

Correlation of activity and stability of CuO/ZnO/Al₂O₃ methanol steam reforming catalysts with Cu/Zn composition obtained by SEM–EDAX analysis [☆]

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Abstract

A series of CuO/ZnO/Al₂O₃ catalysts were prepared and characterized by TPR, surface area, metal area, XRD and SEM–EDAX analysis. These systems were evaluated in the development of a methanol steam reforming catalyst (MSR). A correlation of activity and stability of MSR catalysts with the Cu/Zn ratio derived by SEM–EDAX analysis is observed. The stable activity of these catalysts is also supported by the method of preparation, low temperature reducibility and the presence of reversibly oxidizable Cu species observed by TPR of fresh and used catalysts. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Steam reforming of methanol reaction ($\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 3\text{H}_2$) is a current interest of research to produce hydrogen for fuel cell

applications. A fuel cell drive system based on methanol as the fuel consists of a methanol reformer, a catalytic burner and a gas purification unit which reduces the CO content of the hydrogen rich gas and feeds fuel cell. The use of methanol as a liquid fuel avoids the problems concerning the on board storage of hydrogen as an ideal fuel for the fuel cell. The number of publications on this subject in the recent times is an evidence that serious efforts are being made for the development of an integrated reformer [1–5]. However, development

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of a compact reformer is always a challenge as the amount of hydrogen required for this application is high and there is a need for the development of highly active and selective catalysts with stable life. Though methanol synthesis catalysts are used for studying steam reforming of methanol, no specific claim is made till date. Several reports discussed the preparation, characterization and evaluation of CuO/ZnO based catalysts for steam reforming of methanol and these studies show the effect of method of preparation, pH, temperature of precipitation, aging of precipitate on the nature of precursors obtained, reducibility (TPR profiles), Cu metal area, surface area, copper crystallite size, active copper plane, kinetics, reaction mechanism and in situ studies showing the intermediates [6–12]. Presently our group is working on development of a methanol reformer (integrated) for a 10 kW fuel cell. During the investigation we have optimized several parameters that controlled the structural characteristics of the CuO/ZnO/Al₂O₃ catalysts. A catalyst prepared with the same bulk composition varying preparative conditions showed difference in the Cu:Zn composition of the surface and sub-surface (EDAX analysis) during the course of reaction and an attempt has been made in the present investigation to study the effect of Cu/Zn ratio of the surface and sub-surface on the activity and stability of methanol steam reforming catalysts. This communication also highlights the extensive use of SEM–EDAX to derive the Cu:Zn composition of active and stable methanol steam reforming catalysts.

2. Experimental

Cu–Zn–Al oxide catalysts for steam reforming of methanol were prepared by co-precipitation of metal ions from their nitrate salt solution with 0.5 M Na₂CO₃. The precipitation was carried out either at constant pH 7 or increasing pH up to 8, maintaining temperature around 65–70 °C. Aluminum is either co-precipitated at pH 7 along with Cu and Zn or precipitated separately at pH 8 and was then admixed. Preparations were repeated to check the factors affecting the reproducibility of catalysts. Precipitates allowed to settle in mother

liquor for 10–15 min were filtered and dried in oven over night at 110 °C. The dried catalyst precursors were calcined in air at 350 °C for 6 h. Powder diffraction patterns were measured by a Siemens D-5000 X-ray diffractometer using Cu K α radiation. DTA of the samples were recorded using Leeds and Northup (USA) unit at a heating rate of 10 °C/min in air.

Prior to TPR studies the catalyst samples were activated in N₂ flow for a period of 2 h at 350 °C and cooled to room temperature. TPR studies were carried out by passing 10% H₂/N₂ at a flow of 10 ml/min over 20 mg of the catalyst sample fixed in a micro-reactor. The temperature of the catalyst was increased at a rate of 5.5 °C/min to 250 °C and maintained at 250 °C for 1 h. Water formed during the reduction was removed by a molecular sieve trap and the hydrogen consumption (TPR-1) was monitored by TCD connected to an on-line GC.

The copper metal areas were determined by N₂O decomposition, as described by Bond and Namijo [13]. Prior to N₂O decomposition, the sample (20 mg) reduced in TPR-1 as described above was cooled to 90 °C in nitrogen flow and the catalyst was treated with 6% N₂O (balance He) at that temperature for 1 h. N₂O flow was then replaced by pure N₂ and the sample was cooled to room temperature. This sample was subjected to another TPR and a profile was obtained due to the reduction of Cu₂O formed during N₂O decomposition. The hydrogen consumption measured in this experiment was used to calculate the surface Cu atoms and metal areas were calculated assuming 1.46×10^{19} Cu atoms m⁻² as described earlier [14].

