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Introduction

Biomass is a vast renewable resource suitable as a potential replacement of fossil fuels for the development of a sustainable society. Naturally produced lignocellulosic biomass (a dry plant-based material) with an intricate polymeric structure consists of various oxygenated functionalities. One of the targeted strategies for the implementation of bio-feedstock is upgradation of the raw materials through the reduction of oxygen content using defunctionalisation processes, which include hydrogenation, dehydration, and hydrodeoxygenation; in addition, decarbonylation is an effective transformation process; however, it is currently less studied for biomassderived compounds. As a major step towards the development of effective catalysts, metal-based homogeneous systems with different ligands, the use of CO scavengers for

Accelerated decarbonylation of 5-hydroxymethylfurfural in compressed carbon dioxide: a facile approach[†]

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Herein, decarbonylation of biomass-based 5-hydroxymethylfurfural (HMF) in compressed CO₂ with an unexpected acceleration of the reaction rate and excellent catalytic activity is reported. Without any additive, CO surrogates, or any organic solvents, *via* the developed method, an excellent conversion of 99.8% and highest selectivity of furfuryl alcohol (99.6%) in 4 h at 145 °C were achieved using an alumina-supported Pd catalyst (Pd/Al₂O₃). The superior activity is due to the unique characteristics (miscibility of reactant gases and high diffusivity) of compressed CO₂ and the synergy between CO₂ and Pd/Al₂O₃, where CO₂ plays an interesting role in accelerating the reaction by enhancing the diffusion of CO and furfuryl alcohol (both products have high solubilities in CO₂), consequently shifting the equilibrium to the forward direction. Characterisation of the catalyst suggested its direct interaction with the substrate and provided an indication of the possible reaction path. Thus, a mechanism was outlined. Compared to the results obtained using organic solvents, the results obtained using compressed CO₂ were superior in terms of activity, selectivity, and reaction rate. This strategy highlights easy product separation, improved catalyst life, and a simple sustainable process. The efficiency of this protocol is confirmed by its potential application to a series of aldehydes with various substituents to produce decarbonylated products in good to excellent yields.

improved activity, and acceptor-less conditions^{1–3} have been investigated. The drawbacks associated with the developed catalytic systems are mainly related to the recovery of the catalysts after the reaction, harsh reaction conditions, and the requirement of high-boiling solvents, which make the decarbonylation process incompatible with a sustainable reaction procedure.

In this regard, heterogeneous catalysts would be of significant interest as compared to homogeneous catalysts because they provide straightforward catalyst/product separation through filtration, thus making catalyst recovery easier; however, heterogeneous catalysts exhibit low reaction rates; hence, the selective decarbonylation of different aromatic aldehydes using heterogeneous catalysts in the gas phase faces the difficulties of tedious reaction conditions, presence of additives, catalytic deactivation, and low product yield.⁴ Thus, the development of suitable decarbonylation process that perform under milder reaction conditions in different organic solvents using metal nanoparticles or supported metal nanoparticles as catalysts was continued;⁵ however, limitations such as the requirement of metal additives, CO scavengers, use of large excess of organic solvents, longer reaction times, and product separation hindered these developments.

Furan-based compounds have the potential to generate a variety of products and may thus be implemented in the bio-

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refinery concept; therefore, several strategies have been developed for their transformation of bio-feedstock into speciality chemicals. As a multifunctional compound, 5-hydroxymethylfurfural (HMF) is beneficial for the production of a wide spectrum of fuel or non-fuel materials through hydrogenation, oxidation, hydrogenolysis of the C–O bond, dehydrogenation, decarbonylation, rearrangement, dissociation, and polymerisation.⁶

Decarbonylation of the -CHO group requires abstraction of the aldehydic hydrogen, which is an endothermic reaction; thus, elevated temperatures are essential for this process. In this context, one of the main challenges is to avoid humin formation (soluble or insoluble polymeric species), which generally occurs at high temperatures and hampers the catalytic activity.7 In addition, the presence of highly active multi-functional groups results in different side reactions and consequently decreases the selectivity of the decarbonylated product. Moreover, the adsorption and desorption of CO causes deactivation of the metal surface. Rauchfuss and coworkers employed an open system using the Pd/C catalyst at comparatively lower temperatures (120 °C), but the presence of oxygen was detrimental to the reduced catalysts as well as to the highly active HMF.8 A heterogeneous Pd catalyst supported on mesoporous silica (SBA-15) provided promising results in cyclohexane,⁹ but necessitated the presence of a molecular sieve (MS 4A) as a CO surrogate (a negative consequence was the regeneration of MS 4A, which was a tedious process and changed the resin composition), required a prolonged reaction time (12 h), and had restricted substrate scope and recyclability. To improve the yield, Meng et al. applied alkali metalmodified Pd catalysts; the decarbonylated product was obtained at 180 °C with a yield of >90% in 16 h of reaction after purging N_2 at an 8 h interval to prevent deactivation.^{10a} The same group also employed 28% water along with 1,4dioxane, which improved the yield of furfuryl alcohol (95.3%) under the same conditions as reported in their previous study, but under a hydrogen atmosphere, i.e. fresh hydrogen was flushed after 8 h;^{10b} hydrogen was used as a carrier gas to distinguish between hydrogenation and decarbonylation as the furfural moiety could be readily hydrogenated on a Pd catalyst, which was not reported in the study. Despite these advances, the decarbonylation reaction conducted using heterogeneous catalysts still has limited success because of the requirement of harsh reaction conditions, longer reaction times, as well as the use of a CO acceptor.

Compressed carbon dioxide (compressed CO_2) is a promising alternative for rapid and selective organic synthesis owing to its unique properties such as enhanced diffusion rates, easy product separation, controlled mass transfer resistance, and improvement of catalyst lifetime. However, reactions with heterogeneous catalysts are still restricted mainly to hydrogenation and oxidation because of the accelerated reaction rates, different product distributions, as well as high selectivity associated with the miscibility of the reactant gases (H₂ and O₂). A combination of heterogeneous catalysts and compressed CO_2 can provide an immense opportunity to develop highly efficient and environmentally and economically beneficial processes for a sustainable extension to the organic synthesis. Geilen *et al.* first reported the decarbonylation of HMF using a homogeneous Ir catalyst ([IrCl (cod)]₂) with different phosphine ligands in 1,4-dioxane with 5 MPa of compressed CO₂. Although HMF was decarbonylated to furfuryl alcohol with 95% selectivity, the reaction required dioxane as a solvent, a very high temperature (220 °C), and a long reaction time (12 h).¹¹

In our previous study, we have successfully developed a strategy to dehydrogenate alcohol over a heterogeneous Rh catalyst in compressed CO_2 using HMF as a model compound.¹² During dehydrogenation, decarbonylation of the aldehyde group was detected as a competing reaction that produced furfuryl alcohol depending on the reaction conditions. While screening different metal catalysts for dehydrogenation, we observed that Pd had the ability to mediate both reactions (dehydrogenation of alcohols and decarbonylation of aldehyde) in one transformation, but the tuning of reaction parameters could direct the reaction in a desired direction.

