



Short communication

Fischer–Tropsch synthesis in a slurry mode using ionic liquids

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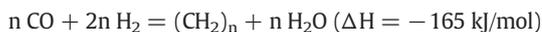
ABSTRACT

The activity of a sodium salt of 4,5-dicarboxyphthalocyanine of cobalt has been studied in Fischer–Tropsch synthesis in a slurry mode (autoclave) using ionic liquids and a mixture of the ionic liquid with perfluorodecaline as solvents. The addition of perfluorodecaline to the reaction mixture resulted in a dramatic increase of the yield of liquid products.

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1. Introduction

The Fischer–Tropsch process is a mature industrial technology to produce hydrocarbons from synthesis gas, no matter whether the syngas is produced from natural gas, biomass or coal:



Typically the composition of products depends on the nature of the active phase (Co, Fe or Ru), catalyst support (oxides or zeolites), and process conditions and includes a broad range of normal or isoparaffins, olefins, or aromatic hydrocarbons with some oxygenates being formed as well (methanol or glycols).

The activity of the catalysts is also governed by the size of metal particles (Co, Fe, Rh or Ru) [1–4]. Different types of reactors are used in the Fischer–Tropsch process. Recently the intensive development of the three-phase process (the slurry process) with the suspended catalyst in a liquid phase has been documented [5,6]. The advantages of this technology have been demonstrated at the industrial scale by SASOL [7–9].

The reactions involving CO were shown to proceed in solutions and ionic liquids (IL), including preparation and stabilization of metal nanoparticles [10–13]. The method of preparation of a Ru-catalyst for Fischer–Tropsch synthesis has been developed, which is based on dispersion of $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ in a solution of a co-polymer

stabilizing IL-containing agent poly[(N-vinyl-2-pyrrolidone)-co-(1-vinyl-3-allylimidazolium chloride)] in methanol with further dissolution of the suspension in another IL-1-butyl-3-methylimidazolium tetrafluoroborate. After this methanol was removed and reduction of ruthenium was carried out in hydrogen at 100–200 °C [14]. Ionic liquids are now considered as benign solvents and catalysts for diverse catalytic processes, including CO reactions, due to their unique and tunable physicochemical properties, as well as preparation of Co nanoparticles in ionic liquids [15–17].

Ionic liquids have been also used as size- and shape-regulating solvents for the synthesis of cobalt nanoparticles. One example of the use of IL in the preparation of Co nanoparticles (7.7 nm) as catalysts for the Fischer–Tropsch reaction is described in [17]. Thermal decomposition of $[\text{Co}_2(\text{CO})_8]$ dispersed in 1-alkyl-3-methyl imidazolium ionic liquid resulted in ligand-free cobalt nanocubes or spherical nanoparticles, depending on the nature of ionic liquid and the process conditions. Such nanoparticles act as selective catalysts in the Fischer–Tropsch reaction. The nanoparticles are easily prepared by the decomposition of $[\text{Co}_2(\text{CO})_8]$ in the ionic liquid at 150 °C and can be reused at least three times. One more relevant example of the published research concerns methanol synthesis from synthesis gas using Cu, Zn and Cu–Zn metal nanoparticles synthesized from amidinate precursors in ionic liquids [18].

To the best of our knowledge, the publications on the direct use of ionic liquids in the Fischer–Tropsch reaction are very limited, except for some rare papers devoted to the preparation of catalysts using IL at certain stages [15–17]. The only paper by Silva et al. [17] presents some data on the activity of Co nanoparticles prepared in BMIM-TFSI ionic liquid and used in Fischer–Tropsch synthesis as being dispersed

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CO conversion, %

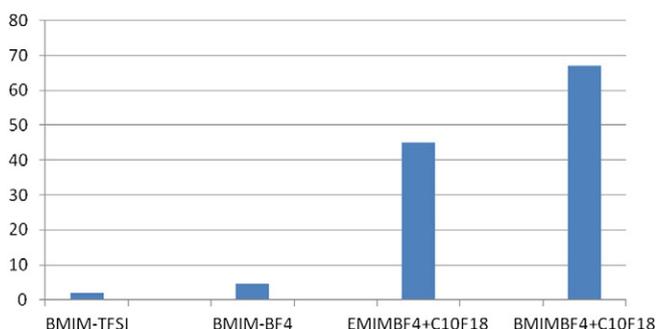


Fig. 1. CO conversion in Fischer–Tropsch synthesis carried out in ionic liquids and a mixture of BMIM-BF₄ and perfluorodecaline (280 °C, 30 atm).

in the same ionic liquid. However, the conversion is given only for the isolated Co nanoparticles (not the dispersion in the ionic liquid) and the conversion is rather low 10–30% during the 10–20 h time on stream.

In our opinion, the lack of such publications can be explained by the very poor solubility of CO and H₂ in ionic liquids even at enhanced reaction pressures. The other reason may be the thermal stability of ionic liquids that may start to decompose at a high reaction temperature of 200–300 °C.

