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*Published in:*  
ChemSusChem (Print)

*Link to article, DOI:*  
[10.1002/cssc.201702411](https://doi.org/10.1002/cssc.201702411)

*Publication date:*  
2018

*Document Version*  
Peer reviewed version

[Link back to DTU Orbit](#)

*Citation (APA):*  
Khokarale, S. G., He, J., Schill, L., Yang, S., Riisager, A., & Saravanamurugan, S. (2018). Selective Hydrodeoxygenation of Alkyl Lactates to Alkyl Propionates with Fe-based Bimetallic Supported Catalysts. *ChemSusChem (Print)*, 11(4), 681-687. <https://doi.org/10.1002/cssc.201702411>

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**To be cited as:** *ChemSusChem* 10.1002/cssc.201702411

**Link to VoR:** <http://dx.doi.org/10.1002/cssc.201702411>

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# Selective Hydrodeoxygenation of Alkyl Lactates to Alkyl Propionates with Fe-based Bimetallic Supported Catalysts

Santosh Govind Khokarale,<sup>[a]</sup> Jian He,<sup>[ab]</sup> Leonhard Schill,<sup>[a]</sup> Song Yang,<sup>[b]</sup> Anders Riisager,<sup>[a]\*</sup> and Shunmugavel Saravanamurugan<sup>[ac]\*</sup>

**Abstract:** Hydrodeoxygenation (HDO) of methyl lactate (ML) to methyl propionate (MP) were performed with various base metal supported catalysts. A high yield of 77% MP was obtained with bimetallic Fe-Ni/ZrO<sub>2</sub> in methanol at 220 °C at 50 bar H<sub>2</sub>. A synergic effect of Ni increased the yield of MP significantly when using Fe-Ni/ZrO<sub>2</sub> instead of Fe/ZrO<sub>2</sub> alone. Moreover, the ZrO<sub>2</sub> support contributed to improve the yield as a phase transition of ZrO<sub>2</sub> from tetragonal to monoclinic occurred after metal doping giving rise to fine dispersion of the Fe and Ni on the ZrO<sub>2</sub>, implying the higher catalytic activity of the material. Intriguingly, it was observed that Fe-Ni/ZrO<sub>2</sub> also effectively catalyzed methanol reforming to produce *in situ* H<sub>2</sub>, followed by HDO of ML, yielding 60% MP at 220 °C with 50 bar N<sub>2</sub> instead of H<sub>2</sub>. Fe-Ni/ZrO<sub>2</sub> also catalyzed HDO of other short chain alkyl lactates to the corresponding alkyl propionates in high yields around 70%. No loss of activity of Fe-Ni/ZrO<sub>2</sub> occurred in five consecutive reaction runs demonstrating the high durability of the catalyst system.

## Introduction

The demand for fossil-based resources are continuously increasing as the need for commodity chemicals, fuels and energy ascend along with a growing world population [1]. Concomitantly, the limited availability of fossil resources will steadily be diminishing in the coming decades, striving industries

and academia to find alternative renewable resources that potentially can replace fossil-based chemicals and fuels [2]. In this connection, terrestrial biomass - in particular the lignocellulosic fraction - has been identified as a renewable, abundant carbon-neutral resource for making chemicals and fuels [3]. However, the direct transformation of lignocellulosic component to targeted chemicals, such as cellulose to lactic acid, is generally tedious and challenging [4]. Conversions of cellulosic sugar-derived platform chemicals to commodity chemicals seems more promising and feasible, as this allow us to improve the yield and selectivity of the targeted products [5].

Lactic acid is a bio-platform chemical derived from glucose, which can be produced by well-established fermentative or alternative chemo-catalytic processes [6]. Lactic acid is an important feedstock to make biodegradable plastics, but can also serve as a feedstock for producing precursors (e.g., methyl propionate, MP) for existing large-volume acrylic plastics, e.g. poly(methyl methacrylate), PMMA. Currently, MP is preferentially made for PMMA production in industry by methoxycarbonylation of ethylene with carbon monoxide in methanol using a Pd-phosphine based homogeneous catalyst in a batch process [7]. The major drawbacks of this process are cautious handling of reactant (e.g., poisonous CO gas, expensive metal complex, reactive phosphine ligand) as well as tedious catalyst recovery and recycling.

Hydrodeoxygenation (HDO) is one of the important transformations to reduce the oxygen content by cleaving C-O bonds with hydrogen to produce value-added chemicals from bio-based substrates [8]. It has been widely studied with regard to hydrogenolysis of polyols to corresponding partly or fully deoxygenated product with a wide range of solid catalyst including base metals such as Ni and Co [9]. In connection with this, hydrogenolysis of  $\alpha$ -hydroxy acids/esters to propylene glycol, 1-propanol and propionic acid/ester have also been reported [10]. Here propylene glycol was predominantly formed with Ru, Pd, Ni, Cu on various supports such as carbon, TiO<sub>2</sub>, alumina and silica, and no selective hydrogenolysis of lactic acid or its ester(s) toward propionic acid or its esters were achieved. Hence, only up to 23% product selectivity of propionic acid was attained at 74% conversion of lactic acid with 10 wt% Cu/SiO<sub>2</sub> [10e]. The reaction selectivity towards ethyl propionate improved to 66% when replacing Cu with Co and Fe in the catalyst, but with very poor conversion of ethyl lactate (9%) [11]. These previous studies inspired us to search for base metal-containing

