SURFACE ENGINEERING OF METAL OXIDES INTERACTIONS AND DEFECT SITES FOR ENHANCED METHANOL SYNTHESIS FROM CO, CO2, AND CO-RICH SYNGAS IN A SLURRY REACTOR: A RATIONAL CATALYTIC DEVELOPMENT APPROACH

VAIBHAV PANDEY

DEPARTMENT OF CHEMICAL ENGINEERING

INDIAN INSTITUTE OF TECHNOLOGY DELHI

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by

VAIBHAV PANDEY

Department Of Chemical Engineering

Submitted

In fulfilment of the requirements of the degree of **DOCTOR OF PHILOSOPHY**

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Certificate

This is to certify that the thesis entitled "**Surface Engineering of Metal Oxides Interactions and Defect Sites for Enhanced Methanol Synthesis from CO, CO_2, and CO-Rich Syngas in a Slurry Reactor: A Rational Catalytic Development Approach**" submitted by **Mr. Vaibhav Pandey** to the Indian Institute of Technology Delhi for the award of the degree of **Doctor of Philosophy**, is a record of the original bona-fide 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.

Prof. Kamal K Pant
Supervisor
Department of Chemical Engineering
Indian Institute of Technology Delhi

Prof. Sreedevi Upadhyayula
Co-Supervisor
Department of Chemical Engineering
Indian Institute of Technology Delhi

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Vaibhav Pandey

Abstract

Heterogeneous catalysts play a pivotal role in large-scale industrial processes, yielding significant economic benefits by facilitating the production of value-added chemicals such as methanol. Methanol stands as a crucial building block for petrochemical industries and finds diverse applications. The development of catalysts and processes is imperative to address energy demands and mitigate the climate crisis, aligning with the urgency outlined in the Sustainable Development Goals (SDGs), of particular relevance are SDG-7, emphasizing 'Affordable and Clean Energy,' and SDG-13, focusing on 'Climate Action.' These underscore three primary concerns: reducing CO_2 emissions, closing the anthropogenic CO_2 cycle, and exploring alternatives to fossil fuels. Given the challenges associated with pure CO_2 feed conversion, including higher activation barriers and stable CO_2 molecules, attention shifts towards CO_2 co-fed syngas as a potential solution. This approach not only aids in closing the anthropogenic CO_2 cycle but also facilitates the formation of C1 chemicals, representing a form of CO_2 utilization. Furthermore, CO_2 co-feeding with syngas has been shown to improve catalytic activity. In industrial settings, methanol production typically occurs in fixed bed reactors (FBRs) operating at 200-300°C and 50-100 bar, employing $CuZnOAl_2O_3$ catalysts. However, FBRs are prone to catalyst deactivation primarily due to sintering and coke formation induced by excessive heat and inadequate temperature control. These drawbacks are addressed by slurry reactors, which maintain isothermal conditions and mitigate catalyst deactivation, thereby enhancing the efficiency of methanol production.

In this study, an investigation was conducted to examine the influence of solvent, basicity, and defect sites on a Cu-based catalyst synthesized via combustion, with subsequent performance testing in a stirred tank slurry reactor. Experimental findings were corroborated by theoretical insights, shedding light on the significance of moderate polarity in CO hydrogenation. Multicomponent Cu-based catalysts incorporating ZnO, MgO, and CeO_2 were synthesized using the solvent combustion method. The catalyst activity test was conducted for the hydrogenation of CO, CO_2, and mixed feed to methanol. The promotional effects of ZnO, CeO_2, and MgO on the physicochemical and structural properties were investigated, alongside their correlation with catalytic activity in the slurry reactor. The CuMgCe catalyst exhibited notable performance, achieving a conversion rate of 49.8%, methanol selectivity of 95%, and a space-time yield (STY) of 646 $g_{MeOH}/kg_{cat}\text{-}h^{-1}$. Furthermore, methanol-assisted synthesis led to a 5% increase in STY.

Additionally, the promotional role of CeO_2 on the CuZnMg catalyst demonstrated enhanced turnover frequency (0.0074 s^{-1}) and stability compared to CuMgCe.

