Directing the Cleavage of Ester C—O Bonds by Controlling the Hydrogen Availability on the Surface of Coprecipitated Pd/Fe₃O₄

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The ready availability of esters from natural sources makes them promising substrates for the sustainable production of key intermediates of the chemical industry. In this context, methods to selectively cleave the alkoxy or ester C–O bond to obtain either alkane + acid or alcohol + aldehyde were investigated. Using Pd/Fe₃O₄^(r) [(r) = reduced] as the catalyst of choice and either 2-propanol—as indirect H source—or molecular hydrogen—as ample H source—the hydrogen coverage on the

Introduction

The directed cleavage of one of the two different C–O single bonds in esters derived from natural sources represents one of the major challenges in green chemistry.^[1] Recent reports concern the synthesis of long- and short-chain alcohols^[2] from natural fats and oils,^[3] acetates and formiates as well as diesters.^[4] To accelerate the hydrogenolysis reaction various transitionmetal catalysts have been used.^[5,6] Nickel has found widespread application in the hydrotreatment of vegetable oils to produce diesel-range alkanes.^[7] Copper-based catalysts are employed commonly for cleaving C–O bonds in esters^[2] to form alcohol products but require harsh reaction conditions. Similarly, homogeneous^[8] and heterogeneous^[9] catalysts have been used for cleaving the C–O bond in aryl ethers to arenes and alcohols including the depolymerization of soft- and hardwood lignin.^[8,9]

Recently, coprecipitated Pd/Fe₃O₄^(r) [(r) = reduced] has been claimed to give superior performance in a number of reactions, including C–O reduction,^[10] aqueous-phase reforming of ethylene glycol,^[11] and hydrogenolysis of glycerol^[12] and ethylene glycol.^[13] Furthermore Pd/Fe₃O₄^(r) has been used in the catalytic

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transfer hydrogenolysis of polyalcohols employing 2-propanol as H source.^[14] As 2-propanol can be obtained from biological sources, it is a particularly "green" reductant that can be dehydrogenated readily to acetone in the presence of an appropriate catalyst. The use of such alternative hydrogen donors has recently gained increased attention to improve the sustainability and economics of hydrogenation reactions.^[15] In the hydrogenolysis of esters, the cleavage of the alkoxy C–O bond provides alkane and acid, while cleavage of the ester C–O bond provides alcohol and aldehyde (Scheme 1). If aromatic esters are used as substrates, a high chemoselectivity to hydrogenolysis of the ester group versus hydrogenation of the aromatic ring is also essential.



Scheme 1. Options for the cleavage of the two different CO bonds in 2phenylethylacetate (PEA); under the conditions of ester hydrolysis, the acid and aldehyde are converted to the corresponding *i*Pr-ester and alcohol.

In the present study, coprecipitated Pd/Fe₃O₄^(r) was explored as a catalyst for the hydrogenolysis of 2-phenylethylacetate (PEA). The principal goal was to develop a methodology for the directed cleavage of one of the ester C–O single bonds, at the same time avoiding the concurrent hydrogenation of the



aromatic ring. 2-Propanol was chosen as indirect H source and molecular hydrogen as readily available H source. Depending on the choice of the H source, a surprising switch in selectivity with respect to the cleavage of either the alkoxy or the ester C–O bond was observed. To study the significance of the distance between phenyl ring and ester group and the influence of the phenyl ring, substrates with different length of the linker as well as alkylacetates were tested under similar reaction conditions.

Results and Discussion

Catalyst preparation and characterization

A sample of Pd/Fe₃O₄^(*i*) with a Pd loading of 8.7 wt % was prepared by coprecipitation of palladium chloride and iron nitrate followed by calcination and reduction with molecular hydrogen.^[10-14] The obtained catalyst had a high BET surface area of 170 m²g⁻¹. Palladium nanoparticles were well dispersed on the surface as shown by X-ray diffraction and high-resolution transmission electron microscopy. Analysis of the particle size distribution revealed a bimodal distribution with a majority of particles of 1.2 nm diameter and a second population of slightly larger palladium particles with 2.3 nm average diameter (Figure 1). X-ray photoelectron spectroscopy (see the Supporting Information) revealed that the Pd 3d_{5/2} binding energy was



Figure 1. Size distribution of the palladium nanoparticles and high-resolution transmission electron micrograph of the $Pd/Fe_3O_4^{(r)}$ catalyst (inset).