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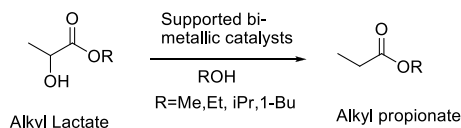
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catalysts, which selectively can hydrodeoxygenate alkyl lactates to alkyl propionates in respective alcohols. Especially, inexpensive Ni and Fe metals and  $\text{ZrO}_2$  as support have some advantageous properties in terms of activity and stability during the reaction. Ni/ $\text{SiO}_2$  has previously been reported to efficiently hydrogenate furfural to furfuryl alcohol, whereas Fe-containing Ni catalysts favoured C-O cleavage by hydrogenolysis to form methyl furan [12a]. Similarly, Ni on carbon nanotubes (CNT) exhibited good reactivity for converting 5-hydroxymethylfurfural to 2,5-furandimethanol (FDM). Concurrently, Ni-Fe/CNT favoured the formation of 2,5-dimethylfuran instead of FDM [12b]. Moreover, it is recognized that Ni has the ability to dissociate hydrogen easily for hydrogenation/hydrogenolysis reactions [12c]. On the other hand, applying  $\text{ZrO}_2$  as support has several advantageous due to its amphoteric and redox properties as well as its high thermal and hydrolytic stability [12e-g]. These viewpoints encouraged us to explore the activity of base metals, including Fe-Ni on  $\text{ZrO}_2$ , for HDO of alkyl lactate to alkyl propionate.



**Scheme 1.** HDO of alkyl lactate to alkyl propionate in alcohol

Here, we report a selective and effective HDO reaction with base metal supported catalysts for converting alkyl lactates to the corresponding alkyl propionates in high yields in alcohols (Scheme 1). A maximum yield of 77% MP was obtained from methyl lactate (ML) using Fe-Ni/ $\text{ZrO}_2$  catalyst. A phase transition of zirconia was confirmed by XRD analysis after incorporation of Fe and Ni metals, suggesting that the metals were incorporated well into the zirconia network thereby possibly enhancing the activity of the material. Notably, a good yield of MP (60%) was also obtained from ML without added hydrogen gas, implying that hydrogen can be generated from methanol reforming with Fe-Ni/ $\text{ZrO}_2$ . Other parameters like e.g., influence of metal content, reaction temperature and time, concentration of ML, and the recyclability of Fe-Ni/ $\text{ZrO}_2$  have also been explored.

## Results and Discussion

### Preliminary studies with precious metals

Catalyst screening for the transformation of ML to MP with Ru or Re on activated carbon (Ru/AC or Re/AC) at 200 °C at 50 bar  $\text{H}_2$  resulted in poor yield of 7 and 3%, respectively, with low conversion of ML (around 10%). However, previous work suggest that the presence of Re in combination with other metals, including Ru, can promote the yield for similar HDO reactions [13]. In line with this, the yield of MP enhanced significantly from

7 to 20% with bimetallic Ru-Re/AC catalyst and to 32% when using reduced Ru-Re/AC catalyst at 220 °C (Table S1). In order to improve the MP yield further catalysts based on common oxide supports (e.g.,  $\text{TiO}_2$ ,  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{ZrO}_2$ ) were examined and the results are presented in Table S1. Ru-Re/ $\text{SiO}_2$ , Ru-Re/ $\text{Al}_2\text{O}_3$  and Ru-Re/ $\text{ZrO}_2$  gave here comparable MP yield, but since  $\text{ZrO}_2$  is more stable than the other oxides [12g] it was chosen as preferred support to study alternative precious metals for the HDO reaction of ML to MP.

Various  $\text{ZrO}_2$ -supported catalysts with precious metals (Rh, Ag, Au, Ir, Pd and Pt) in combination with Re were tested for the conversion ML to MP, and the results are compiled in Table S2 and XRD patterns of the materials shown in Figures S1 and S2. Among the employed catalysts, Au-Re/ $\text{ZrO}_2$  and Ir-Re/ $\text{ZrO}_2$  proved particularly active yielding 54 and 46% of MP, respectively, while the other catalysts yielded between 20-40% of MP. These interesting results prompted us to substitute the precious metals in the  $\text{ZrO}_2$  catalysts with much cheaper and readily available base metals like Fe, Mo, Mn, Ni, Co, Cu, Zn, and Ni. The good to excellent HDO results obtained with these catalysts are compiled in Table 1, and the corresponding XRD patterns of the materials are given in Figure S3.

