

Solid Catalyst with Ionic Liquid Layer (SCILL) for the direct hydrogenation of CO₂ into methanol

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Introduction

The potential of converting CO₂ into valuable products, such as methane, dimethyl ether, methanol, and gasoline-range hydrocarbons, offers a promising solution for reducing CO₂ emissions and addressing fossil fuel depletion. This study aimed to pioneer a novel approach by developing a Solid Catalyst with Ionic Liquid Layer (SCILL) for the direct hydrogenation of CO₂ into methanol. This was achieved by applying an ionic liquid (IL) layer to a commercial Cu/ZnO/Al₂O₃ catalyst. Initially, a thorough assessment of the thermal stabilities of various ILs was carried out using both static and dynamic thermogravimetric analysis (TGA). The ILs demonstrating exceptional thermal stability were chosen to create SCILL catalysts with a 10% IL loading. During reaction testing, the SCILL catalysts exhibited superior CO₂ conversion, outperforming the commercial catalyst's activity under similar conditions. Furthermore, the introduction of Li[NTf₂] in the SCILL systems effectively stabilized the system, countering the negative effects of water deactivation observed in the undoped SCILL.

Materials and Methods

This study involved a comprehensive set of various ionic liquids (ILs) (eg. [PPh₄][C₄F₉SO₃], [SPH₃][C₈F₁₇SO₃], [SPH₃][C₄F₉SO₃], [PPh₄][NTf₂], [SPH₃][NTf₂] and copper-based methanol synthesis catalyst (CZA), for the development of Solid Catalyst with Ionic Liquid Layer (SCILL) systems. The SCILL preparation entailed the mixing of CZA and IL in methanol, while the doped SCILL systems were created by adding Li[NTf₂]. Extensive material characterization was carried out using various techniques like inductively coupled plasma optical emission spectroscopy (ICP-OES), BET analysis, X-ray diffractor (XRD), and temperature programmed reduction (TPR). The thermal stability of ILs was assessed through dynamic and isothermal TGA, and their degradation kinetics were determined. The study included an examination of the stability of ILs under actual reaction conditions, specifically in a hydrogen-rich atmosphere. Finally, reactor tests (250°C and 20 bar, CO₂/H₂ 1:3) for CO₂ hydrogenation were conducted using both the commercial CZA catalyst and SCILL catalysts, providing insights into the performance and stability of the SCILL systems in practical applications.

Results and Discussion

The study investigated the hydrogenation of carbon dioxide using a commercial copper zinc alumina (CZA) catalyst and compared it with a Solid Catalyst with Ionic Liquid Layer (SCILL)

system. Before the reaction tests, a series of ionic liquids (ILs) were synthesized and characterized to determine their suitability, particularly their thermal stability, for use in the SCILL system. Two ILs capable of withstanding temperatures exceeding 250°C were identified as the most promising candidates: [PPh₄][C₄F₉SO₃] and [PPh₄][NTf₂]. The study then investigated the degradation rate of these ILs, using a zero-order degradation rate and Arrhenius's law to calculate activation energy (E_a) and pre-exponential factors. This analysis revealed that [PPh₄][NTf₂] had the highest E_a, confirming its exceptional stability (Table 1).

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 ₄ F ₉ SO ₃]	139.9	2.38·10 ¹²	0.9903	273	0.64
[PPh ₄][NTf ₂]	182.2	4.98·10 ¹⁵	0.9922	295	0.04

The thermal stability of PPh₄[C₄F₉SO₃] and [PPh₄][NTf₂] was examined at 250°C and 20 bar in a nitrogen atmosphere for 10 hours, demonstrating high stability. However, degradation occurred when exposed to a CO₂/H₂/H₂O mixture. To enhance stability and prevent degradation under reaction conditions, SCILLs were doped with Li[NTf₂]. This doping improved stability, and the doped systems retained their CO₂ absorption capabilities at 250°C and 20 bar. After the doping, the SCILL systems were used for CO₂ hydrogenation reaction test, resulting in a visibly stable system. The conversion rates and selectivity of the doped SCILL systems were evaluated over 35 hours of operation. [PPh₄][C₄F₉SO₃] doped with Li[NTf₂] exhibited the highest conversion rate (25%) compared to CZA (10%) and [PPh₄][NTf₂] doped with Li[NTf₂] (2%) (Table 2). However, the doped system showed decreased selectivity for methanol production and increased selectivity for CO production. NMR analysis revealed structural changes in [PPh₄][NTf₂] due to the degradation of the phenyl group.

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 ₃ OH	CO
CZA	10.0	0	1.61	8.86	21.9	67.62
[PPh ₄][C ₄ F ₉ SO 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

Significance

This study aimed to advance Solid Catalyst with Ionic Liquid Layer (SCILL) catalysts for CO₂ hydrogenation to methanol. Initial reactions showed reduced methanol production, possibly due to SCILL system stability. Li[NTf₂] doping significantly improved performance, increasing methanol conversion compared to conventional CZA catalysts. It also enhanced system stability in the presence of water. These findings mark a promising step toward more efficient and sustainable catalytic processes, reducing CO₂ emissions and aiding methanol production.

References

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