[ENE04] Formulation and Characterization of Cu-Zn-V-Al Oxides Catalyst in Auto Thermal Reforming of Methanol.

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Introduction

Nowadays the world concern about the alternative solutions to the combustion engine due to the problem of the decreasing resources of crude oil and its recent environmental impact. One of the attention that are paid by most of the automotive industries is proton exchange membrane fuel cell (PEMFC). To comply with the modern automobiles a fast and highly responsive supply of hydrogen with no by-product other than carbon dioxide must be found. The high selectivity requirement emanate from the sensitivity of the PEM containing Pt as the catalyst for proton exchange.

These concerns led the researchers to search for on-board hydrogen supply methods such as by pressurized hydrogen cylinder, metal hydrides, gas reforming and liquid reforming. However the problem of supplying hydrogen to the refueling station and its mechanical problems while refueling the vehicles, the limited driving range and source amount, the high weight of the storage cylinder and safety concern of carrying a high-pressure cylinder of hydrogen came into view at a commercial level.

As the result, most of them selected liquid reforming method. Four most potential sources, which have been discussed for on-board liquid reforming, are methanol, ethanol, gasoline and diesel. Using gasoline and diesel will not resolved the problem of the diminishing world oil reserves and the present global warming instead of their impurities such as sulphur and nitrogen oxides and producing more coke that will create the soot formation which poisons the reforming catalyst. Methanol has higher hydrogen-to-carbon ratio than ethanol as well as no carbon-carbon bond which make the steam reforming of methanol energetically favorable solution and possible to be soot formation free.

Hence methanol is the best candidate that contains high energy without possessing high toxicity level. (B. Lindström and L. Petterson, 2001). Hydrogen production via steam reforming of methanol (SRM) using commercial methanol synthesis catalyst, co-precipitated Cu-Zn-Al oxide, had mostly been studied as a promising solution for fuel cell vehicle application. However the problem of high CO formation (≥ 20ppm) and high external energy input to the endothermic reaction has yet to be improved [1].

To overcome this the exothermic partial oxidation of methanol (POM) that also produces hydrogen was added by using V-promoted Cu-Zn-Al oxides catalyst. Vanadia has good track record as a commercial moderate oxidizing catalyst in most oil, gas and petrochemical industry for the dehydrogenation and partial oxidation of hydrocarbon and alcohol. The potential of the quaternary catalyst are characterized and observed by using X-Ray Diffraction (XRD), Brunauer-Emmett-Teller (BET), Temperature Programmed Reduction (TPR) and Scanning Electron Micrograph with Energy Dispersive X-Ray (SEM-EDX) method. Finally the potential of the catalyst was tested to produce hydrogen via SRM and auto thermal reforming of methanol (ATRM) reaction.

Materials and methods

Mixture Design – Simplex Centroid.

Designing the experiment from the beginning by using mixture design method, namely the simplex centroid design was being carried out by using Design Expert© 6. 3 compositions of metal: Cu, Zn and V (Fig. 1) were manipulated as Scheffe model in a triangle where BET surface area, the lowest reduction temperature, the hydrogen yield and the reaction temperature responded according to the cubic equation (1). Al was excluded from the design because its function just as a support and is inactive in SRM or ATRM reaction. Al ratio

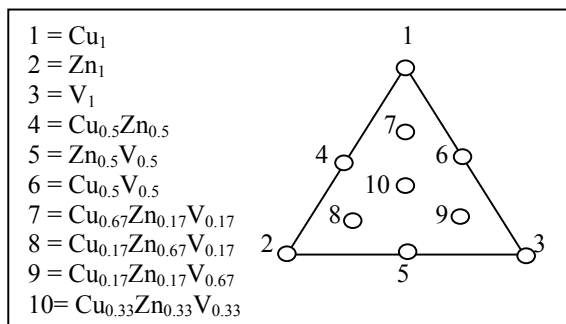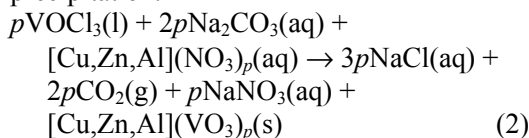was fixed to 40% by weight out of other metals,

