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An ordinary nickel catalyst becomes completely selective for partial hydrogenation of 1,3-butadiene when coated with tributyl(methyl) phosphonium methyl sulfate

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ABSTRACT

Performance of an ordinary supported nickel catalyst was tuned to reach an almost complete selectivity for partial hydrogenation of 1,3-butadiene by coating it with a phosphonium-type ionic liquid (IL), tributyl(methyl) phosphonium methyl sulfate, $[P_{4441}][MeSO_4]$. Thanks to high chemical and thermal stability of $[P_{4441}][MeSO_4]$, the reaction conditions could be pre-optimized for high partial hydrogenation performance before the deposition of the IL coating. When the catalyst was coated with IL, it provided a total butene selectivity of 99.5 \pm 0.2%, a record high partial hydrogenation selectivity ever reported for a nickel-based catalyst. X-ray photoelectron spectroscopy results illustrated that the IL donates electrons to nickel sites and makes them selective for partial hydrogenation. The conductor like screening model for realistic solvents (COSMO-RS) calculations indicated that the IL coating also exerts a filter effect, which helps to maintain this high partial hydrogenation selectivity at all conversion levels.

1. Introduction

Partial hydrogenation of 1,3-butadiene is an important industrial process. It paves the way to the feedstocks for the units producing polymers and/or high-octane number gasoline components. Moreover, it also helps to clean up the feeds in which 1,3-butadiene is present together with valuable C4 olefins. This way the corresponding feed becomes ready for further processing on different catalysts, which, otherwise, would be poisoned if 1,3-butadiene remains in the stream [1,2]. Currently, palladium-based catalysts are considered as the best catalysts for this reaction because of their high yields for partially hydrogenated products [3,4]. However, the cost of palladium is quite high and it has stability problems. Because of these drawbacks, there is a strong need for developing an efficient inexpensive catalyst for this reaction. Nickel, one of the cheapest metals, can be a very good candidate for this reaction. However, it is too active for hydrogenation reactions; hence, it is very challenging to control its performance for partial hydrogenation.

A promising report by Kernchen et al. [5] illustrated that the partial hydrogenation performance on a commercial nickel catalyst can be improved when the surface of the catalyst was coated with an ionic liquid (IL). Accordingly, the selectivity of cyclooctene in the hydrog-

enation of cyclooctadiene increased from 40 to 70%, when the catalyst was coated with 1-n-butyl-3-methylimidazolium octylsulfate, [BMIM] [OS]. Moreover, the same group extended this approach to a commercial Pd catalyst and coated it with different imidazolium-type ILs. Their results on partial hydrogenation of 1,3-butadiene showed improved partial hydrogenation performance [6-8]. Motivated with these reports, we worked on a commercial nickel catalyst and coated it with a different IL (1-n-butyl-3-methylimidazolium tetrafluoroborate, [BMIM] [BF₄]) and used this coated catalyst for the partial hydrogenation of 1,3-butadiene at 40 °C and atmospheric pressure [9]. The performance measurements illustrated a partial hydrogenation selectivity of 96%. Even though these results illustrated the high potential of coating nickel-based catalysts with ILs, the limited thermal stability of the IL coatings poses a major limitation on the applicability of this novel concept. In this respect, the imidazolium type ILs might not be a suitable family because of their limited thermal stabilities, which become even more limited when the ILs are supported on metal oxides [10-12]. Moreover, the unsaturated C=C bonds present on the imidazolium ring of the IL are susceptible to hydrogenation especially when the IL is coated on a hydrogenation catalyst at high temperatures and under high hydrogen partial pressures [9]. Moreover, the imidazolium ring can also undergo different reactions with the reactants present under

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the reaction condition over the different components of supported catalysts (support or metal). For instance, Bauer et al. illustrated this possibility during ethene hydrogenation on a Pd/Al_2O_3 catalyst coated with 1-ethyl-3-methlimidazolium ethylsulfate. Their results indicated that ethene was incorporated into the imidazolium moiety in a reaction catalyzed by palladium [13].

