

## Promoting Effect of Admixed $Ce_xZr_{1-x}O_2$ with Cu-ZnO- $Al_2O_3$ Methanol Synthesis Catalyst on Catalytic Performance: Influence of Ce/Zr Ratio

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Methanol (MeOH) is widely used as a feedstock such as a basic chemical and an alternative fuel which is cleaner and more efficient in fuel cell applications.<sup>1</sup> Commercially, MeOH is produced from synthesis gas ( $H_2/CO/CO_2$ ) using mainly Cu/ZnO based catalyst,<sup>2</sup> since zinc oxide has played an important role in modifying the electronic properties of metallic copper and results in changing the catalytic activity.<sup>3</sup> To enhance the catalytic activity on MeOH synthesis, the selection of appropriate support not only provides a good configuration of active metals but also provides some function in modulating the interactions between the active components and support. Several types of supports such as silica,<sup>4</sup> zinc oxide<sup>5,6</sup> or fluorite-type oxides like ceria, zirconia and thoria<sup>2</sup> have been numerously investigated. In addition,  $CeO_2$ - $ZrO_2$  mixed oxide is widely used due to the improved characteristics of oxygen storage capacity of  $CeO_2$ , redox property, thermal resistance and active metal dispersion for  $CO_2$  reforming with methane (CDR) reaction.<sup>7</sup> Furthermore, Cu/ZnO based catalyst can be modified with various promoters to improve catalytic performance in MeOH synthesis reaction<sup>8</sup> and it is usually prepared by co-precipitation or impregnation method.<sup>9</sup>

In the present investigation,  $Ce_xZr_{1-x}O_2$  is selected as an admixture for improving the dispersion of active components and the catalytic performance on MeOH synthesis. The catalyst is prepared by using co-precipitation method in the slurry of  $Ce_xZr_{1-x}O_2$  powder. The aim of this investigation is to obtain the optimum Ce/(Ce+Zr) weight ratio in  $Ce_xZr_{1-x}O_2$  mixed oxides on the activity of co-precipitated Cu/ZnO/ $Al_2O_3$  catalyst in terms of the combined effects of copper particle size and acidity of  $Ce_xZr_{1-x}O_2$  oxide.

### Catalyst Preparation, Characterization and Activity Test

The metal oxide of  $Ce_xZr_{1-x}O_2$  was prepared by Pechini method using  $Ce(NO_3)_3 \cdot 6H_2O$  and  $ZrO(NO_3)_2 \cdot 6H_2O$  precursors at a desired weight ratio of Ce/Zr. Ethylene glycol (EG) and citric acid (CA) were used to make the gel at the weight ratio of EG/CA at 4 : 1. The mixed gel was obtained by keeping the solution at 60 °C for 30 min and the gel was finally calcined at 500 °C for 4 h with a stepwise calcination at 100, 200, 300 and 400 °C for 1 h. The prepared mixed oxide is represented as  $Ce_xZr_{1-x}O_2$ , where x denotes weight ratio of Ce/(Ce+Zr) as 0.05,

0.08, 0.15, 0.30 and 0.50 and it corresponds to molar ratio of Ce/(Ce+Zr) as 0.033, 0.054, 0.103, 0.218 and 0.394. The catalysts were synthesized by co-precipitation method in an aqueous solution containing Cu, Zn and Al metal precursors (copper acetate, zinc acetate and aluminum nitrate with the weight ratio of CuO/ZnO/ $Al_2O_3$  = 61.5/31.6/7.0) and  $Na_2CO_3$  solution as a precipitating agent at 70 °C in a slurry of  $Ce_xZr_{1-x}O_2$ . The final pH of solution was maintained at around 7 and the precipitate was further aged for 3 h at 70 °C followed by calcination at 300 °C for 5 h. The final catalysts are denoted as CZA(x), where CZA represent CuO, ZnO and  $Al_2O_3$ , and x is weight ratio of Ce/(Ce+Zr) on  $Ce_xZr_{1-x}O_2$ . The weight ratio of CZA oxide components to  $Ce_xZr_{1-x}O_2$  is fixed to 5.

