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Article

The Combination of Calcium Oxide and Cu/ZrO$_2$ Catalyst and their Selective Products for CO$_2$ Hydrogenation

Soipatta Soisuwan[1,a,b,*], **Wilasinee Wisaijorn**[1], **Chalida Nimnul**[1],
Orawan Maunghimapan[1], **and Piyasan Praserthdam**[2]

1 Department of Chemical Engineering, Faculty of Engineering, Burapha University, 169 Long-Hard Bangsaen Road, Saensuk Sub-District, Muang District, Chonburi, 20130, Thailand
2 Center of Excellence in Catalysis and Catalytic Reaction Engineering, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Phayathai Road, Pathuwan District, Bangkok 10330, Thailand
E-mail: [a]soipatta@buu.ac.th (Corresponding author), [b]soipatta@eng.buu.ac.th

Abstract. The catalytic activities of Cu/ZrO$_2$_CaO catalysts were investigated on CO$_2$ hydrogenation. The CO$_2$ hydrogenations were carried out over combination of calcium oxide and Cu/ZrO$_2$ catalyst. Two calcination temperatures were chosen at 300 and 650 °C according to thermal decomposition results. The catalysts were characterized by means of N$_2$ adsorption-desorption, H$_2$ temperature programmed reduction and X-ray diffraction. The CO$_2$ hydrogenation under atmospheric pressure and at 250 °C was carried out over copper-based catalysts combined with calcium oxide namely i.e. Cu/ZrO$_2$_CaO300, Cu/ZrO$_2$_CaO650, Cu/ZrO$_2$_Cu/CaO and Cu/ZrO$_2$+CaO. The catalytic activities over all catalysts were consistent for 4 hours. The catalytic reaction rates over copper-based catalysts were in the range of 21.8 – 47.4 μmol L^{-1} s^{-1} g cat^{-1}. The modification of calcium oxide can improve the catalytic activity of copper-based catalysts to 47.4 μmol L^{-1} s^{-1} g cat^{-1}. The calcination temperature can cause a difference in active species that impact on product selectivity. The CaO consisting in copper-based catalysts, i.e. Cu/ZrO$_2$_CaO650, facilitate the growth of long chain hydrocarbon, whereas Cu/ZrO$_2$_CaO300 favors the formation of carbon monoxide plausibly arising from reverse water gas shift reaction. Directly combined calcium oxide with Cu/ZrO$_2$ via physically mixing, i.e. Cu/ZrO$_2$+CaO, can improve the rate of methanol production.

Keywords: Calcium oxide, copper-based catalyst, CO$_2$ hydrogenation.

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1. Introduction

The increasing rate of energy consumption is one of the severe impacts on environmental topics nowadays because of large population growth and their demand for sustenance, transportation and novel technology which are an exploitation of natural resources, such as fossil fuel that can directly convert to energy with emission of greenhouse gas i.e. CO_2. The incremental amount of carbon dioxide impacts highly on global environment owning to high heat capacity of CO_2 that can rise the global temperature up and change the global climate [1]. The CO_2 utilization is thus of interest for many researchers. The conversion of CO_2 to energy source molecules can considerably benefit both in reduction of CO_2 and production of clean energy source. The hydrogenation of carbon dioxide can occur essentially over catalytic surface of metal to produce the molecules of long chain hydrocarbon and/or alcohol [2–5]. The complete combustion of these fuels emits only carbon dioxide, non hazardous gas, and this carbon dioxide compensates carbon content in ecosystem [1]. The principle catalyst widely used in CO_2 hydrogenation is copper based catalyst since it was selective towards methanol and hydrocarbon. The coupling copper catalyst with special oxide such as ZnO [6–8], or support such as Al_2O_3 [7] or ZrO_2 [7, 9, 10], can effectively increase the hydrogenation rates. Zirconium oxide was employed as catalytic promoter or support because of its notable chemical stability giving good active metal size dispersion and resulting in high production rate [11, 12]. The use of zirconium oxide as copper catalyst support can enhance the catalyst stability while prolonging CO_2 hydrogenation as it can prevent sintering of active metal sites. F. Arena et.al. found textural and chemical effects of zirconia support that conferred superior performance on Cu-ZnO/ZrO_2 system compared with Al_2O_3- and CeO_2-systems because the oxide carriers can control texture and metal surface exposure and adsorption property of CO_2 and H_2 [13]. The primary role of metal/oxide interface in copper-based catalysts on CO_2 to CH_3OH hydrogenation arises from a synergism of metal Cu hydrogenation and oxide basic sites [14]. The hydrogenation of CO_2 to methanol was preferable apparently owning to La addition in ZrO_2 supported copper based catalysts [15]. Additional La existing in Cu/ZrO_2 can improve the number of strong base which facilitates adsorption of CO_2 contributing the formation of methanol. The hydrogenolysis strongly depends on the basicity of Cu-based catalysts and performance of hydrogen spill over [16]. By this reason, we are interested to elucidate a role of basic sites existing in Cu/ZrO_2 for CO_2 hydrogenation selectively convert to products, calcium oxide derived from natural material, i.e. oyster shell, therefore was employed as additional oxide in zirconium oxide supported copper catalysts. The CO_2 hydrogenation was carried out under atmospheric pressure and low temperature 250 ^oC. The selective products of CO_2 hydrogenation to methanol and hydrocarbon were investigated.

