



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, [P₄₄₄₁][MeSO₄]. Thanks to high chemical and thermal stability of [P₄₄₄₁][MeSO₄], 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 ± 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 hydrogenation 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/Al₂O₃ catalyst coated with 1-ethyl-3-methylimidazolium 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 ¼-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

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