Highly Active SiO2-supported Cu–ZnO Catalysts Prepared by Combustion Methods for Low-temperature Methanol Synthesis: Comparative Activity Test with or without SiO2 Support

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Nanostructured (Cu-ZnO/SiO2 and Cu/ZnO) catalysts are prepared by sol-gel and surface impregnation combustion methods with inexpensive raw materials and easily-operated conditions. The X-ray diffraction patterns and SEM analysis reveal that Cu crystallite and particle sizes prepared by surface impregnation combustion method are rather smaller. During the combustion process, the support SiO2 can absorb heat and promote heat transfer, realizing a significantly mild and smooth catalyst-preparation process. As-prepared catalysts are tested in low-temperature methanol synthesis from syngas containing CO2, with ethanol as a catalyst and solvent at 443 K and 5.0 MPa for 8 h. The activity and methanol selectivity of the supported Cu-ZnO/SiO2 catalyst are much higher, which are closely related the metallic Cu surface area and Cu crystalline sizes. The different properties of as-prepared catalysts are investigated by XRD, TG-DTA, FT-IR, Raman spectrum, SEM, BET and N2O chemisorption techniques in detail. Here, the support SiO2 has a function of heat transfer to make catalysts preparation process much smoother, besides the dispersion effect.

Keywords
Sol-gel, Combustion method, Methanol synthesis, Metallic catalyst, Supported copper-based catalyst

1. Introduction

Syngas produced from methane reforming, biomass gasification, or coal gasification can be catalytically converted in-situ via methanol synthesis (CO + 2H2 = CH3OH; CO2 + 3H2 = CH3OH + H2O), which exhibits excellent atomic economy, since the oxygen atom in CO is included in the products and CO2 can be blended into syngas as a reactant. Methanol is a kind of feedstock that is widely used in energy and chemical industries1,2). Methanol is also one type of important liquid fuels that can be supplied to modified internal combustion engines or fuel cells3,4).

The worldwide demand of methanol about 50 Mtons per year is industrially manufactured under high temperature and elevated pressure (523-573 K, 5-10 MPa)5), mainly using Cu/ZnO/Al2O3 catalysts developed by ICI. However, the conversion of one-pass methanol activity is severely limited by thermodynamics because methanol synthesis is an extremely exothermic reaction. According to our knowledge, one-pass conversion of an ICI plant is limited to only 14 % and about zero if the reaction temperature is lower than 473 K. Tsubaki et al. proposed a new route of low temperature methanol synthesis from CO/CO2/H2 on Cu/ZnO based catalysts using different lower alcohols as both catalysts and solvents, by which methanol is produced at 443 K and 5.0 MPa6,7).

For Cu-based catalysts used in methanol synthesis, it is well-accepted that crystallite size, BET surface area, metallic Cu0 surface area, and different preparation methods are important factors affecting catalytic activity and methanol selectivity. These factors are obviously influenced by different catalyst preparation methods. Verneker et al. reported a sol-gel auto-combustion technique based on the principles of propellant chemistry10) to produce high-purity, homogeneous, and crystalline oxide powders11-13). Few reports were available on combustion methods using urea or glycine as complex-
ant to prepare CuO-ZnO-ZrO₂ catalysts for CO₂ hydrogenation [14, 15], and on the usage of acetylacetonates of Cu, Zn, and Al to prepare catalysts to CO₂ hydrogenation [60] for methanol synthesis under higher reaction temperatures from 493 to 513 K. In our former report [17], a sol-gel auto-combustion method is proposed to prepare Cu/ZnO catalysts applied in low-temperature methanol synthesis. The effects of metals to citric acid mole ratios on the properties of Cu/ZnO catalysts and catalytic activity are systematically studied by multiple characterization methods. This technique proceeds via a combination of chemical sol-gel and subsequent combustion processes. First, an aqueous solution containing Cu and Zn nitrates with citric acid forms a gel through a sol-gel process. For this process, multi-carboxylic citric acid is the chelated reagent to form homogeneous precursors. Afterwards, the gel is ignited at a certain temperature in air to combust, yielding a voluminous and fluffy product. However, the combustion process of this sol-gel method is rather severer, which leads to extremely higher flame temperature, resulting in very larger Cu crystalline sizes and smaller metallic Cu surface area. Consequently, the activity and methanol selectivity are significantly influenced.