2. Experimental

2.1. The Catalyst Preparation and Characterization

The combination of calcium oxide and Cu/ZrO_2 was prepared via wetness impregnation. The copper precursor was 99.99% copper nitrate trihydrate ($Cu(NO_3)_2.3H_2O$). The precursor was loaded on solid mixture of zirconium oxide and calcium oxide via wetness impregnation to designate 10%wt copper on support. The solid mixture of Tosoh-ZrO_2 and CaO were simultaneously ground at 10%wt CaO in a mortar. A certain amount of copper nitrate trihydrate was dissolved in deionized water. The resulting solution mixed with given support was heated at 110 ^oC and stirred to slightly evaporate water. The slurry became humid paste, afterwards it was dried at 110 ^oC in an oven overnight. The degradation of as-synthesized catalysts was investigated by thermogravimetric analysis (TGA model TGA850 METTLER TOLEDO) and the catalysts were calcined at temperature according to TGA results. Thermogravimetric analysis was employed additionally to investigate the H_2 Temperature Programmed Reduction (H_2-TPR) behaviour of all catalysts [17]. The results obtained from thermalgravimetric analysis of the catalysts that were carried out under nitrogen flowing gas compared to the results of the catalysts that were tested under 5%hydrogen containing in nitrogen gas, were used to determine the reduction behaviour of all catalysts. The experimental temperature was ramped from 30 to 800 ^oC with heating rate at 10 ^oC/min. The hydrogen temperature programmed reduction was determined in the range of temperature that catalysts were only decomposed under 5% hydrogen containing in nitrogen carrier gas, meanwhile the weight did not alter under the condition of inert nitrogen gas.

2.2. Catalyst Nomenclature

The copper based catalyst supported by ZrO_2 or CaO was namely Cu/ZrO_2 or Cu/CaO, respectively. The copper-based catalysts combined with 10% wt calcium oxide calcined at given temperature i.e. xxx ^{o}C was designated Cu/ZrO_2_CaOxxx. The combination of Cu/ZrO_2 with 10% wt Cu/CaO by mechanically mixing was designated Cu/ZrO_2_Cu/CaO. The direct combination of Cu/ZrO_2 with 10% wt CaO by mechanically mixing was namely Cu/ZrO_2+CaO.

2.3. CO_2 Hydrogenation Testing

1 gram of fresh oxide catalyst was mounted to tubular reactor and CO_2 hydrogenation was carried out under atmospheric pressure at 250 ^{o}C, the catalyst was fully oxidized under pre-treating oxygen gas at 350^{o}C for 3 hours. The flow rate of CO_2/H_2/N_2 was at 30/10/10 ml/min. Nitrogen was used as internal standard gas for gas chromatography. The reactants and products were analyzed by VARIAN gas chromatography connecting with automatic ten-port sampling valves. The influent stream was separated by consecutive two columns i.e. i) molecular sieve for N_2, CO, CO_2 and CH_4 and the long chain HC column for hydrocarbon and methanol. The stepwise influent flow to those columns was automated via STAR software. The effluent stream was consecutively analyzed by thermal conductivity detector (TCD) and flame ionization detector (FID). The conversion of carbon dioxide, rate of reaction and product selectivity were calculated as follows.

$$\mathrm{CO_2 conversion} = \frac{[\dot{C}_{\mathrm{CO_2,input}} - \dot{C}_{\mathrm{CO_2,\,output}}]\ (\mathrm{mol\ L^{-1} s^{-1}})}{\dot{C}_{\mathrm{CO_2,\,input}}\ (\mathrm{mol\ L^{-1} s^{-1}})} \times 100\% \tag{1}$$

$$\text{Rate of reaction} = \frac{((\frac{\%\mathrm{CO_2 conversion}}{100}) \times \dot{C}_{\mathrm{CO_2,\,input}}\ (\frac{\mathrm{mole}}{\mathrm{L.\ s}})}{W_{\mathrm{cat}}(\mathrm{g})} \tag{2}$$

$$\text{Selectivity of } \mathrm{CH_3OH} = \frac{\text{Concentration of } \mathrm{CO_2}\text{convert to } \mathrm{CH_3OH}}{\text{Concentration of } \mathrm{CO_2} \text{ fed into reactor}} \times 100\% \tag{3}$$