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1 = Cu₁                                    1
2 = Zn₁
3 = V₁                                      ○
4 = Cu₀.₅Zn₀.₅                         7 ○
5 = Zn₀.₅V₀.₅              4 ○            ○ 6
6 = Cu₀.₅V₀.₅                  10 ○
7 = Cu₀.₆₇Zn₀.₁₇V₀.₁₇     8 ○       ○ 9
8 = Cu₀.₁₇Zn₀.₆₇V₀.₁₇  2 ○     ○      ○ 3
9 = Cu₀.₁₇Zn₀.₁₇V₀.₆₇          5
10= Cu₀.₃₃Zn₀.₃₃V₀.₃₃
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FIGURE 1 The simplex centroid design

the best composition ($Cu_{30}Zn_{30}Al_{40}$) of the lowest CO formation, as reported by J. Agrell et. al (2002).

$$E(Y) = \sum_{i=1}^{q} \beta_i x_i + \sum_{i=1}^{q} \sum_{j=i+1}^{q} \beta_{ij} x_i x_j +$$

$$\sum_{i=1}^{q} \sum_{j=i+1}^{q} \sum_{k=j+1}^{q} \beta_{ijk} x_i x_j x_k \qquad (1)$$
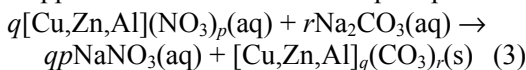
Catalyst preparation

Cu-Zn-V-Al oxides catalysts were prepared as proposed by M. Begum (2000) and J. B. Russell (1992), which 200ml $VOCl_3$ and Cu, Zn and Al nitrates aqueous were co-precipitated by 1.1 of required stoichiometry of Na_2CO_3 with maintained pH 7 → 8 under vigorous stirring as equation 2 and 3. The resulted sludge was dried at 120°C in a ventilated oven overnight prior to the crushing. Then the dry sludge was calcined at 500°C for 3 hrs in a furnace inerted with pure nitrogen.

vanadia and copper or zinc or aluminum precipitation.
$pVOCl_3(l) + 2pNa_2CO_3(aq) +$
    $[Cu,Zn,Al](NO_3)_p(aq) \rightarrow 3pNaCl(aq) +$
    $2pCO_2(g) + pNaNO_3(aq) +$
    $[Cu,Zn,Al](VO_3)_p(s)$ (2)

Copper or zinc or aluminum co-precipitation.
$q[Cu,Zn,Al](NO_3)_p(aq) + rNa_2CO_3(aq) \rightarrow$
    $qpNaNO_3(aq) + [Cu,Zn,Al]_q(CO_3)_r(s)$ (3)

Catalyst characterization

Crystallinity of each 1g sample was characterized by using SIEMENS X-Ray Diffractometer (D5000) facilitated with CuKΩ and Ni filter at 40kV acceleration and 30mA current within the angle range of 2° → 60°. Species phases of the signal peak were identified according to the international diffraction data file.

BET and TPR characterization of 800 → 900mg of each sample were carried out by using catalyst characterization apparatus AMI 200. All samples were treated by flowing nitrogen (BET) and argon (TPR) at 120°C for 1hr. BET surface area were obtained by flowing 3 ratio (10%, 20% and 30%) of N_2 in He via the over-cooled sample in U tube immersed in liquid N_2. TPR trend was obtained by flowing 5% H_2 in Ar at the ramping temperature of 50 → 600°C. Each effluent would then flow through a thermal conductivity detector (TCD) and the signal was plotted verses time or temperature. Finally, the signal was interpreted by referring the average of pulses of the same amount and ratio feed into a calibrated volume (526μL) of spiral tube.

SEM-EDX photo and the spectrum and mapping of the surface metal composition of the calcined samples were obtained by using Electron Microscope LEO 1450VP and interpreted by Inca© software. The sample were coated with gold in argon prior to be scanned under 1000X, 10,000X dan 15,000X magnification. The beam of electron accelerated at 12kV in vacumm space to the coated sample from various angle and the reflection was then being collected by a probe which was adjusted around 9 → 13 mm from the sample. The dispersive energy x-ray was also used to measure the surface metal concentration as well as to map the metal component at the focused area at the certain sublayer.