Besides, the imidazolium type ILs do not provide any significant cost benefits. Hence, the potential of ILs from different families should be investigated. Here, we aimed to explore the potential of phosphonium type ILs, this family of ILs are thermally and chemically more stable compared to their imidazolium-based counterparts [14]. Thus, they can potentially offer opportunities to operate at higher temperatures than imidazolium ILs do. Moreover, phosphonium-based ILs are manufactured on a multi-ton scale and are at least one-order of magnitude cheaper than the imidazolium type ILs [15,16]. However, the utilization of these ILs in catalysis [17–19] is limited with only a few reports, most of which use them as solvents to dissolve metal complexes in homogenous catalysis applications [18,19].

Here, to contribute filling this gap, we coated a commercial supported nickel catalyst with tributyl methyl phosphonium methyl sulfate, [P₄₄₄₁][MeSO₄], and tested the performance for 1,3-butadiene hydrogenation. Because this phosphonium IL offers a higher thermal stability limit than the imidazolium ILs do, it offers a flexibility on setting the reaction conditions. Thus, we first started with optimizing the reaction conditions for high partial hydrogenation selectivity on the uncoated catalyst focusing on relatively high temperatures, which would not be possible with imidazolium-type IL coatings. Then, we coated the catalyst with [P4441][MeSO4] and tested its performance under these optimized conditions. Results illustrated that the ordinary commercial supported nickel catalyst becomes almost completely selective for partial hydrogenation upon coating it with this phosphonium-type IL. To the best of our knowledge, this stable partial hydrogenation selectivity presented here is the highest ever reported on a supported nickel catalyst and presents the benefits of using phosphonium type ILs as coatings over supported metal catalysts.

2. Experimental and computational methods

2.1. Materials and synthesis

65 wt.% Ni on silica-alumina (commercial catalyst, Ni65), silica, and [P4441] [MeSO4] were purchased from Sigma-Aldrich. Ni65 was first reduced at 650 °C for 2 h under pure hydrogen (Linde, 99.99 vol%) flow. Reduced Ni65 was then passivated in 4 vol.% O2 (balance He, Air Liquide, 99.9 vol%) for 20 min. at room temperature. The IL-coated sample was prepared by dipping 50 mg of activated and passivated Ni65 into 284 mg of [P₄₄₄₁][MeSO₄] and stirred for 1 h. Later, this mixture was mixed with 182 mg of calcined SiO₂ to dry the suspension by absorbing the excess IL. The resulting solid sample prepared as a physical mixture in powder form has an overall IL and Ni loadings of 55 and 6.2 wt.%, respectively. Table S1 in Supporting Information, SI, compares the pore volume, average pore diameter, and surface area of these physical mixtures with or without the IL. Based on the data presented in Table S1, the pore filling degree was calculated as approximately 96% (calculated by dividing the IL volume into the pore volume of the physical mixture in the absence of IL) [7].

2.2. Catalyst characterization

2.2.1. Temperature programmed reduction (TPR)

A Micromeritics AutoChem II 2920 automated catalyst characterization system coupled with an MKS Cirrus II mass spectrometer was employed for the TPR measurement. The samples were first dried in He flow at 100 °C for 30 min. Then, the samples were heated up to 700 °C at a ramp rate of 5 °C/min in flowing H₂, while the effluent gas stream was monitored by a TCD detector and a mass spectrometer.

2.2.2. Thermal stability

Thermal stabilities of the bulk [P4441] [MeSO4] and [P4441] [MeSO4]coated catalysts were determined by thermogravimetric analysis (TGA) using a TA Instruments TGA Q500 model instrument. Approximately 15 mg of each sample was subjected to a heat treatment at 100 °C for 4 h in flowing nitrogen at a rate of 60 ml/min. Then, the temperature was raised to 600 °C at a ramp rate of 2 °C/min (in high resolution mode of the equipment). T'_{onset} values were considered as the short-term thermal stability limits, as reported before [10,12,20]. After determining the decomposition temperatures under inert atmospheres, the [P₄₄₄₁] [MeSO₄]-coated catalyst was subjected to additional stability tests under H₂ environment as discussed in a previous work [9]. For this purpose, the IL-coated sample was exposed to isothermal treatment at 150 °C for 30 min in flowing H₂ (30 ml/min) in a ¹/₄-in stainless steel reactor heated in a Thermcraft three-zone resistively heated furnace (model # XST-3-0-18-3 V) equipped with PC-controlled temperature controllers. Then the resulting samples were analyzed spectroscopically to identify any structural changes.