3. Results and Discussions

3.1. Thermal Decomposition of the Catalysts Before Calcination

The decomposition of fresh copper precursor loading on various supports, i.e. Tosoh ZrO_2, CaO and ZrO_2-CaO, were investigated under flowing oxygen gas. The gravimetric analysis was observed during ramping temperature to 1000 ^{o}C. Pure copper precursor ($Cu(NO_3)_2.3H_2O$) was clearly decomposed at 180 and 265 ^{o}C ascribed to dehydration and decomposition of nitrate [18]; however nitrate precursor–support interaction plausibly can cause a difference in decomposition temperature of pre-calcined Cu/ZrO_2, Cu/CaO and Cu/ZrO_2-CaO catalysts. The copper nitrate was decomposed only at 240 ^{o}C over zirconia support and the weight decomposition ended before 300 ^{o}C, while broad decomposition peaks were given apparently at 400 and 475^{o}C over Cu/CaO. These two decomposition steps may possibly own to decomposition of copper precursors loaded on chemically unstable CaO support consisting slightly of $Ca(OH)_2$; however, the weight was found to be thermally stable after 650^{o}C. The results are in good accordance with the decomposition peaks obtained from Cu/ZrO_2-CaO possessing the synergetic effects of copper loaded on ZrO_2 and CaO at 212 ^{o}C and 480 ^{o}C, respectively. Two interesting calcination temperature were therefore chosen according to the decomposition behaviours of copper precursor loaded on ZrO_2 and CaO supports, i.e. 300 and 650 ^{o}C.

3.2. Physicochemical Properties of the Catalysts

The calcined catalysts and their specific surface areas are shown in Table 1. The original Tosoh ZrO_2 gave specific surface area of 14 m^2/g (not shown in Table 1). The surface area decreased slightly to 11.9 m^2/g while loading copper catalyst to ZrO_2 support and surface area of the catalysts sharply lost to 2.8-5.8 m^2/g owning to a presence of calcium oxide in ZrO_2 support as shown in Table 1. The crystalline structure of the catalysts exhibited in Table 1. The tetragonal crystalline phase was the main structure of Tosoh ZrO_2 support, while monoclinc phase was slightly found in the X-ray diffraction patterns and it apparently transformed to tetragonal phase after calcination at 650 ^{o}C as illustrating in the diffraction pattern of

Cu/ZrO_2-CaO650 and this is in good agreement with availability of the thermodynamically stable tetragonal phase at higher temperature [19]. The diffraction patterns of commercial calcium oxide revealed cubic phase which sharply remained after calcination at 650°C for Cu/CaO650, whereas 10 percentage of additional cubic calcium oxide in copper-based catalyst was unnoticeable for Cu/ZrO_2-CaO300. Two small peaks of cubic CaO were found slightly at $2\theta = 32^{o}$ and 54^{o} in the diffraction pattern of Cu/ZrO_2-CaO650. The cubic calcium oxide is likely to facilitate a formation of small copper metal peak at $2\theta = 44^{o}$, while the copper-based catalyst mainly supported by ZrO_2 possessed the small diffraction patterns of CuO at $2\theta = 39^{o}$ [20]. The weight decompositions representing as the behaviour of temperature programmed reduction over Cu/ZrO_2, Cu/CaO and Cu/ZrO_2_Cu/CaO were found at temperature lower than 400 °C as shown in Fig. 1(A), while the weight loss due to water evaporation of unstable catalyst over Cu/ZrO_2_CaO300 gave at 100 °C and plausibly at 470°C as shown in Fig. 1(B), these were not the reduction behavior since these decomposition results concurrently appeared under the conditions of inert nitrogen and 5% hydrogen in nitrogen gases. The profiles of hydrogen consumption derived from the weight decomposition over Cu/ZrO_2, Cu/CaO and Cu/ZrO_2_Cu/CaO was illustrated in Figure 2. The Cu/ZrO_2_CaO650 gave weight decomposition resulting from the hydrogen reduction at 280 °C as shown in Fig. 1(C), although it was very small peak compared to other catalysts in Fig. 2. According to low ability of the hydrogen reduction, it may note that the hydrogen reduction may not take place during CO_2 hydrogenation and copper oxide species were the main active species possibly over Cu/ZrO_2_CaO650. The Cu/CaO, Cu/ZrO_2 and Cu/ZrO_2_Cu/CaO exhibited the hydrogen reduction peaks especially at low temperature as shown in Fig. 2 (<400 °C). These catalysts are likely to give active metal sites during CO_2 hydrogenation. It may note that Cu/ZrO_2 combined with calcium oxide in different routes gave the difference in the reduction behaviour. The catalyst prepared at high calcination temperature 650 °C was hardly reduced according to the strong interaction between metal and support formed at the high temperature calcination [21], likewise the reduction peak was unidentified over the copper based catalyst supported by close combination of ZrO_2 and calcium oxide which was fired at 300 °C (Cu/ZrO_2_CaO300) in Fig. 1(B). The reduction behaviour of Cu/ZrO_2_Cu/CaO was similar to maternal Cu/ZrO_2 and Cu/CaO catalysts when directly combining Cu/ZrO_2 and Cu/CaO catalysts via physically mixing as shown in Fig. 2, while the close combination of calcium oxide to Cu/ZrO_2 catalyst via wetness impregnation route, calcined at different temperature, seems not to urge the hydrogen reduction.

