Wacker oxidation of 1-hexene in 1-n-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]), supercritical (SC) CO_2, and SC CO_2/[bmim][PF_6] mixed solvent

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Oxidation of 1-hexene by molecular oxygen is conducted in 1-n-butyl-3-methylimidazolium hexafluorophosphate [bmim][PF_6], supercritical (SC) CO_2, SC CO_2/[bmim][PF_6] mixed solvent, and in the absence of solvent. The selectivity to the desired product 2-hexanone is much higher when the reaction is carried out in the mixed solvent, and the catalysts is more stable in SC CO_2/[bmim][PF_6] mixed solvent than in SC CO_2.

1. Introduction

The use of supercritical (SC) CO_2 as a substitute for toxic and flammable organic solvents already represents an important method for waste reduction in green chemistry.[1,2] SC CO_2 changes back to gas after reducing the pressure, which makes it easy to recover and reuse. Recently, many catalytic reactions in SC CO_2have been performed with unique properties.[3–5]

Room temperature ionic liquids (ILs) have recently attracted more and more attention.[6–10] They can be considered as green solvents due to their high thermal stability and negligible vapour pressure under ambient conditions. Very recent work has demonstrated that SC CO_2 is highly soluble in some ILs, while the ILs are insoluble in SC CO_2.[11,12] This feature of CO_2/IL systems has been successfully used to separate SC CO_2 soluble products from the ILs in some reaction processes.[13–16]

Biphasic catalytic reaction systems for homogenous catalysis typically consist of a lower phase solvent that is able to dissolve the catalyst and an upper phase solvent that carries the reactants into the reaction phase. Some of the catalytic reactions in SC CO_2/IL biphasic systems have been investigated.[14–16]

Oxidation of alkenes to methyl ketones using oxygen has been developed in synthetic organic chemistry as well as in industrial processes.[17] A well-known example is the Wacker process using $PdCl_2$ and $CuCl_2$ as catalysts,[18,19] and acidic water or organic solvents are usually used as solvents. Recently, Wacker oxidation of olefins in SC CO_2 has also been reported.[20]

Both SC CO_2 and ILs can be used as solvents for chemical reactions, and each of them has their own unique properties. Combination of the advantages of the two classes of solvents is a new and interesting topic. In this work, the Wacker oxidation of 1-hexene in IL [bmim][PF_6], SC CO_2, and SC CO_2/[bmim][PF_6] mixed solvent, and in the absence of solvent is studied.

2. Experimental

The room temperature ionic liquid 1-n-butyl-3-methylimidazolium hexafluorophosphate, [bmim][PF_6], was synthesized according to the procedure in the literature.[21] The IL was dried and degassed under vacuum at 70 °C for 48 h prior to use. The experimental apparatus and procedures were similar to those reported in the literature.[15] Briefly, it consisted mainly of CO_2 and O_2 cylinders, a high-pressure pump, a stainless steel reactor, a constant temperature oil bath, a pressure gauge, a cold trap, and a flow meter. The procedure to conduct reaction in CO_2/IL mixed solvent is described because that in other solvents is similar. In each experiment, 1.5 g [bmim][PF_6], 0.032 g $PdCl_2$, 0.25 g $CuCl_2$, 1 ml 1-hexene, and 2 ml methanol which serves as a nucleophilic reagent (the reaction can not occur without the nucleophilic reagent) were charged into the 18 ml reactor. The reactor was placed into the oil bath at 333.2 K. O_2 was charged into the reactor up to 21 bar and then CO_2 was added to the desired pressure. After a suitable reaction time, the vapour phase was released slowly passing though the cold trap containing isopropanol as absorbent. The CO_2-soluble components in the reactor were extracted by SC CO_2 at 110 bar. Our experiments showed that 100 g CO_2 was required to extract all extractable substances into the cold trap. The sample in the cold trap was analysed by GC (GC112, Shanghai Analytical Instrument Factory). After the extraction process the ionic liquid and the catalysts were left in the reactor. The metal concentration (Pd, Cu) in the extracted sample was analysed by atomic absorbance spectroscopy (Model AAS 6).