0.4 eV higher than that reported for metallic palladium.^[14] Analysis of the extended X-ray absorption fine structure revealed that some iron was alloyed into the palladium nanoparticles forming Pd–Fe bimetallic ensembles.^[13] Both findings imply that also strong interactions between the palladium nanoparticles and the iron oxide support were present (Supporting Information).

Hydrogenolysis of 2-phenylethylacetate over Pd/Fe₃O₄^(r)

The hydrogenolysis of the ester C–O bond in PEA was studied in detail as model reaction. In principle, the hydrogenolysis of PEA may give rise to two possible reaction sequences (Scheme 2). Cleavage of the alkoxy C–O bond produces ethylbenzene (EBE) and acetic acid (route A). Cleavage of the ester C–O bond yields phenylethanol (PET) and ethanol (route B). In a successive reaction, phenylethanol can be reduced to EBE. Moreover, the aromatic ring of PEA as well as of any of the reaction intermediates that occur in the two reaction pathways may be hydrogenated.

An initial exploratory study on the best reaction conditions for heterogeneous palladium catalysts showed that harsher reaction conditions were required (150 °C) for the cleavage of C–O bonds in phenyl alkyl esters than for benzylesters (benzyl-acetate, BAC: 50 °C, 10 bar H₂, see below).^[16]

- Using Pd/Fe₃O₄^(r) as catalyst, the reduction of 2-phenylethylacetate with 2-propanol as H source proceeded rapidly at 150 °C (94% conversion in 24 h). Ethylbenzene was obtained as the main product with 93% selectivity (Table 1, entry 1). Acetic acid, formed during the reaction as byproduct, reacted with 2-propanol to isopropyl acetate. Traces of 2-phenylethanol were detected. Products, where the aromatic ring had been hydrogenated, were not observed.
- 2) For comparison, the reduction of 2-phenylethylacetate was also studied over $Pd/Fe_3O_4^{(r)}$ in the presence of molecular hydrogen at 150 °C (Table 1, entry 2). The reaction proceeded more slowly and, though unexpected, 2-phenylethanol was obtained with a high selectivity of 98%.





Scheme 2. Alternative pathways for the C–O bond cleavage in 2-phenylethylacetate in the presence of $Pd/Fe_3O_4^{(f)}$ as catalyst. With 2-propanol as H source, route A prevails (left) whereas the use of molecular hydrogen as H source directs the reaction pathway to route B (right).

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Entry	Catalyst	H source	Conversion	Selectivity [%]		Selectivity [%]		Chemoselectivity [%]				
			[%]	C–O bonds	Aromatic ring	route A	route B	EBE	PET	HEX	HET	HEA
1	Pd/Fe ₃ O ₄ ^(r)	<i>i</i> PrOH ^[b]	94	100	0	93	7	93	7	0	0	0
2	$Pd/Fe_3O_4^{(r)}$	H ₂ ^[a]	66	100	0	0	100	2	98	0	0	0
3	Pd/C	<i>i</i> PrOH ^[b]	4	100	0	50	50	50	50	0	0	0
4	Pd/C	H ₂ ^[a]	88	54	46	0	100	34	5	15	0.1	46
5	CuCr	<i>i</i> PrOH ^[b]	0	-	-	-	-	-	-	-	-	-
6	CuCr	H ₂ ^[a]	3	100	0	(0)	(100)	10	90	0	0	0

nol led to cleavage of the alkoxy bond (Scheme 2, route A), the use of molecular hydrogen involved nearly exclusive cleavage of the ester C–O bond (Scheme 2, route B).

To corroborate its hydrogen donor ability under our reaction conditions, 2-propanol was heated in the presence of Pd/ $Fe_3O_4^{(r)}$ for 24 h to 150 °C. Acetone was obtained as main product, confirming the ability of 2-propanol to release hydrogen.^[14] Thus, the different product selectivity must be related to differences in the elementary steps that take place on the catalyst surface (see below).

