	177	0.54	121	–
pyridine used	160	0.48	120	–
1-methylimidazole fresh	175	0.57	126	–
1-methylimidazole used	153	0.40	106	–
[MMIM][MeOSO₃] fresh	87	0.29	132	4.7
[MMIM][MeOSO₃] used	106	0.36	134	4.2
[MMIM][NTf₂] fresh	56	0.25	182	8.6
[MMIM][NTf₂] used	101	0.36	142	0.0
[MePsec-Bu₃][MeOSO₃] fresh	42	0.21	199	4.7
[MePsec-Bu₃][MeOSO₃] used	85	0.27	128	2.0

under high-angle annular dark-field conditions (HAAD) and chemisorption with H_2 and CO.

The results of the BET analysis can be seen in Table 4. It is quite apparent that with the uncoated catalyst there is a decrease in the surface area, pore volume and pore width of the catalyst from the freshly prepared catalyst to the used catalyst. This is most likely the result of strongly adsorbed carbonaceous deposits produced during the hydrogenation reaction. The pyridine-modified catalyst also reveals lower BET values for the used catalyst compared to the freshly prepared catalyst. However, the difference is less than that of the uncoated catalyst. The 1-methylimidazole-modified catalyst also follows this trend; however, the values are similar to those of the pyridine-modified catalyst. Interestingly, the ionic-liquid-modified catalysts all show an increase in surface area from the freshly prepared catalysts to the used catalysts. This is also the case for the pore volumes of these catalysts, but the opposite trend occurs with the pore widths. In general, this suggests that there may be a loss in the content of the ionic liquid layer during the reaction.

To determine if the ionic liquid layers of the ionic-liquid-modified catalyst were removed from the catalyst surface, TGA-DSC, DRIFTS and ICP-OES were used to analyse the used catalysts. The TGA-DSC analysis and DRIFTS spectra of the ionic-liquid-modified catalysts are shown in Figure 4.

Absorption bands in the region of $\tilde{v} = 1060$ and $1000\ cm^{-1}$ in the DRIFTS spectra are characteristic of S—O and S=O groups. The spectra of the ionic-liquid-modified catalysts reveal some peaks in these areas that may originate from the ionic liquid. The absorption bands in the region of $\tilde{v} = 2960$–2850 and $1470\ cm^{-1}$ are characteristic of CH_n stretching frequencies, which are most likely present because of the reaction products and reactants adsorbed onto the catalyst surface as well as the ionic liquid substituents or decomposition products thereof. These results suggest that the ionic liquid, or remnants of it, may still be present on the catalyst surface, at least as a thin molecular layer.
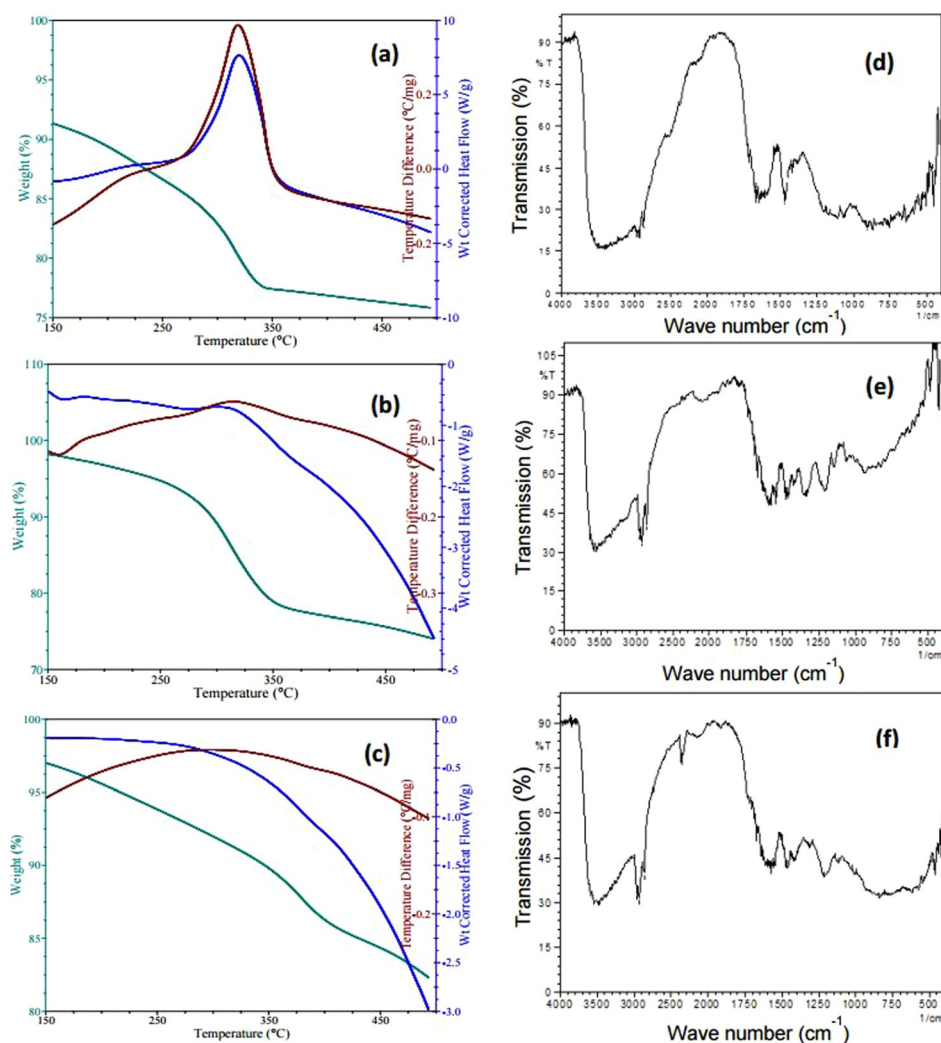