3.3. Effect of Calcium Oxide on CO_2 Hydrogenation

The carbon dioxide hydrogenation was carried out at 250 °C under atmospheric pressure 1 bar. The catalytic activity of carbon dioxide hydrogenation over all copper based catalysts exhibits in Table 2 and Fig. 4. The catalytic activities were consistent for 4 hours. The carbon dioxide hydrogenation can occur despite no hydrogen reduction prior to the hydrogenation took place. The hydrogen chemisorptions were carried out for $Cu/ZrO_2$650, Cu/CaO and Cu/ZrO_2_CaO300 catalysts after hydrogen reduction at 250 °C for 3 h. The amount of active metal sites was slightly found due to small amount of hydrogen adsorbed (0.0000 molecule/g), thus the catalytic activity and product selectivity for these catalysts was possibly dependence on copper oxide and its neighbouring species. Although the copper-based catalyst loaded on ZrO_2 exhibited % CO_2 conversion similarly to the copper-based catalyst loaded on CaO, both copper-based catalysts were selective to different products. The Cu/CaO preferred route of methanation, while Cu/ZrO_2 gave oxygenate compound, i.e. methanol, and longer chain hydrocarbon as shown in Table 2. The hydrocarbon compounds were found over copper-based catalysts consisting both of ZrO_2 and CaO i.e. Cu/ZrO_2, Cu/CaO, Cu/ZrO_2_CaO300 and Cu/ZrO_2_CaO650. Temperature of calcination had an impact on difference in product selectivity probably accrediting to formation of different calcium oxide species. The calcium oxide can occur in amorphous form or fine particles dispersed well enough in the catalysts owning to no detection of X- ray diffraction. The thermal stability of calcium oxide species in Cu/ZrO_2_CaO650 was up to 600 °C according to thermal degradation results in Fig. 1(C), while the less stability exhibited in Cu/ZrO_2_CaO300. Pre-treating at 350 °C prior to CO_2 hydrogenation can cause thermal decomposition of Cu/ZrO_2_CaO300 catalyst and the decomposition can change surface chemistry of calcium oxide and may affect on interfacial interaction of calcium oxide species and its neighbouring particles such as copper oxide and ZrO_2. This would facilitate the reaction toward reverse water gas shift or consecutive methanol decomposition paths causing formation of carbon monoxide [13]. This is in good agreement with the results obtained by M.C. Román-Martinéz et. al. reported positive effect of Pt-Ca combination on CO_2 hydrogenation presenting high selectivity to CO [22]. The close combination of calcium oxide in copper based catalysts can cause the formation of methanol, but directly mixing calcium oxide at 10% wt to copper-based catalyst, Cu/ZrO_2, gave a superior formation of methanol as shown in Fig. 4(a), strongly emphasizing the activity of La modified copper-based catalysts [15] and a dual site L-H mechanism proposed by *Arena F. et al.* [13], involving hydrogenation and basic oxide sites at the surfaces of metal and oxide phase.

Table 1. Physical properties of copper-based catalysts combined with commercial CaO.

