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Synthesis of Mixed Alcohols from Syngas over
Cs-modified Cu/Ce_{1-x}Zr_xO₂ Catalysts

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Cu/Ce_{1-x}Zr_xO₂ ($x = 0-1$) was prepared by a coprecipitation-decomposition method using NH₃·H₂O as precipitant (to avoid residues of alkali metals), followed by a boiling process to eliminate NH₃ and decompose [Cu(NH₃)₄]²⁺ complex. Then Cs was introduced to Cu/Ce_{1-x}Zr_xO₂ by the impregnation method. The prepared CsCu/Ce_{1-x}Zr_xO₂ catalysts (Cs: 1.0 wt%; Cu: 20 wt%) were used to catalyze the synthesis of mixed alcohols in a high-pressure fixed-bed flow reactor under reaction conditions of $T = 573$ K, $P = 3$ MPa, H₂/CO = 2/1, and GHSV = 2400 h⁻¹. CsCu/CeO₂ showed higher CO conversion than the industrial catalyst CsCu/ZnO due to the reducibility of the CeO₂ support. Moreover, the STY of higher alcohols over CsCu/CeO₂ was much higher than that over CsCu/ZnO due to the oxygen storage capacity of the CeO₂-based compounds. Introduction of Zr⁴⁺ ions into CeO₂ lattices increased the reducibility and the oxygen storage capacity of the CeO₂-based compounds, so the STY of higher alcohols over CsCu/Ce_{0.8}Zr_{0.2}O₂ was larger than that over CsCu/CeO₂. CO conversion increased but selectivity for methanol decreased with higher reaction temperature over CsCu/Ce_{0.8}Zr_{0.2}O₂. The selectivity for higher alcohols was maximum at 573 K over CsCu/Ce_{0.8}Zr_{0.2}O₂. Both CO conversion and selectivity for higher alcohols increased with higher reaction pressure over CsCu/Ce_{0.8}Zr_{0.2}O₂ for the synthesis of mixed alcohols from syngas.

Keywords

Coprecipitation decomposition method, Copper catalyst, Ceria-zirconia support, Cesium promoter

1. Introduction

The synthesis of mixed alcohols from syngas has attracted much attention because syngas can be obtained from biomass, coal, and natural gas by gasification and/or reforming^{1,2)}. The obtained mixed alcohols are important as fuels and chemicals. For example, methanol can be used to produce biodiesel by reaction with vegetable oil; ethanol can be directly added to gasoline as a fuel; and isobutanol can be used to produce methyl tertiary-butyl ether (MTBE, a high-octane additive for gasoline) by reaction with methanol.

Four types of catalysts are available for the synthesis of mixed alcohols from syngas: Rh-based catalysts^{3,4)}, Mo-based catalysts^{5)~8)}, modified Fischer-Tropsch (F-T) synthesis catalysts^{9,10)}, and modified methanol synthesis catalysts^{11)~13)}. Rh-based catalysts provide high selectivity for ethanol but Rh metal is too expensive. Mo-

based catalysts have high catalytic performance but require high reaction pressures (> 5 MPa) and usually involve a long activity induction period during the reaction. Modified F-T synthesis catalysts produce large amounts of hydrocarbons, which results in decreased alcohol yield. Modified methanol synthesis catalysts can provide increased selectivity for higher alcohols (C₂+OH). Cu/ZnO is an industrial catalyst for methanol synthesis, and the addition of alkali metals (especially Cs) to Cu/ZnO greatly increases the selectivity for higher alcohols. Therefore, CsCu/ZnO is a typical modified methanol synthesis catalyst for the synthesis of mixed alcohols from syngas^{11)~13)}.