To verify the outstanding selectivity of the Pd/Fe₃O₄^(r) catalyst for cleaving the ester C–O bond, EBE and PET were subjected to the same reaction conditions as employed for PEA (Supporting Information). In both cases, very low conversions were obtained; products derived from aromatic ring hydrogenation were not observed. This confirms that, under the conditions employed in this study, Pd/Fe₃O₄^(r) is highly selective to hydrogenolysis of the C–O bond versus hydrogenation of the aromatic ring.

Comparison of Pd/Fe₃O₄^(r) with other catalysts

The performance of Pd/Fe₃O₄^(r) was compared with Pd/C and CuCr as benchmark catalysts. In the hydrogenolysis of PEA over Pd/C in the presence of 2-propanol, an unexpectedly low conversion was obtained (4%, Table 1, entry 3). The ester C-O and the alkoxy C-O bond were equally cleaved. Products derived from aromatic ring hydrogenation were not detected. In contrast, in the presence of H_2 at 10 bar (entry 4), the reaction proceeded to 88% conversion, and a mixture including ring hydrogenated products was obtained (2-cyclohexylethylacetate, HEA, 46%; EBE, 34%; HEX, 15%; PET, 5%). In a reference experiment, PET was subjected to the same reaction conditions (Supporting Information). Within 24 h, PET was fully converted to EBE (79%) and HEX (13%). Formation of HET was not observed. This suggests that hydrogenolysis of the alcohol C-O bond precedes the hydrogenation of the aromatic ring (Scheme 2). Hydrogenolysis of PEA over CuCr in the presence of 2-propanol or molecular hydrogen provided very low conversion of PEA to a mixture of PET and EBE (Table 1, entries 5, 6). This is in agreement with reports on the low activity of the CuCr catalyst.^[2]

Reversing the selectivity in the hydrogenolysis of 2-phenylethylacetate

In the next step, the effect of temperature and pressure on the product selectivity was investigated for the $Pd/Fe_3O_4^{(r)}$ catalyst.

- 1) In the presence of 2-propanol, an appreciable conversion (51%) and excellent selectivity towards EBE (97%) was achieved also at temperatures as low as 100°C (Supporting Information).
- In the presence of molecular hydrogen, the conversion in the hydrogenolysis of PEA increased, as expected, with increasing temperature in the range from 100 to 200°C (Figure 2). PET was the main product at low temperatures,



Figure 2. Product selectivity in the hydrogenolysis of 2-phenylethylacetate over Pd/Fe₃O₄⁽ⁿ) as a function of temperature (reaction at 10 bar of H₂).

whereas an increasing fraction of EBE was formed at higher temperatures. This suggests that for $Pd/Fe_3O_4^{(r)}$ the activation energy for cleavage of the ester C–O bond in PEA is much lower than that for cleavage of the alkoxy C–O bond.

Upon increasing the initial hydrogen pressure from 10 to 40 bar while keeping the temperature at 150 °C, there was a slight decrease in conversion of PEA though the selectivity to PET remained above 95%. Such decrease in conversion with increasing hydrogen pressure was also reported for other hydrogenolysis reactions over supported palladium catalysts and is attributed to progressive displacement of the substrate adsorbed on the surface of the catalyst by hydrogen.^[17]



Upon exploring the effect of the availability of hydrogen, a surprising change in chemoselectivity was observed, if the reaction was performed at lower hydrogen pressures. Whereas PET was the main product at pressures as low as 5 bar, a mixture of PET and EBE was obtained at 2 bar. Noteworthy, EBE was also obtained as the main product if 2-propanol was used as H source. Hydrogen chemically bound in 2-propanol is less available and, thus, resembles the use of molecular hydrogen at low pressures. This implies that it is the availability of hydrogen that determines the selectivity in the cleavage of C–O bonds as outlined in Figure 3.



Figure 3. Effect of the availability of hydrogen on the product selectivity in the hydrogenolysis of 2-phenylethylacetate over Pd/Fe_3O_4 upon varying between the use of 2-propanol and different pressures of molecular hydrogen.

