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Alkaline modifiers as performance boosters in citral hydrogenation over supported ionic liquid catalysts (SILCAs)

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ABSTRACT

Supported ionic liquid catalysts (SILCAs) consist of nano-scale catalytic species immobilized in an ionic liquid layer which, in turn, is immobilized on a solid support. In this work, novel SILCAs containing various inorganic alkaline modifiers (e.g. potassium hydroxide) were prepared and applied in citral hydrogenation reactions. The supported ionic liquid catalyst systems demonstrated enhanced reaction rates and improved selectivities toward citronellal in citral hydrogenation. With the addition of an alkaline modifier into ionic liquid layer, the catalyst selectivity increased from 16% to 74%. In fact, a highly selective reaction route toward citronellal was accomplished.

1. Introduction

Ionic liquids (ILs) may be referred as molten salts in which either the cation or the anion is of organic origin. Because of their tunable solvation properties, thermal stability and usually low vapor pressure, ionic liquids have already found a number of different application areas such as electrolytes in supercapacitors, batteries and in solar cells; solvents for lignocellulose species; synthesis media for unconventional metal alloys, just to mention a few [1,2]. Another important evolving field of ionic liquids is in heterogeneous catalysis, where those may act as catalyst but also as solvent at the same time [3,4]. The concept of catalysis in supported ionic liquids involves catalytically active species immobilized in a thin layer of ionic liquid, which in turn, is immobilized on a solid support material. The catalytically active species can be solid metal nanoparticles that are suspended or homogeneous catalyst (metal complexes) or even enzymes dissolved in ionic liquids [5–7]. One of the benefits for supported ionic liquid catalysis is the elimination of difficult and costly catalyst separation from the liquid reaction matrix [5,6].

Immobilization of ionic liquids can be achieved by different methods such as simple impregnation, grafting, sol–gel method or polymerization [8–11]. Immobilization of ionic liquids via impregnation of the support material with an ionic liquid is a simple and straightforward route toward supported catalysts. An ionic liquid and a metal compound are both dissolved in a molecular solvent (e.g. acetone) which is then poured over the solid support material. The molecular solvent is evaporated, leaving only a layer of ionic liquid on the support, into which metal compounds are dissolved. In addition, complexes, modifiers and other active species can be dissolved into the ionic liquid layer [12]. Organometallic compounds (e.g. $Pd(acac)_2$) can be reduced to solid metallic nanoparticles e.g. by means of a hydrogen treatment under elevated temperatures as proposed earlier for supported ionic liquid catalyst (SILCA) materials (Fig. 1) [8,12]. Though the concept works quite well for a number of different reactions, two limitations of supported IL catalysts must be mentioned. First, the reaction temperature is limited by the decomposition temperature of the ionic liquid and thermal stability of other species. Secondly, if the ionic liquid is not covalently bonded to the surface of support, the ionic liquid and the organic phase must form an immiscible biphasic system meaning that the ionic liquid should not be miscible with the reaction solvent [13]. Because the ionic liquid is non-covalently immobilized on the active carbon support, the leaching of the catalytic and ionic media must be investigated.

Selective hydrogenation of α,β-unsaturated aldehydes (e.g. citral) is a very important reaction in the preparation of different kinds of products and intermediates in fine chemical industry. Citral and its hydrogenation products are widely used in the fine chemical and perfumery industries [14]. The activity boost by ionic liquids has been observed in the hydrogenation of alkenes, citral and other α,β-unsaturated aldehydes [6,8]. The ionic liquids can influence the concentrations of compounds and intermediates on the surface of the solid catalyst [13]. Ionic liquids have different hydrogen

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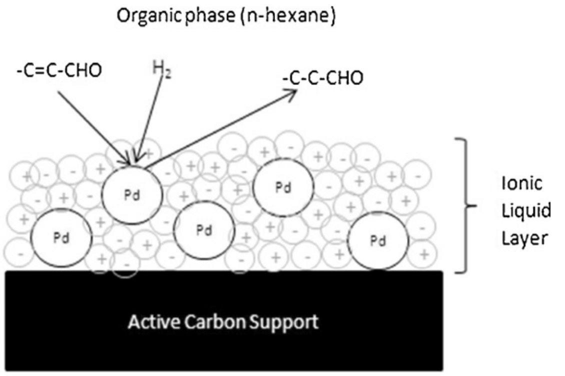

Fig. 1. The principle illustration of supported ionic liquid catalyst used in hydrogenation of citral. Palladium nanoparticles residing in an ionic liquid layer immobilized on an active carbon cloth (ACC).

solubilities and reactant solubilities. This might be one explanation for the selectivity and activity differences observed for systems comprising of various ionic liquids [6,8]. The reason for improved activity could also be that the ionic liquids are non-coordinating solvents and that is why the reactants have a better access to the catalytically active metal particles [6]. It has to be noted that the choice of ionic liquid anion can determine the coordinative or non-coordinative character of the ionic liquid. Preparation of metal nanoparticles in ionic liquids is preferred because the ionic liquid acts as a stabilizer. Also, stabilization of metal nanoparticles with ionic liquids to suppress aggregation can be an important factor contributing to the catalytic activity [15]. Supported ionic liquid catalysts are based on the stabilizing effect of ionic liquids.

