

Electronic Supplementary Information (ESI)

Parahydrogen-induced polarization in alkyne hydrogenation catalyzed by Pd nanoparticles embedded in a supported ionic liquid phase

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MATERIALS AND METHODS

1. Materials

Activated carbon fibres (ACF) cloth (AW1101, KoTHmex. Taiwan Carbon Technology) were used as supports for catalyst preparation. Fabrics of ACF present high mechanical strength, but can be easily cut to fit the reactor dimensions. The BET specific surface area (SSA) and pores size distribution (PSD) of the supports and catalysts were measured using N₂ adsorption–desorption at 77 K via a Sorptomatic 1990 (Carlo Erba) instrument. The samples were set in the ampoule in woven form. The SSA of the samples was calculated employing the BET method, while the Dollimore/Heal method was applied for the calculation of PSD. The SSA of the ACF cloths was 880 m²/g with an average pore diameter of 2.0 nm.

Hydroxyl-functionalized 1-butyl-3-methylimidazolium N-bis(trifluoromethanesulfonyl)imidate [bmimOH][Tf₂N], was synthesized as reported elsewhere.¹ 1-Butyl-3-methylimidazolium hexafluorophosphate, [bmim][PF₆] (Alfa Aesar, 99%), and other chemicals (Fluka, Aldrich, >98%) and gases for the preparation of catalysts (Carbagas, >99.99%) were used as received. Propylene (ca. 99%) and H₂ (99.99%) purchased from local vendors and propyne (Sigma-Aldrich, >99%) were used in hydrogenation reactions without any additional purification.

2. Preparation of the catalysts

Four different SILP on ACF catalysts have been used: Pd/[bmimOH][Tf₂N]/ACF with 5 nm particles, Pd/[bmim][PF₆]/ACF with 10 nm particles, Pd(acac)₂/[bmimOH][Tf₂N]/ACF (1.97% Pd(acac)₂ loading) and Pd(acac)₂/[bmim][PF₆]/ACF (2.03% Pd(acac)₂ loading).

The deposition of the active phase on the ACF support was carried out using a mixture of IL, Pd precursor and acetone, as reported elsewhere.² Briefly, the ACF support was heated up to 700 °C overnight under inert atmosphere (He or Ar) in order to remove the oxygen containing groups from the surface. The wet capacity (WC) of the support, i.e. the quantity of liquid which can be absorbed in weight percent, was found to be ~ 253 wt%. The desired quantity of Pd precursor in IL can be deposited on the support by mixing it with an appropriate amount of acetone. A mixture containing 2 wt.% of Pd(acac)₂ in IL was prepared. The appropriate quantity of acetone needed in order to load 9 wt.% of IL containing the precursor on the support, was found from the mass balance:

$$V_{\text{acetone}} = \frac{WC - ILload}{ILload} \cdot \frac{m_{Pd+IL}}{\rho_{\text{acetone}}}$$

After impregnation, the catalyst was placed for 30 min in a vacuum oven at 30°C in order to evaporate acetone. Finally, the catalyst was reduced to obtain Pd-nanoparticles at 150°C overnight at atmospheric pressure with 30% H₂ in Ar (total flow 150 ml(STP)/min) for [bmim][PF₆] and with Ar (flow 100 ml(STP)/min) for [bmimOH][Tf₂N].

3. Preparation of gaseous mixtures

The parahydrogen enrichment was performed by passing normal hydrogen (para/orto ratio is ca. 3/1) through a spiral copper tube containing FeO(OH) powder and immersed in a liquid nitrogen dewar.³ This procedure allows one to produce a continuously flowing stream of hydrogen enriched with parahydrogen to ca. 50%. It is then stored in an aluminum cylinder to which propyne or propylene is later added. For propyne hydrogenation experiments, a mixture consisting of 86% H₂ and 14% propyne with a total pressure of 6 atm was prepared. For propylene hydrogenation, 74% H₂ and 26% propylene were mixed and stored at the total pressure of 3 atm. Normal H₂ was used in the gaseous mixtures to analyze conversion and product selectivity. The relative amounts of propyne, propylene and propane in the mixtures were evaluated by integrating the corresponding peaks in the ¹H NMR spectra of these mixtures. Parahydrogen-enriched H₂ was used instead when the observation of PHIP effects was attempted.

4. Hydrogenation and NMR experiments

All ^1H NMR experiments were performed on an AV 300 SB 300 MHz Bruker NMR spectrometer. ^1H NMR spectra were detected using 45° -pulses with 128 scans accumulated per spectrum. Heterogeneous hydrogenation reactions were performed in a 10 mm screw cap NMR tube. About 25 mg of the SILP/ACF catalyst was placed at the bottom of the NMR tube and positioned in the NMR probe in such a way that at least some of the catalyst was within the sensitive region of the probe. A variable temperature unit was used to keep the NMR tube and catalyst at 130°C during the reaction. The mixture of gaseous reactants flowed through a $1/8''$ Teflon capillary ending at the bottom of the NMR tube. The gas flow rate was ca. 300 ml/min and NMR spectra were detected without interrupting the flow.

Some gas phase hydrogenation experiments were performed outside the NMR magnet. In this case, about 50 mg of the catalyst was packed inside a small section of $1/4''$ copper tubing used as a reactor which was maintained at 80 - 100°C (propylene and H_2) or 150 - 210°C (propyne and H_2) while the mixture of gaseous reactants flowed through the catalyst and then into the NMR tube positioned in the NMR probe located in the NMR magnet. It was found that Pd/[bmimOH][Tf₂N]/ACF and Pd/[bmim][PF₆]/ACF catalysts are highly active in the gas phase heterogeneous hydrogenation of propyne at 150 - 210°C and hydrogenate propyne into propylene and propane with the molar propyne/propylene/propane ratio of ca. 1/2/1.3. Nevertheless, when parahydrogen-enriched H_2 was used in the reaction and the hydrogenation was carried out outside the NMR instrument, no PHIP effects in the resulting NMR spectra could be observed. One possible explanation of the absence of PHIP in this experiment is that polarization can be destroyed by nuclear spin relaxation processes while the polarized product is transferred from the reactor to the NMR magnet. Moreover, our EPR studies show that the ACF support is paramagnetic, which could also significantly reduce polarization level while the polarized gas travels through the catalyst bed.

References.

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