Reaction study.

Each 500mg-calcined catalyst was tested in a steel micro reactor tube where the reaction was automated by the distributed system controller (DCS) processor, from Zeton Altamira. Methanol which its molar ratio to water and air substrate are respectively 1.3 (SRM and ATRM) and 0.13 (ATRM) was fed to the catalyst at 150°C to 300°C (isothermal) with the interval 25°C and independent pressure from 1 to 2 atm.

The reformate effluent, at the steady state, was then analyzed by the online gas chromatograph (GC). The GC was calibrated with the standard gas prior to the analysis. During the analysis, the reformate was carried along with He to three stage of runs through columns measuring the concentration (ppm) of hydrogen, carbon dioxide, carbon monoxide, water, methanol, oxygen, methane, acetylene, ethane and ethylene.

Results

Catalyst characterization.

Some individual crystal of metal oxides and new crystal were identified in diffractograms given in figure 2. Only 4 XRD trends from 4 samples, representing the other 6 samples, were
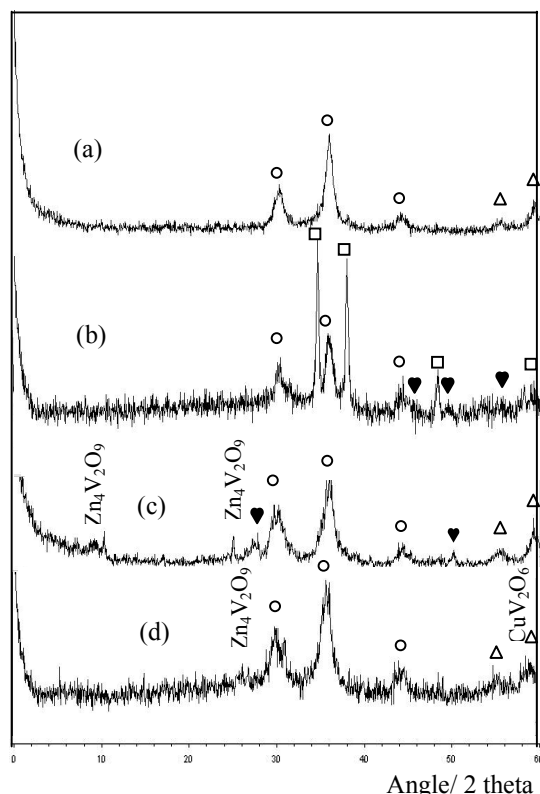
FIGURE 2 The diffractogram of (a) $Cu_{30}Zn_{30}Al_{40}$, (b) $Cu_{30}V_{30}Al_{40}$, (c) $Zn_{30}V_{30}Al_{40}$ and (d) $Cu_{20}Zn_{20}V_{20}Al_{40}$ where o = Al_2O_3, Δ = ZnO, $\square$ = CuO and $\heartsuit$ = V_2O_5

presented here to exhibit the existing species of crystal in the catalyst. The biggest and broadest peak of alumina revealed as the majority and the biggest crystal in all catalysts. This is essential

for the characteristic of support metal. ZnO enhances CuO distribution and thus exists as microcrystalline. Since Cu and CuO plays an important role in steam reforming and partial oxidation of methanol, the size and distribution factor influence significantly the performance of the catalyst. Smaller size and more distribution of crystal may lead to the better performance of the catalyst. Without ZnO, CuO crystal became predominant and exhibited the significant peak as shown in figure 2(b). The catalyst sample containing Zn and V might yield $Zn_4V_2O_9$ and the combination between Cu and V might yield CuV_2O_4 as shown in figure 2(c) and (d), respectively. These two combinations considered as the new species of crystal that possibly have certain effect to the performance of the catalyst.