**Table 1.** HDO of ML to MP with bimetallic catalysts<sup>a</sup>

Entry	Catalyst	ML Conv (%)	MP Yield (%)	MMP Yield (%)	n-PrOH Yield (%)	Carbon balance (%)
1	Ru-Re/ $\text{ZrO}_2$	86	30	7	1	52
2	Fe-Re/ $\text{ZrO}_2$	>99	60	<0.5	10	70
3	Fe-Mn/ $\text{ZrO}_2$	88	33	3	0	48
4	Fe-Cu/ $\text{ZrO}_2$	>99	36	<0.5	0	36
5	Fe-Zn/ $\text{ZrO}_2$	74	40	8	0	74
6	Fe-Mo/ $\text{ZrO}_2$	>99	47	<0.5	0	47
7	Fe-Co/ $\text{ZrO}_2$	>99	71	<0.5	3	74
8	Fe-Ni/ $\text{ZrO}_2$	>99	73	2	0	75
9	Fe-Ni/ $\text{ZrO}_2^b$	87	64	6	0	83
10	Fe/ $\text{ZrO}_2^c$	85	45	2	0	62
11	Ni/ $\text{ZrO}_2^c$	34	4	28	0	98
12	Nano- $\text{Fe}_2\text{O}_3$	44	13	1	0	70
13	$\text{ZrO}_2$	32	0	22	0	90

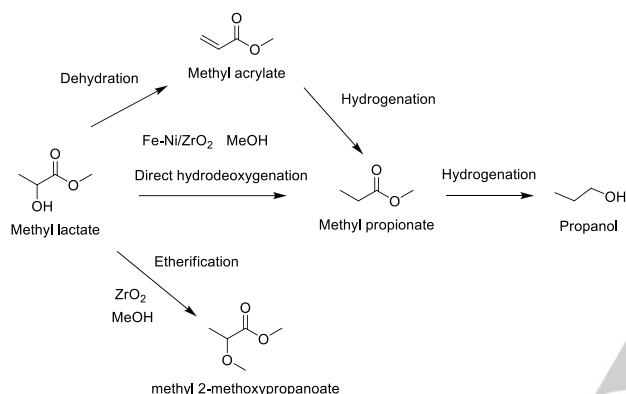
<sup>a</sup> Reaction conditions: 2 mmol ML, 100 mg catalyst (M/Re or Fe/M = 2; 3.6 mol% with respect to ML), 8 g MeOH, 50 bar  $\text{H}_2$ , 12 h, 220 °C. <sup>b</sup> Non-reduced. <sup>c</sup> 2.4 mol % of Fe or Ni with respect to ML.

### Study with nonprecious metal on the yield of MP

Replacing Ru in Ru-Re/ $\text{ZrO}_2$  with the Group 8 analog Fe to obtain Fe-Re/ $\text{ZrO}_2$ , the yield of MP substantially increased from 30 to 60% at quantitative conversion of ML (Table 1, Entries 1 and 2). In order to assess the role of Fe alone, an experiment was also performed with Fe/ $\text{ZrO}_2$  which yielded 45% of MP (Table 1, Entry 10), i.e. 15% higher than what was obtained with bimetallic Ru-Re/ $\text{ZrO}_2$ . When replacing Re with the lighter Group 7 metal Mn in Fe-Mn/ $\text{ZrO}_2$ , an adverse effect was observed as

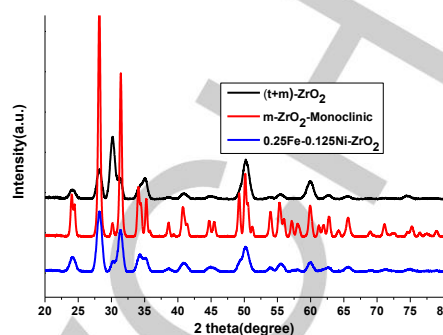
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the yield of MP descended from 60 to 33% (Table 1, Entry 3) confirming that Mn demoted the activity of Fe/ZrO<sub>2</sub>. Other identified by-products such as methyl 2-methoxypropanoate (MMP) and n-propanol were also quantified to account for the carbon balance (Table 1) and the plausible reaction pathway is shown in Scheme 2. Moreover, gas samples collected after the reactions were subjected to GC-MS analysis and showed the formation of CO<sub>2</sub> and propane (m/z of 44), revealing that decarboxylation of methyl propionate (or propionic acid) and complete hydrogenation of methyl lactate took place, respectively. This could account for the rest of the carbon balance to some extent.



**Scheme 2.** Plausible reaction pathway for the conversion of ML with Fe-Ni/ZrO<sub>2</sub>.

The catalytic effect of other base metals (Zn, Co, Ni, Mo, and Cu) in place of Re in Fe-Re/ZrO<sub>2</sub> was also investigated (Table 1). Among the catalysts studied, Fe-Ni/ZrO<sub>2</sub> gave the highest yield of 73% MP at full ML conversion (Table 1, Entry 8). Notably, when the support was altered to SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, spinel or AC only poor to moderate yields of 3-47% MP was obtained (Table S3) indicating a synergistic activity effect of the ZrO<sub>2</sub> support for Fe-Ni. In addition, methyl acrylate (MA) was also used as substrate to probe its reactivity if formed as an intermediate during the reaction. Here, Ni/ZrO<sub>2</sub> gave a higher yield of MP (71%) whereas Fe/ZrO<sub>2</sub> and ZrO<sub>2</sub> alone yielded 52 and 49%, respectively. This clearly indicated that Ni favored hydrogenation compared to Fe leading to the speculation that Fe/ZrO<sub>2</sub> partly promoted the dehydration of ML to form MA followed by hydrogenation on Ni to form MP. Fe/ZrO<sub>2</sub>, Ni/ZrO<sub>2</sub>, Fe-Ni/ZrO<sub>2</sub> and ZrO<sub>2</sub> were by NH<sub>3</sub>-TPD analysis found to have available acid sites of 0.498-0.627 mmol/g with the former possessing about 20% more acid sites than Ni/ZrO<sub>2</sub> (Table S4). Moreover, Fe/ZrO<sub>2</sub> revealed a slightly higher T<sub>max</sub> (200 °C) compared to Ni/ZrO<sub>2</sub> (160 °C) (Figure S4), indicating that Fe/ZrO<sub>2</sub> possessed slightly stronger acid sites which could facilitate the dehydration of ML to MA (Scheme 2).

