

**ELUCIDATING THE ROLE OF METAL OXIDE
INTERACTIONS AND OXYGEN VACANCY DEFECTS IN
TUNING THE METHANOL AND DME SELECTIVITY DURING
CO₂ HYDROGENATION**

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TUNING THE METHANOL AND DME SELECTIVITY
DURING CO₂ HYDROGENATION**

by

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Certificate

This is to certify that the thesis entitled “**Elucidating the role of metal oxide interactions and Oxygen vacancy defects in tuning the methanol and DME selectivity during CO₂ hydrogenation**” submitted by Mr. Rajan Singh to the Indian Institute of Technology Delhi for the award of the degree of Doctor of Philosophy, is a record of the original bonafide research work carried out by him. He has worked under my supervision and has fulfilled the requirements, which to my knowledge, has reached the requisite standard for the submission of this thesis. The results contained in this thesis have not been submitted in part or full to any University or Institute for the award of any degree or diploma



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Abstract

To satisfy the energy demand of an increasing population fossil fuel reserves are being exploited at an unprecedented rate. The burning of these fossil fuels produces CO₂, which is the main constituent of greenhouse gases and leads to global warming. Therefore, use of CO₂ as feed for methanol and DME production can be a possible route to close the anthropogenic carbon cycle. The reverse water gas shift reaction (RWGS) poses major challenge to the design of methanol selective catalyst. Recently oxygen deficient catalytic system like In₂O₃, ZnO-ZrO₂ and Zn₂Ga₂O₄ have been documented to be very selective for methanol synthesis reaction even at high temperature (300°C). The oxygen defective sites are helpful in CO₂ activation. However, the catalytic activity of these oxygen deficient catalytic system is low due to absence of metallic sites for H₂ adsorption. Studies reporting interaction between the metallic Cu and oxygen deficient supports, and its consequence in the catalytic performance are a few.

In this regard, a comparative study to investigate the role of oxygen vacancies and basic site density in tuning methanol selectivity during CO₂ hydrogenation over Cu/CeO₂, CuZrO₂ and Cu/ZnO catalyst was performed. The catalysts were prepared by constant pH co-precipitation method and their catalytic performance was evaluated in a fixed bed tubular reactor. The methanol selectivity over Cu/CeO₂ catalyst reaches 90% at 220°C, 30 bar and 2400 mL g_{cat}⁻¹ h⁻¹. The abundance of oxygen defects on the Cu/CeO₂ catalyst surface facilitates formation of unidentate carbonate species, which leads to selective methanol synthesis. The concentration of the oxygen vacancies was altered by preparing Cu/CeO₂ catalyst with co-precipitation, surfactant assisted co-precipitation and sol-gel method. The improved catalytic activity of Cu/CeO₂ catalyst prepared by sol-gel method is ascribed superior physicochemical properties like Cu surface area, small Cu particle size, strong basic site density and oxygen vacancy defects. The H₂-TPR and XPS results confirms partial reduction of Ce⁴⁺ to Ce³⁺. This reduced

CeO₂ promotes CO₂ adsorption and activation. The methanol space time yield for Cu/CeO₂-SG catalyst reaches 70.8 g kg_{cat}⁻¹ h⁻¹ at 30 bar, 260 °C, 7200 mL kg_{cat}⁻¹ h⁻¹ and CO₂:H₂ ratio 1:3. Further as CeO₂ supported Cu catalyst was more selective towards methanol synthesis reaction. CeO₂ was incorporated as promoter into the conventional Cu/ZnO catalyst and for a constant Cu wt% (70 wt%), the ratio of Zn/Ce was optimized. The catalytic activity of Cu/ZnO/CeO₂ catalyst reached maximum for Zn/Ce ratio of 2:1 and was 106.4 g kg_{cat}⁻¹ h⁻¹ at 30 bar, 250°C, 3000 mLg_{cat}⁻¹ h⁻¹ and 1:3 H₂/CO₂ ratio. The kinetic data was measured within 220°C-310°C temperature, 10-30 bar pressure, 3000-7500 mLg_{cat}⁻¹ h⁻¹ GHSV and 1:1, 1:2, 1:3, 1:4 and 1:5 CO₂:H₂ ratio. The dual site LHHW model with formate hydrogenation as the rate determining step fitted well to the experimental results.