The goal of this communication is to provide the first indication of the application of the ionic liquid in the Fischer–Tropsch synthesis, with the original idea being related to the use of a mixed solvent containing ionic liquid and perfluorodecaline, the latter is known to be a good solvent of oxygen (a blood substituent). It was assumed that the solubility of both CO and H₂ can be increased by using such a mixture.

2. Experimental

The disodium salt of 4,5-dicarboxyphthalocyanine of cobalt (Na-DC-PC-Co) has been used as a catalyst in Fischer–Tropsch synthesis in a slurry mode (autoclave) using ionic liquids and a mixture of the ionic liquid with perfluorodecaline as solvents. A powder dispersed in the ionic liquid or a mixture of the ionic liquid with perfluorodecaline was tested.

The catalyst (0.4 g) and the solvent (10 mL) were loaded in a PARR-300 autoclave. 1-Ethyl-3-methylimidazolium tetrafluoroborate (EMIM-BF₄), 1-butyl-3-methylimidazolium tetrafluoroborate (BMIM-BF₄), and 1-butyl-3-methylimidazolium bis-trifluorosulfonylimide (BMIM-TFSI, the ionic liquids were purchased from Merck, the purity was >99%) or their 1:1 (vol.) mixtures with perfluorodecaline were used as solvents. The loaded autoclave was purged with nitrogen and then filled with synthesis gas (H₂/CO = 2/1) at the pressure of 30 atm, then the autoclave was heated until 280 °C during 40 min under stirring (500 rpm) and the reaction mixture was kept at this temperature for 1 h. Then the autoclave was cooled down to room temperature and liquid or gas products were analyzed by gas chromatography. In some cases, the liquid products formed were extracted from the layer of the ionic liquid using 2,3-dimethylpentane as a solvent (or toluene). Gas and liquid products were analyzed using a 3700 model gas chromatograph with a flame-ionization detector and an SE-54 capillary column (25 m) in the temperature-programmed mode (60 °C, 8 min, then the temperature was increased to 180 °C with the rate of

Table 1
Composition of gas products.

| Content, % wt. | | | |
|-----------------|----------------|----------------|--|
| CH ₄ | C ₂ | C ₃ | paraffins C ₄ /olefins C ₄ |
| 52.2 | 31.4 | 10.6 | 5.4/0.5 |

Table 2
Composition of liquid products.

| Content, % wt. | | | | | | | |
|----------------|----------------|----------------|----------------|----------------|-----------------|-----------------|------------------|
| C ₅ | C ₆ | C ₇ | C ₈ | C ₉ | C ₁₀ | C ₁₁ | C ₁₂₊ |
| 6.0 | 11.5 | 9.1 | 27.8 | 10.1 | 15.2 | 7.1 | 13.2 |

8 °C/min). Analysis for hydrogen and CO was performed using the same chromatograph using a packed column with molecular sieves 5A (3 m) and a thermal conductivity detector. The conversion of CO was determined by the method of absolute calibration.

3. Results and discussion

The use of the ionic liquid (or a solvent, in general) allows a better dispersion of the catalyst and a better heat transfer, since the Fischer–Tropsch reaction is highly exothermic. The tests carried out with the chosen ionic liquids (EMIM-BF₄, BMIM-BF₄ and BMIM-TFSI) or perfluorodecaline as single solvents using the Na-DC-PC-Co catalyst demonstrated a poor activity of the system, with the CO conversion not exceeding 2–3%. Noteworthy that the [BMIM]-TFSI-perfluorodecaline system showed about the same poor performance (the CO conversion 3.5%). The yield of liquid products is typically below 1% and the gas formed in the process contains a C₁–C₈ fraction with predominance of n-octane. It should be noted that perfluorodecaline does not mix with the ionic liquid (BMIM-TFSI).

The second system (Na-DC-PC-Co in BMIM-BF₄-perfluorodecaline), which forms a homogenous phase, demonstrated very promising results, unlike the first system as well as the tests when individual ionic liquids or perfluorodecaline served as solvents. In this case, the role of perfluorodecaline is rather related not to the extraction of the hydrocarbons formed but the better solubility of both gases (CO and H₂) in the mixed solvent. The yield of the liquid products reached 0.7 g, whereas the CO conversion was as high as 65% (Fig. 1). The product distribution for this test in the gas and liquid phases (toluene was used as an extracting agent) is shown in Tables 1 and 2. The liquid products contain mostly normal paraffins C₅–C₁₆, which is very similar to conventional Fischer–Tropsch systems based on Co catalysts. The catalyst was recycled 3 times without any activity loss. Noteworthy that the use of EMIM-BF₄ resulted in a lower activity, perhaps, due to the higher polarity of this ionic liquid.

4. Conclusions

The data obtained provide some ideas on how to better design the slurry process of production of liquid hydrocarbons from synthesis gas using mixed solvents containing ionic liquids and fluorinated solvents. The use of perfluorodecaline in a mixture with miscible ionic liquids seems to be responsible for the improved solubility of CO and hydrogen in the solvent mixture.

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