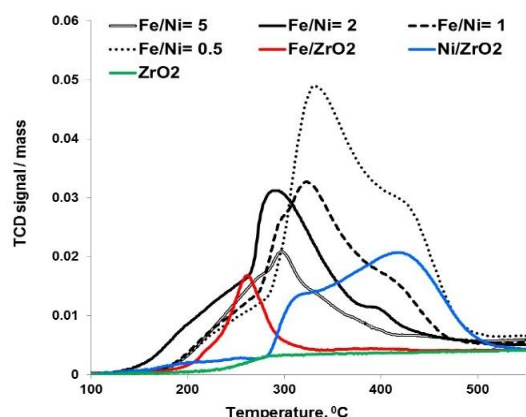


**Figure 1.** XRD patterns of ZrO<sub>2</sub> and Fe-Ni/ZrO<sub>2</sub> (2.7 wt% Fe and 1.4 wt% Ni).

To get insight into the promoting role of ZrO<sub>2</sub>, the support and the Fe-Ni/ZrO<sub>2</sub> catalyst were subjected to XRD analysis and part of the measured diffractograms are shown in Figure 1. ZrO<sub>2</sub> derived from Zr(OH)<sub>4</sub> showed an intense diffraction peak at 2θ of 30.2° corresponding to (111) of the tetragonal phase along with two minor peaks at 2θ of 28.2 and 31.4° ascribed to (11-1) and (111) of the monoclinic phase [14]. To ascertain formation of the monoclinic phase, ZrO<sub>2</sub> was treated at 900 °C and the XRD pattern of the resulting sample clearly indicated increased intensity of the 28.2 and 31.4° peaks at the expense of the peak at 30.2° from the tetragonal phase. A similar XRD pattern was apparently seen for the Fe-Ni/ZrO<sub>2</sub> catalyst, substantiating that the two metals were well dispersed into the network of ZrO<sub>2</sub> transforming the support predominantly to the monoclinic phase (Figure 1 and Table S5) as in accordance with previous report [15], which possibly contributed to the superior catalyst activity observed in the HDO reaction of ML. Moreover, no clear or distinct peak corresponding to metallic Fe or Ni, FeNi alloy or mono- or mixed metal oxides were observed in the XRD patterns as those peaks might also have been overlapped with support ZrO<sub>2</sub> if formed [16,12b,17]. In line with this, TEM analysis revealed formation of small particles with sizes around 2 nm for Fe-Ni/ZrO<sub>2</sub> as well as for the Fe-Mn/ZrO<sub>2</sub>, Ir-Re/ZrO<sub>2</sub> and Pt-Re/ZrO<sub>2</sub> catalysts (Figure S5). In contrast, no particles were visualized for the active Au-Re/ZrO<sub>2</sub> and Fe-Co/ZrO<sub>2</sub> catalysts, indicating that the size of the particles was less important for obtaining the synergic role of the Fe and Ni on ZrO<sub>2</sub>. Furthermore, the Fe-Ni/ZrO<sub>2</sub> catalyst with Fe/Ni ratio of 2 was subjected to XPS analysis before and after the HDO of ML to MP (Table S6). Before the reaction, the existing oxidation states of surface Fe and Ni were Fe<sup>2+</sup>(68%)/Fe<sup>3+</sup>(32%) and Ni<sup>2+</sup>(25%)/Ni<sup>3+</sup>(75%), respectively [18]. After reaction, the distribution of oxidation states for Fe remained unchanged, while no reliable results were obtained for Ni due to lack of surface Ni on the ZrO<sub>2</sub>. This confirmed that no metallic Fe and Ni were present on the ZrO<sub>2</sub> surface, but did not rule out presence of metallic species in the interior part of the support.



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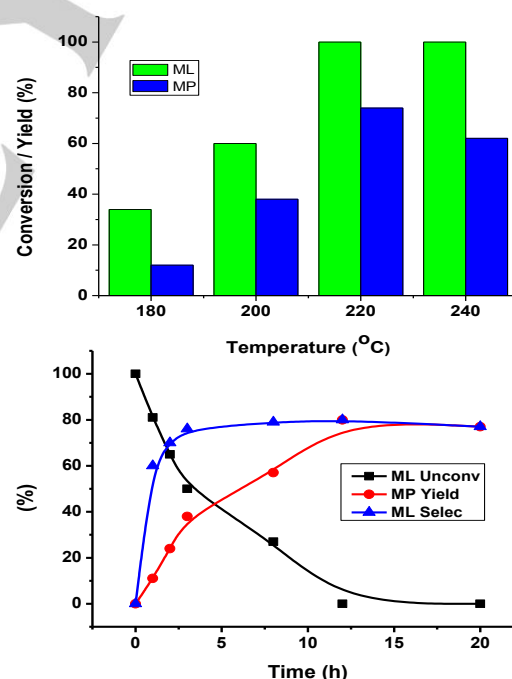
**Figure 2.** H<sub>2</sub>-TPR profile of Fe and/or Ni containing ZrO<sub>2</sub> materials.