Single step DME synthesis poses additional advantage of overcoming the thermodynamic barrier for CO₂ hydrogenation to methanol. However, excess water produced in the methanol dehydration deactivates catalytic performance. Therefore, mildly hydrophobic ZrO₂ is used as promoter to the Cu/ZnO catalyst. The synergistic effect between Cu, Zn and Zr oxides leads to higher DME selectivity and consequently inhibit the side reactions over the bifunctional catalyst. The ZnO-ZrO₂ interaction leads to formation of oxygen defective sites and improve the activity of bifunctional catalyst. The methanol and DME selectivity reach up to 19% and 60% respectively with 14% CO₂ conversion at 30 bar, 260°C, 2400 mLg_{cat}⁻¹ h⁻¹ and 1:3 CO₂/H₂ ratio. Altogether the tuning metal oxide interactions and oxygen vacancy defects is the keys to enhance methanol yield by CO₂ hydrogenation.

सारांश

एक बढ़ती हुई आबादी की ऊर्जा मांग को पूरा करने के लिए जीवाश्म ईंधन का अभूतपूर्व दर से दोहन किया जा रहा है। इन जीवाश्म ईंधनों के जलने से CO_2 पैदा होती है, जो ग्रीनहाउस गैसों का मुख्य घटक है और ग्लोबल वार्मिंग की ओर ले जाती है। इसलिए, मेथनॉल और डीएमई उत्पादन के लिए फ़ीड के रूप में CO_2 का उपयोग मानवजनित कार्बन चक्र को बंद करने का एक संभावित मार्ग हो सकता है। रिवर्स वॉटर गैस शिफ्ट रिएक्शन (RWGS) मेथनॉल चयनात्मक उत्प्रेरक के डिजाइन के लिए बड़ी चुनौती है। हाल ही में ऑक्सीजन अभावपूर्ण उत्प्रेरक जैसे In_2O_3 , ZnO-ZrO_2 और $\text{Zn}_2\text{Ga}_2\text{O}_4$ को उच्च तापमान (300 डिग्री सेल्सियस) पर भी मेथनॉल संश्लेषण प्रतिक्रिया के लिए बहुत चयनात्मक होने के लिए प्रलेखित किया गया है। ऑक्सीजन दोषपूर्ण स्थल CO_2 सक्रियण में सहायक होते हैं। हालांकि, H_2 अवशोषण के लिए धातु स्थलों की अनुपस्थिति के कारण इन ऑक्सीजन की कमी वाले उत्प्रेरकों की उत्प्रेरकता गतिविधि कम है। धातुयुक्त सहायकों और ऑक्सीजन दोषपूर्ण समर्थन के बीच संवेदनशीलता में अवसरों की रिपोर्ट करने वाले अध्ययनों परिणाम बहुत कम हैं।

इस संबंध में, Cu/CeO_2 , CuZrO_2 और Cu/ZnO उत्प्रेरक पर CO_2 हाइड्रोजनीकरण के दौरान मेथनॉल चयनात्मकता समायोजन में ऑक्सीजन रिक्तियों और बुनियादी साइट घनत्व की भूमिका की जांच करने के लिए एक तुलनात्मक अध्ययन किया गया था। उत्प्रेरक निरंतर पीएच सह-वर्षा विधि द्वारा तैयार किए गए थे और उनके उत्प्रेरक प्रदर्शन का मूल्यांकन फिक्स्ड बेड ट्यूबलर रिएक्टर में किया गया था। Cu/CeO_2 उत्प्रेरक पर मेथनॉल चयनात्मकता 220°C , 30 बार और $2400 \text{ mL gcat}^{-1} \text{ h}^{-1}$ पर 90% तक पहुंच जाती है। Cu/CeO_2 उत्प्रेरक सतह सुविधाओं पर ऑक्सीजन दोषों की प्रचुरता एकरूप कार्बोनेट प्रजातियों का निर्माण करती है, जो चयनात्मक मेथनॉल संश्लेषण की ओर ले जाती है। सह-वर्षा, सर्फैक्टेंट सहायक सह-वर्षा और सोल-जेल विधि के साथ Cu/CeO_2 उत्प्रेरक तैयार करके ऑक्सीजन रिक्तियों की एकाग्रता को बदल दिया गया था। सोल-जेल विधि द्वारा तैयार Cu/CeO_2 उत्प्रेरक की बेहतर उत्प्रेरक

