Effect of Y_2O_3 binder on the methanol steam reforming activity of Cu/ZnO catalyst

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For compact reactor systems, catalyst is usually washcoated onto either honeycomb or microchannel of the reactors. In this study, a house-prepared Cu-ZnO/Al_2O_3 catalyst was used to prepare the ink for washcoat using Y_2O_3 sols as the binder. The effect of Y_2O_3 binder was examined on the methanol steam reforming activity of the Cu-ZnO/Al_2O_3 catalyst. Within the range of ink recipe that provided good adhesion on a stainless-steel substrate, the added Y_2O_3 binder was found to increase the per-gram catalyst activity. This effect is more obvious when the Cu-ZnO/Al_2O_3 catalyst had a larger particle size of CuO. Analyses indicated that CuO redispersion occurred during the ink preparation likely due to certain interaction with Y_2O_3. Increase in binder dosage or in ink agitation time resulted in denser washcoat. The specific surface area increased while the average pore size decreased in denser washcoat. Such changes did not affect the steady state activity when dry ink powders were tested in a packed-bed reactor but could influence the performance of the washcoat in a microchannel reactor.

1. Introduction

Hydrogen is considered as a clean energy carrier. The so-called hydrogen economy covers the production, the storage, the transportation, and the uses of hydrogen. Although water is proposed as the most environmental friendly source of hydrogen, the efficiency of hydrogen production from water is still low. The reforming of hydrocarbons is a long-known technology that can be used to produce syn gas and hydrogen-rich gases. It, especially the steam reforming, serves as an effective way for the production of hydrogen from H-containing compounds. Methanol is one of the more studied raw materials for uses of steam reforming to produce hydrogen. This is because of the relatively low cost of methanol and, more importantly, that there is no C-C bond breaking in methanol steam reforming.

For portable devices using fuel cells, the hydrogen supply needs not only to meet the capacity and purity requirements but also to match a portable size. One way of making a portable methanol steam reformer is to washcoat catalyst powders to a microchannel reactor. Microchannel reactors are considered to provide uniform temperature via good

heat conduction (Kawamura, 2006, Holladay, 2004) and, consequently, are considered more effective. The wash coat requires a binder and the ink preparation is critical. Good adhesion of catalyst powders to the substrate and maintaining good catalyst performance are two important issues. In this study, we report the use of Y_2O_3 sols to bind house-prepared Cu-Zn/Al_2O_3 catalysts onto stainless steel substrates. The catalytic performance of catalyst powders and the dry ink powders was also compared. It was found that the activity per-gram catalyst depends on the ink preparation conditions.

2. Experimentals

2.1 Catalyst Preparation

The Cu-ZnO/Al_2O_3 catalyst was prepared by a sequential precipitation method using a commercial γ-Al_2O_3 support (Kaiser, 99 %). The support dispersed in deionized water was heated to 343 K and then 0.1 M $Zn(NO_3)_2$ (Aldrich, 98 %) was added dropwise at a control pH of 9 (by NaOH addition). After 2-h aging, 0.1 M $Cu(NO_3)_2$ (Aldrich, 98 %) was added dropwise at a control pH of 9 and the mixture was agitaed for another 2 h. The filtered solids were washed with deionized water, dried at 378 K and then calcined at 673 K. Two heating rates, 20 and 5 K/min, were used during calcinations, and the obtained catalyst is named as CuZnAl-1 and CuZnAl-2 respectively. The composition of the prepared catalyst was 40 % CuO, 50 % ZnO, and 10 % Al_2O_3.

2.2 Catalyst Ink Preparation

The desired amount of Cu-ZnO/Al_2O_3 catalyst was mixed with a commercial Y_2O_3 sol (NYACOL, Y_2O_3 14 wt%, acetic acid 9 %, water 77 %, Y_2O_3 size 2 - 10 nm) at room temperature. The aqueous suspension was always kept at a constant solid content of 20 wt %, although the catalyst/binder (C/B) ratio varied. After agitation for a certain time, the suspension was either filtered and dried or brush coated onto a 304 stainless steel microchannel plate. The dry ink was calicined at 623 K for 2 h.