The reducibility of the catalysts was evaluated by temperature programmed reduction (TPR) with hydrogen and the results correlated with catalytic activity. Figure 2 shows H<sub>2</sub>-TPR profiles of the Ni- and/or Fe-containing ZrO<sub>2</sub> catalysts. Ni/ZrO<sub>2</sub> (yielding only 4% MP from ML) revealed a very broad profile with reduction peaks at  $T_{\max}$  of 310 and 420 °C assigned to the reduction of NiO and support interacting NiO, respectively, to metallic Ni [19]. On the other hand, a distinct sharp peak appeared at  $T_{\max}$  of 266 °C for Fe/ZrO<sub>2</sub> (yielding 45% MP from ML) corresponding to the reduction of Fe<sub>2</sub>O<sub>3</sub> to Fe<sub>3</sub>O<sub>4</sub> in line with previous reports [20]. For the bimetallic Fe-Ni/ZrO<sub>2</sub> catalysts reductions occurred already at around 150 °C and a major peak appeared between the  $T_{\max}$  of Fe/ZrO<sub>2</sub> and Ni/ZrO<sub>2</sub> depending on the catalyst composition. An analogous Ni-induced lowering of the reduction temperature of iron oxides was seen for Fe-Ni/SiO<sub>2</sub> (Fischer-Tropsch catalyst), implying that Ni facilitated hydrogen activation [21]. A similar observation was also found for Fe-Ni/TiO<sub>2</sub> resulting in enhanced catalytic activity for synthesis gas conversion compared to Fe/TiO<sub>2</sub> [22]. The marked shift in reduction temperature in the present study suggests that more isolated oxide species had formed which were easily reduced at low temperatures, thus inferring a concerted effect of Ni in Fe/ZrO<sub>2</sub> on the yield of MP (73%). Furthermore, H<sub>2</sub> consumption was drastically reduced in the high temperature region above 400 °C compared to Ni/ZrO<sub>2</sub>, revealing the formation of isolated and low temperature reducible species that also partly could contribute to the enhanced catalytic activity.

#### Influence of reaction time, temperature and Fe to Ni ratio

The catalytic activity of Fe-Ni/ZrO<sub>2</sub> catalysts with Fe/Ni mole ratios from 0.5-25 was investigated after optimizing the reaction temperature and time (Figure 3) and the obtained results are summarized in Table 2. The corresponding XRD patterns of the catalysts are presented in Figure S6. The highest yield of 77% MP was obtained with the catalyst having a Fe/Ni mole ratio of 1, when using a total metal loading of 4.9 mol% with respect to

ML. Interestingly, when decreasing the Ni content five-fold relative to Fe (i.e. Fe/Ni ratio of 5) the yield of MP (72-73%) was almost maintained no matter if the Fe loading was kept or doubled, manifesting that small amount of Ni was adequate to promote MP formation and demonstrating the importance of optimizing both the metal ratio and the metal loading towards maximizing the MP yield. XPS analysis of the Fe-Ni/ZrO<sub>2</sub> catalysts with the various Fe/Ni ratios (Table S6) further revealed that the contribution of Ni<sup>2+</sup>, but not Fe<sup>2+</sup>, significantly descended as the Fe/Ni ratio in the catalyst increased while the yield of MP decreased. Moreover, it can be inferred that the catalyst with a Fe/Ni ratio of 1 possessed the highest relative amount of Ni<sup>2+</sup>, which could be easily reduced and contribute during reaction to obtain the highest MP yield (77%) among the employed catalysts. According to the TPR results and previous relevant reports, Ni can accelerate the reduction of iron oxide by activating hydrogen [21,22], thus suggesting a synergetic role between Ni and Fe for activating hydrogen and the HDO reaction of ML to MP, respectively. When the concentration of ML was increased from 2.5 to 6.1 wt% (i.e. 2 to 5 mmol ML) the MP yield descended from 73 to 41% whereas the selectivity remained almost similar. The initial high yield could however be obtained at prolonged reaction time of 24 h (Table S7).



**Figure 3.** The influence of reaction temperature (top) and time (bottom) on the yield of MP. Reaction conditions: 2.0 mmol ML, 100 mg catalyst (Fe/Ni = 2, 3.6 mol% with respect to ML), 8 g MeOH, 50 bar H<sub>2</sub>. Catalysts activated at 450 °C in static air followed by reduction at 300 °C for 3 h under former gas flow (10 vol. % H<sub>2</sub> in N<sub>2</sub>, 50 ml/min).

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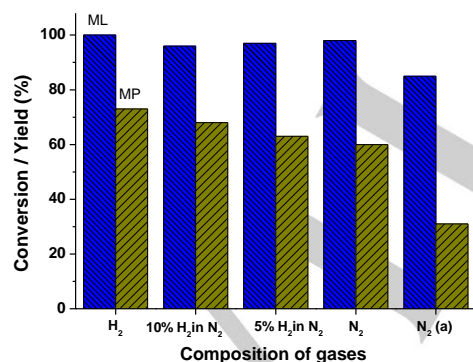
**Table 2.** The influence of metal composition of Fe-Ni/ZrO<sub>2</sub> on the yield of MP<sup>a</sup>

