Solid Catalyst with Ionic Liquid Layer (SCILL) for Direct CO_2 Hydrogenation to Methanol: Enhancing Performance and Stability

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Significance and Relevance

This research investigates the use of **S**olid **C**atalysts with **I**onic **L**iquid Layers (**SCILL**) for CO_2 direct hydrogenation to methanol with copper-based methanol synthesis catalysts (CZA). Ionic liquids (ILs), known as "designer solvents" for their tunable properties, offer excellent gas solubility, particularly for CO2, making them ideal for enhancing catalytic processes like hydrogenation and enabling efficient, high-temperature applications. Initial results indicated lower methanol yields compared to the uncoated heterogeneous catalyst, likely due to stability issues with the **SCILL** system in the presence of water. However, the introduction of Ionic liquid Li[NTf_2] doping led to a significant improvement in catalytic performance, enhancing CH_3OH conversion rates compared to traditional CZA. Additionally, this doping increased system stability, especially in the presence of water. These results highlight the potential of SCILL catalysts as a more efficient and stable solution for CO_2 hydrogenation, contributing to sustainable methanol production and CO_2 mitigation.

Preferred and 2nd choice for the topic:
1st choice: CO_2 utilization and recycling;
2nd choice: Sustainable and clean energy production and transport.
Preferred presentation: *Poster*

Introduction and Motivations

This study explores an innovative method for CO_2 hydrogenation to methanol, aiming to enhance conversion efficiency through a Solid Catalyst with Ionic Liquid Layer (SCILL). By integrating an ionic liquid (IL) layer onto a commercial $Cu/ZnO/Al_2O_3$ catalyst, we aim to improve both stability and catalytic performance. Initially, various ILs were evaluated for their thermal stability using advanced thermogravimetric analysis (TGA). The most stable ILs were selected to form SCILL catalysts with a 10% IL loading. When tested for CO_2 hydrogenation, the SCILL catalysts exhibited significantly improved CO_2 conversion rates compared to conventional catalysts. Furthermore, the incorporation of Li[NTf_2] into the SCILL system enhanced its stability, mitigating the adverse effects of water deactivation observed in untreated SCILL catalysts.

Materials and Methods

In this work, several ionic liquids (ILs), including [PPh_4][$C_4F_9SO_3$], [SPh_3][$C_8F_{17}SO_3$], [SPh_3][$C_4F_9SO_3$], [PPh_4][NTf_2], and [SPh_3][NTf_2], were explored alongside a copper-based catalyst (CZA) to develop Solid Catalysts with Ionic Liquid Layers (SCILL). The SCILL catalysts were prepared by combining CZA with ILs in methanol, while doping with Li[NTf2] further modified the system. A thorough characterization of the materials was conducted using techniques such as ICP-OES, BET surface area analysis, XRD, and TPR. The stability of the ILs was studied through dynamic and isothermal TGA, and their degradation behavior was analyzed. The study also assessed the performance and longevity of these ILs under reaction conditions rich in hydrogen. Finally, reactor tests for CO_2 hydrogenation were carried out at 250°C and 20 bar (CO_2/H_2 ratio of 1:3) to evaluate both the SCILL catalysts and the commercial CZA catalyst, providing insights into their practical applications and stability.

Results and Discussion

This study investigates the hydrogenation of CO_2 using a commercial copper-zinc-alumina (CZA) catalyst and a Solid Catalyst with Ionic Liquid Layer (SCILL) system. A range of ionic liquids (ILs), including $[PPh_4][C_4F_9SO_3]$, $[SPh_3][C_8F_{17}SO_3]$, $[PPh_4][NTf_2]$, and others, were synthesized and characterized to assess their thermal stability for SCILL applications. Two ILs, $[PPh_4][C_4F_9SO_3]$ and $[PPh_4][NTf_2]$, were identified as the most thermally stable, with $[PPh_4][NTf_2]$ showing the highest activation energy (Ea) and pre-exponential factor, suggesting excellent thermal stability under reaction conditions.

Table 1. *Results from Arrhenius plots and errors calculated through validation of the kinetic model*

IL	Activation Energy [kJ/mol]	Pre-exponential factor [h^{-1}]	R^2	Validation T [°C]	Mass error after 10 h [%]
$[PPh_4][C_4F_9SO_3]$	139.9	$2.38 \cdot 10^{12}$	0.9903	273	0.64
$[PPh_4][NTf_2]$	182.2	$4.98 \cdot 10^{15}$	0.9922	295	0.04

These ILs were subjected to thermal stability tests in nitrogen at 250°C and 20 bar over 10 hours, where they showed good resistance. However, degradation was observed in a $CO_2/H_2/H_2O$ mixture. To enhance the system's stability, SCILLs were doped with $Li[NTf_2]$, which significantly improved stability, allowing the doped systems to retain CO_2 absorption capabilities under harsh reaction conditions.

The performance of these doped SCILL systems was evaluated in CO2 hydrogenation reactions (250°C, 20 bar, CO_2/H_2 1:3) over 35 hours. $[PPh_4][C_4F_9SO_3]$ doped with $Li[NTf_2]$ achieved a 25% CO_2 conversion rate, outperforming both the commercial CZA catalyst (10%) and the undoped $[PPh_4][NTf_2]$ (2%). However, the doped system showed a shift in selectivity, favoring CO production instead of methanol. NMR analysis revealed degradation of the phenyl group in $[PPh_4][NTf_2]$, contributing to changes in the product distribution. These results demonstrate the potential of SCILL systems to enhance CO_2 hydrogenation efficiency while highlighting the trade-off in selectivity.

Table 2. *Results of catalytic testing at 250°C and 20 bar, CO2/H2 1:3*

	X CO_2 (%)	Selectivity (%)				
		CH_4	Acetone	DME	CH_3OH	CO
CZA	10.0	0	1.61	8.86	21.9	67.62
$[PPh_4][C_4F_9SO_3]$ doped $Li[NTf_2]$	25.0	0	0	0.15	0.03	99.83
$[PPh_4][NTf_2]$ doped $Li[NTf_2]$	3.4	0.05	0	1	2.88	96.06

References

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