In the present work, surface impregnation combustion method is proposed to prepare highly pure and dispersed Cu-ZnO/SiO₂ catalyst, which exhibits rather higher activity and methanol selectivity if compared with those prepared by previous reported sol-gel auto-combustion method [17]. Here, the support SiO₂ has a function of heat transfer to make catalysts preparation process significantly smoother, besides dispersion effect, determining in smaller Cu crystalline sizes and larger metallic Cu surface area.

2. Experimental

2.1. Preparation of Catalysts

A schematic flow chart of the catalyst prepared by surface impregnation combustion method is presented in Fig. 1. Analytical-grade Cu(NO₃)₂·3H₂O, Zn(NO₃)₂·6H₂O and citric acid are used as raw materials. The metal nitrates with the mole ratio of Cu/Zn = 1/1 (noted as M, M = Cu²⁺ + Zn²⁺) and citric acid (noted as CA) are first dissolved in distilled water with M/CA molar ratio of 1/1.4, because the as-mentioned catalyst (M/CA = 1/1.4) was formerly proved [22] to exhibit better reaction results. The solutions are adjusted using ammonia to reach a pH value of 7. Stirring and refluxing at 353 K for 4 h ensure that the citric acid is completely chelated with the metal ions. Subsequently, the neutralized solution is evaporated at 343 K on a hot plate by continuously stirring until 10 mL dark blue solution with the concentration of 0.57 mol/L Cu²⁺ and Zn²⁺ is left. Afterwards, this dark blue solution is impregnated on 5 g silica (Caract Q-3, Fuji Silysia Co., specific surface area: 546 m²/g, pore volume: 0.3 mL/g) with 15 wt% Cu-ZnO loading. The precursor is dried at 393 K for 40 h. Then, the precursor is loaded in a muffle oven. The temperature is increased to about 493 K in air at a heating rate of 2 K/min, leading to the ignition of the precursor, which burns in a self-propagating combustion manner until completely burns out to form homogeneous powders. Subsequently, the temperature is continuously increased to about 723 K at a heating rate of 2 K/min and maintained for 3 h in air. The burnt catalyst is reduced by a flow of 5 % hydrogen in nitrogen at 523 K for 10 h and successively passivated by 1 % oxygen diluted by nitrogen, noted as Cₐ₁ZₓSₓ. For comparison, former reported Cu/ZnO catalyst prepared by sol-gel auto-combustion method is selected as reference and denoted as Cₐ₂Zₓ.

2.2. Characterization Techniques

The characterization conditions and methods of X-ray diffraction, scanning electron microscopy, temperature-programmed reduction, thermogravimetry differential thermal analysis, Fourier transform infrared spectroscopy, Raman analysis, Brunner-Emmett-Teller, and N₂O pulse techniques are the same as those reported in previous work [17].

2.3. Catalytic Activity Tests

A batch reactor with 85 mL inner volume and a stirrer is used to study the catalytic activity. Approximately 1 g catalyst and 40 mL ethanol are first poured in the autoclave. The air inside is purged by the reactant gas, Ar/CO/CO₂/H₂ = 3.13/33/5.23/58.64. Then, the pressure in the reactor is raised to 5.0 MPa at 298 K. The reaction conducts at 443 K for 8 h. The stirring speed is fixed at 2000 rpm to prevent the diffusion-controlled regime. All products are determined on gas chromatograph-mass spectrometer (GC-MS, Shimadzu GCMS).
A thermal conductivity detector (TCD, Shimadzu GC-320) and a flame ionization detector (FID, Shimadzu GC-8A) are used to analyze the gasous and the liquid products, respectively. The CO, CO₂, total carbon conversions, and the selectivity of the liquid products are calculated as follows:

\[
\text{CO conv.} = \frac{100 \times ([\text{CO/Ar in feed}] - [\text{CO/Ar in effluent}])}{[\text{CO/Ar in feed}]} \quad (1)
\]

\[
\text{CO₂ conv.} = \frac{100 \times ([\text{CO₂/Ar in feed}] - [\text{CO₂/Ar in effluent}])}{[\text{CO₂/Ar in feed}]} \quad (2)
\]

Total carbon conv. = \[
\text{CO conv.} \times a \times (a + b) + \text{CO₂ conv.} \times b \times (a + b) \quad (3)
\]

where a and b are the contents of CO and CO₂ in the feed gas.