Entry	Catalyst Fe-Ni/ZrO <sub>2</sub>	Fe/Ni mole ratio	Fe content (mol%) <sup>b</sup>	Ni content (mol%) <sup>b</sup>	ML Conv. (%)	MP Yield (%)
1	Fe <sub>1</sub> Ni <sub>2</sub>	0.5	2.44	4.76	>99	67
2	Fe <sub>1</sub> Ni <sub>1</sub>	1	2.44	2.44	>99	77
3	Fe <sub>1</sub> Ni <sub>0.5</sub>	2	2.44	1.23	>99	73
4	Fe <sub>1</sub> Ni <sub>0.4</sub>	2.5	2.44	0.01	>99	71
5	Fe <sub>1</sub> Ni <sub>0.2</sub>	5	2.44	0.58	>99	72
6	Fe <sub>1</sub> Ni <sub>0.04</sub>	25	2.44	0.001	78	57
7	Fe <sub>1</sub> Ni <sub>0.2</sub>	5	4.76	0.01	>99	73
8	Fe <sub>1</sub> Ni <sub>1</sub>	1	0.10	0.01	57	26

<sup>a</sup> Reaction conditions: 100 mg catalyst, 2.0 mmol ML, 8 g MeOH, 50 bar H<sub>2</sub>, 12 h. <sup>b</sup> Mol% with respect to ML. Catalyst activated at 450 °C in air followed by reduction at 300 °C for 3 h under former gas flow (10 vol. % H<sub>2</sub> in N<sub>2</sub>, 50 ml/min).

**Influence of partial pressure of H<sub>2</sub>**

The influence of the partial pressure of H<sub>2</sub> on reaction progression was also studied with Fe-Ni/ZrO<sub>2</sub> in methanol at constant total pressure of 50 bar (Figure 4). Only a slight decrease in the yield of MP (71-67%) was found with 10% H<sub>2</sub> in N<sub>2</sub> ( $P_{H_2}$  = 5 bar) or with 5% H<sub>2</sub> in N<sub>2</sub> ( $P_{H_2}$  = 2.5 bar) instead of pure H<sub>2</sub> atmosphere (73%). Notably, even under pure N<sub>2</sub> atmosphere without external H<sub>2</sub> supply a MP yield of 61% was obtained (30% without catalyst pre-reduction), clearly indicated that H<sub>2</sub> for the reduction had evolved *in situ* by methanol reforming under the reaction conditions, and further demonstrating that transfer hydrogenation with methanol took place. To substantiate this rationale, reactions were performed with d<sub>4</sub>-methanol as solvent and the reaction mixtures subjected to GC-MS analysis. The resulting MS spectra revealed a major molecular ion peak at 90 m/z (MP-D<sub>2</sub>) as well as 91 (M+1) and 92 m/z (M+2), corroborating the decomposition of CD<sub>3</sub>OD and incorporation of D<sub>2</sub> into MP.



**Figure 4.** Influence of partial pressure of H<sub>2</sub> on the yield of MP. Reaction condition: 2.0 mmol ML, 100 mg catalyst (Fe-Ni/ZrO<sub>2</sub>, Fe = 0.05 mmol or 2.68 wt.%, Ni = 0.025 mmol or 1.40 wt.%), 8 g MeOH, 220 °C, 12 h, total pressure 50 bar. <sup>a</sup> Non-reduced catalyst.

**Influence of substrate reactivity and recyclability**

The HDO reaction with Fe-Ni/ZrO<sub>2</sub> was also extended to other alkyl lactates (ALs) and the results are presented in Table 3. The reactivity towards ethyl, isopropyl and butyl lactates were almost similar to ML yielding around 70% of the corresponding alkyl propionates (APs), implying that the activity of the catalyst was unaffected by the chain length of the substrate. Moreover, in case of ethyl lactate the formation of 2-ethoxypropionate (5%) was observed, whereas the corresponding alkoxylated by-products with 2-propyl lactate and 1-butyl lactate did not form.

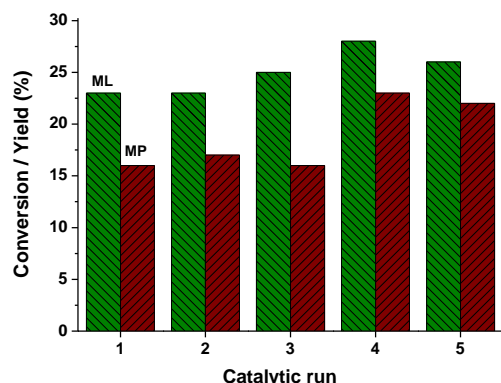
**Table 3.** HDO of alkyl lactates (ALs) with Fe-Ni/ZrO<sub>2</sub><sup>a</sup>

Entry	Alkyl lactate	AL Conv. (%)	AP Yield (%)
1	Methyl lactate	>99	72
2	Ethyl lactate	>99	68
3	2-Propyl lactate	>99	71
4	1-Butyl lactate	>99	67

<sup>a</sup> Reaction condition: 2.0 mmol alkyl lactate, 100 mg catalyst (Fe = 0.05 mmol or 2.68 wt% and Ni = 0.01 mmol or 0.58 wt%), 8 g alcohol, 12 h, 220 °C, 50 bar H<sub>2</sub>.