Catalyst nomenclature	**Calcination Temperature (°C)**	**Specific Surface Area (m^2/g)**	**Crystalline structure**		
			ZrO_2	**CaO**	**CuO/Cu**
Cu/ZrO_2	300	11.9 ± 0.3	T,M	-	CuO
Cu/CaO	650	2.9 ± 0.3	-	Cubic	Cu
Cu/ZrO_2_CaO300	300	5.8 ± 0.7	T,M	-	CuO
Cu/ZrO_2_CaO650	650	9.4 ±0.5	T	-	CuO
Cu/ZrO_2_Cu/CaO	300, 650	-	-	-	-
Cu/ZrO_2+CaO	300	-	-	-	-

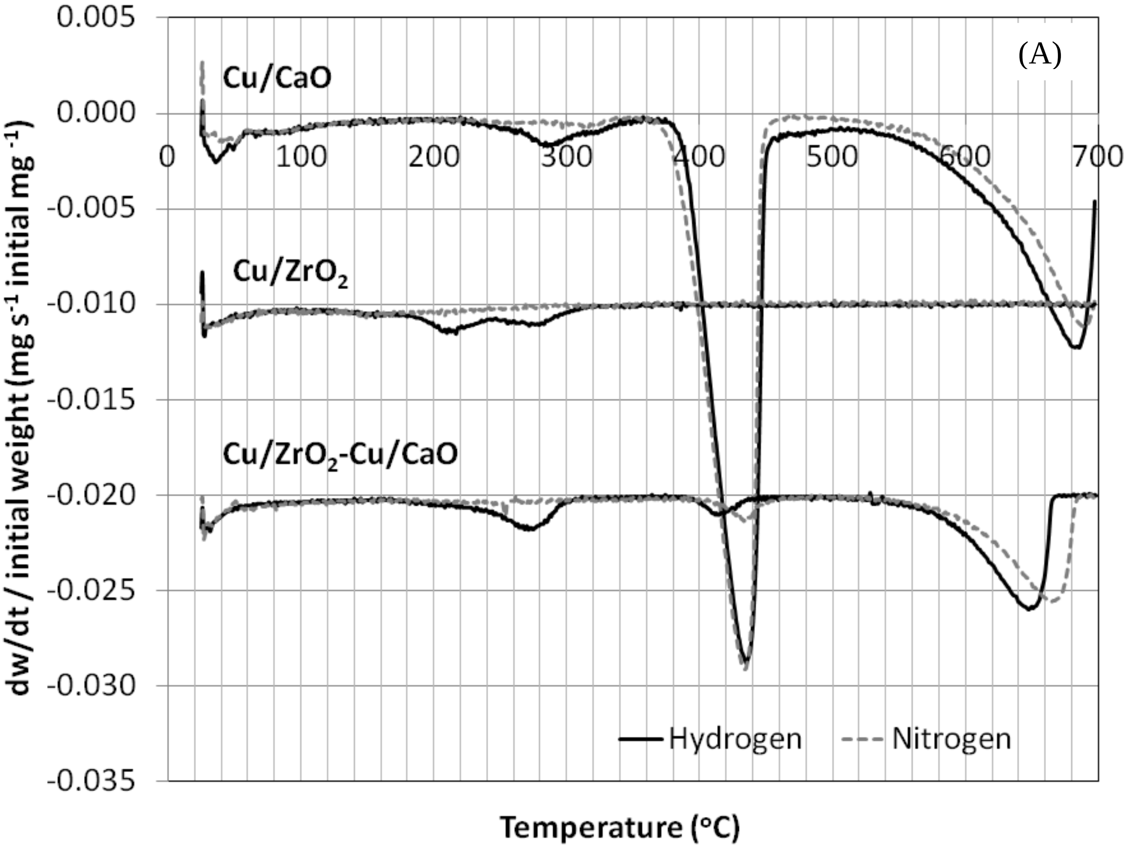

Fig. 1. (A) The rate of weight decomposition by TGA under 5% H_2 in N_2 flowing gas i.e. Cu/CaO, Cu/ZrO_2 and Cu/ZrO_2-Cu/CaO.