Herein, we attempted the decarbonylation of HMF using a commercially available Pd/Al_2O_3 catalyst, focusing on the use of only compressed CO_2 to play the dual role of a solvent and a surrogate to the generated gases, especially CO. Specifically, the goal of this study was to ensure the suitability of compressed CO_2 in the development of a simple process through the intelligent tuning of the advantageous physicochemical properties that could be helpful in building a compact system to achieve desired transformation under mild reaction conditions without any additional components.

Results and discussion

As abovementioned, HMF can undergo different types of reactions, which affect the selectivity of a particular product, and eventually, a separation step is required to obtain the desired compounds. However, the sensitivity of each process strongly depends on the reaction conditions; hence, careful modulation of the reaction parameters has an utmost importance in shifting the reaction path towards the preferred direction. Scheme 1 represents the general transformation routes of



Scheme 1 A general reaction pathway for the HMF transformation.

HMF, which can be converted to furfuryl alcohol and 2,5-diformylfuran (DFF) *via* decarbonylation and dehydrogenation, respectively. In addition, DFF can be transformed to furfural again through decarbonylation followed by hydrogenation to furfuryl alcohol. Furthermore, the dehydrogenation of furfuryl alcohol can produce furfural, which can be decarbonylated to furan.

Optimisation of different reaction parameters

CO₂ pressure. In the first step of optimisation, selection of proper pressure is essential to tune the properties of compressed CO₂. To elucidate the effect of CO₂ pressure on the catalytic performance of Pd/Al₂O₃, a series of reactions were performed with pressure varying from 4 to 16 MPa while maintaining a constant temperature (145 °C) and reaction time (4 h) in the presence (Fig. 1a) and in the absence of air (Fig. 1b). As shown in Fig. 1a, the reaction proceeded with a change in catalytic activity depending on the applied pressure; a very low conversion of ~9% was observed at 4 MPa, which started to increase with the increasing CO₂ pressure and reached 38% at 16 MPa. From the product distribution, it can be seen that the selectivity of DFF is comparatively higher (25% at 16 MPa); this suggests that dehydrogenation as another route competes with decarbonylation. Thus, it is reasonable to conduct the reaction in the absence of air to avoid the formation of unwanted by-products.

Fig. 1b shows the excellent pressure (density)-dependent performance in the absence of air (an inert atmosphere). The conversion of HMF increased significantly even at a low pressure of 4 MPa (79.9%). After reaching a maximum of >99% at 6 MPa, the conversion remained almost constant until 8 MPa. Surprisingly, the conversion of HMF dropped substantially to 54.6% when the pressure was increased to 16 MPa. As CO_2 is a compressed gas, at a fixed temperature of 145 °C, there is a huge change in the density from 0.054 g ml^{-1} (vapour) to 0.259 g ml⁻¹ (supercritical) (NIST chemistry web book) with an increase in pressure (4 to 16 MPa) that subsequently affects the solubility of the substrate. Thus, it is reasonable to understand the experimental environment (phase behaviour) inside the reactor that can provide an explanation for the CO₂ pressure-based activity of the present reaction. Because of the technical constraints related to the reactor used to perform the reaction, video monitoring of the phase behaviour was conducted in a separate setup. After replicating the applied conditions, the video is expected to offer an actual scenario of the number of phases present in the system during the reaction. Fig. 2a-f show the images of the phase behaviour





Fig. 1 Effect of CO₂ pressure on the decarbonylation of HMF using the Pd/Al_2O_3 catalyst; (a) presence of air and (b) N₂ atmosphere. Reaction conditions: Catalyst : substrate = 1:10; temperature = 145 °C, and reaction time = 4 h.

Fig. 2 Images obtained during the phase observation of the HMF-CO₂ system in a view cell at 145 °C. (a) Empty, (b) HMF in cell at various CO₂ pressure (c) 6 MPa, (d) 8 MPa, (e) 12 MPa, and (e) 16 MPa. For 12 and 16 MPa, the image obtained taken during stirring is presented, which clearly shows the status of HMF. Dotted red line represents the liquid meniscus.

obtained at various CO₂ pressures. Fig. 2a and b represent the images of the cell before and after the introduction of HMF, respectively. Naked eye observation indicates a sharp change in the system environment with a change in CO₂ pressure (Fig. 2c-f); at 6 MPa, the view cell is mainly filled with vapour, and a liquid phase is evident below the stirrer bar (Fig. 2c). Interestingly, as the CO₂ pressure was increased beyond 8 MPa, the liquid phase started to diminish (as can be seen from the change in the meniscus position) (Fig. 2d and e), and finally, a single phase was obtained at 16 MPa. By correlating the phase behaviour with the catalytic activity, it was logical to suggest that the adsorption of the substrate on the catalyst surface controlled the reaction¹³ because the substrate was more concentrated around the catalyst when the CO₂ pressure was low, and the reaction progressed with an accelerated rate. On the other hand, at higher pressures, the increased solubility of HMF in compressed CO₂ caused a decrease in the substrate concentration near the catalyst surface and generated a HMF-enriched CO_2 phase (Scheme 2); this could explain the reduced catalytic performance related to a change in the mass transfer properties.14

Effect of temperature. As abovementioned, decarbonylation of aldehyde is an endothermic reaction; hence, most of the studies have revealed an exceptionally high temperature regime for catalytic decarbonylation. By conducting the reaction in compressed CO₂, the temperature can tune the density and consequently the solubility, which in turn affects the phase behaviour. The conversion of HMF was investigated in the temperature range from 80 °C to 150 °C at a fixed pressure of 6 MPa (Fig. 3). Notably, the vapour state of CO₂ was maintained in the temperature range studied herein, and there was a nominal change in the density from 0.110 g ml⁻¹ (80 °C) to 0.0835 g ml $^{-1}$ (145 °C) at the fixed pressure of 6 MPa. Thus, no significant change was observed in the phase behaviour. The results presented in Fig. 3a revealed an unexpectedly poor conversion of HMF (6.1%) at 80 °C that increased monotonically with temperature and plateaued at or above 145 °C. Almost quantitative conversion of HMF (>99%) was achieved at 145 °C. There was a significant difference in the product selectivity depending on the temperature; as seen in Fig. 3a, the product selectivity transferred from dehydrogenation (DFF) to decarbonylation (FA) at 130 °C; the formation of DFF was favoured at low temperatures, and DFF was the major product



Scheme 2 Schematic of the possible scenario inside the reactor under (a) low and (b) high pressure conditions.