We previously reported that Cu/CeO₂ is a highly active catalyst for the steam reforming of methanol^{14,15)}. The support and metal (SISM) show strong interaction in the CeO₂-supported metal catalysts which induces high activity for the synthesis of methanol in Pd/CeO₂ or Cu/CeO₂ catalysts^{16,17)}. Modifying the CeO₂ support with Zr⁴⁺ ions improves the catalytic activity of CeO₂-supported metal catalysts for the decomposition of methanol and the steam reforming of ethanol^{18,19)}. Moreover, CeO₂-TiO₂ catalyst is effec-

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tive for the synthesis of isobutane from syngas²⁰). In the present study, we investigated the catalytic performance of Cs-modified Cu/Ce_{1-x}Zr_xO₂ catalysts for the synthesis of mixed alcohols from syngas.

2. Experimental

2.1. Catalyst Preparation

Cu/Ce_{1-x}Zr_xO₂ ($x = 0-1$) was prepared by the coprecipitation-decomposition method using NH₃·H₂O as the precipitant to avoid residues of alkali metals. Some Cu²⁺ ions formed deep blue [Cu(NH₃)₄]²⁺ complexes with NH₃ during the precipitation process, so we designed a boiling step followed the precipitation step to eliminate NH₃ and decompose the complex. In a typical process, Ce(NO₃)₃·6H₂O, ZrO(NO₃)₂·8H₂O, and Cu(NO₃)₂·3H₂O were dissolved in distilled water in a beaker. 28 wt% NH₃·H₂O was added dropwise to the aqueous solution of mixed metallic nitrates with strong stirring at room temperature until the pH reached 9.5. The slurry was then boiled for 6 h with stirring until the pH reached 5.5. Distilled water was added to the beaker to maintain the liquid level during the boiling process. The resulting precipitate was then filtered off, washed with distilled water, dried at 373 K for 12 h, and finally calcined at 723 K for 3 h. The Cu loading was 20 wt% in the sample.

CsCu/Ce_{1-x}Zr_xO₂ was prepared by impregnating Cu/Ce_{1-x}Zr_xO₂ in a CsOH aqueous solution. After the water was eliminated by heating at 363 K, the solid sample was dried at 373 K for 12 h and calcined at 723 K for 3 h. The Cs loading was 1.0 wt% in the sample.

CsCu/ZnO was prepared by impregnating Cu/ZnO in a CsOH aqueous solution¹¹). Cu/ZnO was prepared using the coprecipitation-decomposition method through an aurichalite precursor^{11,15}). The Cu loading was 20 wt% and the Cs loading was 1.0 wt% in the sample.

2.2. Catalyst Characterization

X-ray powder diffraction (XRD) patterns were measured using a MAC Science MXP-18 diffractometer with Cu-K α radiation. Inductively coupled plasma (ICP) analyses were measured by a Thermo Jarrel Ash IRIS/AP instrument. The CO adsorptions (for calculating the sizes of Cu metal particles) and the N₂ adsorptions (for calculating the BET surface areas) were carried out using a BELCAT-B automatic instrument.

2.3. Catalyst Measurement

The catalytic reaction was carried out in a high-pressure fixed-bed flow type reactor (dia. 10 mm) at 523-623 K under a total pressure of 2-6 MPa. 1.0 g catalyst and 2.0 g quartz sand were mixed uniformly, and packed in a tubular reactor. After reduction in hydrogen at 573 K for 1 h, the reaction was started at a gas hourly space velocity (GHSV) of 2400 h⁻¹. The

feed gas contained 60% H₂, 30% CO and 10% N₂ (as an internal standard). The products were analyzed by four on-line gas chromatographs (GC) during the reaction. H₂, N₂, CO, and CO₂ were analyzed by a thermal conductivity detector (TCD) GC equipped with a New Carbon-ST column; light hydrocarbons (C₁-C₄) were analyzed by a hydrogen flame ionization detector (FID) GC equipped with a CP-Al₂O₃/KCl capillary column; heavy hydrocarbons (C₅+) were analyzed by a FID GC equipped with a UA-DX capillary column; and oxygenated compounds were analyzed by a FID GC equipped with a Stablewax capillary column. CO conversion was determined by the changes of the percentage concentrations of CO and N₂ (internal standard) in the mixed gases before and after the reaction. Product selectivities were reported in terms of carbon efficiencies which were calculated using the formula $n_i C_i / \sum (n_i C_i)$ where n_i is the carbon atom number of the compound. The analytical results agreed well with the carbon monoxide material balance.