गतिविधि को Cu सतह क्षेत्र, छोटे Cu कण आकार, मजबूत बुनियादी साइट घनत्व और ऑक्सीजन रिक्ति दोष जैसे बेहतर भौतिक-रासायनिक गुण दिए गए हैं। H₂-TPR और XPS परिणाम Ce₄₊ के Ce₃₊ में आंशिक कमी की पुष्टि करते हैं। CO₂ विज्ञापन और सक्रिय करने को बढ़ावा दिया है। Cu/CeO₂-SG उत्प्रेरक के लिए मेथनॉल स्पेस टाइम यील्ड 70.8 g kg_{cat}⁻¹ h⁻¹ 30 बार, 260 °C, 7200 mL kg_{cat}⁻¹ h⁻¹ और CO₂:H₂ अनुपात 1: 3. इसके अलावा CeO₂ समर्थित Cu उत्प्रेरक मेथनॉल संश्लेषण प्रतिक्रिया के प्रति अधिक चयनात्मक था। CeO₂ को पारंपरिक Cu/ZnO उत्प्रेरक में प्रमोटर के रूप में शामिल किया गया था और स्थिर Cu wt% (70 wt%) के लिए, Zn/Ce के अनुपात को अनुकूलित किया गया था। Cu/ZnO/CeO₂ उत्प्रेरक की उत्प्रेरक गतिविधि 2:1 के Zn/Ce अनुपात के लिए अधिकतम पहुंच गई और 30 बार, 250°C, 3000 mLg_{cat}⁻¹ h⁻¹ पर 106.4 g kg_{cat}⁻¹ h⁻¹ थी और 1:3 H₂/CO₂ अनुपात। काइनेटिक डेटा को 220°C-310°C तापमान, 10-30 बार प्रेशर, 3000-7500 mLg_{cat}⁻¹ h⁻¹ GHSV और 1:1, 1:2, 1:3, 1:4 और 1: 5 CO₂:H₂ अनुपात के भीतर मापा गया था। दर निर्धारित करने वाले चरण के रूप में फ़ॉर्मेट हाइड्रोजनीकरण के साथ दोहरी साइट LHHW मॉडल प्रयोगात्मक परिणामों के लिए अच्छी तरह से फिट है।

सिंगल स्टेप डीएमई संश्लेषण से मेथनॉल में CO₂ हाइड्रोजनीकरण के लिए उष्मागतिकी बाधा पर काबू पाने का अतिरिक्त लाभ मिलता है। हालांकि, मेथनॉल निर्जलीकरण में उत्पादित अतिरिक्त पानी उत्प्रेरक प्रदर्शन को निष्क्रिय कर देता है। इसलिए, हल्के जलविरोधी ZrO₂ का उपयोग Cu/ZnO उत्प्रेरक के प्रवर्तक के रूप में किया जाता है। Cu, Zn और Zr ऑक्साइड के बीच सहक्रियात्मक प्रभाव उच्च DME चयनात्मकता की ओर ले जाता है और परिणामस्वरूप द्विभाजित उत्प्रेरक पर पार्श्व प्रतिक्रियाओं को रोकता है। ZnO-ZrO₂ अन्योन्य क्रिया ऑक्सीजन दोषपूर्ण साइटों के गठन की ओर ले जाती है और द्वि-कार्यात्मक उत्प्रेरक की गतिविधि में सुधार करती है। 30 बार, 260°C, 2400 mLg_{cat}⁻¹ h⁻¹ और 1:3 CO₂/H₂ अनुपात में 14% CO₂ रूपांतरण के साथ मेथनॉल और DME चयनात्मकता क्रमशः 19% और

60% तक पहुंच जाती है। कुल मिलाकर ट्यूनिंग मेटल ऑक्साइड इंटरैक्शन और ऑक्सीजन रिक्ति दोष CO_2 हाइड्रोजनीकरण द्वारा मेथनॉल उपज बढ़ाने की कुंजी है।

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