Finally, the recyclability of Fe-Ni/ZrO<sub>2</sub> was evaluated by subjecting the catalyst to reuse in the HDO of ML at conditions where relatively low ML conversion was obtained (Figure 5). For the first three reactions runs, the yield of MP was unchanged around 16% whereas it increased to 22-23% for the fourth and fifth run, confirming that Fe-Ni/ZrO<sub>2</sub> apparently remained stable in the consecutive reaction cycles. After the fifth reaction run the catalyst was recovered, calcined and subjected to XRD analysis. An identical diffraction pattern as for the pristine catalyst was here measured demonstrating that the material structure was intact (Figure S7).

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**Figure 5.** Recyclability of Fe-Ni/ZrO<sub>2</sub> for the conversion of ML to MP. Reaction conditions: 2.53 wt% of ML in MeOH, mass ratio of ML to catalyst = 2:1 (Fe = 0.1 mmol and Ni = 0.02 mmol with respect to ML), 3 h, 220 °C, 50 bar H<sub>2</sub>.

## Conclusions

The supported base-metal catalyst Fe-Ni/ZrO<sub>2</sub> has been demonstrated to be a versatile, selective and efficient catalyst for HDO and transfer hydrogenation of alkyl lactates with molecular hydrogen and methanol, respectively, in methanol. Under optimized reaction conditions (220 °C, 50 bar H<sub>2</sub>) the catalyst yielded 77% of MP from ML and about 70% products from other alkyl lactates, suggesting a general high reactivity for  $\alpha$ -hydroxy esters. In contrast, alternative base-metal catalysts (Zn, Co, Ni, Mo, and Cu) mostly gave significantly lower catalytic activity. Ni synergistically promoted the catalytic HDO activity of Fe-Ni/ZrO<sub>2</sub> to enhance the yield of MP as Fe/ZrO<sub>2</sub> and Ni/ZrO<sub>2</sub> only gave 45 and 4% MP, respectively (Table 1). This effect correlated with H<sub>2</sub>-TPR results, where Fe-Ni/ZrO<sub>2</sub> exhibited lower reduction temperature than Fe/ZrO<sub>2</sub> and Ni/ZrO<sub>2</sub>. Moreover, XRD analysis revealed that doping of Fe and Ni into the ZrO<sub>2</sub> network facilitated formation of the monoclinic ZrO<sub>2</sub> phase, which could also be partly responsible for the improved catalytic activity of Fe-Ni/ZrO<sub>2</sub> by accelerating hydrogen activation with Ni. Intriguingly, the transformation of ML to MP in methanol with Fe-Ni/ZrO<sub>2</sub> took place (61% yield) via methanol hydrogen transfer reaction as substantiated by performing experiment under N<sub>2</sub> atmosphere without external H<sub>2</sub> and by a isotopic labeling experiment in deuterated methanol. Interestingly, a recyclability study showed that the activity of Fe-Ni/ZrO<sub>2</sub> was maintained in at least four consecutive reaction runs, and XRD analysis confirmed the structural integrity of the spent catalyst. The developed catalyst system combines inexpensive and abundant base-metals with excellent durability, thus making its potentially attractive for conversion of other biomass-derived substrates containing hydroxyl group(s) of industrial importance.

## Experimental Section

### Catalyst Preparation

All the supported mono- and bimetallic catalysts were prepared by wetness impregnation by adapting the following procedure: Aqueous solution(s) of appropriate amount of respective metal(s) (Mn, Ni, Co, Cu, Mo, Zn, Rh, Ru, Pd, Pt, Au, Ag or Ir) precursors were mixed with support materials (ZrO<sub>2</sub>,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, SiO<sub>2</sub>, activated carbon (AC) or MgAl<sub>2</sub>O<sub>4</sub>) and the obtained slurries were thoroughly mixed for 30 mins and dried in the oven at 110 °C for 4 h (details on chemicals and materials in Supporting Information). The dried catalyst was then calcined at 450 °C with a ramp of 3 °C/min for 4 h in a static air, except activated carbon as support which instead was treated under Ar flow at a rate of 50 ml/min. Commercially available 5wt.% Ru/AC was used to prepare Ru-Re/AC catalysts by following the same procedure as mentioned above. All the catalysts were reduced at 300 °C with a ramp of 3 °C/min for 3 h with a flow of formier gas (10 vol.% H<sub>2</sub> in N<sub>2</sub>, 50 ml/min) prior to catalytic test, unless otherwise mentioned.

### Catalyst Characterization

H<sub>2</sub>-temperature programmed reduction (TPR) studies were performed on a Micrometrics Autochem-II instrument. In a typical procedure, approximately 100 mg of the dried sample was placed in one arm of a U-shaped quartz tube sample holder on quartz wool. The sample was pretreated by flushing with 5 vol.% H<sub>2</sub> and balance Ar (Air Linde) at 50 °C for 30 min prior to the measurement, and then TPR analysis was carried out with a reducing mixture (50 ml/min) consisting of 5 vol.% H<sub>2</sub> in Ar (Air Linde) from 60 to 550 °C (10 °C/min.). A thermal conductivity detector (TCD) was used to monitor the hydrogen concentration in the effluent stream and the H<sub>2</sub> consumption values were calculated based on calibration experiments.

X-ray powder diffraction (XRPD) of activated catalysts were performed on a Huber G670 powder diffractometer using Cu K $\alpha$  radiation with a 2 $\theta$  range of 2-80° at the rate of 0.02°/sec.