3. Results and Discussion

3.1. Characterization of Various Samples

Figure 1 shows the XRD patterns of various samples after calcination at 723 K for 3 h. The Cu loading was

A: CsCu/CeO₂; B: CsCu/Ce_{0.9}Zr_{0.1}O₂; C: CsCu/Ce_{0.8}Zr_{0.2}O₂; D: CsCu/Ce_{0.7}Zr_{0.3}O₂; E: CsCu/Ce_{0.5}Zr_{0.5}O₂; F: CsCu/Ce_{0.2}Zr_{0.8}O₂; G: CsCu/ZrO₂. (●): CeO₂; (▼): CuO; (◆): ZrO₂.

Fig. 1 XRD Patterns of Various Samples (with 20 wt% Cu and 1.0 wt% Cs) after Calcination at 723 K

Fig. 2 Lattice Constant of CeO_2 in the $\text{CsCu/Ce}_{1-x}\text{Zr}_x\text{O}_2$ (with 20 wt% Cu and 1.0 wt% Cs) after Calcination at 723 K

20 wt% and the Cs loading was 1.0 wt% for each sample. CsCu/CeO_2 showed four strong reflections of the CeO_2 support corresponding to the (111), (200), (220) and (311) crystallographic planes, indicating that the CeO_2 support had a fluorite structure with cubic (fcc) cells. CsCu/ZrO_2 also showed four strong reflections corresponding to cubic ZrO_2 cells in the XRD pattern, but the peak positions were obviously different to those of CsCu/CeO_2 . The Cs phase could not be observed in the XRD patterns due to low Cs loading in the samples. On the other hand, two small peaks of a CuO phase could be observed at 35-40 degrees in the XRD pattern for each sample.

Figure 2 shows the lattice constants in $\text{CsCu/Ce}_{1-x}\text{Zr}_x\text{O}_2$ ($x = 0-0.5$) with changing Zr^{4+} content. The lattice constants were calculated based on the four main reflections of CeO_2 -based compounds in the XRD patterns. The lattice constant of CsCu/CeO_2 was 0.5402 nm. Introducing small Zr^{4+} (ionic radius: 0.84 nm) into the position of Ce^{4+} (ionic radius: 0.96 nm) caused a decrease in the lattice parameter when x was less than 0.2. On the other hand, the lattice constant remained constant at 0.5358 nm when $x > 0.2$ in $\text{CsCu/Ce}_{1-x}\text{Zr}_x\text{O}_2$ ($x = 0-0.5$). These results indicated that Zr^{4+} ions could enter the CeO_2 lattice to form a homogeneous solid solution when x was less than 0.2. In the $\text{CsCu/Ce}_{1-x}\text{Zr}_x\text{O}_2$ ($x = 0-0.5$) samples with $x > 0.2$, part of the Zr^{4+} ions probably entered the CeO_2 lattice to form a solid solution and the remainder of the Zr^{4+} ions formed ZrO_2 particles on the catalyst surface.

Figure 3 shows the BET surface areas and the Cu particle sizes of the $\text{CsCu/Ce}_{1-x}\text{Zr}_x\text{O}_2$ ($x = 0-1$) catalysts after reduction in H_2 at 573 K for 1 h. Doping Zr^{4+} ions into CeO_2 lattices or doping Ce^{4+} ions into ZrO_2 lattices decreased the crystallization degree of the $\text{CsCu/Ce}_{1-x}\text{Zr}_x\text{O}_2$ samples (as shown in Fig. 1), which resulted in the increase of the BET surface area¹⁸⁾.

(●): Surface area; (■): Cu particle size.