Role of the distance between phenyl ring and ester group

To explore the substrate scope, the length of the alkyl linker between the phenyl ring and the ester group was varied (Table 2). Benzylacetate (BAC) was not converted at all over Pd/ $Fe_3O_4^{(r)}$ using *i*PrOH as H source at 50 °C. The same reaction



performed at high temperatures (150 °C) showed full conversion. Toluene was obtained as the only product (route A). In contrast, at 50 °C using molecular H₂ (10 bar) as H source, full conversion and a selectivity of >99% for the cleavage of the C–O alkoxy bond was achieved.^[16] Toluene and acetic acid (detected as isopropyl acetate) were the only products (route A). This exemplifies that *i*PrOH is a potent hydrogen donor only at high reaction temperatures, whereas molecular hydrogen functions as a readily available H source at low reaction temperatures.

Reaction of 3-phenylpropylacetate (PPA) with *i*PrOH in the presence of Pd/Fe₃O₄^(r) at 150 °C showed a conversion of 14%, with a selectivity of 92% to phenylpropanol (PPO) and of 8% to propylbenzene (prB) (route B). The reaction performed in the presence of H₂ at 10 bar provided a conversion of 19% and a selectivity to PPO and prB of 98 and 2%, respectively (route B). Thus, the experimental data demonstrate that for BAC and PPA as well as for PEA, Pd/Fe₃O₄^(r) has a high selectivity towards C–O cleavage, while the phenyl ring is not converted.

For comparison, BAC and PPA were also tested in the presence of Pd/C. The hydrogenolysis of BAC with *i*PrOH over Pd/C at 50 °C provided no conversion of BAC similar to the reaction over Pd/Fe₃O₄^(r) while at 150 °C a conversion of 10% was observed. Toluene was obtained as the only product (route A). By contrast, the hydrogenolysis of BAC at 50 °C with molecular H₂ provided a conversion of >99% with complete selectivity to toluene >99% (route A).

The hydrogenolysis of PPA in the presence of *i*PrOH over Pd/C at 150 °C provided a conversion of 23% and a selectivity of 10 and 89% to PPO and prB, respectively (route A). The reaction in the presence of molecular H_2 (10 bar) over Pd/C at 150 °C provided a very high conversion (99%) with a selectivity of 84% to propylcyclohexane (PCH) resulting from consecutive hydrogenolysis of the C–OH bond of PPO, and some minor products (15%).

The influence of the pressure of molecular hydrogen was also investigated for the hydrogenolysis of PPA over Pd/Fe₃O₄^(r) (150 °C) in comparison to *i*PrOH as H source. The conversion of PPA increased from 14%, when *i*PrOH was used as H source, to 21 and 19% in the presence of molecular H₂ (5 and 10 bar, respectively). In all cases, the selectivity to PPO was very high (84–98%). In the presence of Pd/C, the conversion of PPA increased markedly from 23% upon using *i*PrOH to 79 and >99% using molecular hydrogen at 5 and 10 bar, respectively. Noteworthy was that the selectivity was reversed and prB was obtained as main product upon using *i*PrOH, while 37 and 84% of PCH were obtained at a H₂ pressure of 5 and 10 bar, respectively. Thus, in the hydrogenolysis of PPA the influence of the H source is much more pronounced for Pd/C than for Pd/Fe₃O₄^(r).

Upon raising the temperature, the conversion of PPA in the presence of *i*PrOH (Pd/Fe₃O₄) increased from 7, 14 to 86% (100, 150 to 200 °C, respectively), while the selectivity to the major product PPO increased from 82% (100 °C) to 92% (150 °C) and then decreased to 52% (200 °C). With the increase in temperature, the selectivity to prB also varied (18, 8, 46%,



respectively) indicative of consecutive hydrogenolysis of the C-OH group in PPA. The reaction performed in the presence of H₂ (10 bar) gave very similar conversions (5, 19 and 96%) and selectivities to PPO (97, 98 and 61% at 100, 150 and 200°C, respectively).

The hydrogenolysis of PPA with *i*PrOH in the presence of Pd/C showed a rise in conversion from 7, to 23% and full conversion upon increasing the temperature from 100 to 150°C and then to 200°C. The selectivity for the major product prB decreased from 92, 89 to 7% (100, 150 to 200°C). In the presence of molecular hydrogen, complete conversion was obtained independent of the temperature applied, whereas the selectivity to propylcyclohexane (PCH) decreased from 91, 84 to 72% (100, 150 to 200°C) in favor of the formation of prB (20% at 200°C, route A).