The physical view of component crystal is shown in figure 3. The white matter is considered as Al_2O_3 or ZnO crystal. Some crystal is clearly identified such as CuO in
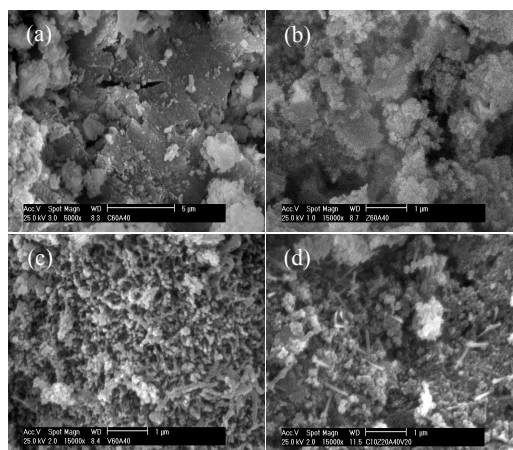

FIGURE 3 The SEM photo of (a) $Cu_{60}Al_{40}$, (b) $Zn_{60}Al_{40}$, (c) $V_{60}Al_{40}$ and (d) $Cu_{20}Zn_{20}V_{20}Al_{40}$ at 10,000x magnification.

figure 3(a), ZnO in figure 3(b) V_2O_5 among alumina in figure 3(c), monoclinic $Zn_4V_2O_9$ among alumina in figure 3(d). The pore characteristic of every crystal contributed to the higher surface area of catalyst. This could be explained by referring to BET analysis.

The oxide metal species and properties regarding the temperature can be observed from TPR analysis. The TPR profiles obtained from Cu-Zn-V-Al oxides are illustrated in figure 4.
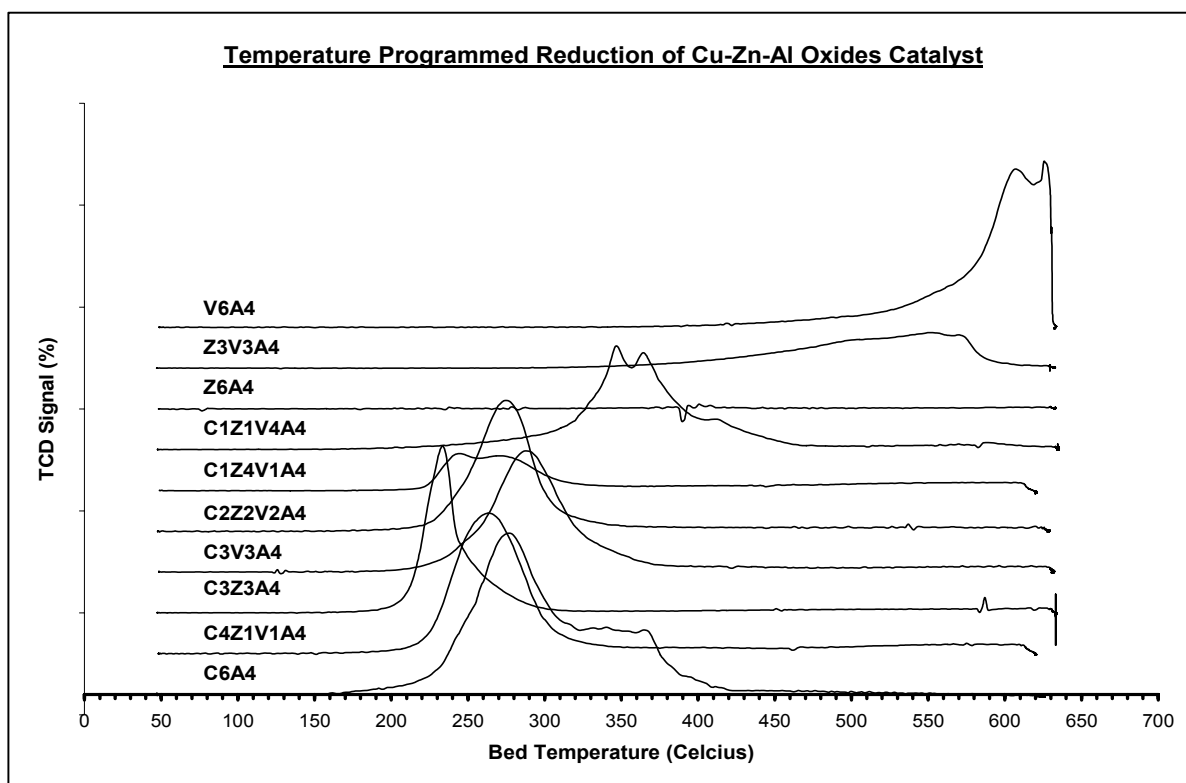
FIGURE 4 10 TPR trend of samples (from AMI 200) where C, Z, V, A and numbers denote Cu, Zn, V, Al and the weight ratio of mixture respectively.