Fig. 3 BET Surface Areas and Cu Particle Sizes in the $\text{CsCu/Ce}_{1-x}\text{Zr}_x\text{O}_2$ Catalysts (with 20 wt% Cu and 1.0 wt% Cs) after Reduction at 573 K

Therefore, $\text{CsCu/Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ had a higher BET surface area than CsCu/CeO_2 due to doping Zr^{4+} ions in CeO_2 lattices, and $\text{CsCu/Ce}_{0.2}\text{Zr}_{0.8}\text{O}_2$ had a higher BET surface area than CsCu/ZrO_2 due to doping Ce^{4+} ions in ZrO_2 lattices. On the other hand, $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ is a physical mixture but is not a solid solution, so $\text{CsCu/Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ had a lower BET surface area than $\text{CsCu/Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ and $\text{CsCu/Ce}_{0.2}\text{Zr}_{0.8}\text{O}_2$. The actual Cu loadings, which were measured by ICP analysis, were similar to the designed Cu loadings in the various catalysts. The Cu particle size was calculated from the actual Cu loading and the amount of adsorbed CO molecules for each catalyst. The Cu particle size remained almost constant (about 10.2 nm) when x was less than 0.2 but increased with increasing Zr amount when x was larger than 0.2 in $\text{CsCu/Ce}_{1-x}\text{Zr}_x\text{O}_2$.

3. 2. Catalytic Performances of Various Catalysts for the Synthesis of Mixed Alcohols

The catalytic performances over various catalysts for the synthesis of mixed alcohols at 573 K are summarized in Table 1. Cu/CeO_2 showed a CO conversion of 23.5%, which was higher than that of Cu/ZnO (17.2%). Both Cu^0 species and Cu^+ species are important in the synthesis of methanol over Cu-based catalysts. The support effect of a Cu-based catalyst is decided by the amount ratio of Cu^+ to Cu^0 on the support surface for the synthesis of methanol²¹⁾. Reaction active intermediates are probably adsorbed on the surface of Cu^0 species, and the role of Cu^+ species is the stabilization of any oxygenates near the Cu^+ sites²¹⁾. CeO_2 -based compounds are reducible and a redox equilibrium ($\text{Ce}^{4+} + \text{Cu}^0 \leftrightarrow \text{Ce}^{3+} + \text{Cu}^+$) exists between the CeO_2 support and Cu particles in Cu/CeO_2 , so both Cu^0 species and Cu^+ species can be stabilized in Cu/CeO_2 ^{14),15)}. The stabilization of Cu^0 species and Cu^+ species at the same time effectively improves the CO conversion over Cu/CeO_2 catalyst. The selectivity for

Table 1 Catalytic Performance of Various Catalysts for the Synthesis of Mixed Alcohols at 573 K^{a)}

Catalyst ^{b)}	CO conv. [%]	Selectivity [%]					C ₂ +OH/MeOH ^{f)}
		Alc ^{c)}	CH ₄	HC ^{d)}	CO ₂	Other ^{e)}	
Cu/ZnO	17.2	78.4	8.8	1.1	9.7	1.9	0.05
Cu/CeO ₂	23.5	82.5	6.7	1.0	8.1	1.7	0.13
CsCu/ZnO	16.5	77.9	8.2	2.8	9.3	1.8	0.53
CsCu/CeO ₂	22.2	81.3	6.3	2.9	7.9	1.6	0.71
CsCu/Ce _{0.8} Zr _{0.2} O ₂	34.8	83.8	6.1	2.1	6.2	1.7	0.87

a) Reaction conditions: $n(\text{H}_2)/n(\text{CO}) = 2$; $P = 3$ MPa; GHSV = 2400 h⁻¹.

b) Cu: 20 wt%; Cs: 1.0 wt% (if applicable).

c) Total alcohols.

d) C₂+ hydrocarbons, mainly isobutane and ethane.

e) Other oxygenates, mainly DME and methyl formate.

f) Mass ratio.

alcohols over Cu/CeO₂ catalyst was 82.5%, which was higher than that over Cu/ZnO (78.4%). Methane and carbon dioxide were the main by-products for the synthesis of mixed alcohols over various catalysts. Although both Cu/ZnO and Cu/CeO₂ produced methanol as the dominant product, Cu/CeO₂ formed a larger amount of higher alcohols (C₂+OH) than Cu/ZnO (because the mass ratio of C₂+OH to MeOH was 0.13 for Cu/CeO₂ and 0.05 for Cu/ZnO). In comparison with the industrial methanol synthesis catalyst Cu/ZnO, Cu/CeO₂ is more suitable for the synthesis of mixed alcohols by modifying with promoters.