The selectivity of the liquid products is calculated as follows:

\[
\text{Selectivity} = 100 \times \sum P_i \text{ yield} \quad (4)
\]

where \(P_i\) is the carbon mol number of each liquid product from reactants.

TOF is the total carbon turnover frequency:

\[
\text{TOF \ (batch reaction)} = \frac{\left(85 - 40\right) \times 50 \times 38.23 \% \times \text{total carbon conv} \times 6.02 \times 10^{23}}{\left(3600 \times 1000 \times 22.4 \times S_\text{Cu} \times \text{catalyst weight} \times \text{reaction hours} \times \text{Cu atom numbers of per square meter}\right)} \quad (5)
\]

where Cu atom numbers of per square meter is \(1.4 \times 10^{19}\).

3. Results and Discussion

3.1. Activity of the As-prepared Catalysts

The activity of the as-prepared \(CZ\) and \(CZ/S\) catalysts is investigated at 443 K and 5.0 MPa in batch reactor for 8 h in this new low-temperature slurry-phase methanol synthesis, which allows the use of solid catalysts, and syngas containing CO₂ and H₂O directly from an industrial reformer or biomass gasifier without deep purification. Characterization results of the as-prepared \(CZ\) and \(CZ/S\) catalysts, and batch reaction results for slurry-phase methanol synthesis are exhibited in Table 1. It is clear that the BET surface area of \(CZ/S\) catalyst is much larger than that of \(CZ\) catalyst. The larger BET surface area of \(CZ/S\) catalyst is mainly contributed by the SiO₂ support. As displayed in Table 1, the total carbon conversion of \(CZ/S\) is much higher than that of \(CZ\). This variation trend of the activity is in agreement with that of the copper (Cu⁰) surface area determined from N₂O pulse chemisorption method. According to the literatures, larger Cu⁰ surface area provides more active sites for hydrogenation. For this new route of methanol synthesis, metallic Cu⁰ is just the active site for the rate-determining step. According to the composition of the as-prepared catalysts, the weight ratio of Cu in \(CZ\) is about 44 wt%. However, the weight ratio of Cu in \(CZ/S\) is only about 4.4 wt%, which is about 10% of that in \(CZ\). But as displayed in Table 1, the metallic Cu⁰ surface area of \(CZ/S\) (10.7 m²/g) is significantly larger than that of \(CZ\) (7.7 m²/g), indicating that Cu⁰ particles are well dispersed on the surface of SiO₂.

It is notable in Table 1 that the methanol selectivity and yield are closely related to the variation of Cu crystalline sizes. As compared by both catalysts, the methanol selectivity significantly increases from 77.1 to 89.2% with Cu crystalline sizes decreasing from 34 (\(CZ\)) to 17 nm (\(CZ/S\)). The proposed mechanism in our previous work is that Cu⁺ and ZnO are active sites for the formation of formic esters and ethyl formate. However, only metallic Cu⁰ is the active site for the hydrogenation of ethyl formate to reach methanol. The smaller crystalline size and larger surface area of metallic Cu⁰ is beneficial in methanol formation, exhibiting higher hydrogenation capability. Consequently, \(CZ/S\) exhibits higher methanol selectivity than \(CZ\) with lower Cu dispersion.

3.2. Studies on the Thermal Behaviors by TG-DTA Analysis in Air

The thermal behavior of pure citric acid, and the precursors of \(CZ\) and \(CZ/S\) catalysts is investigated by thermogravimetry-differential thermal analysis (TG-DTA) measurements at 10 K/min from 293 to 1073 K.