Fig. 3 Effect of temperature on the (a) catalytic activity and selectivity and the rate of (b) decarbonylation (TOF_{FA}) and dehydrogenation (TOF_{DFF}) over the Pd/Al₂O₃ catalyst. Reaction conditions: catalyst: substrate = 1:10, P_{CO_2} = 6 MPa, and reaction time = 4 h. TOF = Turnover frequency (TOF) = number of moles reacted/moles of metal *x* time (calculated on the basis of the lowest conversion of around 6%).

from 80 °C (selectivity ~80%) to 100 °C (selectivity 61%) (Fig. 3a), but decarbonylation dominated above 130 °C.

We evaluated the temperature-dependent reaction rate corresponding to dehydrogenation (TOF_{DFF}) and decarbonylation (TOF_{FA}) in terms of turnover frequency (TOF) at the conversion level of ~6%. Fig. 3b shows a comparison between the rate of formation of furfuryl alcohol (TOF_{FA}) and that of DFF (TOF_{DFF}) with the applied temperature. At 80 °C, TOF_{FA} $(1.6 h^{-1})$ was lower than TOF_{DFF} $(4.8 h^{-1})$, but started to increase with temperature and reached a maximum of 92.0 h⁻¹ at 145 °C. When the temperature was further increased to 150 °C, the TOF was slightly improved to 94.1 h^{-1} . On the other hand, except those at 80 °C, all TOF_{DFF} values were lower than the TOF_{FA} values (Fig. 3b) and further reduced at higher temperatures (12.4 h^{-1} ; 145 °C). This suggests that the activation energies of the two paths leading to the formation of furfuryl alcohol and DFF are different. Therefore, the obtained results underline the importance of the applied temperature to dictate the dominance of the kinetically or thermodynamically controlled path.¹⁵ Hence, kinetics is a straightforward explication for the increase in TOF_{FA} with temperature rather than the correlation of the reaction rate with the phase change model,

as described in Fig. 2. Based on the results presented in Fig. 3a and b, a temperature of 145 °C was used as the optimum temperature for HMF decarbonylation.

Reaction time versus catalytic performance. Fig. 4a presents the time profile of the reaction (temperature of 145 °C and P_{CO_2} of 6 MPa). With the variation of reaction time from 15 min to 8 h, the activity of the catalyst changed (Fig. 4a). There was no detectable transformation right after the introduction of the substrate (0 min). At the shortest time (15 min), the conversion of HMF was low (6.1%), but started to increase with time, which reached a maximum of >99% in 4 h and then remained almost constant. The change in conversion was also associated with the alteration of the product selectivity; after 15 min, the product mixture contained 76.7% furfuryl alcohol and 23.3% DFF. No other products were observed in the detectable range. As the reaction progressed, the selectivity of furfuryl alcohol increased to 99.6%, whereas the selectivity of DFF decreased to 0.4%. This observation suggests that the transformation of HMF to furfuryl alcohol can occur (i) via direct decarbonylation and (ii) through DFF. The yield vs. conversion curve provides further possibility to distinguish between the primary and secondary reactions. The curve with a linear approach from the origin represented the primary product; on the other hand, the product recognised by an increased followed by a decreased yield corresponded to the secondary reaction.¹⁶ The conversion-dependent yield plot (Fig. 4b) revealed



Fig. 4 Time profile of the (a) catalytic decarbonylation of HMF and (b) yield vs. conversion on Pd/Al₂O₃ catalyst. Reaction conditions: catalyst : substrate = 1:10, $P_{CO_2} = 6$ MPa, and temperature = 145 °C.

that at the lowest conversion, furfuryl alcohol and DFF were obtained with a yield of 3.9% and 1.4%, respectively. The yield of furfuryl alcohol increased steadily with conversion (major path), but DFF disappeared after reaching a maximum (4.4%)at 20% conversion (minor path of the HMF transformation). Notably, we also detected furfural with a very low yield (0.6%)at 50% conversion that disappeared in the final product. According to Scheme 1, furfural can be obtained from the decarbonylation of DFF or through the dehydrogenation of furfuryl alcohol. Herein, we can ignore the possibility of the direct formation of furfuryl alcohol from HMF by hydrogenolysis, which requires the presence of water and CO₂.¹⁷ In a controlled experiment, DFF was completely converted mainly to furfural (86.3%) (Table 2; entry 7). On the other hand, furfuryl alcohol was converted to 36.9% furfural although with a very poor conversion (5.1%) (Table 2; entry 8). Based on the results of the controlled experiments, DFF has emerged as a possible source of furfural that can be further hydrogenated to furfuryl alcohol using surface hydrogen, which has also been confirmed by another experiment with trace amounts of hydrogen (Table 2; entry 9). Hence, the transformation of HMF to furfuryl alcohol can occur through direct decarbonylation (major) as well as via DFF (minor) under the present conditions.