Cs is an excellent promoter to improve the selectivity for higher alcohols of Cu/ZnO catalyst^{11)~13)}. As shown in **Table 1**, the mass ratio of C₂+OH to MeOH over CsCu/ZnO was 0.53, which was much higher than that over Cu/ZnO (0.05). Moreover, the mass ratio of C₂+OH to MeOH greatly increased from 0.13 to 0.71 by introducing 1.0 wt% Cs in Cu/CeO₂. On the other hand, the CO conversion over CsCu/ZnO (16.5%) was slightly lower than that over Cu/ZnO (17.2%), and the CO conversion over CsCu/CeO₂ (22.2%) was also slightly lower than that over Cu/CeO₂ (23.5%). Therefore, Cs promoter greatly improved the formation of higher alcohols but only slightly decreased the formation of methanol over the Cu-based catalysts. CsCu/CeO₂ catalyst showed higher CO conversion and higher mass ratio of C₂+OH to MeOH than CsCu/ZnO catalyst. On the other hand, CsCu/Ce_{0.8}Zr_{0.2}O₂ showed a higher CO conversion (34.8%) than CsCu/CeO₂ (22.2%) for the synthesis of mixed alcohols. Moreover, the mass ratio of C₂+OH to MeOH increased to 0.87 over CsCu/Ce_{0.8}Zr_{0.2}O₂. Therefore, Zr is an effective promoter for CsCu/CeO₂ catalyst for the synthesis of mixed alcohols.

Figure 4 shows the effect of Zr content in CsCu/Ce_{1-x}Zr_xO₂ catalysts for the synthesis of mixed alcohols. Either the STY of total alcohols or the STY of higher alcohols was maximum at $x = 0.2$ in CsCu/Ce_{1-x}Zr_xO₂. CeO₂-based compounds have high oxygen storage capacity and reducibility, which induces high

(●): STY of total alcohols; (▲): STY of MeOH; (■): STY of C₂+OH. Reaction conditions: $n(\text{H}_2)/n(\text{CO}) = 2$; $T = 573$ K; $P = 3$ MPa; GHSV = 2400 h⁻¹.

Fig. 4 Effect of Zr Amount in CsCu/Ce_{1-x}Zr_xO₂ (Cu: 20 wt%; Cs: 1.0 wt%) for the Synthesis of Mixed Alcohols

activity for some reactions^{19),22)}. The addition of ZrO₂ to CeO₂ leads to improvements in oxygen storage capacity and reducibility, due to the partial substitution of Ce⁴⁺ by Zr⁴⁺ in the lattice of CeO₂, resulting in formation of a solid solution^{22),23)}. The XRD patterns indicate that small Zr⁴⁺ ions could be introduced in the Ce⁴⁺ positions up to $x = 0.2$ in CsCu/Ce_{1-x}Zr_xO₂. The remainder of the Zr⁴⁺ ions formed ZrO₂ particles on the catalyst surface when x was larger than 0.2 in CsCu/Ce_{1-x}Zr_xO₂. Therefore, neither Ce_{0.7}Zr_{0.3}O₂ nor Ce_{0.5}Zr_{0.5}O₂ is a solid solution. Ce_{0.2}Zr_{0.8}O₂ support is a solid solution with the largest amount of Zr⁴⁺ ions, so CsCu/Ce_{0.8}Zr_{0.2}O₂ showed the highest catalytic performance among the various CsCu/Ce_{1-x}Zr_xO₂ catalysts for the synthesis of mixed alcohols.