Hydrogenolysis of alkyl acetates

To better understand the importance of the aromatic group in the cleavage of the C–O bond, the cleavage of alkyl acetates varying in the length of the alkyl chain was investigated (Table 3). Butylacetate (BTA) and octylacetate (OCA) were con-



verted at 150 °C over Pd/Fe₃O₄^(r) using 2-propanol as H source. The conversion was 8.4 and 15%, respectively, with a selectivity of 100% to the corresponding alcohols 1-butanol and 1-octanol (route B). The same reactions performed in the presence of 10 bar of H₂ provided similar conversion (7.6% for butylacetate and 14% for octylacetate) as well as 100% of selectivity to the corresponding alcohols. In contrast, the use of methyl butyrate (MBT) as substrate led to even lower conversion at similar high selectivities (>80%) to 1-butanol. Thus, route B dominated for alkylacetates. The surprisingly low reactivity of aliphatic substrates demonstrates that the adsorption of the aromatic ring on the Pd/Fe₃O₄^(r) catalyst plays a key role. In comparison, the conversion for all three alkylacetates was very low (1%) in the presence of Pd/C both in the presence of isopropanol and mo-

lecular hydrogen as H source. This low reactivity of alkylacetates is consistent with a previous study in which very harsh conditions were needed for hydrogenolysis of alkylacetates to alkanes, CO₂, and alcohols.^[18]

Mechanism of C–O bond cleavage

An important difference between the two H sources is the different availability of hydrogen and, consequently, the very different hydrogen coverage on the surface of the Pd/Fe₃O₄^(r) catalyst. Even though hydrogen can be transferred from 2-propanol to the metal surface, the rate of 2-propanol dissociation limits the surface coverage with hydrogen atoms.^[19] In contrast, in the presence of an increasing pressure of molecular hydrogen the palladium surface becomes increasingly saturated with hydrogen atoms ($E_{ad} = -2.96 \text{ eV}$ for Pd–H).^[19a] Furthermore, interstitial octahedral sites of the palladium lattice can be occupied.^[19b] Consequently, different reaction pathways appear more likely in dependence of the choice of the reductant.

For 2-propanol, a large number of free Pd sites enables ready coordination of the substrate PEA ($E_{ad} = -0.21 \text{ eV}$),^[20] whereby it is likely that both oxygen atoms of the ester group interact with Pd. Owing to steric constraints, the adsorption of PEA involves an agostic interaction of the α -methylene group with a neighboring Pd atom (Scheme 3) thereby enhancing the positive partial charge at the carbon atom. In contrast, the aromatic ring is adsorbed preferentially onto exposed Fe atoms in vicinity ($E_{ad} = -1.10 \text{ eV}$ for benzene).^[21]

We propose that the reaction proceeds through a transfer hydrogenation mechanism^[22] without involvement of surfacebound H-atoms. Transfer of the α -hydrogen atom of 2-propanol to the α -methylene moiety of adsorbed PEA is promoted by the activation of the neighboring OH-group of 2-propanol through coordination to Pd. The agostic interaction in adsorbed PEA leads to weakening of the alkoxy C–O bond, enabling simultaneous transfer of the α -hydrogen atom and cleavage of the alkoxy C–O bond. Subsequently, the 2-propanol OH proton is transferred to the acetate moiety. Overall, the surface-assisted transfer hydrogenation enables cleavage of the PEA alkoxy C–O bond to provide EBE and acetic acid.

In the presence of H_2 , a large number of Pd sites are occupied by hydrogen atoms, and the substrate PEA is adsorbed preferentially through the aromatic ring onto exposed Fe atoms of the $Fe_3O_4^{(r)}$ support (Scheme 4). Transfer of two hydrogen atoms from Pd to the ester functionality leads to cleavage of the ester C–O bond to provide PET and acetaldehyde. The latter is then hydrogenated rapidly to ethanol.