Catalyst/substrate ratio. Like the case of other parameters (temperature, pressure, etc.), the optimisation of the catalyst to substrate ratio under the studied reaction conditions is also important. Investigations on the variation of catalyst : substrate (wt) ratio was carried out from 1:1 to 1:30 at a fixed reaction time of 1 h (Fig. 5a). At a low ratio of 1:1, complete conversion was observed, but it dropped significantly (4.9%) as the substrate amount increased 30 times that of the catalyst. At the lowest conversion (\sim 5%), the TOF is enhanced from 18 h⁻¹ (1:1) to 116 h⁻¹ (1:30); thus, to achieve a high performance after maximising the substrate concentration, appropriate reaction conditions are necessary. In this context, increasing the reaction time can also enhance the conversion. Fig. 5b presents the catalytic activity and product selectivity after 4 h of reaction. The result shows that except for the case of the 1:1 system, in which the conversion dropped (70.2%) because of the generation of black polymeric substances, the conversion increased after extending the reaction time to 4 h. A highest conversion of >99% was achieved using the 1:10 ratio, whereas a vast improvement (40.2%) was observed for maximum substrate concentration (1:30). A comparison of the product distributions (Fig. 5a and b) indicated that at a low substrate concentration (1:1), the selectivity of furfuryl alcohol dropped from 93.7% (1 h) to 80.2% (4 h); this might be attributed to the longer reaction time that led to the substrate scarcity near the catalyst surface and triggered other side reactions. On the other hand, although a higher ratio (1:30)showed improved selectivity of furfuryl alcohol from 52.8% (1 h) to 87% (4 h), unwanted products (dehydrogenated, condensation, etc.) were also detected. Thus, at high substrate concentrations, the overcrowded surface resulted in the increased selectivity of DFF that might be related to a change in the adsorption geometry that influenced the activity and selectivity



Fig. 5 Effect of the catalyst : substrate ratio (wt.) on the activity of Pd/ Al₂O₃ catalyst at (a) 1 h and (b) 4 h. Reaction conditions: $P_{CO_2} = 6$ MPa and temperature = 145 °C.

of the reaction.¹⁸ As the reaction progressed, the transformation of DFF to furfuryl alcohol occurred, and the selectivity increased. Hence, in the applied protocol, the catalyst: substrate ratio is a critical parameter to control the activity and selectivity. To achieve maximum conversion and selectivity to furfuryl alcohol, an optimum ratio of 1:10 was used throughout the experiment.

Different organic solvents and solvent-CO₂. After optimizing the reaction parameters, different organic solvents, such as tetrahydrofuran (THF), cyclohexane, and hexane, were tested

for the decarbonylation of HMF under the present reaction conditions. Notably, a nonpolar and a borderline (THF) solvent were chosen to compare the activity with that of compressed CO₂, and the results are shown in Table 1. Under the same reaction conditions, the conversion of HMF varied depending on the solvent used and followed the order: hexane (92.5%) > cyclohexane (85.2%) > THF (59.1%) (Table 1; entries 1 to 3). Furfuryl alcohol was detected as the major product independent of the solvent used, and the selectivity order was hexane (95.6%) > cyclohexane (76.9%) > THF (50.1%), showing a clear trend depending on the solvent polarity. No DFF was detected in hexane and cyclohexane (Table 1; entries 1 and 2), but 43% of DFF-enriched product mixture was found in THF (Table 1; entry 3).

After applying a fixed pressure of CO_2 (6 MPa) to the abovementioned solvents, a change was observed, especially in the selectivity of furfuryl alcohol (Table 1; entries 4 to 6). The selectivity increased to 90% and 92% in THF and cyclohexane, respectively, (Table 1; entries 4 and 5) after suppressing the other side reactions observed in the absence of CO₂; however, hexane maintained a constant selectivity (95%). A positive influence was also observed on the conversion of HMF in THF, which increased significantly to 70%, but slightly dropped in the other two solvents. This might be attributed to the presence of a co-solvent that affected the solvation of CO₂ molecule, and the activity decreased.¹⁹ Hence, by comparing the results with those obtained using non-polar solvents, it can be inferred that compressed CO₂ has a decisive influence on the catalytic activity, and it is possible to achieve a significantly improved performance regarding the selectivity of furfuryl alcohol.

Effect of the support materials. It has to be mentioned that the catalyst support has a wide range of effects that originate from direct involvement and influence the particle size (dispersion), charge transfer between metal and support (metal support interaction), redox property *etc.*, which can influence the activity of the catalyst.²⁰ To elucidate the role of the support material in the decarbonylation of HMF in compressed CO_2 , we examined Pd supported on different types of materials (Table 2). In each case, the metal concentration was

Table 1	Decarbonylation of HMF i	n different organic solvents and in solv	vent + CO ₂ using the Pd/Al ₂ O ₃ catalyst
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Entry	Solvent	Conv. (%)	Product selectivity (%)			
			Furfuryl alc.	DFF	Furfural	Others
Organic solv	ent					
1	THF	59.1	60.1	32.9	6.9	_
2	Cyclohexane	85.2	76.9	_	5.2	17.9
3	Hexane	92.5	95.6	_	4.4	_
Organic solv	$ent + CO_2$					
4	THF	70.0	90.9	5.5	3.3	_
5	Cyclohexane	81.4	92.0	3.4	4.6	_
6	Hexane	84.0	95.5	—	4.5	—

Reaction conditions: catalyst : substrate = 1 : 10; P_{N_2} = 0.1 MPa; Temp. = 145 °C; reaction time = 4 h; metal content ~5 wt%; entries 1–3: solvent = ~7 ml (corresponds to the moles of CO₂ used); entries 4–6: P_{CO_2} = 6 MPa.

Entry	Catalyst	Dispersion ^{<i>a</i>} (%)	Conv. (%)	Product selectivity (%)		
				DFF	Furfuryl alc.	Other
1	Pd/Al ₂ O ₃	21.4	99.8	0.4	99.6	_
2	Pd/MCM-41	5.6	22.8	26.1	73.9	_
3	Pd/Al-MCM-41	4.8	45.6	9.1	90.9	_
4	Pd/C	12.1	86.0	10.4	86.6	2.7
5	Pd/hydrotalcite	20.2	65.2	58.3	37.9	3.8
6	Al_2O_3	_	_	_	_	_
7^b	Pd/Al_2O_3	_	>99.0	_		>99.0 ^c
8^d	Pd/Al_2O_3	_	5.1	_	_	>99.0 ^e
9^f	Pd/Al ₂ O ₂		>99.0	_	97.8	

Reaction conditions: Catalyst: substrate = 1:10; $P_{CO_2} = 6$ MPa; $P_{N_2} = 0.1$ MPa; Temp. = 145 °C; reaction time = 4 h; 0.05 mol% of Pd. ^{*a*} Approximate expression of metal dispersion = 0.9/diameter (in nm); [see ref. 36]. ^{*b*} DFF as substrate. ^{*c*} 86.3% = furfural and 13.7% = other. ^{*d*} Furfuryl alcohol as substrate. ^{*e*} 36.9% furfural and 63.1% condensation products. ^{*f*} Controlled experiment with DFF in the presence of trace amounts of hydrogen for 1 h.