Cu-Al and V-Al exhibits the reduction temperature at minimum 278°C and above 600°C respectively. Cu-Al exhibits two broad peaks that may be attributed to the stepwise reduction of copper oxide (Cu^{2+} (Cu+ (Cu0) (Lindstrom et. al 2002). Zn-Al could not be reduced at all observed temperature since both are more electropositive than hydrogen. The Zn addition enhanced Cu crystal dispersion on alumina (Agrell et. al 2003) and decreased the reduction temperature of Cu-based catalyst (Lindstrom et. al 2002) which were exhibited by C4Z1V1A4 and C3Z3A4 trends whereas the addition of V increased the reduction temperature might be due to the high reduction temperature of vanadia as exhibited by C1Z1V4A4 and C3V3A4 trends. Similarly C2Z2V2A4 reduction exhibits slightly higher temperature than C4Z1V1A4. The loading of Vanadium seemed to start increasing the reduction temperature between 10% and 20% which might be below 20% as reported by K. Inumaru et. al (1997) who prepared V-Al by using incipient wetness impregnation method. V-Al (V6A4) or with the lower copper loading (C1Z4V1A4 and C1Z1V4A4) exhibits two peaks, which attributed to the stepwise reduction of vanadia (V2O5 (VO2 (V2O3) as reported by I. L. Botto et. al (1997). In general a low loading vanadia (below 40%) exhibits the single tall peak that reveals the prefect combination by giving single reduction property.
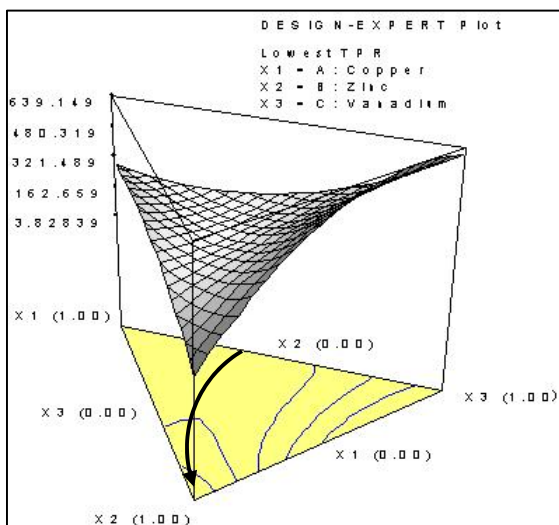
FIGURE 5 The lowest reduction temperature (RT/°C) versus the composition of the catalyst component (w/w).

The lower reduction temperature (RT) corresponds to the easier SRM occurrence hence producing more hidrogen. For instant, the lowest RT from TPR result of all calcined catalyst is presented in the form of surface function on the designed triangle of the simplex centroid design. After replication of the sample 1, 2, 3 and 7 (figure 1) for checking purpose and confirmation using the ANOVA and studentized residue, the profile is shown in figure 3 where the bottom variable is the composition of the metal and vertical variable is the lowest RT. The lines in the bottom triangle represent the surface contour. As referred to figure 3, Zn exhibits the lowest RT because Zn60Al40 is not active for all. From Cu (X 1) axis the RT is 275oC, decreasing until the bottom valley from 290oC to 0oC that denoted by the arrow line. The arrow is pointing towards the lowest RT (Zn). Passing the arrow line towards V the RT starts increasing very rapidly until at the axis of V the RT which is 623oC.