Figure 4. The TGA-DSC profile for the used catalysts modified with a) [MMIM][MeOSO₃], b) [MMIM][NTf₂] and c) [MePsec-Bu₃][MeOSO₃]; DRIFTS spectra for the used catalysts modified with d) [MMIM][MeOSO₃], e) [MMIM][NTf₂] and f) [MePsec-Bu₃][MeOSO₃].

However, TGA-DSC of these catalysts (Figure 4) revealed dramatic differences between them. The [MMIM][MeOSO$_3$]-modified catalyst reveals a weight loss of approximately 18% with an associated exothermal peak at 323 °C. The exothermal peak is characteristic of a decomposition, and the corresponding temperature is fairly close to that reported for the decomposition temperature of pure [MMIM][MeOSO$_3$].[16] This indicates that the ionic liquid is still intact and that a significant amount of it has remained. This is confirmed by the sulfur content analysis by ICP-OES (Table 4). TGA-DSC of the [MMIM][NTf$_2$]-modified catalyst reveals a slight exotherm at 312 °C with an associated weight loss of around 17%. However, the sulfur content analysis (Table 4) indicates that the ionic liquid has not remained intact; this is supported by the relatively small exotherm found by DSC. The weight loss may simply be caused by carbonaceous material formed by an in situ decomposition or alteration of the ionic liquid. Notably, the gradual loss of weight between 150 and 500 °C with an associated gradual endotherm has been attributed to a gradual loss of carbonaceous materials.[17] TGA-DSC of [MePsec-Bu$_3$][MeOSO$_3$]-modified catalyst reveals no exotherms characteristic of ionic liquid decomposition, however, there is a slight differential weight loss that starts at approximately 350 °C. The sulfur content analysis (Table 4) reveals that a fair amount of sulfur remains on the catalyst. This implies that the ionic liquid layer has not survived intact and that an in situ decomposition has taken place to leave sulfur fragments on the catalyst.

These results reveal that the in situ preparation of ionic-liquid-modified catalysts can result in dramatic differences in the surface characteristics of the catalysts, which depends on the type of ionic liquid used and may translate into differences in catalyst performance.

HRTEM analysis, particle size analysis by STEM and chemisorption of the used catalysts were conducted to determine if the in situ preparation and use of organically modified catalysts have any effect on the morphological and chemical properties of the Pd crystallites. The results of these analyses can be seen in Table 5 and Figure 5. An example of an image obtained by HRTEM can be seen in Figure 5a. The crystallites present are of a uniform nature, that is, whole crystallites with no observable defects, apart from plane interfaces. This was
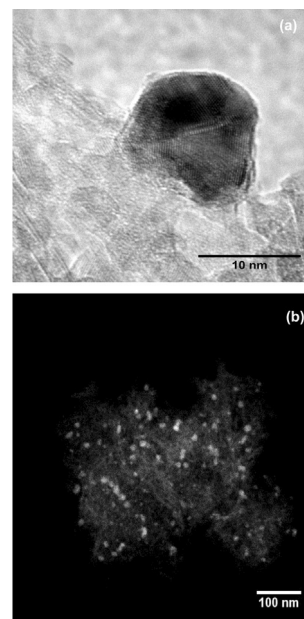

Figure 5. a) HRTEM image and b) STEM image under HAAD conditions of a Pd crystallite from a 5% Pd on alumina catalyst.

found with all the catalysts analysed. Furthermore, an image obtained for STEM analysis under HAAD conditions is shown in Figure 5b, a minimum of 300 particle measurements over 20 images were used to calculate the average particle size (Table 5).