The fact that hydrogenation of the aromatic ring is not observed is most likely related to the strong preference for adsorption of the aromatic ring onto exposed Fe atoms of the $Fe_3O_4^{(r)}$ support. This preference results from the electronic structure of Fe_3O_4 that remains unaffected by the interactions with the palladium nanoparticles.^[21] Thereby, the orbitals of the Fe atoms are electronically oriented in such a way that they readily overlap with the aromatic system. In contrast, the interaction with the $Fe_3O_4^{(r)}$ support leads to strong deviation





Scheme 3. Hydrogen transfer mechanism proposed for the hydrogenolysis of the alkoxy C–O bond of 2-phenylethylacetate over $Pd/Fe_3O_4^{(r)}$ in the presence of 2-propanol.



Scheme 4. Reaction mechanism proposed for the hydrogenolysis of the ester C–O bond of 2-phenylethylacetate over $Pd/Fe_3O_4^{(r)}$ in the presence of molecular hydrogen.

of the Pd d-band of the palladium nanoparticles from the Fermi level.^[21] In a reference experiment, PEA was allowed to react over the parent Fe_3O_4 in the presence of molecular hydrogen (10 bar). No conversion of the substrate was observed confirming that the presence of Pd nanoparticles is essential for the hydrogenolysis reaction to occur.

As a measure for the relative bond strengths, the IR vibrations of the substrates as well as the NMR data were analyzed in detail. For the aromatic acetates (Figure 4) the carbonyl stretch vibration ν_{st} (C=O) was observed at a similar position (1734-1735 cm⁻¹). The C–O stretch vibration of BAC was found at 1221 cm⁻¹, whereas the C–O stretch vibration was observed at 1231 cm⁻¹ for PEA and PPA. Lower wave numbers correspond to a weakened bond^[23] and it appears reasonable that the alkoxy C–O bond of benzylacetate is relatively easy to break compared to those of PEA and PPA. The ¹³C NMR signal of the CH₂ group of BAC was observed at 66.2 ppm. In comparison, the corresponding alkoxy carbon of PEA was observed at higher fields (64.0 ppm). Similarly, the chemical shift of the alkoxy carbon was 63.8 ppm for PPA. Thus, the alkoxy C–O bond becomes less polarized in the series BAC–PEA–PPA consistent with the increasing propensity for route B. A low electron density on the carbon atom, as in the case of BAC, renders the C–O bond more exposed to the approach of a negatively polarized hydrogen atom. In contrast, increased electron density on the carbon atom, as in the case of PPA, results in a less polarized and stronger alkoxy C–O bond allowing the Pd-H species to react more readily with the C=O carbon atom.

For the aliphatic acetates, the carbonyl stretch vibration v_{st} (C=O) was blueshifted to 1736–1742 cm⁻¹ relative to that of the aromatic acetates (Figure 5) indicative of a stronger C=O bond. The C–O stretch vibration was broadened or involved two vibration modes, whereby the absorbance maximum was observed at varying frequencies (1174, 1227, and 1169 cm⁻¹, MBT, BTA, and OCA, respectively). The ¹³C NMR signal of the methyl group neighboring the carbonyl group in MTB (CH₃-





Figure 4. FTIR analysis of the aromatic acetate esters employed in this study and selected NMR data.



Figure 5. FTIR analysis of the aliphatic acetate esters employed in this study and selected NMR data.

 $OC(O)^{n}Pr$) was observed at 52.3 ppm and compares to a position of the signal assigned to the methylene group in BTA and OCA at 64.0 and 64.9 ppm, respectively. The low fields of the ¹³C NMR signals of the CH₃ group of MTB and the CH₂ group of BTA and OCA are comparable to that of the aromatic acetates. The preference for cleavage of the ester C–O bond in ali-

phatic acetate esters (route B) and the low reactivity must therefore be related to the absence of an aromatic group facilitating the coordination of the substrate on the catalyst surface.

As compared to PEA (route A or B dependent on the reaction conditions), the selectivity of the C–O bond cleavage is specific for BAC (route A), PPA (route B), and alkyl esters (route B). This suggests that the electronic state of the carbon in the (R–CH₂–O–) group plays a synergistic role. The decisive factors controlling the selectivity include (i) coordination of the aromatic ring to the Fe atoms of the Fe₃O₄^(f) support, (ii) the availability of hydrogen on the surface of the palladium nanoparticles as well as (iii) the electronic factors in the substrate. For PEA, the control of the availability of hydrogen enables the specific hydrogenolysis of either the alkoxy or the ester C–O bond.