2. Experimental

2.1. Catalyst preparation

A simple straightforward catalyst preparation method was applied [5]. Approximately 150 mg of ionic liquid and 50 mg of palladium acetylacetonate (Pd(acac)$_2$) (Aldrich, 99%) were both dissolved into acetone (Merck, p.a.). With alkaline-modified catalysts, an alkaline modifier (e.g. KOH or Na_2CO_3) was dissolved into methyl alcohol (Merck, p.a.). The mole fraction of KOH and ionic liquid was 4:1 whereas the mole fraction of Na_2CO_3 and ionic liquid was 2:1. The solutions were mixed together and then poured over a pre-dried active carbon cloth (ACC) Kynol® (approximately. 1.2 g). The wetted catalysts were kept in an oven, at 80 °C, for 2 h so that all solvents (acetone and methyl alcohol) evaporated. As the next step the SILCAs were pre-reduced prior to the hydrogenation experiments in a high-pressure semi-batch reactor (Parr Inc.). Pretreating was performed at 120 °C under hydrogen flow of 10 bar. Consequently, the catalyst containing palladium nanoparticles in an ionic liquid immobilized on ACC was obtained. The ionic liquids used in the preparation of SILCAs were N-butyl-4-methylpyridinium tetrafluoroborate ([C_4C_1Py][BF_4], Merck, 98%) and N-(3-hydroxypropyl)pyridinium bis(trifluoromethylsulfonyl)imide ([(C_3OH)Py][N(CF_3SO_2)$_2$], Merck, 98%), stored under inert atmosphere and used without further purification.

2.2. Hydrogenation experiments

The supported ionic liquid catalysts were used in the hydrogenation of citral (Aldrich, 95%). Hydrogenation experiments were performed in a semi-batch reactor (Parr Instrument Company). The total volume of the reactor was 600 ml whereas the effective liquid volume was 250 ml. The temperature and stirring rate were controlled by a Parr 4843 control unit (Watlow control series 982). All experiments were performed at a constant pressure and temperature. Approximately 3 g of citral (0.02 mol) was dissolved in 250 ml of n-hexane (Merck, >99%). In the beginning of each experiment, the reactor was heated to a desired temperature and, at the same time, the hydrogen pressure was also adjusted to desired level. After the citral solution was injected to the reactor, the stirring was commenced and this was considered as the starting point for the reaction.

Citral hydrogenation products were identified by means of gas chromatography (Hewlett Packard 6890 GC with FI detector). In addition, a gas chromatograph coupled to a mass-spectrometer (Agilent 6980N GC with Agilent 5973 MS detector) was used to identify the peaks of citral hydrogenation products. The peaks in the chromatogram were identified with the following reference substances: (±)-citronellal (Fluka, 80–90%), nerol (Fluka, >90%), geraniol (Alfa Aesar, 97%), (+)-neomenthol (Fluka, 98.5%), (−)-isopulegol (Aldrich, 99%), tetrahydrogeraniol (Aldrich, 99%), menthol (Aldrich, 99%), (+)-isomenthol (Fluka, >99%), and (±)-β-citronellol (90–95%, Fluka). The progress of citral hydrogenation reaction was monitored by taking samples from the reactor and analyzing them by means of gas chromatography. In the case of standard samples and samples taken from reactor, 500 μl of internal standard (0.02 M cyclohexanone in cyclohexane) was added into a 500 μl of sample. The GC column used was an Agilent DB-5 with a length of 60 m, inner diameter of 0.32 mm and a film thickness of 1 μm. The following temperature program was applied: 10 min at 100 °C, then raised 5 °C/min to 160 °C. Temperature was then held 10 min at 160 °C. At the end the temperature was increased 13 °C/min to 200 °C and kept constant for 1 min.

2.3. Catalyst characterization

Both fresh and spent catalysts were analyzed by means of energy-filtered transmission electron spectroscopy (EFTEM Leo912 OMEGA, 120 kV, LaB_6 filament). Prior to the characterization, the samples were crushed, dispersed in n-hexane or in water and then drop cast on copper grids (coated with formvar). The leaching behavior of ionic liquids has been already determined in our earlier studies [8]. Accumulation of different hydrogenation decomposition products on the catalyst surface was studied by extracting spent catalyst with 2-propanol and analyzing this solution by means of gas chromatography, as shown in the case of the citral hydrogenation samples.

The surface area and micropore volume of the catalysts were characterized by means of automatic physisorption–chemisorption apparatus (Carlo-Erba Instruments, Sorptometer 1900). Dollim.–Heal method was used to calculate the micropore volume of the catalysts whereas the Dubinin method was used to calculate the surface area of the catalysts.

3. Results and discussion

3.1. Catalyst activity and selectivity

Citral hydrogenation experiments were carried out in a semi-batch reactor. The stirring rate was adjusted to 1200 rpm in order that the external mass-transfer limitations from the bulk liquid to the catalyst surface were suppressed, as confirmed by our earlier studies [8]. The hydrogenation of citral was studied over unmodified and alkali-modified supported ionic liquid catalysts. In all experiments, total conversion of citral was obtained. The plausible citral hydrogenation reaction scheme is presented in Scheme 1.