Chemisorption studies of SCILL Pd on silica catalysts have been conducted before,[18] however, these were unused ex situ prepared catalysts (pre-reduced catalysts, followed by a coating of ionic liquid) with intact ionic liquid layers, analysed to confirm the assumption that a layer of ionic liquid (known for their low solubilities of H$_2$ and CO) will reduce the amount of absorbed H$_2$ and CO on the catalyst.

To the best of our knowledge, this is the first time a comparison has been made between used in situ prepared (coated catalysts reduced in situ) SCILL Pd on alumina catalysts and those modified by traditional organic modifiers with the hope to correlate catalyst performance. As part of our investigation, we used a standard model for crystallite size determination (for ease of comparison between H$_2$ chemisorption, CO chemisorption and STEM analysis) using an assumption of complete coverage by the gases and a stoichiometry factor of 1 for CO and 2 for H$_2$. These factor values are used commonly, although the most accurate values are disputed.[13]

The crystallite size analysis by STEM for the uncoated catalyst reveals an average size of around 10 nm. This is supported by the H$_2$ chemisorption analysis, which reveals a good correlation between the two techniques. CO chemisorption, however, gave a much larger average crystallite size at approximately 26 nm, and the ratio between the STEM analyses is 1:2.5. CO has multiple bonding conformations to transition metals, for example linear on top, bridged or hollow bonding using 5δ and 2π* orbitals.[13a] The

Table 5. Crystallite size and metal surface area analysis by STEM and chemisorption techniques.					
Coating	STEM [nm]	Crystallite size [nm]		Metallic surface area [m^2 g^{-1}]	
		CO	H$_2$	CO	H$_2$
uncoated	10±3[a]	26±4[b]	10±3[b]	19±4[b]	49±3[b]
pyridine	7±2[a]	18±4[b]	7±2[b]	48±4[b]	72±2[b]
1-methylimidazole	7±4[a]	21±2[b]	9±3[b]	24±2[b]	59±3[b]
[MMIM][MeOSO$_3$]	10±3[a]	39±5[b]	15±3[b]	13±5[b]	34±3[b]
[MMIM][NTf$_2$]	7±2[a]	28±5[b]	7±4[b]	18±5[b]	69±4[b]
[MePsec-Bu$_3$][MeOSO$_3$]	10±4[a]	35±4[b]	13±1[b]	14±4[b]	38±1[b]
[a] Standard deviation. [b] Percentage error.					

different energies associated with these bonding modes result in the dependence of the amount of CO bonded on the coverage (that is, relative pressure of CO).[13b] In addition, the relative numbers of different bonding sites (that is, plateau, hollow, terrace or steps; Figure 5a reveals some of these sites) affects the amount of CO bonded.[13b] The electronic state of the metal caused by modifications may also have a direct influence on the bonding of CO.[13c] This, along with the data obtained, suggest that a stoichiometry factor of 2 for CO is an accurate value. However, as there are already many in-depth investigations into the nature of CO chemisorption on palladium catalysts,[13a,b,e,f] this study will focus on the differences in chemisorption of CO (seen as changes in crystallite size) between the different catalysts as a potential measure on the catalytic performance of the catalysts with regards to the binding and reaction of carbonyl compounds.[13g] Interestingly, the pyridine- and 1-methylimidazole-modified catalysts have an average crystallite size of around 7 nm (by STEM analysis). This suggests that these modifiers may have an effect on the size of the Pd crystallites. H_2 chemisorption analysis confirms this for the pyridine-modified catalyst. However, the H_2 chemisorption results for the 1-methylimidazole-modified catalyst reveal a larger average crystallite size, which is potentially the result of a hindrance in H_2 adsorption because of the chemically modified surface, and may be in part responsible for the differences in the intrinsic activity observed between these two catalysts. A similar observation can be seen from the CO chemisorption analysis, in which the ratio of STEM analysis to CO chemisorption analysis is 1:2.6 and 1:2.9, respectively. If we take the crystallite sizes measured directly (STEM analysis) into account, the ratio of these and the uncoated catalyst tend to follow the trend in intrinsic activity of octanal conversion.