2.2.3. Fourier transform infrared (FTIR) spectroscopy

A Bruker Vertex 80v FTIR spectrometer was used for the FTIR measurements. Approximately 30 mg of catalyst was pressed between two KBr windows and loaded into a transmission cell. The resolution of each spectra was set to 2 cm⁻¹ with an average of 256 background scans and 512 sample scans under vacuum (employed by evacuating the sample chamber of the spectrometer).

2.2.4. X-ray photoelectron spectroscopy (XPS)

A ThermoScientific K-Alpha spectrometer with an aluminum anode (Al K α = 1468.3 eV) at an electron take-off angle (between the sample surface and the axis of the analyzer lens) of 90° was used for the XPS measurement. Data was recorded using Avantage 5.9 software. The binding energy calibration was performed based on the C1s signal at 284.3 eV.

2.2.5. Elemental analysis

For quantitative analysis of carbon, nitrogen, and sulfur contents in samples, a Thermo Scientific Flash 2000 CHNS/O Analyzer was used. Under continuous supply of oxygen, samples were placed in a reactor at a temperature of approximately 1000 °C. Oxidation of the samples produces elemental gas, which are separated by chromatography equipped with thermal conductivity detector.

2.2.6. Brunauer-Emmet-Teller (BET) surface Area

To determine the BET surface area, a Micromeritics ASAP 2020 physisorption analyzer was used. For each analysis, approximately 150 mg of sample was used. At first, the samples were degassed at 125 °C under vacuum for overnight. After degassing, free space measurement of samples was performed using He gas at 77 K. Volumetric adsorption of N₂ gas was obtained between 10^{-6} and 1 bar, and the pressure steps between 0.05 and 0.3 bar were fit to BET equation to estimate the surface areas of samples. The pore volume of the samples were derived using the *t*-plot method from N₂ adsorption isotherm measured at 77 K.

2.2.7. Catalytic activity testing

The as-received Ni65 catalyst was first reduced at 650 °C in a ¼-inch stainless steel tubular reactor in H₂ (Linde, 99.9 vol.%) flow (30 ml/min) for 2 h. A Thermcraft three-zone resistively heated furnace was used to maintain reactor temperature. Then, the reactor was cooled down to the room temperature in He flow (Air liquid, 99.9 vol%) and the catalyst was passivated in 4% O₂ (balance He) for 15 min. The passivated catalysts were then activated in H₂ flow at 150 °C for 30 min. Electronic mass flow controllers (Aalborg, model GFC17) were employed to control the flow rates. The uncoated sample was diluted with SiO₂, which was calcined in static air at 500 °C for 5 h, at a ratio of

1:300 g:g. The coated catalyst was used as-prepared without further diluting with silica. The reaction was carried out at ambient pressure and various temperature and partial pressures of H₂ and 1,3-butadiene (1,3-butadiene, Linde, 99.6 vol.%). The concentration of reactants and products at the exit stream were quantified by an online gas chromatograph (Agilent GC 7890 A) with a GS-Alumina column (50 m × 530 µm) and a flame ionization detector (FID) at a constant column temperature of 130 °C and He flow at a rate of 6.5 cm³/sec, and having sample injections every six min. The conversion was controlled by varying the space velocity from 4.09 (1.13 × 10⁻¹) to 3.75 × 10⁻¹ (7.6 × 10⁻³) (mol of 1,3-butadiene) × (mol of Ni × s)⁻¹ for uncoated (coated) Ni65 catalyst under constant temperature and partial pressures.

2.3. COSMO-RS calculations

COSMOThermX (version 1601) software was employed for estimating the relative solubilities of butenes and 1,3-butadiene in the IL using the Ionic Liquid Screening Module and setting the temperature at 145 °C. The structures of 1,3-butadiene, 1-butene, *cis/trans*-2-butene were first optimized by density functional theory (DFT) calculations performed at a level of B3LYP with 3-21G + basis sets using Gaussian09 [21] software and used as input files [22]. The input geometries for butane and IL were obtained from the COSMO and COSMO-IL database, respectively. Calculations were performed using TZVP parameterization (full geometry optimized with DFT and medium sized basis set for 1,3-butadiene). The inverse of activity coefficients at infinite dilution [23] in [P₄₄₄₁][MeSO₄] for each gas was considered as the capacity. Mathematically, the capacity is defined as:

$$C_i^{\infty} = \frac{1}{\gamma_i^{\infty}}$$

where C_i^{∞} is the solvent capacity at infinite dilution for component "*i*" in [P₄₄₄₁][MeSO₄], while γ_i^{∞} is activity coefficient of component "*i*" at infinite dilution in [P₄₄₄₁][MeSO₄].