2.3 Catalyst Characterization

The XRD (x-ray diffraction) was carried out using a commercial instrument (Shimadzu, LabX 6000, with Cu Kα-source). The particle size of CuO and ZnO was calculated by Scherrer equation using the half width of CuO(111) and ZnO(100). The Cu dispersion of the 523K-reduced Cu-Zn/Al_2O_3 catalysts and dry ink powders was analyzed by flowing N_2O for 30 min, purging with He for 30 min, and then the surface oxide was reduced by temperature-programmed H_2 reduction. The amount of hydrogen consumption was used to calculate Cu dispersion by assuming $O_{ad}/Cu_s = 1/2$. The BET surface area and the average pore size were analyzed by N_2 adsorption at liquid N_2 temperature using a commercial instrument (Micromeritics, ASAP2020). Scanning electron microscope (SEM) images were taken by using a commercial instrument (JOEL, JSM-6701) typically at 15 kV.

2.4 Methanol Steam Reforming Reaction Tests

Powders of catalysts or of dry inks in the range of 80-120 mesh size were loaded into a glass U-tube reactor which is then connected to a house-made microreactor system via a 4-way valve. The powders were reduced in-line by H_2 at 523 K for 1h before reaction test. The reactant methanol (Merck, 99.95 %) was premixed with water to a H_2O/methanol ratio of 1.3 (mole), fed to the preheated foreline by a syringe pump and carried into the reactor by He carrier gas. The reactor effluent was constantly monitored

by in-line GC using a 6-port valve. The reaction was carried out at atmospheric pressure having 22 % methanol, 28 % H_2O and 50 % He. The WHSV (weight hourly space velocity, g methanol/g catalyst/h) tested covers $1 - 15$ h^{-1}.The reactor temperature was
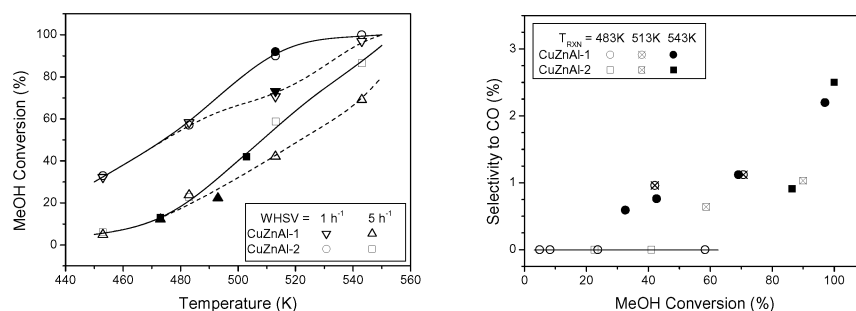

Figure 1.Effect of heating rate during calcination on the methanol steam reforming reaction over house-prepared Cu-ZnO/Al_2O_3 catalyst at WHSV of 1 and 5 h^{-1}: (a) methanol conversion as a function of temperature, and (b) CO selectivity as a function of methanol conversion. CuZnAl-1 represents the catalyst calcined with a heating rate of 20 K/min while CuZnAl-2 represent the one with 5 K/min. Open symbols indicate data taken during heating sequence while filled symbols are data taken during cooling sequence.

subjected to a stepwise heating-cooling sequence in which methanol and water was fed only at constant-temperature segments. Data reported in this study are averaged of steady state data from 30 to 90 min onstream at each temperature.

3. Results and Discussion

The methanol steam reforming activity of the house-prepared Cu-ZnO/Al_2O_3 was found to depend on the heating rate during its calcination. Figure 1a shows that CuZnAl-1 (using a faster heating rate at 20 K/min) is less active than CuZnAl-2 (using a slower heating rate at 5 K/min) at reaction temperatures above 480 K. However, the activity at below 480 K is independent of the heating rate. Both XRD and N_2O chemisorption analysis, shown in Table 1, indicated that CuZnAl-2 contains Cu at higher dispersion. That the Cu dispersion is higher when the calcination was carried out at a slower heating rate is consistent with previous reports (Fujita, 2001). The selectivity to CO as a function of methanol conversion is indicated in Figure 1b. The CuZnAl-2 with higher dispersion seems to give slightly lower CO selectivity. However, the difference is relatively insignificant compared to the effect of reaction temperature. The selectivity to CO increased with the reaction temperature and methanol conversion.