fixed to ~0.05 mol%. The dispersion of Pd was calculated from the particle size distribution (ESI; Fig. S6[†]), which varied from 5% to ~21% depending on the support used. An inert support such as MCM-41 (only Si) provided <25% conversion (Table 2; entry 2); however, after modification with Al, the conversion reached ~46% (Table 2; entry 3). A very high conversion of 86% was observed on Pd/C (Table 2; entry 4), whereas 65.2% HMF was converted over Pd/hydrotalcite, which was a basic support (Table 2; entry 5). The product distribution also highlights the support effect. Under the applied conditions, furfuryl alcohol was the major product on MCM-41 (73.9%) as well as on Al-MCM-41 (90.9%) (Table 1; entries 2 and 3). In addition, Pd/C also offers an excellent selectivity of furfuryl alcohol (86.6%) accompanied by DFF (10.7%) and 2.7% of other by-products (Table 2; entry 4). Although Pd/Al₂O₃ and Pd/hydrotalcite exhibit comparable Pd dispersion, dehydrogenation predominates over decarbonylation on hydrotalcite; DFF is obtained as a major product with a selectivity of 58.3% (Table 2; entry 5). The conversion and selectivity of furfuryl alcohol among the catalysts were investigated; they followed the order Al₂O₃ > C > hydrotalcite > Al-MCM-41 > MCM-41 and $Al_2O_3 > C > Al-MCM-41 > MCM-41 > hydrotalcite, respectively.$ From these results, it can be suggested that all the catalysts are active under the studied conditions. Furthermore, the nature of the support material plays an important role; acidic supports are more efficient than basic supports; this can be explained by their role in the modification of active sites (Pd) through the enhancement of the electron deficiency of noble metals.²¹ The excellent performance of Pd/Al₂O₃ may be related to the possible interaction of Pd with Al₂O₃²² as Al₂O₃ itself is completely inactive in the reaction (Table 2, entry 6). However, the present results do not allow us to reach a precise conclusion, which requires a detailed study. Previously, a support-dependent activity has also been observed in the gasphase decarbonylation of furfural.⁴

Scope of the developed method. After successful application of the developed method in the decarbonylation of HMF, the process was further extended to other heterocyclic aldehydes

under the optimised reaction conditions (temperature of 145 °C, reaction time of 4 h, and P_{CO_2} of 6 MPa) (Table 3). In each case, the decarbonylated product was detected as the sole product. Furfural and 5-methylfurfural were converted to their corresponding decarbonylated compounds with an excellent yield of >99% and 92.5%, respectively (Table 3; entries 1 and 2). Furthermore, in addition to furanic compounds, pyrrole aldehyde also underwent decarbonylation to produce pyrrole (56.2% yield) (Table 3; entry 3). The method was then extended to a series of substituted benzaldehyde. Depending on the presence of electron-withdrawing and electron-donating groups, the activity of the compound varied; nitro-substituted benzaldehydes exhibited good to excellent yields based on the position of the substituent, which followed the sequence *p*- (100%) > *m*- (90.6%) > *o*- (26.8%) (Table 3; entries 4, 5, and 6). The presence of -OH and -OMe groups in p-substituted benzaldehyde also affords the corresponding decarbonylated products without affecting the other functional groups; p-hydroxybenzaldehyde shows tolerance to the -OH group and is successfully converted to phenol with 64.4% yield (Table 3; entry 7). On the other hand, 76% anisole was generated smoothly from the decarbonylation of p-anisaldehyde (Table 3; entry 8). Moreover, 55% toluene was obtained from p-tolylaldehyde (Table 3; entry 9). Interestingly, styrene reached an excellent yield of 99% from the decarbonylation of trans-cinnamaldehyde (Table 3; entry 10). Indole-3-carboxaldehyde, a bicyclic compound, also decarbonylated to indole with a high yield of 68.3%. Thus, the efficiency of the developed method was confirmed by the powerful performance of a wide range of aldehydes to achieve quantitative selectivity of the targeted decarbonylation products.

Catalyst recycling

Recycling is one of the most advantageous factors of a heterogeneous catalyst for the environmental and economic sustainability of a process. In the decarbonylation process, it is considered that the catalytic deactivation can originate from the adsorption of CO on the metal surface. Thus, to assess the

Entry	Substrate	Product yield (%)
1 ^a	0 0 0	↓ H
2		(>99.0)
3	A Contraction of the second se	(92.5) Нн
4	0 ₂ N-0	(56.2) $O_2N \longrightarrow H$
5	0 ₂ N 0	(>99.0) _{O2N} H
6		(90.6)
7		(26.8) нон
8		(64.4)
9	-<->	(75.8) — (52.7)
10		(53.7)
11 ^b	0 N H	(98.9)

Reaction MPa: Te decarbonylated product was detected as the sole product.

efficiency of the spent catalyst, it was recycled after separation from the product mixture by filtration (ESI; Fig. S1[†]). The used catalyst retained its activity until the 5th recycle, which then dropped slightly without affecting the product selectivity. After confirming the stability of the metal by a hot filtration test, surface characterisation of the catalyst was conducted using different spectroscopic techniques.

Table 3 Substrate scope of the decarbonylation reaction on the Pd/ Al₂O₃ catalyst

		mesh cata
	↓ H	4.2 ± 0.4
	(>99.0)	butions, t
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		sition of o
ц	(92.5)	0.3 nm wa The F
	N H	obtained
		Fig. S2a a
	(56.2)	section†).
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		tangle in
	(>99.0)	activation
		CO in cor
O ₂ N	O ₂ N H	the cataly
	(90.6)	gaseous
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		ESI†). The
	(75.8)	HMF, wh
	Щ	
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	(98.9)	
0=	ң	
	< <u>∽</u> ∥	
Ĥ	H (68-3)	20 nm
	(00.5)	
h conditions: catalyst : substrate = 1 : $mp_{e} = 145 \text{ °C}$: time = 4 h, a = 6.5 h	10; $P_{CO_2} = 6$ MPa; $P_{N_2} = 0.1$ b = 12 h; in each case, the	(b)
,,,,,,, _		12102.00

Transmission electron microscopy (TEM) images of the fresh and used catalysts and the corresponding particle size distributions are shown in Fig. 6a and b, respectively. In the fresh catalyst, spherical Pd particles with an average size of nm were detected on the Al₂O₃ surface (Fig. 6a). from the calculation of the particle size distrithe TEM image of the spent catalyst (Fig. 6b) did not y sign of agglomeration of metal particles or depocarbonaceous materials, and the particle size of 4.8 \pm as almost retained.