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| Catalysts | \(S_{\text{BET}}\) [m²/g] | \(S_{\text{Cu}}\) [m²/g] | Cu dia. [nm] | Conversion [%] | TOF \(b\) \(10^{-3} \text{ s}^{-1}\) | Selectivity [%] | Yield [%] |
|-----------|-----------------|-----------------|-------------|----------------|----------------|----------------|----------|
| \(CZ\)    | 28.9            | 7.7             | 34          | 52.0           | 75.6           | 55.3           | 4.0      |
| \(CZ/S\)  | 394.2           | 10.7            | 17          | 59.2           | 77.6           | 61.7           | 3.2      |

Reaction conditions: \(T = 443\ K, P = 5.0\ MPa\), catalyst weight: 1 g, ethanol solvent: 40 mL, stirring speed: 2000 rpm, reaction time: 8 h, syngas: Ar/CO/CO₂/H₂ = 3.13/35/23/58.64.

a) Determined by N₂ physical adsorption-desorption at 77 K.
b) Determined from N₂O pulse chemisorption.
c) Calculated by Scherrer formula.
d) TOF is the total carbon turnover frequency.
e) HCOOR is ethyl formate.
in air with about 5 mg sample. During the combustion process, all the gels exhibit rapid self-propagating combustion manner until completely burning out to form homogenous precursors with uniform colors when the temperature increases up to about 493 K.

For comparison, the TG-DTA curve of pure citric acid is shown in Fig. 2a. The DTA plots exhibit two endothermic and one exothermal peaks, at 430, 473, and 683 K, respectively. The endothermic peak at 430 K is attributed to the melting of pure citric acid, because no weight loss is observed from the TG plots. Another endothermic peak at 473 K comes from the decomposition of citric acid accompanied by releasing a large amount of H₂O and CO₂. Meanwhile, the TG plots display the dominated weight loss. The exothermal peak at higher temperature (683 K) arises from the combination of amorphous carbon oxidation and pyrolysis of residue organics in air.

As compared in Fig. 2b for the precursor of CZ, the DTA plots display one extremely sharp exothermal peak and a shoulder peak at about 493 K in a very narrow temperature range. Meanwhile, the TG curves present an abrupt weight loss, suggesting that a severe redox reaction is proceeding wherein citric acid is the reductant, while nitrate ions and O₂ (in the air) are oxidants. During the combustion process, large amounts of gases, such as CO₂, H₂O, N₂, and NO₂ are liberated, which is confirmed by TG-MS analysis. The shoulder peak at lower than 493 K is derived from the overlapped accumulation of the energy absorbed by the decomposition of citric acid (as compared in Fig. 2a at about 473 K) and the energy released from the combustion process. The second exothermal peak at about 590 K arises from the oxidation of amorphous carbon, which is in good agreement with the experiment phenomena reported by Liu et al. and Pranda et al. The third exothermal peak at about 653 K is attributed to the pyrolysis of residue organics in air, which are further proven by Fourier transform infrared (FT-IR) and Raman spectrum.

Compared with the combustion process of CZ in Fig. 2b, the exothermal peak area of the precursor for CZS, which shifts to lower temperature, at about 486 K in Fig. 2c, is much smaller, suggesting that the combustion process is remarkably smoother and milder. Because during the combustion process, the generated heat, which contributes to the higher flame temperature, is rapidly transferred and absorbed by the support SiO₂, resulting in lower flame temperature. Cu crystalline sizes are significantly influenced by the flame temperature and the continued duration of high temperature. These results are in agreement with X-ray diffraction (XRD) analysis in Table 1 that metallic Cu⁰ crystalline size of CZ (34 nm) is rather larger than that of CZS (17 nm). For the preparation of CZ catalyst, carbon oxidation and pyrolysis of residue organics also contribute to the continued duration of high temperature. However, the second exothermal peak in Fig. 2c is also rather smaller and broader, indicating that carbon oxidation and pyrolysis of residue organics of CZS are much milder and smoother. In conclusion, combustion, carbon oxidation, and pyrolysis of residue organics processes of the precursor for CZS are very gentler. The support SiO₂ here has a function of heat absorption and diffusion to make catalyst preparation process rather smoother, besides the dispersion effect, resulting in smaller Cu crystalline size and larger metallic Cu sur-
3.3. XRD Analysis of CZ and CZ/S

The XRD patterns of the as-prepared CZ and CZ/S catalysts after reduction are compared in Fig. 3. Cu crystalline sizes of the as-prepared catalysts which are calculated by Scherrer equation are shown in Table 1. All diffraction peaks of CZ are attributed to Cu and ZnO phases in Fig. 3a, but Cu, ZnO and SiO2 phases are observed in Fig. 3b. The small embossment in Fig. 3a at about 27° was a baseline drift. Cu crystalline size of CZ/S (Cu-ZnO/SiO2) is only 17 nm, significantly smaller than that of CZ without support, suggesting that Cu-ZnO phase is well dispersed on SiO2 support. This phenomenon is in agreement with TG-DTA analysis that energy released from the catalyst preparation processes is rapidly absorbed and transported by the support. Consequently, heat cannot be accumulated to induce higher temperature. Hence, the Cu and ZnO crystalline sizes of the supported catalyst CZ/S (Cu-ZnO/SiO2) is much smaller.