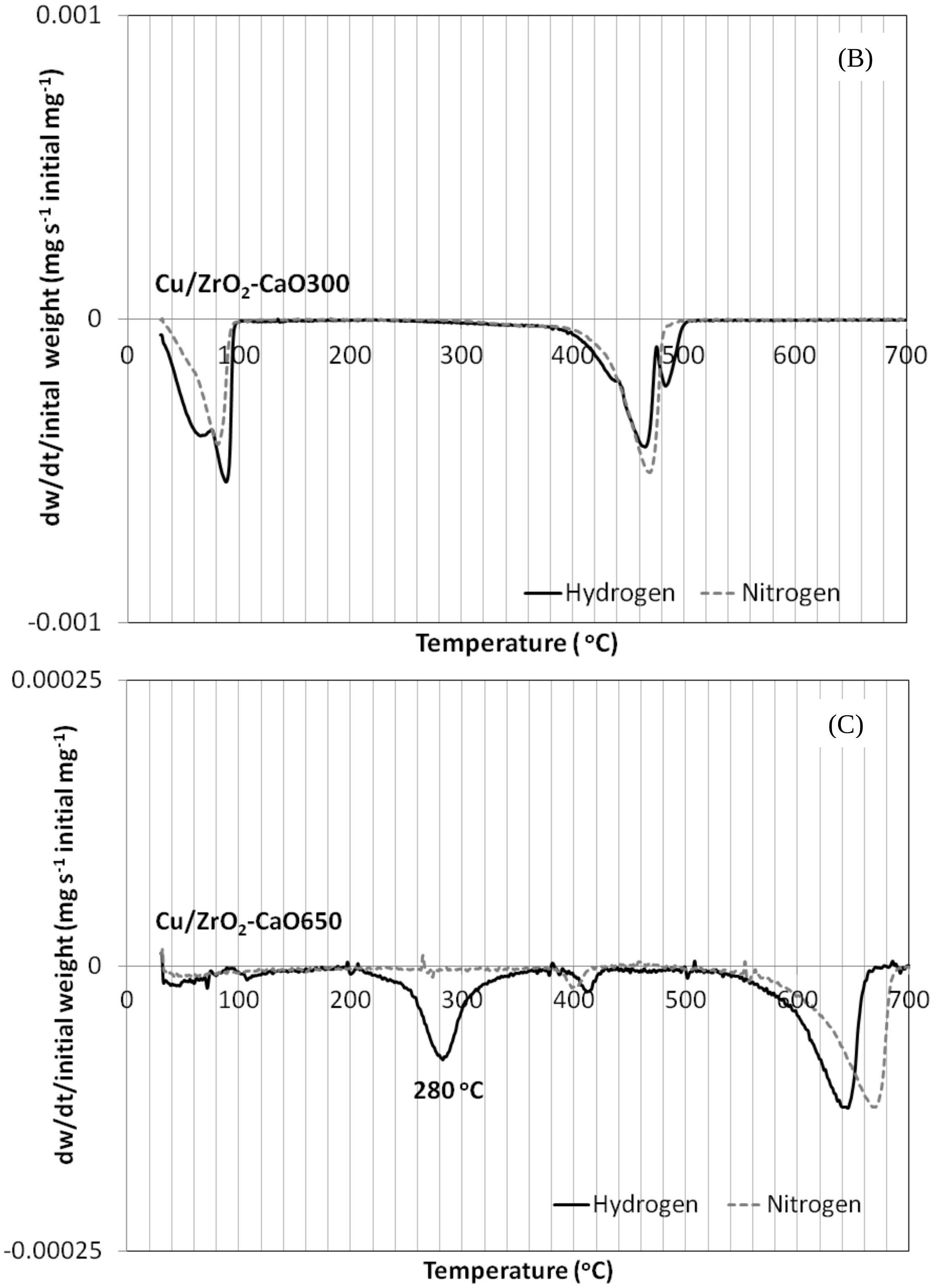

Fig. 1. (Cont.) The rate of weight decomposition by TGA under 5% H_2 in N_2 flowing gas i.e. (B) Cu/ZrO_2-CaO300 and (C) Cu/ZrO_2-CaO650.