3. Results and discussion

Conversion and selectivity in different solvents

The experiments showed that the main products of the reaction were 2-hexanone and 3-hexanone, and 2-hexanone was the desired product. The data of the conversion of 1-hexene and the selectivity to 2-hexanone in different solvents and in the absence of solvent are listed in Table 1. The selectivity is defined as moles of the desired product divided by the total moles of all the products. In all the solvents the conversion approaches 100% after a reaction time of 17 h. It is very interesting that the selectivity in SC CO_2/[bmim][PF_6] mixed

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Table 1 Conversion and selectivity of the reaction in different solvents at 333.2 K with a reaction time of 17 h

Solvents	P/bar	Conversion (%)	Selectivity (%)
SC CO_2	125	98.9	70.5
SC CO_2 + IL	125	98.2	91.9
IL		97.0	64.2
Without solvent		99.9	63.2

solvent to the desired product 2-hexanone is much higher than those in SC CO_2 and in the IL, or in the absence of solvent. This is discussed in the following.

3-Hexanone is generated from 2-hexene which is produced from the isomerization of the reactant (1-hexene).[22] The catalysts $PdCl_2$ and $CuCl_2$ are not soluble in SC CO_2, and they exist in the IL-rich phase. SC CO_2 is soluble in the IL, and the IL is insoluble in SC CO_2.[11,12] 1-Hexene is soluble in both SC CO_2 phase and the IL phase, and thus the reactant is distributed in the two phases. Considering these facts, it can be deduced that SC CO_2 in the reaction system has at least two functions. One is that the SC CO_2-rich phase serves as a "reservoir" for the reactant, which supplies the reactant for the IL-rich phase continuously and keeps lower concentration of the reactant in the IL-rich phase that contains the catalysts. In other words, less amount of the reactant contacts with the catalysts, and the degree of isomerization of the reactant is reduced. As a result, the amount of 3-hexanone produced is reduced. Second, the dissolution of CO_2 in the IL can reduce the viscosity and enhance the mass transfer of the IL, which may also reduce the isomerization reaction. In addition, the catalyst–reactant, solvent–reactant, and catalyst–solvent interactions in CO_2/IL mixed are different from those in pure CO_2 or IL, which may favor increasing selectivity for 2-hexanone.

Effect of reaction time on the conversion and selectivity

Fig. 1 shows the dependence of the conversion and selectivity on the reaction time in SC CO_2 and the SC CO_2/IL mixed solvent at 125 bar. Our phase behavior experiments using an optical cell[23] showed that only one fluid phase existed in the reaction system when SC CO_2 was used as the solvent, *i.e.*, the reactants, products, and the nucleophilic reagent (methanol) were dissolved in SC CO_2. When CO_2/IL mixed solvent was used, there were two fluid phases in the mixed solvent system, a CO_2-rich phase and an IL-rich phase, and the reactants, products, and the nucleophilic reagent were distributed between the CO_2-rich phase and the IL-rich phase.

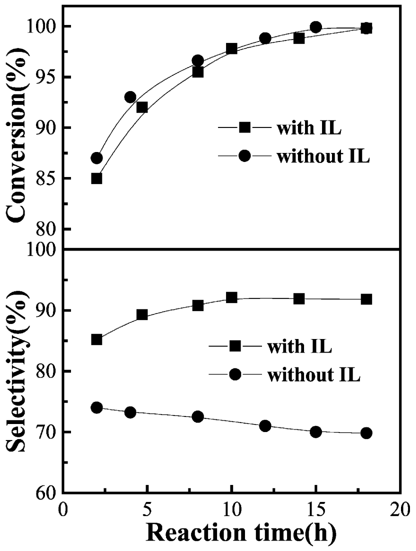

Fig. 1 The dependence of conversion and selectivity on reaction time at 333.2 K and 125 bar; IL: ionic liquid [bmim][PF_6].