Table 2 lists the STY of various alcohols over CsCu/ZnO, CsCu/CeO₂, and CsCu/Ce_{0.2}Zr_{0.8}O₂ at 573 K. The STY of total alcohols over CsCu/CeO₂ (159.8 g·L⁻¹·h⁻¹) was larger than that over CsCu/ZnO (106.5 g·L⁻¹·h⁻¹) due to the high CO conversion. Moreover, the STY of isobutanol over CsCu/CeO₂

Table 2 STY of Various Alcohols over Various Catalysts at 573 K^{a)}

Catalyst ^{b)}	Alcohol STY [$\text{g} \cdot \text{L}^{-1} \cdot \text{h}^{-1}$]					
	Total	MeOH	EtOH	PrOH	<i>i</i> -BuOH	C ₅ +OH
CsCu/ZnO	106.5	69.8	9.8	6.5	16.2	4.6
CsCu/CeO ₂	159.8	93.5	12.6	9.2	41.8	2.7
CsCu/Ce _{0.8} Zr _{0.2} O ₂	185.4	99.1	13.5	9.9	59.5	3.4

a) Reaction conditions: $n(\text{H}_2)/n(\text{CO}) = 2$; $P = 3$ MPa; GHSV: 2400 h^{-1} .

b) Cu: 20 wt%; Cs: 1.0 wt%.

($41.8 \text{ g} \cdot \text{L}^{-1} \cdot \text{h}^{-1}$) was much higher than that over CsCu/ZnO ($16.2 \text{ g} \cdot \text{L}^{-1} \cdot \text{h}^{-1}$), which is the main reason for the high mass ratio of C₂+OH to MeOH over CsCu/CeO₂ (as shown in Table 1). The CeO₂-based compounds have oxygen storage capacity, so are active catalysts for the synthesis of isobutane from syngas (so-called as isosynthesis)²⁰. Isobutane is a thermodynamically stable hydrocarbon and isobutanol is a thermodynamically stable alcohol. CeO₂ support with the oxygen-storage capacity can achieve thermodynamic equilibrium rapidly during the reaction. Therefore, we think that the oxygen storage capacity of the CeO₂ support allowed the high STY of isobutanol over CsCu/CeO₂ in the synthesis of mixed alcohols. Both the reducibility and the oxygen storage capacity were increased by introducing Zr⁴⁺ ions into CeO₂ lattices to form solid solutions^{22,23}. Increased reducibility improved the CO conversion and increased oxygen storage capacity increased the STY of isobutanol, so that CsCu/Ce_{0.8}Zr_{0.2}O₂ showed the highest STY of total alcohols ($185.4 \text{ g} \cdot \text{L}^{-1} \cdot \text{h}^{-1}$) and the highest STY of isobutanol ($59.5 \text{ g} \cdot \text{L}^{-1} \cdot \text{h}^{-1}$). Isobutanol is used for synthesizing MTBE by reaction with methanol (obtained from the reaction), so the STY of isobutanol is an important parameter for evaluating modified methanol synthesis catalysts for the synthesis of mixed alcohols²⁴. Therefore, CsCu/Ce_{0.8}Zr_{0.2}O₂ is a promising catalyst for the synthesis of mixed alcohols from syngas.

3.3. Synthesis of Mixed Alcohols over CsCu/Ce_{0.8}Zr_{0.2}O₂ Catalyst

Figure 5 shows the effect of Cs loading in CsCu/Ce_{0.8}Zr_{0.2}O₂ (Cu: 20 wt%) for the synthesis of mixed alcohols at 573 K. The STY of methanol decreased with higher Cs loading in CsCu/Ce_{0.8}Zr_{0.2}O₂, so Cs decreased the formation of methanol. On the other hand, the introduction of Cs into Cu/Ce_{0.8}Zr_{0.2}O₂ greatly increased the STY of higher alcohols from 15.7 to $66.3 \text{ g} \cdot \text{L}^{-1} \cdot \text{h}^{-1}$ as the Cs loading increased from 0 to 1.0 wt% in CsCu/Ce_{0.8}Zr_{0.2}O₂. However, both the STY of higher alcohols and the STY of total alcohols decreased with increasing Cs loading higher than 1.0 wt% in CsCu/Ce_{0.8}Zr_{0.2}O₂. Overall, 1.0 wt% Cs loading is optimum for the CsCu/Ce_{0.8}Zr_{0.2}O₂ catalyst in the synthesis of mixed alcohols.