Transmission electron microscopy (TEM) studies of reduced Fe-Ni/ZrO<sub>2</sub> (Fe/Ni molar ratio = 2) were performed using a Tecnai T20 G2 and Titan instrument (Hillsboro, OR, USA) operated at 200 and 120 kV, respectively. The Titan was fitted with a field-emission electron source and a spherical aberration corrector on the condenser lens system. Reduced catalyst was dispersed on plain carbon-coated Cu grids (Agar Scientific, Stansted, UK) prior to analysis.

X-ray photoelectron spectra (XPS) were acquired ex-situ with a ThermoScientific system at room temperature using Al K $\alpha$  radiation (1484.6 eV). Sample charging effects were eliminated by correcting the observed spectra with the C1s binding energy value of 284.8 eV of adventitious carbon. Peak integration and deconvolution were performed with the Avantage 4.87 software using "Smart" background correction. The molar concentrations of Zr, O, Fe and Ni were obtained using the areas of the corresponding peak in conjunction with their sensitivity factors (Zr3d: 7.04; O1s: 2.93; Fe2p: 16.42; Ni2p: 22.18). Fe2p spectra were deconvoluted using mixed Gaussian-Lorentzian (L share: 30%) functions. Both the Fe2p<sub>3/2</sub> and Fe2p<sub>1/2</sub> peaks were fitted using peaks for Fe<sup>2+</sup> and Fe<sup>3+</sup> plus their respective shake-up peaks resulting in a total of eight peaks [18a]. The share of Fe<sup>3+</sup> was calculated using the relative areas of the Fe2p<sub>3/2</sub>(III) and Fe2p<sub>3/2</sub>(II) peaks. Likewise, Ni oxidation states were obtained by deconvoluting the Ni2p<sub>3/2</sub> signals using four peaks representing Ni<sup>2+</sup>, Ni<sup>3+</sup> and their respective shake-up peaks [18b].



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## Catalytic Hydrodeoxygenation (HDO) of Alkyl Lactates

HDO of alkyl lactates was performed in a 50 ml stainless steel Parr reactor equipped with a pressure transducer and a temperature controller. In a typical catalytic study, 2 mmol of methyl lactate (ML), 100 mg of reduced catalyst and 8 g of methanol were placed in the reactor and flushed with H<sub>2</sub> or N<sub>2</sub> gas three times before pressurized to 50 bar H<sub>2</sub> or N<sub>2</sub> or mixtures of H<sub>2</sub> and N<sub>2</sub>. The reaction mixture was heated and stirring started (350 rpm) after reaching a temperature 20 °C lower than the set temperature. The reaction solvent was changed from methanol to ethanol and 2-propanol and 1-butanol when changing the substrate from ML to ethyl lactate, 2-propyl lactate and 1-butyl lactate, respectively. After a reaction time of 12 h, the reaction mixture was rapidly quenched by placing the reactor in ice-cold water. Naphthalene was used as an internal standard and added to the reaction mixture prior to analysis. Carbon balance was calculated by adding unconverted ML and yield of MP, MMP and n-propanol.

## Reactant and Product Analysis

Aliquots of the reaction mixtures were subjected to GC-FID analysis using an Agilent 6890N instrument with HP-5 capillary column (30.0 m x 320 µm x 0.25 µm). An Agilent 6850 GC system coupled with an Agilent 5975C mass detector was used to identify the formed products. Conversion of AL and yield of alkyl propionates (APs) were calculated based on series of individual standards for ALs and APs with naphthalene as internal standard in respective alcohols.

## Recycle Study

Recyclability of the Fe-Ni/ZrO<sub>2</sub> catalyst was tested in five consecutive HDO reaction runs of ML to MP. The Fe-Ni/ZrO<sub>2</sub> catalyst was removed by filtration from the reaction mixture after each catalytic run and dried at 110 °C overnight. The dried catalyst was then reactivated at 450 °C for 4 h under static air, followed by reduction at 300 °C for 3 h under H<sub>2</sub> flow rate of 50 ml/min. After each run, the amount of ML and methanol were adjusted based on the recovered amount of Fe-Ni/ZrO<sub>2</sub>.

## Acknowledgements

The Danish Council for Independent Research – Technology and Production Sciences (project no. 11-106979) has supported the work. S.S. gratefully thank Department of Biotechnology (Government of India) New Delhi, India for support.

**Keywords:** Alkyl lactate • base metal catalysts • alkyl propionate • value-added chemicals • heterogeneous catalysis

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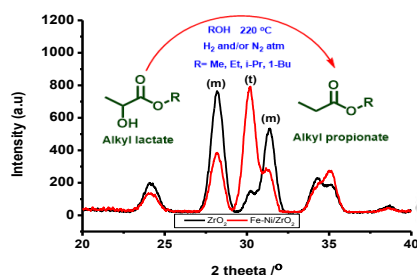
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**Hydrogenolysis:** A high yield of methyl propionate (77%) from methyl lactate is obtained with base-metal containing catalyst Fe-Ni/ZrO<sub>2</sub> in methanol in the presence of H<sub>2</sub> atmosphere via hydrodeoxygenation and methanol hydrogen transfer reactions.



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Leonhard Schill, Song Yang, Anders  
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**Selective Hydrodeoxygenation of  
Alkyl Lactates to Alkyl Propionates  
with Fe-based Bimetallic Supported  
Catalysts**