Fig. 1 illustrates that the difference in conversion at various reaction times in SC CO_2 and in the CO_2/IL mixture is not considerable. One of the main reasons may be that the catalysts are well dispersed in the IL-rich phase in the presence of the IL, which favors enhancement of the reaction rate in the CO_2/IL system. On the other hand, the liquid/vapor interface exists in the CO_2/IL system, which does not favor increasing the reaction rate due to the interface mass transfer. The two opposite factors compensate each other, and thus the conversion is similar. The effect of reaction time on the selectivity in the two solvents is not significant, as can be seen from the figure. However, in the CO_2/IL mixed solvent the selectivity to the desired product is much higher than that in SC CO_2. Moreover, the selectivity in the mixed solvent increases slightly with reaction time, while the selectivity decreases slowly with reaction time in SC CO_2.

Dependence of pressure on the conversion and selectivity

It is known that the properties of supercritical fluids (SCFs) are sensitive to pressure, and thus pressure may influence the conversion and selectivity of the reaction. In this work, we also explore the effect of the pressure on the conversion and the selectivity in CO_2/IL mixed solvent, and the results are given in Fig. 2. In the pressure range studied, the conversion is very high and is nearly independent of pressure. However, the selectivity increases with pressure significantly, especially in the low-pressure range. A very rough explanation is that the solvent power of CO_2 increases with increasing pressure. Therefore, less reactant exists in the IL-rich phase at higher pressure, which favors reduction of the isomerization of the reactant. Meanwhile, the solubility of CO_2 in the IL increases with pressure,[11,12] and so the diffusivity of the solvent is improved more significantly at the higher pressures, which may also enhance the selectivity. This explanation is consistent with the discussion above.

Stability of the catalysts

In order to study the stability of the catalysts in SC CO_2 and CO_2/IL, we repeated the experiment in each solvent six times at 125 bar with a reaction time of 17 h. The results are shown in Fig. 3, which indicates that the catalysts are fairly stable in both solvents. Obviously, the catalysts are more stable in SC CO_2/IL mixed solvent than in CO_2. In other words, the mixed solvent can not only enhance the selectivity to the desired

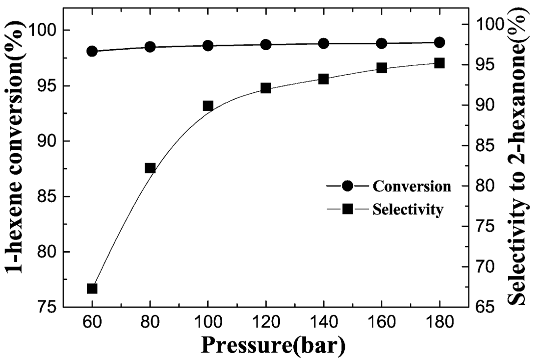

Fig. 2 The dependence of conversion and selectivity on reaction pressure in SC CO_2/IL mixed solvent at 333.2 K with a reaction time of 17 h.

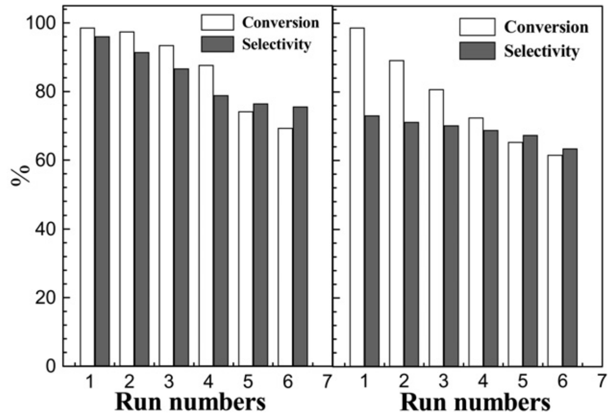

Fig. 3 Effect of run number on the conversion and selectivity in SC CO_2/IL (left) and in SC CO_2 (right)at 333.2 K and 125 bar (in each run the reaction time is 17 h).

product significantly, but also stabilise the catalysts. Atomic adsorption spectroscopy showed that Pd and Cu were not detectable in the extracted sample. This indicates that the fall of the conversion does not result from catalyst losses, and the change of the properties of the catalysts is the main reason.

Acknowledgements

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