The [MMIM][MeOSO$_3$]-modified catalyst has an average crystallite size of around 10 nm, which is similar to that of the uncoated catalyst. However, the H_2 chemisorption analysis revealed an average particle size of around 14 nm. This suggests that the H_2 molecules used in the chemisorption analysis are hindered in their chemisorption to the Pd crystallites, possibly because of the ionic liquid molecular layer or decomposition products. This, in general, correlates with the catalytic results of the intrinsic activity and selectivity versus the iso-conversion of 1-octene between the uncoated and [MMIM][MeOSO$_3$]-modified catalysts. The crystallite size determined by CO chemisorption is approximately 39 nm, and the ratio to STEM analysis is 1:3.9. Interestingly, the catalyst was inactive in the conversion of octanal to octanol.

The [MMIM][NTf$_2$]-modified catalyst has an average crystallite size of 7 nm by STEM analysis, which confirms the H_2 chemisorption analysis. Interestingly, this also correlates with the catalytic intrinsic activity of this catalyst compared to the uncoated catalyst with regards to 1-octene conversion and crystallite size. The CO chemisorption analysis reveals a larger crystallite size compared to the uncoated catalyst. The ratio of STEM analysis to CO chemisorption analysis is 1:3.6. These data fit well with both the 1-octene and octanal conversion results, in which there was a noticeable decrease in the intrinsic activity of octanal conversion compared to the uncoated catalyst, but

not inactivity, with a slight increase in intrinsic activity for 1-octene conversion.

The [MePsec-Bu$_3$][MeOSO$_3$]-modified catalyst has an average crystallite size of approximately 10 nm (STEM analysis). This is similar to that of the uncoated and [MMIM][MeOSO$_3$]-modified catalysts. As with the [MMIM][MeOSO$_3$]-modified catalyst, the H_2 chemisorption analysis reveals a larger Pd crystallite size and the intrinsic activity of the 1-octene conversion is lower than that of the uncoated catalyst. As with the [MMIM][MeOSO$_3$]- and [MMIM][NTf$_2$]-modified catalysts, the CO chemisorption analysis reveals a larger Pd crystallite size compared to the uncoated catalyst, with the ratio of crystallite size to STEM analysis of 3.6; the catalyst was inactive in the conversion of octanal to octanol. These results show that an interesting pattern emerges between the catalytic results and the chemisorption analysis, and it may be possible to anticipate the general catalytic results of ionic-liquid-modified catalysts by chemisorption techniques together with STEM analysis.

Conclusion

The catalytic results from this study reveal that ionic-liquid-modified catalysts have dramatic and specific effects and indicate that they have a place alongside traditional organic modifiers. They also have the ability to alter the catalytic performance between different types of substrates selectively. Catalyst characterisation studies reveal that the BET surface area analysis of these catalysts can give an indication of a possible loss in the content of ionic liquid but cannot be used as a means to predict the behaviour of the intrinsic activity or reactivity of a catalyst.[12] Diffuse reflectance infrared transmittance spectroscopy, inductively coupled plasma optical emission spectroscopy, and thermogravimetric analysis with differential scanning calorimetry analyses of these catalysts reveal that a relatively thick ionic liquid layer can survive the reaction conditions. However, this is not a universal rule and ionic liquid decomposition or removal can indeed occur. The decomposition of the ionic liquid can potentially lead to a very different matrix of surface modification, which depends on the ionic liquid used. In addition to this, the in situ preparation of the catalysts with different organic modifiers can have an effect on the size of the Pd crystallites. However, chemisorption techniques coupled with scanning transmission electron microscopy can reveal the size of the crystallites and potentially give a general method for the anticipation of catalytic results.