3.4. SEM Analysis of CZ and CZ/S

Scanning electron microscope (SEM) micrograph of the as-prepared catalyst CZ is exhibited in Fig. 4a. It is clear that CZ shows highly porous microstructure. The SEM image of the CZ/S is displayed in Fig. 4b. The dots with high brightness are attributed to Cu particles with or without ZnO particles. However, the rest is the surface of the SiO2 support. As observed in Fig. 4b, CZ/S has well-dispersed metallic Cu0 along with or without ZnO particles on the support all over the catalyst. Higher dispersion naturally results in larger active-metal surface area.

3.5. TPR Analysis of CZ and CZ/S before Reduction

The thermal conductivity detector (TCD) signal in accordance with hydrogen consumption from H2-temperature-programmed reduction (TPR) of CZ and CZ/S before reduction is compared in Fig. 5. As compared in Fig. 5a, the main reduction peak of CZ is located at about 518 K. As known, bulk CuO can be reduced at a considerably high temperature (about 573 K). This result suggests that the presence of ZnO could facilitate the reduction of CuO. In Fig. 5b, the reduction peak of CZ/S is abroad and much lower than that of CZ. Considering the results of the XRD patterns and the Cu0 surface area determined by N2O chemisorption, the reduction peak at lower temperature...
represents the well-dispersed CuO species with smaller crystalline sizes, whereas the reduction peak at higher temperature is assigned to the reduction of CuO species with larger crystalline sizes. This conclusion is well supported by the literature\textsuperscript{26},\textsuperscript{27} that the reduction peak of smaller CuO crystalline size prefers at lower temperature.

3.6. FT-IR Analysis of the Precursor, CZ, and CZS

In this metal ion-citric acid system, the pH value of the solution is the key point, which can control the dissociation of carboxylic acid and yield homogeneous products to prevent the hydrolysis of metal ions. In this system, all metal ions (Cu\textsuperscript{2+} and Zn\textsuperscript{2+}) can be chelated at the pH value of 7.0. \textbf{Figure 6} a displays the FT-IR spectrum of the precursor of CZ, which is also the same precursor as that of CZS without support. The transmission band at about 3180 cm\textsuperscript{-1} suggests the presence of adsorbed moisture\textsuperscript{28}. The band at 2376 cm\textsuperscript{-1} comes from the adsorption of CO\textsubscript{2}\textsuperscript{28,29}. The bands at 820 cm\textsuperscript{-1} and 1384 cm\textsuperscript{-1} are attributed to the NO\textsubscript{3}\textsuperscript{-}, and the band at 3034 cm\textsuperscript{-1} is derived from O-H group\textsuperscript{28,29}. Two bands occur at 1620 cm\textsuperscript{-1} and 1400 cm\textsuperscript{-1}, standing for the asymmetric and symmetric stretching vibrations for carboxyl ions (COO\textsuperscript{-}), whereas the bands at 1720 cm\textsuperscript{-1} and 1770 cm\textsuperscript{-1} come from the free carboxylic groups\textsuperscript{30} in the unchelated citric acid.

\textbf{Figure 6} b and c compare the FT-IR spectra of CZ and CZS. Absolutely neither NO\textsubscript{3}\textsuperscript{-} bands at 820 cm\textsuperscript{-1} and 1384 cm\textsuperscript{-1} nor carboxyl bands are observed for both catalysts, indicating that all NO\textsubscript{3}\textsuperscript{-} in the precursors and carboxyl take part in the combustion and pyrolysis processes. As shown in \textbf{Fig. 6} b, a broad band from about 1400 to 1600 cm\textsuperscript{-1}, which is attributed to complicated carbonic residues, is exhibited. The bands at 1428, 1534, 1551, and 1582 cm\textsuperscript{-1} are assigned to the carbonates species (COOO\textsuperscript{31}). The bands at 1352 cm\textsuperscript{-1} and 1580 cm\textsuperscript{-1} come from the symmetric and asymmetric stretches of (OCO) of carbonate species (OCO). However, no bands from 1400 to 1600 cm\textsuperscript{-1} are observed in \textbf{Fig. 6} c for the supported CZS prepared by surface impregnation combustion method. All the bands in \textbf{Fig. 6} c are attributed to the support SiO\textsubscript{2}, which are confirmed with the FT-IR spectrum of pure SiO\textsubscript{2}, indicating that no carbonates are left in the supported catalyst CZS.