Conclusions

The principles allowing for the selective cleavage of either the alkoxy C–O bond or the ester C–O bond over Pd/Fe₃O₄^(r) as catalyst were studied for 2-phenylethylacetate (PEA) as base case. The alkoxy C–O bond was cleaved preferentially in the presence of 2-propanol, whereas cleavage of the ester C–O bond was favored in the presence of molecular hydrogen. Similarly, by using very low H₂ pressures, the selectivity for cleavage of the ester C–O bond was reversed, allowing for the preferential cleavage of the alkoxy C–O bond. This suggests that it is the low availability of hydrogen on the surface of the Pd nanoparticles that makes a surface-assisted hydrogen transfer mechanism likely in the case that 2-propanol is used as H source. This is a variant of the classic hydrogenolysis mechanism that occurs if molecular hydrogen is used.

Noteworthy, a very high selectivity to hydrogenolysis was observed, whereas hydrogenation of the aromatic ring was not observed independent of the choice of the H source or the reaction conditions adopted. This exceptional preference towards cleavage of the alkoxy or ester C–O bond without parallel hydrogenation of the aromatic ring is explained by the strong interaction between the aromatic system and exposed Fe atoms derived from the support. The Pd/Fe₃O₄^(r) catalyst, thus, revealed superior performance for the selective cleavage of C–O bonds in the presence of aromatic rings compared to other heterogeneous catalysts. Furthermore, the activity for conversion of alkylacetates demonstrated Pd/Fe₃O₄^(r) to be an exceptionally active and selective catalyst for C–O bond cleavage.

Experimental Section

Pd/Fe₂O₃^(c) [(c) = coprecipitated] with a nominal palladium loading of 5 wt% was prepared by coprecipitation. Palladium chloride (anhydrous, Fluka, 60 wt% Pd) was dissolved in aqueous HCl (33%). The solution was poured into an aqueous solution of iron(III)nitrate nonahydrate (Fluka). The mixture was then added dropwise to an aqueous solution of Na₂CO₃ (1 m). The precipitate was filtered off, washed with water and dried at 80°C under a partial vacuum for



1 day. Thereafter, the sample was reduced to Pd/Fe₃O₄^(r) by heating for 2 h to 200 °C under flowing hydrogen. Characterization of the Pd/Fe₃O₄^(r) catalyst revealed a Pd loading of 8.7 wt% (ICP), a BET surface of 170 m²g⁻¹ (H₂-chemisorption) and an average particle size for the Pd nanoparticles of 1.2 nm (TEM). The benchmark catalysts Pd/C (5 wt% Pd) and CuCr were purchased from commercial sources and used as received.

Catalytic reactions were performed in a 160 mL stainless-steel reactor (Parr Instruments) equipped with a gas-entrainment stirrer. The reactor was loaded with a suspension of catalyst (0.5 g) in a solution of the desired substrate in 2-propanol (75 mL, 4 wt%). The reactor was purged with N₂ (99.99%), the system was then pressurized with the desired gas (H₂ or N₂), stirred at 500 rpm, and, finally, heated up to the reaction temperature for 24 h. Then, the reactor was cooled to RT, the pressure released and the composition of the organic phase was analyzed by gas chromatography.

Gas chromatographic analyses were performed on a HP 5890 gas chromatograph equipped with a wide-bore capillary column (CP-WAX 52CB, 60 m, i.d. 0.53 mm) and flame ionization detector. Conversion and selectivity to the product i were calculated on the basis of Equations (1) and (2), respectively.

$$Conversion = \frac{n_{ini}(i) - n_t(i)}{n_{ini}(i)} \times 100 \ [\%]$$
(1)

Selectivity =
$$\frac{n_{\rm t}(j)}{n_{\rm ini}(i) - n_{\rm t}(i)} \times 100 \ [\%]$$
 (2)

 n_{ini} = molar amount of substrate *i* at time 0; n_t = molar amount of substrate *i* at time *t*; $n_t(j)$ = molar amount of product *j* at time *t*.

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