

ZrO₂-CeO₂ 担持 Cu 触媒を用いたエタノールの CO₂改質による CO および H₂の製造

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CO and H₂ formation by CO₂ reforming of ethanol using ZrO₂-CeO₂-supported Cu catalyst (Graduate School of Engineering, Mie University) Yuuki Hatooka, Tadanori Hashimoto, ○Atsushi Ishihara

Recently, much attention has been focused on chemical transformation of CO₂ and many attempts have been investigated. Among them, renewable ethanol CO₂ reforming for synthesis gas or hydrogen formation is one of promising processes. In our laboratory, Co as a major active species and CeO₂ and ZrO₂ as supports were used to make Co/CeO₂-ZrO₂ catalysts by the sol-gel method, which were effective in steam reforming of ethanol. When Co/CeO₂-ZrO₂ catalysts were tested in CO₂ reforming of ethanol, high yields of CO and H₂ were not obtained. In the present study, Cu as a major active species and CeO₂ and ZrO₂ as supports were used to make Cu/CeO₂-ZrO₂ catalysts by the sol-gel method, which were tested in CO₂ reforming of ethanol. Copper(II) nitrate trihydrate was used, CeO₂ was a reference catalyst and the precursor of ZrO₂ was zirconium butoxide. When the reaction was performed at Cu 10%, catalyst 0.25g and CO₂:Ethanol = 5mol/mol, conversions of ethanol and CO₂ were high at 650°C and higher and CO and H₂ formation increased with increasing temperature regardless of the ratio of CeO₂ and ZrO₂. When the ratio of CeO₂ and ZrO₂ was 1:1, yields of H₂ and CO at 700°C reached 75% and >100%, respectively. When H₂ and CO are formed according to C₂H₅OH + CO₂ → 3H₂ + 3CO, it seems that coke deposited at lower temperature would be reformed to CO at 700°C.

Keywords : CO₂ reforming of ethanol, ZrO₂-CeO₂-supported Cu catalyst, Formation of CO and H₂

CO₂の化学的変換には大きな関心が寄せられ、多くの試みが検討されている。その中で、再生可能なエタノールの CO₂改質は、合成ガスあるいは水素製造の有望なプロセスである。我々はこれまで、触媒の活性金属に Co、担体として CeO₂と ZrO₂を用いた Co/CeO₂-ZrO₂触媒を sol-gel 法で調製し、エタノールの水蒸気改質に有効であることを報告してきた^{1,2)}。この Co/CeO₂-ZrO₂触媒をエタノールの CO₂改質に用いたが、高い CO および H₂収率が得られなかった、そこで本研究では、触媒の活性金属に Cu、担体として CeO₂と ZrO₂を用いた Cu/CeO₂-ZrO₂触媒を sol-gel 法で調製し、エタノールの CO₂改質を検討した。Cu は硝酸銅(II)三水和物として加えられ、CeO₂は参照触媒、ZrO₂の前駆体は zirconium butoxide であった。Cu 10%、触媒 0.25g、CO₂:Ethanol=5mol/mol の条件で反応を行った結果、CeO₂と ZrO₂の比にかかわらず、エタノールおよび二酸化炭素の転化率は 650°C以上でそれぞれ高い値が得られ、COと水素収量も温度とともに上昇した。CeO₂と ZrO₂の比が 1:1 の時、700°C で H₂収率が 75%、CO収率が 100%を超えた。C₂H₅OH + CO₂ → 3H₂ + 3CO により H₂と CO が生成すると考えると、700°C ではより低温で析出した coke も CO に改質されたと考えられる。

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2) H. Tsujino, et al., *RSC Adv.*, 2021, 11, 8530–8539. DOI: 10.1039/d1ra00141h