3.7. Raman Analysis of CZ and CZS

The Raman spectra of CZ and CZS are compared in \textbf{Fig. 7} in the region from 800 to 1900 cm\textsuperscript{-1}. The bands at about 1110 cm\textsuperscript{-1} in \textbf{Fig. 7} a are attributed to the (CO\textsubscript{3})\textsuperscript{2-} symmetric stretching vibration in carbonates\textsuperscript{32,34}. The Raman spectrum of the (CO\textsubscript{3})\textsuperscript{2-} symmetric stretching modes in the pure carbonates is commonly in the region from 1050 to 1110 cm\textsuperscript{-1}\textsuperscript{35}. These phenomena indicate a part of carbon element is left in CZ in the form of carbonates. However, no bands are observed in \textbf{Fig. 7} b, suggesting that no carbonates are left in CZS. This conclusion is in good accordance with FT-IR findings that no bands are attributed to the carbonate species (COOO) and carboxylate species (OCO) in \textbf{Fig. 6} c. Pure metal/support catalyst without any impurity could be obtained when this surface impregnation combustion method is applied.

4. Conclusions

Nanostructured Cu-ZnO/SiO\textsubscript{2} catalyst, which is prepared by surface impregnation combustion methods with inexpensive raw materials and uncomplicated operation conditions, exhibits significantly higher activity and methanol selectivity, which are closely related to the metallic Cu surface area and Cu crystalline sizes. The support SiO\textsubscript{2} here has a function of heat transfer to make catalysts preparation process much smoother, besides the dispersion effect, resulting in smaller Cu crystalline sizes and larger metallic Cu surface area, and eliminating carbon deposit on the catalyst surface.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig6.png}
\caption{\textbf{Fig. 6} FT-IR Spectrum of (a) the Precursor of CZ, (b) CZ and (c) CZS.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig7.png}
\caption{\textbf{Fig. 7} Raman Analysis of the As-prepared Catalysts (a) CZ and (b) CZS.}
\end{figure}

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要旨

燃焼法から調製された低温メタノール合成用高性能シリカ担持鋼-酸化亜鉛触媒
—シリカの有無に関する比較—

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安価な原料と簡易な方法を用いて、ソル-ゲルの表面合浸燃焼法で Cu-ZnO/SiO₂およびCu-ZnO触媒を調製した。XRDとSEMの測定結果から、表面合浸燃焼法で調製されたCu-ZnO/SiO₂触媒では、Cuの結晶粒子もCu-ZnO粒子も非常に小さいことが明らかになった。触媒調製の燃焼過程において、シリカ担体の共存によって、燃焼熱の吸収ならびに燃焼の拡散が素早く進行し、触媒調製過程の温度変動、熱変化は温和であった。Cu-ZnO/SiO₂およびCu-ZnO触媒を用いて、メタノールを触媒的な溶媒とし、CO₂を含む合成ガスからの低温メタノール合成を行った。反応条件は443 K, 5.0 MPa, 8 hとした。Cu-ZnO/SiO₂触媒はCu-ZnO触媒より高い活性とメタノール選択性を示した。これは、Cu-ZnO/SiO₂触媒の高い鋼表面積と高分散された銅ナノ粒子によるものであると考えられる。XRD, TG-DTA, FT-IR, ラマン, SEM, BET, N₂O化学吸着などのキャラクタリゼーション手法を用いて、この二つの触媒におけるシリカ有無の効果を詳細に比較した。シリカ担体の共存は、Cu-ZnO活性種の高分散を実現しただけでなく、触媒調製過程の燃焼熱をスムーズに拡散した役割も果たした。