Figure 6 shows the effect of Cu loading in CsCu/Ce_{0.8}Zr_{0.2}O₂ (Cs: 1.0 wt%) for the synthesis of mixed

(●): STY of total alcohols; (▲): STY of MeOH; (■): STY of C₂+OH. Reaction conditions: $n(\text{H}_2)/n(\text{CO}) = 2$; $P = 3$ MPa; GHSV = 2400 h^{-1} .

Fig. 5 Effect of Cs Loading in CsCu/Ce_{0.8}Zr_{0.2}O₂ (Cu: 20 wt%) for the Synthesis of Mixed Alcohols at 573 K

(●): STY of total alcohols; (▲): STY of MeOH; (■): STY of C₂+OH. Reaction conditions: $n(\text{H}_2)/n(\text{CO}) = 2$; $P = 3$ MPa; GHSV = 2400 h^{-1} .

Fig. 6 Effect of Cu Loading in CsCu/Ce_{0.8}Zr_{0.2}O₂ (Cs: 1.0 wt%) for the Synthesis of Mixed Alcohols at 573 K

alcohols at 573 K. No alcohol was formed from the reaction over a catalyst containing no Cu. Both the STY of methanol and the STY of higher alcohols increased with higher Cu loading from 0 to 20 wt% over CsCu/Ce_{0.8}Zr_{0.2}O₂. However, the STY of total alcohols decreased with higher Cu loading above

(●): CO conversion; (▲): selectivity for MeOH; (■): selectivity for C₂+OH. Reaction conditions: $n(\text{H}_2)/n(\text{CO}) = 2$; $P = 3 \text{ MPa}$; GHSV = 2400 h⁻¹.

Fig. 7 Effect of Reaction Temperature in the Synthesis of Mixed Alcohols over CsCu/Ce_{0.8}Zr_{0.2}O₂ (Cu: 20 wt%; Cs: 1.0 wt%)

20 wt% in CsCu/Ce_{0.8}Zr_{0.2}O₂. On the other hand, the mass ratio of higher alcohols to methanol was almost constant (around 0.7) over CsCu/Ce_{0.8}Zr_{0.2}O₂ at Cu loadings from 5 to 30 wt%. Overall, 20 wt% Cu loading is optimum for CsCu/Ce_{0.8}Zr_{0.2}O₂ catalyst in the synthesis of mixed alcohols.

Figure 7 shows the effect of reaction temperature in the synthesis of mixed alcohols over CsCu/Ce_{0.8}Zr_{0.2}O₂ (Cu: 20 wt%; Cs: 1.0 wt%). The CO conversion increased from 8.2 to 64.5% with higher reaction temperature from 523 to 623 K. On the other hand, the selectivity for methanol decreased with higher reaction temperature in the synthesis of mixed alcohols. The selectivity for higher alcohols increased with higher reaction temperature from 523 to 573 K but decreased with higher reaction temperature at > 573 K. The selectivity for by-products (hydrocarbons and CO₂) increased when the reaction was carried out at a high temperature over CsCu/Ce_{0.8}Zr_{0.2}O₂. Therefore, 573 K is the optimum reaction temperature for the synthesis of mixed alcohols over CsCu/Ce_{0.8}Zr_{0.2}O₂ catalyst.