3. Results and discussions

As illustrated in Fig. S1 in Supporting Information (SI), the as-received Ni/SiO₂-Al₂O₃ catalyst with a nickel loading of approximately 65 wt% (Ni65) catalyst requires an activation treatment in flowing H₂ at temperatures exceeding 500 °C. However, this activation temperature is quite high for the ILs, most of which decompose below 400 °C under inert atmospheres [10-12]. Consistently, our thermogravimetric analysis (TGA) measurements indicate that the [P4441][MeSO4] starts to decompose at 285 °C in N2 flow (Fig. 1). Moreover, this thermal stability limit slightly decreases to 279 °C, when the IL was coated over the Ni65 catalyst, which was activated at 650 °C and passivated at room temperature prior to be coated with the IL (Fig. 1). Such small decrease in thermal stability limit (slightly larger than the error range of our TGA measurements) might be originated from the presence of interactions between the IL and the supported metal catalysts, consistent with our previous reports [10,11]. We also note that the amount of IL loading was fairly high (approximately 55 wt%), and this might be the reason for why the deviation from the bulk decomposition temperature was not that significant.

Thus, the Ni65 was first activated in flowing hydrogen at 650 °C and passivated at room temperature in very dilute O_2 flow, before being coated with the IL. Temperature programmed reduction (TPR) data confirm that this passivated Ni65 can be reactivated at a temperature lower than 150 °C, as shown in Fig. S1.

Results presented in Fig. 2 compare the IR spectra of IL-coated reduced and passivated catalyst before and after undergoing reactivation treatment for 30 min in flowing H₂ at 150 °C. In [P₄₄₄₁][MeSO₄], the ν (S=O) bands of the anion located at 1161 and 940 cm⁻¹ [24] are susceptible to hydrogenation over Ni in the presence of hydrogen.



Fig. 1. TGA results for bulk $[P_{4441}][MeSO_4]$ (—) and $[P_{4441}][MeSO_4]$ -coated Ni65 (--). Data were collected at a ramp rate of 2 °C/min under flowing nitrogen.



Fig. 2. IR spectra of the activated-passivated IL-coated Ni65: (a) As prepared activated-passivated IL-coated Ni65; (b) after a reactivation treatment at 150 °C in flowing H₂ for 30 min (c) after using the reactivated catalysts for partial hydrogenation of 1,3-butadiene at 145 °C at a 1,3-butadiene:H₂ ratio of 1:2 for a time-on-stream period of 48 h.

Moreover, the band located at approximately 2900 cm^{-1} represents the stretching vibration of the O–CH₃ on the anion, another group that can readily react with hydrogen on a hydrogenation catalyst. Data indicated that these bands (and any other features) do not show any detectable changes upon reactivation; thus, we infered that the IL structure remains intact during the reactivation of the passivated IL-coated Ni65.

After determining a suitable condition for the reactivation without damaging the structure of the IL coating, we focused on investigating the reaction conditions at which the reactivated Ni65 catalyst provides the highest possible selectivity for partial hydrogenation of 1,3-butadiene before depositing the IL coating. The investigated conditions and the consequent results obtained under these conditions are given in Fig. S2 and S3, SI. Accordingly, the selectivity for total butenes (summation of the individual selectivities for 1-butene, and *cis*- and *trans*-2-butenes) on the uncoated catalyst can be increased to approximately 95%, when the partial pressures of 1,3-butadiene and H₂ were 120 and 240 Torr (with balance He), respectively, at 145 °C (Fig. 3a). Data showed that this selectivity remains at this level up to a 1,3-butadiene conversion of 97%. Results further indicated that 1-butene selectivity was



Fig. 3. Change in selectivities of total butenes (\blacktriangle), *trans*-2-butene (\bigcirc), 1-butene (\bigcirc), *cis*-2-butene (+), and butane (\bigcirc) with conversion over (a) uncoated Ni65 catalyst and (b) [P₄₄₄₁][MeSO₄]-coated Ni65. Reaction was carried out in a once-through flow reactor under a 1,3-butadiene and H₂ partial pressure of 120 and 240 Torr (balance He), respectively, at 145 °C and atmospheric pressure in balance helium flow. The conversion was varied by changing the space velocity keeping the other reaction conditions the same.



