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Catalytic Hydrogenation of CO₂ to Formate by Immobilized Ruthenium on Phosphine Catalysts

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PURPOSE OF THE ABSTRACT

1. Introduction

The utilization of CO₂ as abundant C1 building block has attracted considerable attention in times of increasing CO₂ emissions, causing detrimental consequences for the environment and society. Its catalytic conversion with H₂, produced by electrochemical water splitting, establishes a sustainable synthesis of formic acid. Recently, formic acid is intensively discussed as H₂ storage medium and as valuable platform chemicals, which encourages the development of efficient catalysts.[1]

Numerous homogeneous catalysts have been published, achieving high activities and selectivities but significant drawbacks in the catalyst separation, recycling and stability are present. On the other hand, desired heterogeneous catalysts such as bulk metal catalysts and supported metal catalysts suffer from low and inefficient conversions. Therefore, immobilized catalysts based on the grafting or direct immobilization of molecular complexes onto functionalized materials were described.[2] Especially, the heterogenization of phosphorus ligands is of particular interest and the polymeric analogs of PPh₃ (pTPP) and DPPE (pDPPE) already showed high activity in the decomposition of aqueous formic acid.[3] Here, we present the immobilization of molecular [RuCl₂(p-cymene)]₂ on heterogenized phosphorus ligands for the catalytic hydrogenation of CO₂ to formate.[4]

2. Results

Phosphine polymers pTPP, pDPPE and pTPPB were prepared by lithiation of 4,4'-dibromodiphenyl or 1,3,5-tris(4-bromophenyl)benzene followed by reaction with the respective chlorophosphine. The resulting polymers are amorphous, thermally stable and microporous with BET surface areas of 50 - 420 m² g⁻¹. The proposed chemical structures were confirmed by solid-state ¹³C and ³¹P NMR. These polymers were used as support materials for the immobilization of 1 wt% [RuCl₂(p-cymene)]₂. TEM analysis of the prepared catalysts revealed the absence of nanoparticles and XPS measurements confirmed Ru species with an oxidation state of +2. Solid-state MAS ³¹P NMR showed that all phosphine centers are accessible for coordination and mainly bidentate ruthenium complexes are formed.

Ru@phosphine catalysts exhibited excellent productivities in the catalytic hydrogenation of CO₂ under mild conditions in the absence of CO formation (Figure 1). These catalysts exceed the catalytic activity of commercial Ru/C and the homogeneous complexes, while the Ru@pDPPE presented the highest activity of phosphine based catalysts (Figure 2). A maximum TON of 13,170 was obtained after parameter optimization. The catalyst was

already active at 40 °C and a catalyst loading of only 0.0006 mol%.

Recycling experiments revealed a drop in activity after the first run followed by a gradual decrease in the subsequent runs. This is attributed to a change of the catalytically active complex during the hydrogenation reaction. In all runs, the CO formation was suppressed and low leaching was maintained. In addition, a mechanism for the CO₂ hydrogenation to formate was proposed based on the catalyst characterization.

3. Conclusions

The synthesis and characterization of novel phosphine polymers is presented. The immobilization of [Ru(p-cymene)Cl₂]₂ onto these polyphosphines presented a remarkable catalytic productivity and selectivity in the hydrogenation of CO₂ to formate under mild conditions. The best reported catalyst is Ru@pDPPE, reaching a maximum TON of 13,170. The change of coordination environment of Ru was evaluated during the CO₂ hydrogenation and a mechanism is proposed.

4. Acknowledgement

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FIGURES

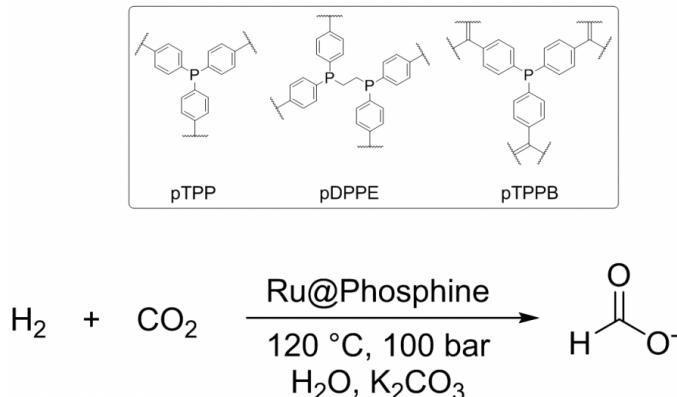


FIGURE 1
Ru-catalyzed CO_2 hydrogenation to formate under mild reaction conditions..
Phosphine polymers as support materials.

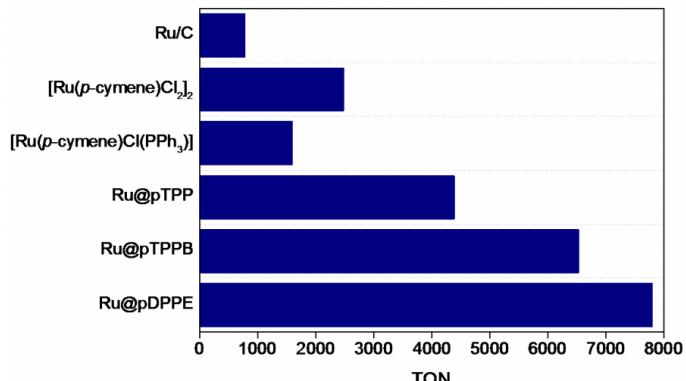


FIGURE 2
Catalytic productivity of Ru immobilized phosphines in comparison to commercial homogeneous and heterogeneous catalysts.
Reaction conditions: 50 mL Hastelloy autoclave, water (10 mL), Ru (0.0026 mol%), 1 wt% Ru@Phosphine, 5wt% Ru@C, 120 °C, 100 bar CO_2/H_2 (1:1 v/v), 2.59M K_2CO_3 , 4 h.
TON=mol(formate) per mol(Ru).

KEYWORDS

CO_2 conversion | Heterogeneous catalysis | hydrogenation | phosphines

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