TIR spectra of the fresh and used catalysts were in the range of 4000-400 cm⁻¹ and are depicted in nd S2b,† respectively (details are provided in the ESI In the spectrum of the spent catalysts (Fig. S2b[†]), no detected in the 1800-2100 cm⁻¹ range (dotted rec-Fig. S2b[†]) corresponding to adsorbed CO on metallic ich is one of the possible factors of catalyst deduring decarbonylation.²⁴ The high miscibility of mpressed CO₂ might prevent the adsorption of CO on yst surface, as confirmed from the analysis of the part after the reaction (ESI; Fig. S3[†]), eventually g the catalyst life. Thus, the decreased catalytic an be related to the loss of catalyst because of handng separation.

fingerprint region (1700–1100 cm⁻¹), the FTIR specthe used catalyst also shows a number of signals at 80, 1400, 1510, 1620, and 1676 cm⁻¹ (an expanded lustrated in ESI; Fig. S4a[†]). The described IR bands o HMF,²⁵ and the assignments can be made from an pectrum of HMF (ESI: Fig. S4b; details are in the e band at 1676 $\rm cm^{-1}$ is due to the carbonyl group of ich shifts to 1665 cm⁻¹ in the used catalyst because



Fig. 6 TEM images and particle size distribution of the Pd/Al₂O₃ catalyst: (a) fresh and (b) used.

of the possible adsorption on Pd, and explains the interaction of HMF with the metal surface through the aldehyde functionality.²⁶ In addition, a very weak band appears at 1620 cm⁻¹, which may be attributed to the C=C stretching vibration of the furan ring bound to the carbonyl group. A small shoulder at 1720 cm⁻¹ indicates the possible C=O stretching of aldehyde (marked with *). Regarding the peaks in the -OH region (3500-3200 cm⁻¹), the signal of the spent catalyst is broader than that of the fresh catalyst with a maxima at 3425 cm⁻¹ because of the possible change upon adsorption of HMF. In addition, the peaks related to the aromatic and aldehyde C-H stretching are observed at 2920 cm⁻¹ and 2860 cm⁻¹, respectively.

To understand the change in the metal environment before and after the reaction, XPS was performed on the fresh and recycled catalysts (ESI; Fig. S5†). Fig. S5a and S5b† exhibit the 3d region spectra of Pd in the fresh and used catalyst, respectively. The Pd 3d core level spectrum of the fresh catalyst contains two well-separated components at 334.9 eV (3d_{5/2}) and 340.3 eV $(3d_{3/2})$ corresponding to Pd⁰, which are also present in the spectrum of the recycled catalyst (335.3 eV (3d_{5/2}) and 340.6 eV $(3d_{3/2})$, respectively). There is no peak related to the PdO_x species in the higher binding energy region. The atomic concentrations calculated in the fresh and recycled catalyst are 4.7% (Pd), 36.8% (Al), and 58.5% (O) and 4.4% (Pd), 37.2% (Al), and 58.7% (O), respectively. In addition, XPS revealed a slight change in the amount of Pd atoms on the surface of Pd/ Al₂O₃ measured in terms of Pd/Al ratio, which increased slightly from the fresh catalyst (0.072) to the recycled catalyst (0.110) and was attributed to a nominal change in the dispersion of the metal on the catalyst surface.²⁷ The XPS spectra of the support materials confirmed the minor changes in the binding energies of the Al 2p and O 1s spectra (ESI[†]).

Possible mechanism

Elucidation of the reaction mechanism is important to understand each reaction step and helpful for further implementation of the developed method. It is difficult to predict a clear cut mechanism for the studied reaction based on the present

Scheme 3 Proposed reaction mechanism.

results; thus, only an outline is proposed (Scheme 3). Herein, the reaction was conducted in compressed CO_2 , and there was every possibility of the chemical participation of CO_2^{28} by direct interaction with the substrate²⁹ and with the catalyst.³⁰ Considering the experimental results, we observed that the highest catalytic activity was obtained in the substrate-rich phase; hence, the possibility of substrate- CO_2 interactions was dismissed. The IR spectrum of the used catalyst shows no bands related to the carbonate species that generally exist in the presence of CO_2 .³¹ Therefore, CO_2 can be considered a CO acceptor in the present system, which causes a shift in the reaction equilibrium and enhances the reaction rate (ESI; Fig. S3†).

The best performance of the catalyst was achieved under the two-phase condition (CO₂-substrate), suggesting a surfacecontrolled reaction; however, only the support surface (Al_2O_3) is completely inactive in the reaction, which requires Pd (Table 2; entry 6). Therefore, we propose that in the first step, HMF is invariably adsorbed on the metal surface through the aldehyde functionality, as confirmed from the product distribution. From the spectral analysis of the used catalysts, we also detected a shift of the aldehyde -C-O band and a change in the aromatic skeletal vibration region (1600 and 1500 cm^{-1}). The transformation of HMF into furfuryl alcohol can be postulated as a consequence of the C-C bond scission between the aryl and aldehyde groups. Previously, Song et al. have reported that the cleavage of a C-C bond is easier than that of a C-H bond in aryl aldehyde due to the strong interaction between the aryl group and the catalyst surface that causes a weakening of the C-C bond.³² In addition, a strong interaction of the aldehyde group and furan ring with the same metal surface was also reported.³³ In the next step, the cleavage of the C-C bond causes decarbonylation followed by reductive elimination and results in the decarbonylated product. The minor dehydrogenation reaction might be the consequence of the interaction of the -OH proton with the neighbouring surface oxygen.³⁴ Furthermore, the role of the support material cannot be ignored, as described in the previous section, which needs further investigations.