Fig. 4. Change in conversion (left vertical axis, black) and selectivity (right vertical axis, blue) on uncoated Ni65 (dotted lines) and $[P_{4441}]$ [MeSO₄]-coated Ni65 (solid lines) in time (hours). Reaction was carried under 1,3-butadiene and H₂ partial pressures of 120 and 240 Torr (balance He), respectively, at 145 °C and atmospheric pressure. The space velocities were adjusted such that the initial conversions are the same on both catalysts. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

approximately 60% throughout the whole conversion range. Similarly, the ratio of *trans*- to *cis*-2-butene was constant at approximately 2.0. Even though these results indicate a high performance for partial hydrogenation, extended time-on-stream runs indicated that the performance was not stable on the uncoated catalyst. The catalyst deactivates slightly within 48 h and this decrease in conversion was accompanied by a decrease in partial hydrogenation selectivity (Fig. 4). Accordingly, the 1,3-butadiene conversion and the selectivity for total butenes decreased from approximately 12 to 9% and 95 to 92%, respectively, at a space velocity of approximately 1.19 (mol of 1,3-butadiene) × (mol of Ni × s)⁻¹ (Fig. 4). Among different possible routes of deactivation, carbonaceous deposit formation might be the dominant one, as sintering might not be possible on a catalyst which was pre-reduced at 650 °C and used at 145 °C.

Following the optimization of reaction conditions for the highest partial hydrogenation selectivity on the uncoated catalyst (even though the time-on-stream data show that this performance was not stable), the performance of [P4441][MeSO4]-coated Ni65 catalyst was measured under the identical partial pressures and temperature. Results presented in Fig. 3b illustrate that the IL-coated catalyst provides an almost complete selectivity (> 99.5 \pm 0.2%) towards partial hydrogenation throughout the whole conversion range. To the best of our knowledge, this is the highest partial hydrogenation selectivity ever reported on a supported nickel catalyst. As it was reported previously [25], improvements in catalytic selectivity are often achieved at the expense of a drop in activity. Consistently, rate of the coated catalyst was lower $(7.4 \times 10^{-3} \text{ (mol of 1,3-butadiene converted)} \times (\text{mol of Ni} \times \text{s})^{-1})$ compared to that of the uncoated sample $(3.2 \times 10^{-2} \text{ (mol of 1,3-bu$ tadiene converted) \times (mol of Ni \times s)⁻¹). However, we also note that the presence of IL coating also induces a mass transfer barrier limiting the reaction rate. Besides, this lower activity might also originate from a change in the electron-density of the metal [26], and/or a simple reduction in the number of accessible active sites by the presence of IL layer. Here, it's also worth mentioning that the partial hydrogenation performance was stable for 48 h (Fig. 4) and the IL structure remains intact as illustrated by the comparison of IR (Fig. 2) and CHNS/O results (Table S2) of the catalysts before and after a time-on-stream period of 48 h. The increase in catalytic stability might be because of the IL layer, which controls the active concentrations of the intermediates/ products; and thus, helps their removal from the surface before getting any chance for forming carbonaceous deposits.

Data on the IL-coated catalyst further indicated that the selectivity of 1-butene was approximately 42% with a corresponding trans- to cis-2-butene ratio of approximately 4.7. An almost complete partial hydrogenation selectivity and such a high ratio of trans/cis isomers of 2butene indicate the presence of a higher electron density on the active sites in the presence of the IL coating compared to that on uncoated catalyst [27]. Aiming at investigating the presence of possible electron donation from IL to the metal sites, we employed XPS on uncoated and coated catalysts (Fig. S4 presents the raw data). Fig. 5 shows high resolution Ni2p spectrum consisting of $2p_{3/2}$ and $2p_{1/2}$ multiplet-split peaks of nickel. In Fig. 5a, the activated-passivated Ni65 catalyst has four peaks in the $2p_{3/2}$ region located at binding energies of 852.6 (Ni [28]), 853.6 (Ni²⁺ [29]), 856.1 (Ni²⁺ [30]), and 860.8 eV (satellite [31]). Upon coating the activated-passivated Ni65 catalyst with [P₄₄₄₁] [MeSO₄], Fig. 5 shows three peaks in the 2p_{3/2} region at binding energies of 852.1, 855.8, and 860.8 eV. The peak at 853.6 eV observed on uncoated catalyst disappeared from the spectra with a simultaneous decrease in the intensity of the Ni peak associated with an increase in the intensity of the peak positioned at 856.1 eV, indicating the presence