These results highlight that the effects of ionic liquid modification of traditional heterogeneous catalysts are many and varied. In addition to any transport and/or modification effects, crystallite size modification may also potentially be a factor. As these varied effects are also dependent on the type of ionic liquid used and the substrate catalysed, a large-scale investigation is required to appreciate the trends and modifications of solid catalysts with an ionic liquid layer fully. This is especially so if different metals and combinations of them are to be considered, as ionic-liquid-modified catalysts from this study and others with different metal catalysts have shown to be effec-

tive to alter reaction product selectivity, intrinsic reactivities and intrinsic activities (compared to the uncoated catalyst).[12]

Experimental Section

Catalyst preparation

Alkylation of 1-methylimidazole with dimethylsulfate:[16] Pyridine and 1-methylimidazole were obtained from Sigma–Aldrich, and [MePsec-Bu₃][MeOSO₃] was obtained from SASOL R&D. [MMIM][NTf₂] was synthesised by an anion exchange of [MMIM][MeOSO₃] with Na(NTf₂). NMR analysis was used to confirm the purity and identity of the synthesised ionic liquids.

A Pd on alumina catalyst (≈5% w/w) was prepared by the wet impregnation of a crushed γ-alumina support with palladium acetate in dichloromethane at 50 °C for 4 h. The resultant paste was dried in an oven at 110 °C for 2 h before it was calcined at 350 °C for 8 h. The catalyst was pelletised to a size distribution between 300 and 600 μm. The resultant catalyst was then coated with the following organic modifiers: pyridine, [MMIM][MeOSO₃], [MMIM][NTf₂], [MePsec-Bu₃][MeOSO₃] and 1-methylimidazole, to the equivalent molar amount of 25 wt% of [MMIM][MeOSO₃], by dissolving the required amounts of modifier in either methanol or dichloromethane in a pill vial before the parent catalyst was introduced. The mixture was allowed to evaporate slowly in a fume hood to obtain a dry powder. The reduced metal catalysts were then generated in situ in the reactor (50 bar H₂, 15 mL min⁻¹ H₂, 180 °C, 4 h) before commencement of the reaction.

Catalyst characterisation

The average Pd crystallite size and crystallite morphology of the organically modified catalysts were determined by using a JEOL 2100 HRTEM, and approximately 300 particles were counted under HAAD and STEM conditions for the crystallite size analysis. ICP-OES (PerkinElmer Optima DV2100) was used to confirm the weight percent loading of Pd as well as the sulfur content of the freshly prepared and used catalysts. The BET pore size distribution and width were determined by using a Micromeritics TRISTAR 3020 to resolve the extent of change in pore volume, pore width and surface area between the freshly prepared and used organically modified and uncoated catalysts, all catalyst were placed under vacuum until a stable 70 Torr was reached. Chemisorption experiments were performed by using a Micromeritics ASAP 2020C using volumetric techniques. The calculation of the crystallite size and metal surface area was performed by using Micromeritics ASAP 2020C software using an established formula.[13f] DRIFTS spectra were obtained by using a Shimadzu IRAffinity-1 FTIR spectrophotometer, and TGA-DSC profiles of the used catalysts were obtained by using a TA SDT Q600.

Catalytic testing

Hydrogenation experiments were performed in a concurrent down-flow trickle-bed reactor with an inner diameter of 14 mm and a length of 250 mm to give a volume of 38.5 cm³. If required, the catalyst was diluted with carborundum (grit size 24) to maintain a constant catalyst bed volume, which prevented aniso-thermal conditions with strongly active catalysts (high LHSV values). The grit size is sufficient to prevent a large pressure drop across the reactor tube. The rest of the reactor was packed with carborundum, and quartz wool was used as a plug at the ends of the car-

borundum and the catalyst bed, which serves as an efficient dispersant of the liquid phase.[19] A 1-octene 2.5% (v/v) with 2.5% (v/v) octanal mixture in hexane was introduced into the reactor by using an HPLC pump. The hydrogen was introduced with mass flow controllers at a constant substrate to hydrogen ratio of 1:2. The feed was dried with molecular sieves[20] and degassed with argon[21] to eliminate water and oxygen from the system. An argon feed was supplied to the head space of the feed bottle to give a slight positive pressure. The temperature and pressure of the reaction system was kept at 50 bar and 130 °C by a temperature-controlled heating jacket with an internal sliding thermocouple. The gas hourly space velocity (GHSV) and LHSV were adjusted concurrently to produce the different iso-conversions of 1-octene and octanal for each of the differently modified catalysts. The product composition was analysed off-line by GC with flame ionisation detection (FID; PerkinElmer Clarus 500). Compositions were calculated using the mass obtained from the off-line GC analysis, and the conversion was obtained by determining the decrease in the composition of the substrate.

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