BET result is presented as same as RT result and shown in figure 4. The highest surface area (115m2/g sample) exhibited by X 1:X 2 = 60:40 (Cu36Zn24Al40). The

light grey (or light yellow) represents the considerable area of BET response, which is higher than 65m2/g sample. Vanadia addition resulted the decreased surface area of catalyst.
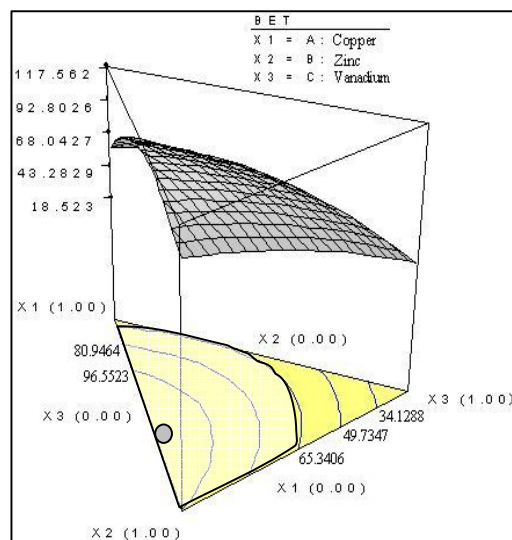

FIGURE 6 BET surface area (m^2/g sample) versus the composition of the catalyst (w/w).

Reaction Study

Since the reaction experiment is still in progress at the moment, the result of hydrogen yield and CO formation is not enough to be fulfilled in the simplex centroid triangle. The
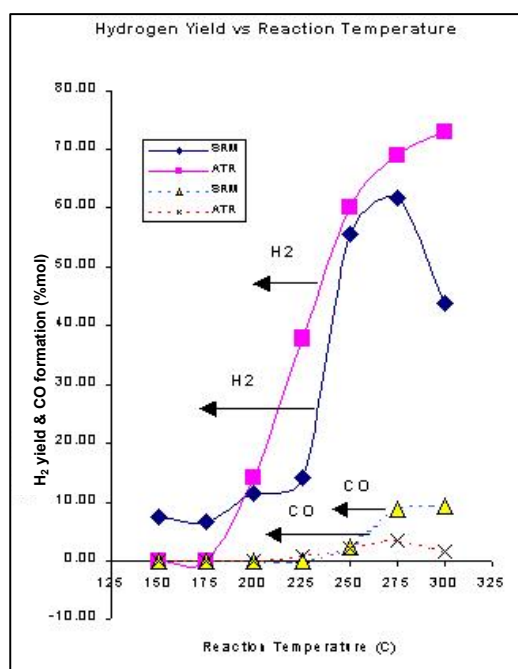

FIGURE 7 Hydrogen yield and CO formation (%mol) versus the reaction temperature by using $Cu_{20}Zn_{20}V_{20}Al_{40}$

present result of $Cu_{20}Zn_{20}V_{20}Al_{40}$ catalyst was given in the figure 7. SRM exhibits the lower reactivity than ATR above 200°C. At 275°C CO formation from SRM reaction became significant (9.4%) as compared to ATR reaction, which is about 3.2% of mol.

Discussion

Promoting vanadia as a moderate oxidizer to the co-precipitated Cu-Zn-Al catalyst seemed to yield new interesting observation. From XRD and SEM-EDX result, the combination of V and Zn formed the plenty of tiny fiber and crystals, which strengthened the physical property of the catalyst. Copper and copper oxide was also well dispersed as combined with Zn and became microcrystalline, which was sometime hard to be identified by using XRD. The reducibility of the catalyst by using hydrogen was decreased after increasing V composition from the design valley (the arrow in figure 5) observed from the point of reduction temperature view. BET surface area was also decreased significantly as seen in figure 6. From the reaction study ATR is better than SRM when the reaction temperature is more than 200°C. The addition of oxygen (air) might also reduce the formation of CO.

Acknowledgements

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