Catalytic activity was tested in a tubular fixed bed reactor (10.2 mm I.D.) with a catalyst of 1.0 g. Prior to the reaction, the catalyst was reduced for 4 h at 250 °C in a flow of 5 vol %  $H_2$  balanced with nitrogen. After reduction, the synthesis gas ( $H_2/CO = 2$ ) was introduced into the reactor. The reaction conditions were as follows; T = 250 °C, P = 5.0 MPa and space velocity (SV) = 4000 mL/ $g_{cat}/h$ . The effluent gas from the reactor was analyzed simultaneously by an online gas chromatograph (YoungLin Acme 6000 GC) employing GS-Q capillary column connected with flame ionized detector (FID) and Carboxen-1000 packed column connected with thermal conductive detector (TCD). The powder X-ray diffraction (XRD) patterns were obtained with a Rigaku diffractometer using Cu-K $\alpha$  radiation to identify the phases of active species before and after reaction. The elemental analysis of calcined CZA(x) catalysts was further carried out using the X-ray fluorescence (XRF; SEA5120). The Cu surface area (defined as  $S_{Cu}$  = exposed metallic copper area ( $m^2/g$ ) of sample) was measured by  $N_2O$  surface titration method.

### Results and Discussion

The catalytic performances on CZA(x) after 15 h on stream are summarized in Table 1. Although the initial activity was found to be around 40% of CO conversion, it stabilized after 4 h on stream in the range of 27.1 - 36.0% and finally showed a stable activity. The CO conversion on the co-precipitated CZA without the addition of  $Ce_xZr_{1-x}O_2$  mixed oxide showed lower value around 26.8%. In general, the slow deactivation is known

**Table 1.** CO conversion and product distribution<sup>a</sup>

Notation <sup>b</sup>	molar ratio Ce/(Ce+Zr)	CO conv. (mol %)	Product distribution (mol%)		
			MeOH	DME	BP <sup>c</sup>
CZA(0.05)	0.033	34.4	97.0	1.7	1.3
CZA(0.08)	0.054	36.0	96.2	2.4	1.4
CZA(0.15)	0.103	35.3	96.6	2.0	1.4
CZA(0.30)	0.218	31.9	96.6	1.6	1.8
CZA(0.50)	0.394	27.1	90.6	7.8	1.6
CZA	-	26.8	93.5	2.7	3.8

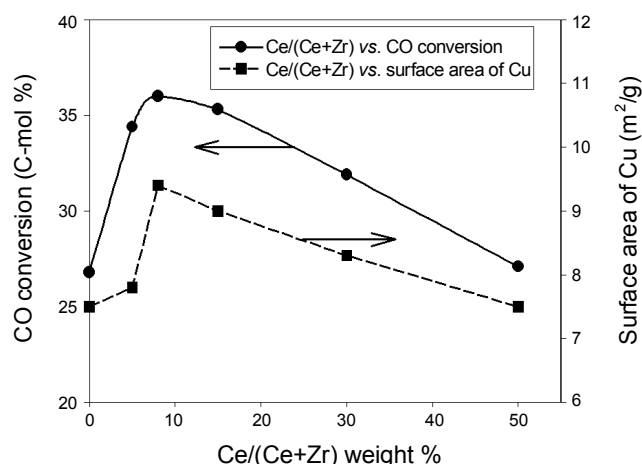
<sup>a</sup>The average values of CO conversion and product distribution were obtained after 15 h on stream which shows stable catalytic performance. <sup>b</sup>The catalyst is denoted as CZA(x) with a different Ce/(Ce+Zr) weight ratio of x on Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub>. CZA stands for CuO/ZnO/Al<sub>2</sub>O<sub>3</sub> component with a fixed weight ratio of 61.5/31.6/7.0. <sup>c</sup>Byproducts (BP) includes CH<sub>4</sub> (main by-product) and a trivial amount of C<sub>2</sub> - C<sub>4</sub> hydrocarbons.