Figure 8 shows the effect of reaction pressure on the synthesis of mixed alcohols over CsCu/Ce_{0.8}Zr_{0.2}O₂ (Cu: 20 wt%; Cs: 1.0 wt%). The CO conversion increased from 3.8 to 48.5% with higher reaction pressure from 0.1 to 6.0 MPa. The selectivity for methanol increased with higher reaction pressure from 0.1 to 3.0 MPa but remained almost constant from 3.0 to 6.0 MPa. On the other hand, the selectivity for higher alcohols increased with higher reaction pressure from 0.1 to 6.0 MPa. Therefore, a high reaction pressure is preferable for producing higher alcohols over CsCu/Ce_{0.8}Zr_{0.2}O₂ in the synthesis of mixed alcohols from

(●): CO conversion; (▲): selectivity for MeOH; (■): selectivity for C₂+OH. Reaction conditions: $n(\text{H}_2)/n(\text{CO}) = 2$; $T = 573 \text{ K}$; GHSV = 2400 h⁻¹.

Fig. 8 Effect of Reaction Pressure in the Synthesis of Mixed Alcohols over CsCu/Ce_{0.8}Zr_{0.2}O₂ (Cu: 20 wt%; Cs: 1.0 wt%)

syngas.

4. Conclusions

CsCu/CeO₂ catalyst had higher STY for higher alcohols than the industrial catalyst CsCu/ZnO for the synthesis of mixed alcohols because CeO₂-based compounds had reducibility and oxygen storage capacity. Introduction of Zr⁴⁺ ions into CeO₂ lattices (to form a solid solution) increased the reducibility and the oxygen storage capacity, whereas CsCu/Ce_{0.8}Zr_{0.2}O₂ showed the highest STY of higher alcohols among the various CsCu/Ce_{1-x}Zr_xO₂ ($x = 0-1$) catalysts. Cs promoter greatly improved the selectivity for higher alcohols but depressed the formation of methanol for the synthesis of mixed alcohols. Reaction at a high temperature improved the CO conversion but decreased the selectivity for methanol, whereas reaction at a high pressure improved the CO conversion as well as the selectivity for higher alcohols.

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要 旨

Cs 修飾した Cu/Ce_{1-x}Zr_xO₂ 触媒による合成ガスから混合アルコールの合成

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アンモニア水共沈殿-沸騰分解法で Cu/Ce_{1-x}Zr_xO₂ を得て、含浸法で Cs を Cu/Ce_{1-x}Zr_xO₂ に導入することによって CsCu/Ce_{1-x}Zr_xO₂ 触媒を調製した。調製した CsCu/Ce_{1-x}Zr_xO₂ 触媒 (Cs: 1 wt%; Cu: 20 wt%) を用い、 $T = 573 \text{ K}$, $P = 3 \text{ MPa}$, $\text{H}_2/\text{CO} = 2/1$, $\text{GHSV} = 2400 \text{ h}^{-1}$ の反応条件において、高圧固定床流通式反応系で合成ガスから混合アルコールの合成を行った。CeO₂ 系化合物は還元性を有するため、CsCu/CeO₂ 触媒は工業触媒 CsCu/ZnO より高い CO 転化率を示した。CeO₂ 系化合物は酸素貯蔵能力を持つため、CsCu/CeO₂ は CsCu/ZnO に比べて高級アルコール (C₂+OH) を多く生成した。Zr⁴⁺ イオンを CeO₂ 格子

に導入することによって、セリア系化合物は還元性と酸素貯蔵能力が向上したため、CsCu/Ce_{0.8}Zr_{0.2}O₂ は CsCu/CeO₂ より高い高級アルコールの STY (空時収率) を得た。CsCu/Ce_{0.8}Zr_{0.2}O₂ 触媒を用いた反応において、反応温度の上昇に伴って CO 転化率は向上したが、メタノールへの選択率は低下した。一方、573 K において CsCu/Ce_{0.8}Zr_{0.2}O₂ 触媒は最も高い高級アルコールへの選択率を示した。さらに、CsCu/Ce_{0.8}Zr_{0.2}O₂ 触媒は高い反応圧力において、CO 転化率や高級アルコールへの選択率が向上したことも分かった。