Conclusion

In conclusion, we have developed an efficient decarbonylation methodology free from any organic solvent or CO scavenger for the selective decarbonylation of biomass-based platform molecules, such as HMF, using a commercially available Pd/Al_2O_3 catalyst in compressed CO_2 . The unique properties of the reaction medium can be beneficially applied in the conversion of HMF to furfuryl alcohol with very high selectivity (99.6%). Indeed, the incorporation of compressed CO_2 significantly improved the catalytic activity. Neither CO_2 nor Pd alone appears suitable for the reaction, but a combination of both provides high catalytic performance and excellent product yield through the proper control of the reaction variables. A minor path through dehydrogenation was also detected, but

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had nominal effect on the product selectivity. This process allows an easy separation of the product simply by depressurisation. Based on the characterisation of the fresh and used catalyst, a reaction mechanism was proposed. The catalytic system provides appreciable reusability and shows tolerance to a series of different types of substrates with various substituents, which generate the corresponding decarbonylated compounds with good to excellent yield without affecting the substituents. Our future challenge is to investigate the role of the oxide support in the presence of compressed CO_2 and to determine the exact reaction mechanism after the proper understanding of the status of the reaction medium.

Experimental

Materials

5-Hydroxymethylfurfural (HMF) (Aldrich) was used as received. Carbon dioxide (>99.99%) was supplied by Nippon Sanso Co. Ltd. 5% Pd/C and 5% and 1% Pd/Al₂O₃ were obtained from Aldrich. Pd(II) sodium chloride was obtained from Aldrich, and ~1% Pd/hydrotalcite was obtained from Wako Pure Chemicals. Cetyltrimethylammonium bromide used as a template for the MCM-41 synthesis was obtained from Aldrich. Tetraethylorthosilicate, which was used as the silica source, was obtained from Wako Pure Chemicals.

The metal catalyst supported on MCM-41 was synthesised in our laboratory using a modified method.³⁵ In each case, the metal content was maintained as ~5%. Unless otherwise stated, all the chemicals were used without further purification. Details of the catalyst characterisation techniques are provided in the ESI.[†]

Phase observation

Video monitoring of the phase behaviour of HMF in compressed CO_2 at 145 °C was performed separately in a 10 ml high-pressure view cell. At first, HMF was introduced into the cell followed by CO_2 after stabilisation of the temperature. For phase observation during the reaction, the content was stirred continuously, and images were obtained at each step.

Catalytic performance

A 50 ml batch reactor placed in a hot air circulating oven was used to test the reaction on the laboratory scale. In a typical experiment, a specified amount of the catalyst and substrate were introduced into the reactor. The reactor was flushed 5 times with nitrogen to remove air. The reactor was heated for a specified amount of time to stabilise to the required temperature (145 °C). After stabilisation, CO_2 was charged into the reactor using a high-pressure liquid pump and then compressed to the desired pressure. The content of the reactor was stirred with a magnetic stirrer bar during the reaction. After the reaction, the reactor was quenched using an ice bath, followed by careful depressurisation and the separation of the solid catalyst from the liquid product simply by filtration. The detailed analytical method is provided in the ESI.[†]

Conflicts of interest

There are no conflicts to declare.

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References

- (a) J. Tsuji, J. Am. Chem. Soc., 1968, 90, 99;
 (b) D. H. Doughty and L. H. Pignolet, J. Am. Chem. Soc., 1978, 100, 7083;
 (c) J. M. O'Connor and J. Ma, J. Org. Chem., 1992, 57, 5075;
 (d) P. Fristrup, M. Kreis, A. Palmelund, P.-O. Norrby and R. Madsen, J. Am. Chem. Soc., 2008, 130, 5206;
 (e) J. J. Adams, N. Arulsamy and D. M. Roddick, Organometallics, 2012, 31, 1439;
 (f) T. Iwai, T. Fujihara and Y. Tsuji, Chem. Commun., 2008, 6215.
- 2 (a) A. Modak, A. Deb, T. Patra, S. Rana, S. Maity and D. Maiti, *Chem. Commun.*, 2012, 48, 4253; (b) K. Ding, S. Xu, R. Alotaibi, K. Paudel, E. W. Reinheimer and J. Weatherly, *J. Org. Chem.*, 2017, 82, 4924.
- 3 (a) M. Kreis, A. Palmelund, L. Bunch and R. Madsen, Adv. Synth. Catal., 2006, 348, 2148; (b) C. M. Beck, S. E. Rathmill, Y. J. Park, J. Chen, R. H. Crabtree, L. M. Liable-Sands and A. L. Rheingold, Organometallics, 1999, 18, 5311.
- 4 (*a*) H. Singh, M. Prasad and R. D. Srivastava, *J. Chem. Technol. Biotechnol.*, 1980, **30**, 293; (*b*) P. Lejemble, A. Gaset and P. Kalck, *Biomass*, 1984, **4**, 263.
- 5 (a) P. K. Kundu, M. Dhiman, A. Modak, A. Chowdhury, V. Polshettiwar and D. Maiti, *ChemPlusChem*, 2016, 81, 1142; (b) V. V. Pushkarev, N. Musselwhite, K. An, S. Alayoglu and G. A. Somorjai, *Nano Lett.*, 2012, 12, 5196; (c) N. Pino, S. Sitthisa, Q. Tan, T. Souza, D. López and D. E. Resasco, *J. Catal.*, 2017, 350, 30.
- 6 (a) A. Corma, S. Iborra and A. Velty, Chem. Rev., 2007, 107, 2411; (b) O. Casanova, S. Iborra and A. Corma, ChemSusChem, 2009, 2, 1138; (c) Y. Roman-Leshkov, J. N. Chheda and J. A. Dumesic, Science, 2006, 312, 1933; (d) H. B. Zhao, J. E. Holladay, H. Brown and Z. C. Zhang, Science, 2007, 316, 1597; (e) G. Yong, Y. G. Zhang and J. Y. Ying, Angew. Chem., 2008, 120, 9485, (Angew. Chem. Int. Ed., 2008, 47, 9345); (f) L. Vanoye, M. Fanselow, J. D. Holbrey, M. P. Atkins and K. R. Seddon, Green Chem., 2009, 11, 390; (g) S. Hu, Z. Zhang, J. Song, Y. Zhou and B. Han, Green Chem., 2009, 11, 1746; (h) J. Lewkowski, ARKIVOC, 2001, 2, 17.
- 7 (a) G. Tsilomelekis, M. J. Orella, Z. Lin, Z. Cheng,
 W. Zheng, V. Nikolakis and D. G. Vlachos, *Green Chem.*,
 2016, 18, 1983; (b) A. Herbst and C. Janiak, *New J. Chem.*,

2016, **40**, 7958; (*c*) B. Girisuta, L. P. B. M. Janssen and H. J. Heeres, *Green Chem.*, 2006, **8**, 701.