**Table 2.** Particle size of Cu species and Cu surface area

Notation	Particle size (nm) <sup>a</sup>		Surface area of Cu (m <sup>2</sup> /g) <sup>b</sup>	weight ratio <sup>c</sup> CuO/ZnO/Al <sub>2</sub> O <sub>3</sub>
	CuO	metallic Cu		
CZA(0.05)	12.1	11.6	7.8	60.1/31.0/8.9
CZA(0.08)	11.3	6.8	9.4	61.6/31.3/7.1
CZA(0.15)	11.5	7.5	9.0	61.8/31.0/7.2
CZA(0.30)	12.6	9.2	8.3	62.1/30.4/7.5
CZA(0.50)	14.8	12.1	7.5	59.8/32.0/8.2
CZA	11.6	11.7	7.5	61.3/31.5/7.2

<sup>a</sup>The particle size of copper oxide and metallic copper was calculated from FWHM values of XRD diffraction peaks at 2θ = 35.5° for CuO on the calcined CZA(x) and 43.3° for Cu on the reacted CZA(x) catalysts. <sup>b</sup>Cu surface area of calcined CZA(x) catalysts was measured by N<sub>2</sub>O titration method. <sup>c</sup>The chemical composition of CZA(x) catalysts was verified by XRF analysis.

by coke formation or sintering of metallic copper during MeOH synthesis reaction.<sup>10</sup> The highest catalytic performance was observed on CZA(0.08) and monotonously decreased with the increase of Ce/(Ce+Zr) weight ratio. In addition, the catalyst performance is directly proportional to the surface area of metallic copper since metallic copper species are known to be active sites for MeOH synthesis.<sup>1,2,8,11</sup> To further understand of catalytic functionality, the calculated particle size of CuO and metallic Cu from Scherrer's equation (FWHM values) using the diffraction peaks measured by XRD analysis are summarized in Table 2. The chemical composition of CZA(x) catalysts after calcination is confirmed by XRF analysis and found to be in the similar composition which has been originally designed values during catalyst preparation. The shift of diffraction peak positions around 30, 50 and 60° (not shown in here) is due to the change of structure of Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> oxide with the variation of Ce/(Ce+Zr) weight ratio. Pokrovski *et al.* suggested that the thermodynamically stable phase of Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> oxide is monoclinic for Zr-rich composition (< 10 at.% Ce) and cubic for Ce-rich composition (> 80 at.% Ce) with a different position of diffraction peaks.<sup>12</sup> These different phases of Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> are eventually influencing the dispersion of Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> components during co-precipitation step. To verify the XRD results, Cu surface area by N<sub>2</sub>O titration method and XRF analysis for

**Figure 1.** Correlation of CO conversion and surface area of Cu with respect to Ce/(Ce+Zr) weight % on CZA/Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> catalysts.

chemical composition was measured and summarized in Table 2. The small particle size on CZA(0.08) of 11.3 nm for CuO and 6.8 nm for metallic copper is observed. The different surface acidity (Bronsted acidic site) on Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> has been previously reported<sup>13</sup> and it can be enhanced on Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> in the range of 0.3 to 0.5 due to the facile reduction of Ce<sup>4+</sup> to Ce<sup>3+</sup>. These different acidity on Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> is responsible for uniform distribution of Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> components leading to small particle size as found on the CZA(0.08) catalyst. The smaller the particle size of CuO and metallic Cu, the higher is the metallic surface area of copper (9.4 m<sup>2</sup>/g) due to the stable monoclinic phase of Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub>, and it is well correlated with CO conversion. CO conversion is found to be in the range of 27.1 - 36.0% which are found to be enhanced on CZA(0.08) catalyst due to small particle size of copper and its high metallic surface area. The correlation with CO conversion and copper surface area according to Ce/(Ce+Zr) weight ratio is shown in Figure 1. The surface area of copper and CO conversion are found to be maximum on CZA(0.08) and the compositional change on Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> mixed oxide are indeed responsible for changing metallic copper surface area which in turn alter the catalytic performance.

## Conclusions

A series of Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> admixed Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalysts were prepared to elucidate the effect of Ce/(Ce+Zr) weight ratio on the physicochemical characteristics and their catalytic performance for MeOH synthesis from syngas. The XRD and copper surface area measurement indicated that the metal surface area is maximum on the catalyst co-precipitated Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> in a slurry of Ce<sub>0.08</sub>Zr<sub>0.92</sub>O<sub>2</sub>. The catalytic activity also shows a maximum value on this catalyst i.e. CZA(0.08). The strong interaction between Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> and Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> indeed influences the admixed phases with the variation of copper dispersion due to the different surface acidity of Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> and it eventually affects the catalytic performance. The further characterization of those catalysts to elucidate the different catalytic performance is under study.

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