In-depth characterization techniques unveiled the formation of CO_2 during CO temperature-programmed desorption coupled with mass spectrometry (CO-TPD-MS) and CO temperature-programmed reduction coupled with mass spectrometry (CO-TPR-MS), attributed to lattice oxygen. This process enhances the presence of surface species $CO_2^{\delta-}$, which serves as a highly active intermediate for the formation of intermediates like formate. Additionally, in-situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) demonstrated that formate intermediates play a significant role in the selective synthesis of methanol on the $CuMgOCeO_2$ catalyst. A mechanistic study elucidated the promotional effect of MgO and CeO_2 on the CuMgCe catalyst, synthesized in the laboratory, in enhancing methanol formation during CO_2-cofed syngas conversion to methanol. Density functional theory (DFT) calculations and in-situ DRIFTS experiments were conducted for micro-level studies and to elucidate the reaction mechanism. CuMgO and $CuCeO_2$ were found to exhibit higher activity for CO and CO_2 hydrogenation, respectively. Furthermore, the role of initial methanol concentration was investigated through in-situ DRIFTS, revealing insights into the mechanism of methanol-assisted synthesis. In summary, optimizing the methanol yield involves considering factors such as defect sites, basicity, initial methanol concentration, and tuning catalyst properties through the effects of supports. These findings underscore the importance of a comprehensive understanding of catalyst characteristics and reaction mechanisms in enhancing methanol synthesis efficiency.

सार

विजातीय उत्प्रेरक बड़े पैमाने पर औद्योगिक प्रक्रियाओं में महत्वपूर्ण भूमिका निभाते हैं, जो मेथनॉल जैसे मूल्यवर्धित रसायनों के उत्पादन को सुविधाजनक बनाकर महत्वपूर्ण आर्थिक लाभ प्रदान करते हैं। मेथनॉल पेट्रो-रसायन उद्योगों के लिए एक महत्वपूर्ण निर्माण खंड के रूप में खड़ा है और इसके विविध अनुप्रयोग हैं। उत्प्रेरक और प्रक्रियाओं का विकास ऊर्जा की मांगों को संबोधित करने और जलवायु संकट को कम करने के लिए अनिवार्य है, जो सतत विकास लक्ष्यों (एसडीजी) में उल्लिखित तात्कालिकता के साथ संरेखित है, विशेष रूप से प्रासंगिक एसडीजी- ७ हैं, जो 'सस्ती और स्वच्छ ऊर्जा' पर जोर देते हैं, और एसडीजी- १३ , जो 'जलवायु कार्रवाई' पर ध्यान केंद्रित करते हैं। ये तीन प्राथमिक चिंताओं को रेखांकित करते हैं: CO_2 उत्सर्जन को कम करना, मानवजनित CO_2 चक्र को बंद करना, और जीवाश्म ईंधन के विकल्पों की खोज करना। उच्च सक्रियण अवरोधों तथा स्थिर CO_2 अणुओं सहित शुद्ध CO_2 निविष्ट रूपांतरण से जुड़ी चुनौतियों को देखते हुए, संभावित समाधान के रूप में CO_2 सह- निविष्ट सिंथेटिक गैस (सिनगैस) की ओर ध्यान जाता है। यह दृष्टिकोण न केवल मानवजनित CO_2 चक्र को बंद करने में सहायता करता है बल्कि C1 रसायनों के निर्माण को भी सुगम बनाता है, जो CO_2 उपयोग का एक रूप है। इसके अलावा, सिनगैस के साथ CO_2 का सह-भक्षण उत्प्रेरक गतिविधि में सुधार करने के लिए दिखाया गया है। औद्योगिक समायोजन में, मेथनॉल उत्पादन आम तौर पर २००- ३०० डिग्री सेल्सियस और ५०- १०० बार पर संचालित फिक्स्ड बेड रिएक्टरों (एफबीआर) में होता है, जिसमें $CuZnOAl_2O_3$ उत्प्रेरक का उपयोग किया जाता है। हालांकि, एफबीआर मुख्य रूप से अत्यधिक गर्मी और अपर्याप्त तापमान नियंत्रण से प्रेरित सिंटरिंग और कोक गठन के कारण उत्प्रेरक निष्क्रियता के लिए प्रवण होते हैं। इन कमियों को स्लरी रिएक्टरों द्वारा संबोधित किया जाता है, जो समतापी स्थितियों को बनाए रखते हैं और उत्प्रेरक निष्क्रियता को कम करते हैं, जिससे मेथनॉल उत्पादन की दक्षता बढ़ जाती है। प्रायोगिक निष्कर्षों की पुष्टि सैद्धांतिक अंतर्दृष्टि द्वारा की गई, जो CO हाइड्रोजनीकरण में मध्यम ध्रुवीयता के महत्व पर प्रकाश डालती है। विलायक दहन विधि का उपयोग करके ZnO, MgO और CeO_2 को शामिल करने वाले बहुघटक Cu-आधारित उत्प्रेरक को संश्लेषित किया गया। CO, CO_2 और मेथनॉल में मिश्रित फ़ीड के हाइड्रोजनीकरण के लिए उत्प्रेरक गतिविधि परीक्षण किया गया। भौतिक और संरचनात्मक गुणों पर ZnO, CeO_2 और MgO के प्रचारात्मक प्रभावों की जांच की गई, साथ ही स्लरी रिएक्टर में उत्प्रेरक गतिविधि के साथ उनके सहसंबंध की भी जांच की गई। CuMgCe उत्प्रेरक ने उल्लेखनीय प्रदर्शन किया, ४९.८ % की रूपांतरण दर, ९५ % की मेथनॉल चयनात्मकता और ६४६ gMeOH/kgcat-h-1 की स्पेस-टाइम उपज (STY) प्राप्त की। इसके अलावा, मेथनॉल-सहायता प्राप्त संश्लेषण से STY में ५% की वृद्धि हुई। इसके अतिरिक्त, CuZnMg उत्प्रेरक पर CeO_2 की प्रचारात्मक भूमिका ने CuMgCe की तुलना में बढ़ी हुई टर्नओवर आवृत्ति (0.00७४ s-1) और स्थिरता का प्रदर्शन किया। गहन लक्षण वर्णन तकनीकों ने CO तापमान-क्रमादेशित विशोषण के दौरान द्रव्यमान स्पेक्ट्रोमेट्री (CO-TPD-MS) और CO तापमान-क्रमादेशित कमी के साथ द्रव्यमान स्पेक्ट्रोमेट्री (CO-TPR-MS) के दौरान CO_2 के गठन का खुलासा किया, जिसका श्रेय जालक ऑक्सीजन को दिया जाता है। यह प्रक्रिया सतह प्रजाति $CO_2^{\delta-}$ की उपस्थिति को बढ़ाती है, जो फॉर्मेट जैसे मध्यवर्ती अणुओं के गठन के लिए एक अत्यधिक सक्रिय मध्यवर्ती के रूप में कार्य करती है। इसके अतिरिक्त, स्वस्थानी डिफ्यूज रिफ्लेक्शन इंफ्रारेड फूरियर ट्रांसफॉर्म स्पेक्ट्रोस्कोपी (डीआरआईएफटीएस) ने प्रदर्शित किया कि फॉर्मेट मध्यवर्ती $CuMgOCeO_2$ उत्प्रेरक पर मेथनॉल के चयनात्मक संश्लेषण में महत्वपूर्ण भूमिका निभाते हैं एक यांत्रिक अध्ययन ने प्रयोगशाला में संश्लेषित CuMgCe उत्प्रेरक पर MgO और CeO_2 के प्रोत्साहन प्रभाव को स्पष्ट किया, जो CO_2- सह- निविष्ट सिंथेटिक गैस के मेथनॉल में रूपांतरण के दौरान मेथनॉल