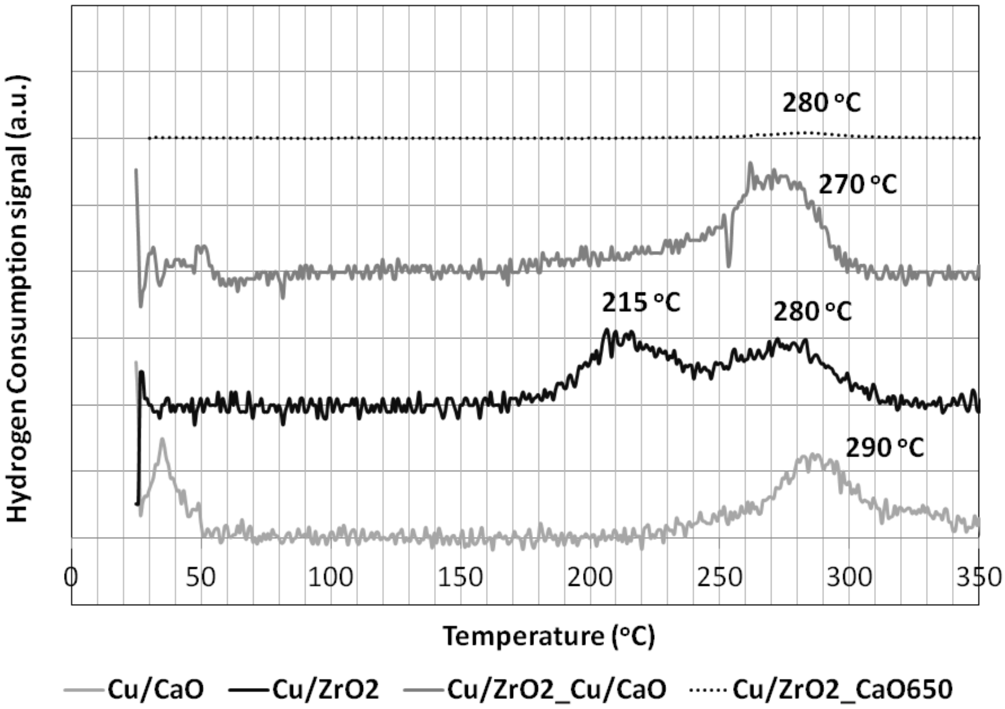

Fig. 2. Hydrogen temperature programmed reduction profiles.

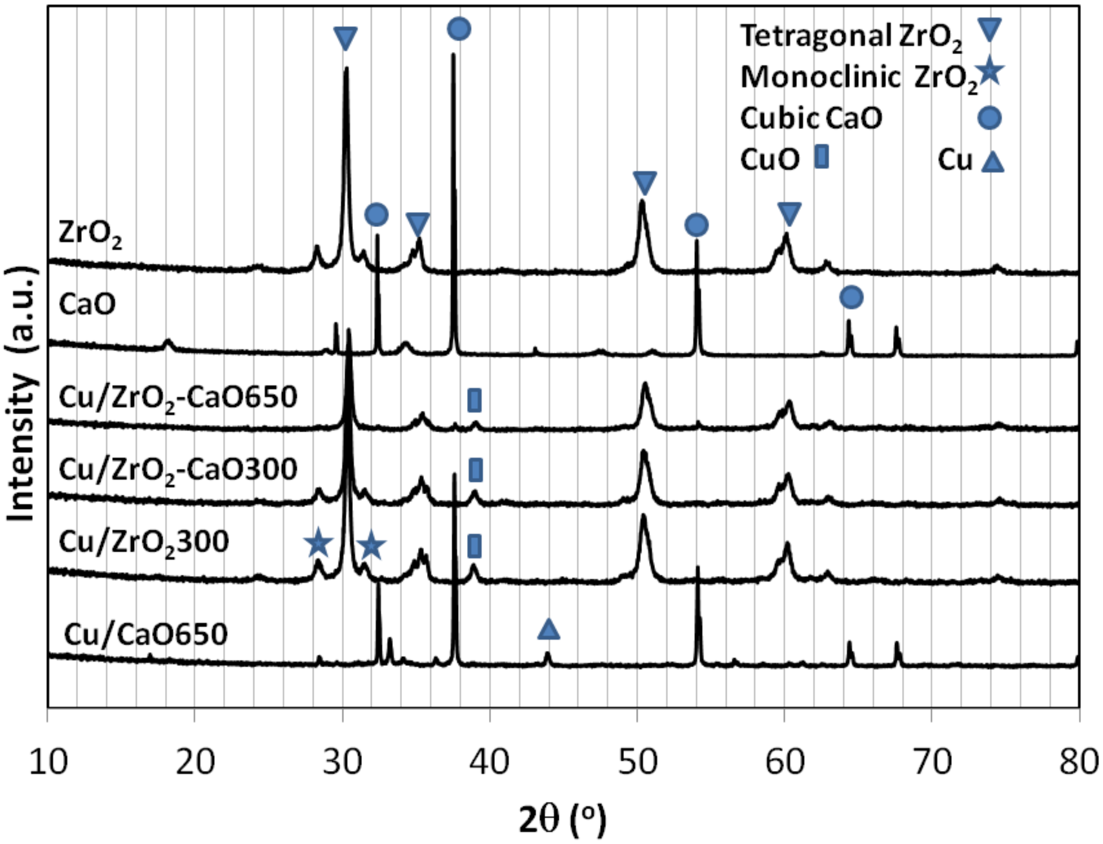

Fig. 3. X-ray diffraction patterns of the catalysts and supports.

Table 2. The catalytic activities and selectivity of products for all catalysts at initial.