The dry ink powders were also tested for the methanol steam reforming reaction using the same packed bed microreactor system. By varying WHSV, the effect of space time on the methanol conversion at 513 K is shown in Figure 2 in which the ink was agitated for only 10 min. The methanol conversion increased with space time as expected from kinetic theory. The kinetic activity can be calculated by the linear relation between

conversion and space time in such a plot. As already shown in Figure 1, CuZnAl-2 is more active than CuZnAl-1 at 513 K. However, the dry ink powders were found more active than the original catalyst and this effect of activity increase by Y_2O_3 dilution Table 1. XRD, N_2O chemisorption, BET specific area, and pore size analysis of the prepared catalysts and their dry ink powders.

Sample	d_{CuO}[1] (nm)	d_{ZnO}[1] (nm)	Cu_s/Cu[2] (%)	Surface Area[3] (m^2/g)	Pore Size[3] (nm)
CuZnAl-1	20.8	47.1	5.1	--	--
C/B 10 (10 min)	20.5	48.9	7.7	--	--
C/B 1.5 (10 min)	13.8	40.0	11.0	--	--
CuZnAl-2	12.4	19.8	7.2	23	51.6
C/B 10 (10 min)	11.9	19.6	--	--	--
C/B 10 (3 h)	12.0	20.0	10.3	--	--
C/B 10 (12 h)	11.8	19.7	10.2	49	13.9
C/B 1.5 (10 min)	10.4	18.7	--	51	5.8

[1] By XRD analysis.

[2] By N_2O chemisorption followed by temperature-programmed H_2 reduction.

[3] By N_2 physisorption.

is more obvious for CuZnAl-1 than for CuZnAl-2. Table 1 shows that the dry ink powders prepared from CuZnAl-1 showed significant decrease in the particle size of both CuO and ZnO. Consistently, an increase in Cu dispersion was observed. Similar trends can be found with CuZnAl-2 but the degree of changes is relatively small, in consistent with data in Figure 2. Figure 3 shows the effect of ink agitation time on the methanol steam reforming activity of dry ink powders prepared from CuZnAl-2. Minor increase of the activity was noticed on an increase of agitation time.

The reason of the redispersion of CuO and ZnO during ink preparation is not known yet. The Y_2O_3 sols used in this study has a pH near 7 and it is not expected to cause dissolution. To examine the possible influence of acetic acid presented in Y_2O_3 sols, we mixed CuZnAl-2 with acetic acid aqueous solution in the exact conditions (solid content and acetic concentration) as in the preparation of C/B 10 ink. No obvious change in
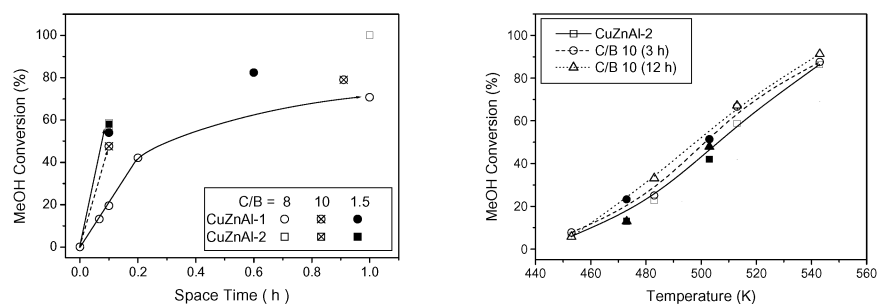

Figure 2. Effect of space time on the methanol steam reforming reaction at 513 K over dry ink powders prepared from Cu-ZnO/Al₂O₃ catalyst at different catalyst/binder wt ratio. The ink was agitated at room temperature for 10 min, then filtered, dried, and

calcined. Please refer to Figure 1 caption for the difference between CuZnAl-1 and CuZnAl-2.