- 8 J. Mitra, X. Zhou and T. Rauchfuss, Green Chem., 2015, 17, 307.
- 9 Y.-B. Huang, Z. Yang, M.-Y. Chen, J.-J. Dai, Q.-X. Guo and Y. Fu, *ChemSusChem*, 2013, 6, 1348.
- 10 (a) Q. Meng, C. Qiu, G. Ding, J. Cui, Y. Zhu and Y. Li, *Catal. Sci. Technol.*, 2016, 6, 4377; (b) Q. Meng, D. Cao, G. Zhao, C. Qiu, X. Liu, X. Wen, Y. Zhu and Y. Li, *Appl. Catal.*, B, 2017, 212, 15.
- 11 F. M. A. Geilen, T. vom Stein, B. Engendahl, S. Winterle, M. A. Liauw, J. Klankermayer and W. Leitner, *Angew. Chem.*, *Int. Ed.*, 2011, **50**, 6831.
- 12 M. Chatterjee, T. Ishizaka, A. Chatterjee and H. Kawanami, *Green Chem.*, 2017, **19**, 1315.
- 13 (a) A. Milewska, A. M. Banet Osuna, I. M. Fonseca and M. Nunes da Ponte, *Green Chem.*, 2005, 7, 726;
 (b) D. Chouchi, D. Gourgouillon, M. Courel, J. Vital and M. Nunes da Ponte, *Ind. Eng. Chem. Res.*, 2001, 40, 2551.
- 14 N. J. Meehan, A. J. Sandee, J. N. H. Reek, P. C. J. Kamer, Piet W. N. M. van Leeuwen and M. Poliakoff, *Chem. Commun.*, 2000, 1497.
- 15 P. Sykes, *A guidebook to mechanism in organic chemistry*, Longman Scientific & Technical, Essex, UK, 6th edn, 1986, pp. 42–43.
- 16 A.-N. Ko and B. Wojciechowski, *Prog. React. Kinet.*, 1983, **12**, 20.
- 17 M. Chatterjee, T. Ishizaka and H. Kawanami, *Green Chem.*, 2014, **16**, 1543.
- 18 (a) F. Delbecq and P. Sautet, J. Catal., 1995, 152, 217;
 (b) D. Loffreda, F. Delbecq, F. Vigné and P. Sautet, J. Am. Chem. Soc., 2006, 128, 1316.
- (a) T. Aizawa, S. Janttarakeeree, Y. Ikushima, N. Saitoh, K. Arai and R. Smith, *J. Supercrit. Fluids*, 2003, 27, 247;
 (b) A. I. Frolov and M. G. Kiselev, *J. Phys. Chem. B*, 2014, 118, 11769.
- 20 (a) T. Ishihara, K. Harada, K. Eguchi and H. Arai, *J. Catal.*, 1992, 136, 161; (b) M. Shekhar, J. Wang, W.-S. Lee, W. D. Williams, S. M. Kim, E. A. Stach, J. T. Miller, W. N. Delgass and F. H. Ribeiro, *J. Am. Chem. Soc.*, 2012, 134, 4700.
- 21 (a) A. Yu. Stakheev and L. M. Kustov, *Appl. Catal.*, A, 1999, 188, 3; (b) R. A. Della Betta, M. Boudart, P. Gallezot and R. S. Weber, *J. Catal.*, 1981, 69, 514.

- 22 (a) J. H. Kwak, J. Z. Hu, D. H. Mei, C. W. Yi, D. H. Kim, C. H. F. Peden, L. F. Allard and J. Szanyi, *Science*, 2009, 325, 1670; (b) D. H. Mei, J. H. Kwak, J. Z. Hu, S. J. Cho, J. Szanyi, L. F. Allard and C. H. F. Peden, *J. Phys. Chem. Lett.*, 2010, 1, 2688.
- 23 (a) F. M. Hoffmann, *Surf. Sci. Rep.*, 1983, 3, 107;
 (b) C. Keresszegi, T. Burgi, T. Mallat and A. Baiker, *J. Catal.*, 2002, 211, 244.
- 24 (a) R. D. Srivastava and A. K. Guha, *J. Catal.*, 1985, 91, 254;
 (b) M. D. Argyle and C. H. Bartholomew, *Catalysts*, 2015, 5, 145.
- 25 N. B. Colthup, L. H. Daly and S. E. Wiberley, *Introduction to Infrared and Raman Spectroscopy*, Academic Press, New York, 1964.
- 26 H.-W. Chen, C.-S. Chen and S.-J. Ham, J. Phys. Chem., 1995, 99, 10557.
- 27 B. Kucharczyk, W. Tylus and L. Kepinski, *Appl. Catal., B*, 2004, **49**, 27.
- 28 M. A. Blatchford, P. Raveendran and S. L. Wallen, J. Am. Chem. Soc., 2002, 124, 14818.
- 29 Y. Jing, Y. Hou, W. Wu, W. Liu and B. Zhang, *J. Chem. Eng. Data*, 2011, **56**, 298.
- 30 (a) J. Szanyi and J. H. Kwak, *Phys. Chem. Chem. Phys.*, 2014, 16, 15126; (b) K. Fottinger, R. Schlogl and G. Rupprechter, *Chem. Commun.*, 2008, 320.
- 31 X. Wang, H. Shi, J. H. Kwak and J. Szanyi, ACS Catal., 2015, 5, 6337.
- 32 R. Song, D. Ostgard and C. V. Smith, in *Catalysis of organic reactions*, ed. J. L. Davis and M. A. Barteau, *Surf. Sci.*, 1987, vol. 187, pp. 387.
- 33 (a) S. Sitthisa, T. Pham, T. Prasomsri, T. Sooknoi, R. G. Mallinson and D. E. Resasco, *J. Catal.*, 2011, 280, 17;
 (b) S. H. Pang and J. Will Medlin, *ACS Catal.*, 2011, 1, 1272.
- 34 (a) L. Nondek and J. Sedlacek, J. Catal., 1975, 40, 34;
 (b) B. Xu, X. Liu, J. Haubrich and C. M. Friend, Nat. Chem., 2010, 2, 61.
- 35 M. Chatterjee, T. Iwasaki, Y. Onodera and T. Nagase, *Catal. Lett.*, 1999, **61**, 199.
- 36 M. Boudart and G. Djega-Mariadassou, *Kinetics of Heterogeneous Catalytic Reaction*, Princeton University Press, Princeton, NJ, 1984.