The 29th North American Catalysis Society Meeting (NAM29)
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SiO_2-Coated Cu-Based Catalysts for Efficient CH_3OH Production from CO_2

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Introduction

Methanol production is traditionally carried out from natural gas or coal via the syngas route. However, renewable methanol production through CO_2 hydrogenation emerges as a promising alternative to reduce greenhouse gas emissions. [1,2] Despite advances in Cu-based catalysts for this reaction, the aggregation of the active phase under reaction conditions remains a challenge. [3] Conventional catalysts like $Cu/ZnO/Al_2O_3$ exhibit limitations in the direct conversion of CO_2. [4] Recent research focuses on improving activity and stability with catalysts such as Cu/ZrO_2 and Cu/CeO_2, where metal-oxide interaction promotes the adsorption and activation of reagents. Chemical promotion with low loads of In_2O_3 has been shown to enhance metal-support interaction. This work explored the improvement of the physical properties of these catalysts through coating with a mesoporous SiO_2 layer.

Materials and Methods

Nanoparticles of $Cu/In_2O_3/CeO_2$ and $Cu/In_2O_3/ZrO_2$ were synthesized and coated with a mesoporous SiO_2 shell, using CTAB and TEOS as precursors. The resulting catalysts were named CuCeIn@mSiO_2 and CuZrIn@mSiO_2, and were compared with the uncoated materials CuCeIn and CuZrIn. The SiO_2 shell accounted for 80% by weight of the composition of the coated catalysts. Structural properties were characterized by X-ray diffraction (XRD) and N_2 adsorption-desorption isotherms. Reducibility was evaluated by temperature-programmed reduction (TPR), and morphology by transmission electron microscopy (TEM). The metallic surface area was accessed through H_2 consumption after controlled oxidation of surface copper with N_2O. Catalytic activity was assessed in CO_2 hydrogenation under various conditions of temperature, pressure, and WHSV. A chemometric analysis was conducted to optimize the reaction conditions.

Results and Discussion

XRD and TEM analyses revealed that the mesoporous SiO_2 coating limited nanoparticle size to up to 3.5 nm, preventing active phase aggregation during thermal treatment. N_2 isotherms showed a considerable increase in the BET surface area and pore volume of the coated catalysts, indicating the presence of the mesoporous structure. TPR profiles of the coated materials exhibited a single narrow peak, suggesting high homogeneity in particle size. Copper dispersion in the coated catalysts was 3 to 4 times higher than in the uncoated ones. The coated catalysts also demonstrated greater basicity. Turnover frequency (TOF) analysis indicated higher efficiency for the coated catalysts, with a significant increase in TOF for methanol and a decrease in TOF for CO, suggesting suppression of the rWGS reaction. Apparent activation energies showed that the chemical nature of the active site is consistent, but the SiO_2 layer prevents surface restructuring. Chemometric analysis revealed that the coated catalysts are particularly advantageous at high temperatures, where particle aggregation is more intense in uncoated catalysts, maintaining high methanol selectivity and leading to significantly higher methanol productivity. Reuse tests under severe conditions confirmed the high productivity and stability of the coated catalysts, with nanoparticle size maintenance.

Table 1. Physical and chemical properties of SiO_2-coated and uncoated CuZrIn and CuCeIn catalysts.

Catalyst	A_{BET} ($m^2 \cdot g^{-1}$)	V_{meso} ($cm^3 \cdot g^{-1}$)	d_{pore} (nm)	Cu dispersion (%)	Basicity ($\mu mol_{CO2} \cdot g^{-1}$)
CuCeIn@mSiO_2	192	0.59	5.4	22.7	288
CuCeIn	46	0.05	-	6.5	242
CuZrIn@mSiO_2	235	0.95	5.4	29.6	194
CuZrIn	29	0.03	-	10.0	126

Table 2. Turnover frequency (TOF) and apparent activation energies for rWGS and methanol synthesis over uncoated and SiO_2-coated CuCeIn and CuZrIn catalysts.

Catalyst	TOF (10^{-3} s^{-1})[a]			Apparent activation energy (kJ mol^{-1})	
	CO (rWGS)	CH_3OH	Total	CO (rWGS)	CH_3OH
CuCeIn@mSiO_2	0.13	3.30	3.43	105.0	37.2
CuCeIn	0.81	1.31	2.12	116.3	43.1
CuZrIn@mSiO_2	0.14	2.94	3.08	92.9	32.6
CuZrIn	0.93	2.23	3.16	97.1	36.0

[a]reaction conditions: T = 498 K, P = 2.5 MPa and WHSV = 14000 $mL \cdot g^{-1} \cdot h^{-1}$, $X_{CO2} \leq 4.2\%$.

Significance

The significance of this work lies in the substantial improvement of Cu-based catalysts for CO_2 hydrogenation to methanol through a mesoporous SiO_2 coating. This strategy limited nanoparticle aggregation, resulting in higher activity and selectivity, especially under severe reaction conditions, and significantly increased methanol yield. The study proposes a novel approach for designing more efficient and stable catalysts for renewable methanol production.

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