Figure 3. Effect of ink agitation time on the methanol steam reforming reaction over dry ink powders prepared from CuZnAl-2 catalyst.
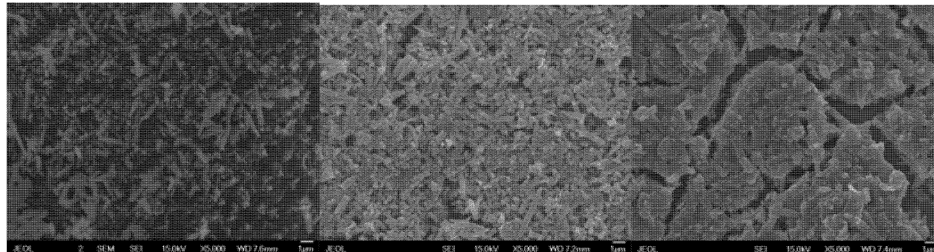

Figure 4. SEM Images of (a) CuZnAl-1, and dry ink powders from CuZnAl-1 with (b) C/B = 10 and (c) C/B = 1.5. Both inks were agitated at room temperature for 10 min.

CuO or ZnO particle size or in Cu dispersion was observed even after agitation for 12 h. It seems that the Y_2O_3 nanoparticles have a strong interaction with CuO and ZnO probably due to the difference in surface free energy and this effect is more obvious when the original CuO and ZnO particles are larger as in CuZnAl-1.

Table 1 indicates that the dry ink powders showed a decrease in the average pore size comparing to the original catalyst while the specific surface area of dry ink powders increases. The increase in surface area can be expected owing to the smaller particle size of Y_2O_3 and, therefore, the specific surface area of dry ink powders should increase with increasing Y_2O_3 content (i.e., decreasing C/B). The decrease in pore size is significant even for the ink of C/B = 10, which is equivalent to 91 % wt of catalyst in the dry ink powders. We found that the catalyst ink became more viscous when either the agitation time was increased or the C/B ratio was decreased. This is likely due to the gelling of the ink suspension. Figure 4 shows the SEM images of dry ink powders at a C/B ratio of 10 and 1.5 and the catalyst powders. It is obvious that denser solid packing can be observed with increasing binder content. The denser solid packing and the reduced pore size with increasing binder content is not desirable because of the possibility to cause mass transfer limitation during reaction. From Figures 2 and 3, mass transfer limitation did not occur in our tests with packed bed reactor. It may be due to the small sample size (less than 100 mg) we used and also the control of sample particle size (from 80 to 120 mesh) in our tests. However, mass transfer limitation was found to play an important role in the washcoat of microchannel reactor when using the same inks in this study. (Yang, 2009) The reactants flow in the same direction as mass diffusion in a packed bed reactor. However, the direction of mass diffusion is perpendicular to the flow direction in a microchannel reactor. This may be a reason for the different performance between a packed bed reactor and a microchannel reactor using the same ink.

4. Conclusions

The heating rate during calcinations of house-prepared Cu-ZnO/Al$_2$O$_3$ catalyst affected the particle size of CuO and of ZnO. A slower heating resulted in higher dispersion. The methanol steam reforming activity increased with increasing Cu dispersion. A washcoating ink was prepared by using Y$_2$O$_3$ sols as the binder. The dry ink powders showed an increase in methanol steam reforming reaction activity per gram of catalyst comparing to the catalyst before the ink preparation. Meanwhile, the particle size of CuO and ZnO in the dry ink powders was found smaller than that of the catalyst. This is attributed to a certain interaction between Y$_2$O$_3$ and CuO. Increase in binder dosage or in ink agitation time resulted in more viscous ink and denser washcoat. In addition, the average pore size of the dry ink powders was found to decrease. Denser washcoat has a tendency to cause mass transfer limitation during reaction.

5. References

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