Ruthenium Nanoparticles with Ionic Liquids Media in Carbon Dioxide Valorisation to Methane

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ABSTRACT

Subject of a sufficient valorisation of carbon dioxide into fuels is an attractive hot topic at academia and industry level. Transformation of carbon dioxide into fuels can suit as an excellent alternative to carbon dioxide capture and sequestration. As such an example we sought to achieve hydrogenation of carbon dioxide towards fuels, namely methane in ionic liquid media. The important role of ruthenium nanoparticles prepared in situ to catalyse the reaction at moderate conditions of temperature and pressure has to be highlighted in order to produce methane selectively and efficiently.

Keywords: nanoparticles, heterogeneous catalyst, in situ, fuels, sustainable chemistry

1 INTRODUCTION

Large amounts of carbon dioxide (CO₂) has to be prevented from being released into the atmosphere. Such a prevention is named as Carbon Capture and Storage, CCS, known also as Carbon Capture and Sequestration. CO₂ produced by large industrial plants is captured and compressed for transportation. Later on, carbon dioxide is injected into deep underground rock to be permanently stored. CCS is a sustainable option in reducing emissions from large scale emission sources. As estimated in the U.S. Inventory of Greenhouse Gas Emissions and Sinks, 40% of CO₂ emissions in the United States come from electric power generation. CCS technologies are available and can significantly reduce by nearly 90% of CO₂ emissions from power coal- and natural-gas-fired plants that burn fossil fuels.[1]

Carbon dioxide is a non-polar stable, chemically inreacted molecule and its reduction can occur at very high not economically favourable temperatures. Using carbon dioxide to produce chemicals, energy, fuels is according the scope of green economy. Carbon dioxide use and utilisation, CCU, aims at transformation of carbon dioxide into valuable products. [2] Illustration of products being of interest from Carbon Dioxide utilisation is presented in Figure 1.

![Figure 1: Valuable products from Carbon Dioxide Utilisation.](image)

Utilisation of carbon dioxide gives possibility to recall carbon within a cycle. The carbon can be trapped in a permanent form to produce construction materials and polymer formation, or stored within an energy vector. Carbon dioxide has to be captured from the air to retain the cycle. Many valuable intermediates including synthesis gas and small molecule organics that can be produced from carbon dioxide.

Carbon dioxide has been utilised to produced methanol, or fuels. Hydrocarbons or oxygenates were produced in heterogeneous or electrochemical way. CO₂ methanation at 160-180 ºC in a continuous flow reactor using ruthenium nanoparticle-loaded TiO₂ is a 100% selective process toward methanol. [4] The importance of the size of the nanoparticles was highlighted as a factor driving the activity of the catalyst. Reduction of CO₂ in biphasic ionic liquid and supercritical CO₂ mixtures is common method applied to produce formic acid [5]. Ruthenium homogeneous catalysts immobilised in ionic liquids were reported to hydrogenate dissolved CO₂ to obtain methanol or formic acid.[6,7] Supercritical carbon dioxide is capable to act as reagent and solvent. Ionic liquids are organic salts with low melting temperature that can be easily tuned by adjustment of their cations and anions to the specific demands. ILs are known as reaction media or as catalysts at high-pressure hydrogenation [8,9]. Ruthenium nanoparticles in ionic liquids were successfully applied to catalyse hydrogenation of arenes.[10]

Taking into account exceptional capability of ionic liquids in formation of various types of nanoparticles, this
work aimed at Ruthenium Nanoparticles formation that catalysed Carbon Dioxide Hydrogenation to Methane in Ionic Liquid Media.\[11\]

2 EXPERIMENTAL PART

The experimental set up consists of a 30 mL stainless steel autoclave that was charged with 0.03 to 0.26 mol% of Ruthenium(II) catalyst precursor. After sealed the autoclave was deoxygenated under vacuum and 40 to 60 bar of H2 were admitted at room temperature. Reactor temperature was increased to 313.15 K and CO2 was admitted until the system reached 80 bar of total pressure. The reaction mixture was heated to 413.15 K in an oil bath and stirred for 12 to 48 h (normally 24 h of reaction time). After reaction, the autoclave was slowly cooled until it reached room temperature and the system is depressurized into an expansion vessel (EV). A sample of the gas phase (1 bar) was recovered into the collecting vessel (CV) for gas chromatography analyses. The ionic liquid phase was analyzed by NMR, UV-Vis and TEM. The data resulting GC analysis is used to calculate the yield of reaction.\[11\]

Figure 2: Photograph of the hydrogenation of carbon dioxide apparatus.

3 RESULTS AND DISCUSSION

This work is devoted to reduction of carbon dioxide at moderate conditions using ruthenium nanoparticles produced in situ and stabilized in ionic liquid medium. Analogically to the work of Leitner, where Ru(cod)methylallyl2 as ruthenium (II) catalysts and Triphos as ligand were used in hydrogenation of carbon dioxide to obtain formic acid, we have performed reactions with Ru(cod)methylallyl2 catalyst and ligand PPh3 dissolved in imidazolium based ionic liquids in various pressure, 20-60 bar of H2 with a total pressure of 80 bar when CO2 was added. Various imidazolium based ionic liquids was tested in the high pressure reduction of carbon dioxide.\[11\]

Selectivity of the reduction of carbon dioxide catalysed by ruthenium nanoparticles in ionic liquid media was found to be dependent on various factors. Formation of methane was found to be dependent upon the temperature, pressure and the type of ionic liquid used. It was discovered that the ionic liquid has to facilitate reduction of ruthenium and stabilise the nanoparticle formed to allow for a successful hydrogenation of carbon dioxide towards methane.

Considering the effect of temperature, minimal temperature that was needed to perform the reaction was 120°C. Increase of the temperature from 120°C to 150°C corresponded to higher catalytical activity. Keeping the same amount of the catalyst, increase of temperature gave a higher yield of the hydrogenation of carbon dioxide in ruthenium nanoparticles formed in ionic liquid media.

Among the same family of ionic liquids, solubility of carbon dioxide in ionic liquid that reduced ionic liquid viscosity is an important parameter in reactions performed in high pressure conditions. The ionic liquid that becomes less viscous could suit as a better stabiliser of the nanoparticles. TEM and UV analyses were used to characterise the nanoparticles formed.

The performed reduction of carbon dioxide was the most effective using 1-methyl-3-octylimidazolium bis(trifluoromethylsulfonyl)imide allowing to produce methane with the highest yield at moderate conditions.\[11\]
4 CONCLUSIONS

A successful hydrogenation of carbon dioxide hydrogenation to methane using ruthenium nanoparticles prepared in situ in the presence of imidazolium based ionic liquid media was accomplished.

5 REFERENCES