Fig. 5. XPS data of (a) activated passivated Ni65 and (b) [P4441][MeSO4] coated activated and passivated catalyst.

of nickel oxide species as expected for a passivated sample. We inferred that because of the presence of IL coating, the surface concentration of nickel-based species decreases resulting in a reduction of peak intensity of Ni phase and subsequent disappearing or agglomeration of peak at 853.6 eV. Furthermore, a shift in the peak position of Ni from 852.6 to 852.1 eV indicating a possible electron donation from IL to the nickel sites. These results are strongly consistent with our previous report on a y-Al₂O₂-supported atomically dispersed single-site iridium catalyst coated with 1,3-dialkylimidazolium ILs. High-energy resolution fluorescence detection X-ray absorption near edge structure (HERFD XANES) measurements on these iridium catalyst presented direct evidence on the presence of electron donation from IL coatings to the active metal sites [25]. These HERFD XANES results indicated a strong correlation between the edge energy of iridium adjusted by the choice of imidazolium IL and the total butene selectivity for the same reaction [25]. Thus, consistent with these previous observations on imidazolium type ILs, we infered that the phosphonium type-IL that we used in this study also works as a ligand to adjust the electronic environment over the nickel sites.

One other possible effect of IL coating is that it can work as a filter over the active sites to control the active concentrations of the reactants and intermediates [32,33]. To investigate the consequences of this effect on the exceptional partial hydrogenation selectivity obtained on ILcoated catalyst, we performed the COSMO-RS calculations. The estimated solubilities of 1,3-butadiene, 1-butene, *cis*- and *trans*-2-butenes, and butane in [P₄₄₄₁][MeSO₄] at 145 °C are listed in Table 1. These results indicate that the solubility of 1,3-butadiene in [P₄₄₄₁][MeSO₄] is approximately 1.5-times higher than those of butene intermediates/ products (Table 1). Such difference might provide an increase in selectivity towards partial hydrogenation. However, even if it does, it

Table 1

Capacity of individual components in $[P_{4441}][MeSO_4]$ at 145 $^\circ C$ as determined by COSMO-RS calculations.

Component	Capacity mol/mol
1,3-butadiene	1.22
trans-2-butene	0.81
1-butene	0.86
cis-2-butene	0.82
Butane	0.58

325

should be very limited, because the relative solubility of 1,3-butadiene is not that significantly high. Thus, we infer that the ligand effect of the IL is the major effect controlling the partial hydrogenation performance. The filter effect, on the other hand, helps to maintain such high partial hydrogenation selectivity at all conversion levels. Thanks to both of these effects, the performance of a commercial supported nickel catalyst could be improved to provide an almost complete partial hydrogenation selectivity. Here, we note that choosing the IL from a family with high chemical and thermal stability offers a great degree of flexibility in optimizing the reaction conditions even before introducing the IL coating.

4. Conclusions

Here, we showed that an ordinary commercial nickel catalyst can be taught to behave like palladium-based catalysts towards partial hydrogenation, when coated with an inexpensive, yet thermally and chemically stable IL. Data illustrate that $[P_{4441}][MeSO_4]$ -coated Ni65 gives a record high selectivity of 99.5 \pm 0.2% towards butenes at any conversion level in 1,3-butadiene hydrogenation under optimized conditions. This almost complete partial hydrogenation selectivity irrespective of conversion is associated with the ligand and filter effects of the IL. XPS results indicated that the IL donates electrons to the nickel sites. Moreover, COSMO-RS calculations showed that butenes are approximately 1.5-times less soluble than 1,3-butadiene in [P4441] [MeSO₄], and this difference in solubility helps to maintain the high partial hydrogenation selectivity at all conversion levels. Results presented here provide opportunities towards controlling the catalytic performance by coating the catalysts with chemically and thermally stable ILs, which offer a flexibility in optimizing the reaction conditions for high performance even before depositing the IL coatings.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.apcata.2018.06.016.

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