निर्माण को बढ़ाता है। सूक्ष्म स्तर के अध्ययनों और प्रतिक्रिया तंत्र को स्पष्ट करने के लिए घनत्व कार्यात्मक सिद्धांत (डी एफ टी) गणना और स्वस्थानी डीआरआईएफटीएस प्रयोग किए गए। CuMgO और $CuCeO_2$ क्रमशः CO और CO_2 हाइड्रोजनीकरण के लिए उच्च गतिविधि प्रदर्शित करते पाए गए। इसके अलावा, स्वस्थानी डीआरआईएफटीएस के माध्यम से प्रारंभिक मेथनॉल सांद्रता की भूमिका की जांच की गई, जिससे मेथनॉल-सहायता प्राप्त संश्लेषण के तंत्र में अंतर्दृष्टि का पता चला। संक्षेप में, मेथनॉल उपज को अनुकूलित करने में उत्प्रेरक के दोष स्थलों, मूलता, प्रारंभिक मेथनॉल सांद्रता और समर्थन के प्रभावों के माध्यम से उत्प्रेरक गुणों को समंजन करने जैसे कारकों पर विचार करना शामिल है। ये निष्कर्ष मेथनॉल संश्लेषण दक्षता को बढ़ाने में उत्प्रेरक विशेषताओं और प्रतिक्रिया तंत्र की व्यापक समझ के महत्व को रेखांकित करते हैं।

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Thesis Contribution

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