Catalyst	% CO_2 Conversion	Rate of Reaction (μmol L^{-1} s^{-1} g cat^{-1})	(%) Product Selectivity				
			CH_3OH	CO	Hydrocarbon		
					CH_4	C_2H_6	C_{3+}
Cu/ZrO_2	3.3	25.7	0.8	0.0	81.8	18.1	0.0
Cu/CaO	2.8	21.8	0.0	0.0	100.0	0.0	0.0
Cu/ZrO_2_CaO300	6.1	47.4	0.4	41.7	48.3	10.1	0.0
Cu/ZrO_2_CaO650	4.3	33.4	0.2	0.0	73.1	24.4	2.4
Cu/ZrO_2_Cu/CaO	3.3	25.7	0.8	0.0	79.8	19.6	0.0
Cu/ZrO_2+CaO	2.9	22.5	1.2	0	98.8	0.0	0.0

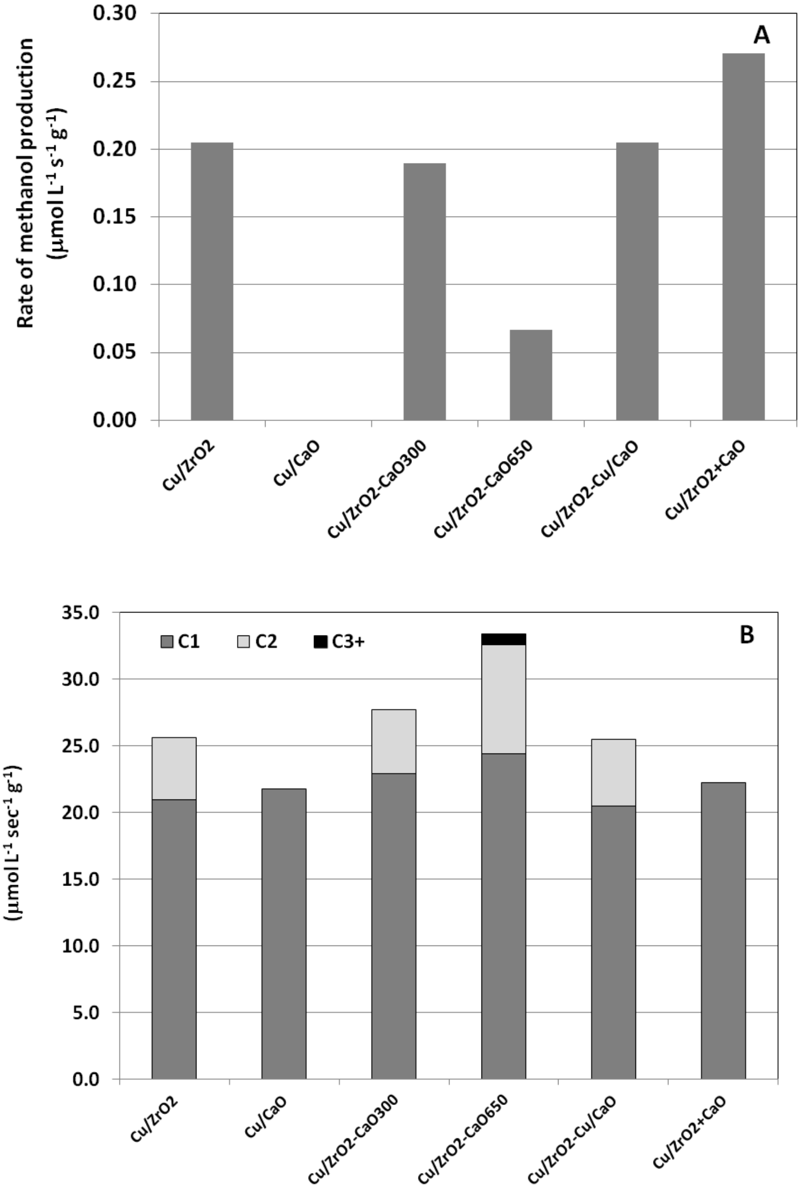

Fig. 4. (A) & (B) The rate of methanol and hydrocarbon produced over copper-based catalysts.

4. Conclusions

The copper-based catalysts modified by 10%wt calcium oxide were prepared by wetness impregnation. The calcination temperature can cause a difference in copper-calcium oxide species that was selective to different product distribution. The CO_2 hydrogenation was carried out after pre-treating the catalyst under oxygen flowing gas at 350 °C. The product distribution of longer chain hydrocarbon, i.e. CH_4, C_2H_6 and C_3H_8, formed at 33.4 μmol L^{-1} s^{-1} g^{-1} over the catalyst with high calcination temperature 650 °C. The majority of product was carbon monoxide (19.8 μmol L^{-1} s^{-1} g^{-1}) and methane (22.9 μmol L^{-1} s^{-1} g^{-1}) over the catalyst with low calcination temperature 300 °C. The methanol production was improved over copper-based catalyst directly mixing to calcium oxide (Cu/ZrO_2+CaO).

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