Another set of TPR experiments was also carried out on used catalysts namely MSR-3, MSR-6, MSR-10 and the TPR profiles of calcined (fresh) and used catalysts (TPR-1) were compared for hydrogen consumption as shown in Table 3. The reduced catalysts of these experiments were passivated at room temperature by allowing air and TPR-2 profiles were recorded to determine the reversibly oxidizable species (Table 3).

For scanning electron microscope studies samples were mounted on an aluminum support using a double adhesive tape, coated with gold in HUS-SGB vacuum coating unit and observed in Hitachi

S-520 SEM unit. Elemental analysis was carried out using Link, ISIS-300, Oxford EDAX detector.

Methanol reforming reaction was carried out in a conventional fixed bed reactor (12 mm dia with 6 mm thermo-well) loaded with 2 g of catalyst (1 mm size). The reactor is provided with a pre-heater, a syringe pump, a cold condenser and a gas flow meter. The conversion of methanol was calculated from the composition of the condensate and the gas composition was determined using a GC with Poropak Q column. Feed containing 1:1.3 mole ratio of methanol to water was maintained to get $10 \text{ l H}_2 \text{ h}^{-1} \text{ g}^{-1} \text{ cat.}$ at 100% methanol conversion. Prior to the reaction, catalysts were reduced in 10% H_2/N_2 in the temperature range of 180–220 °C. The catalyst was reduced initially at 180 °C for 2 h and later at 220 °C for 2 h. Catalyst evaluation was carried out for a minimum of 25 h and maximum of 100 h depending on the stable activity. SEM–EDAX analysis of catalysts was carried out wherever a decline in the activity is observed. Used catalysts were also subjected to XRD and TPR.

3. Results and discussion

3.1. Catalyst characterization

A thorough literature survey on CuO/ZnO/ Al_2O_3 methanol synthesis catalysts reveals that addition of ZnO (10–40 wt%) improves the Cu dispersion and a decrease in the Cu surface area above ZnO contents of 40–50% due to a decrease in Cu content is also well acknowledged [19,21]. Therefore CuO of 50–55 wt% and ZnO of 35–40 wt% were chosen in our Cu–Zn–Al–O catalyst

preparation to maintain the Cu dispersion and typical Cu/Zn ratio in the range of 1.25–1.57. The preparative conditions, surface area and Cu metal area of the catalysts are given in Table 1. It is clear from the table that the method of preparation is affecting the Cu metal area. A co-precipitated catalyst either at constant pH of 7 (MSR-2) or with build up pH to 8 (MSR-1) is showing relatively low metal area compared to a catalyst where Cu–Zn are co-precipitated and alumina precipitated separately is admixed (MSR-3). XRD of the uncalcined catalyst precursors show amorphous or poorly developed layered double hydroxide + aurichalcite patterns (Fig. 3(a)). The DTA patterns of these precursors are almost identical showing a broad dehydroxylation peak (200–350 °C) and a broad/sharp decarboxylation peak (450–550 °C). Cu/Zn ratio of the calcined catalysts obtained by EDAX analysis do not differ from what is used in the preparation and almost fall in the same range. The chemical analysis shows that Al_2O_3 percentage is well maintained whether it is co-precipitated or precipitated separately and admixed.

3.2. Temperature programmed reduction of Cu–Zn–Al–O catalysts

The TPR profiles of calcined catalysts are shown in Fig. 1. The catalysts are showing T_{max} in the range of 230–250 °C. The minute differences in the reduction profiles may be seen as due to different conditions used in the preparation. Co-precipitated catalysts are reduced slightly at higher temperature (MSR-1, MSR-2, MSR-4). The variation in the T_{max} of Cu–Zn–Al–O catalysts co-precipitated at constant pH 7 (MSR-2, 4, 6, 10)

Table 1
Preparation and characterization of Cu–Zn–Al–O catalysts

Catalyst	Method of preparation	Surface area (m ² /gm)	Cu metal area (m ² /gm)
MSR-1	Cu–Zn–Al co-precipitated with build up pH to 8	56	18
MSR-2	Cu–Zn–Al co-precipitated at constant pH 7	40	17
MSR-3	Cu–Zn co-precipitated at constant pH 7, Alumina precipitated at pH 8 and admixed	58	24
MSR-4	Repetition of MSR-2	39	17
MSR-6	Repetition of MSR-2	47	18
MSR-10	Repetition of MSR-2	50	21

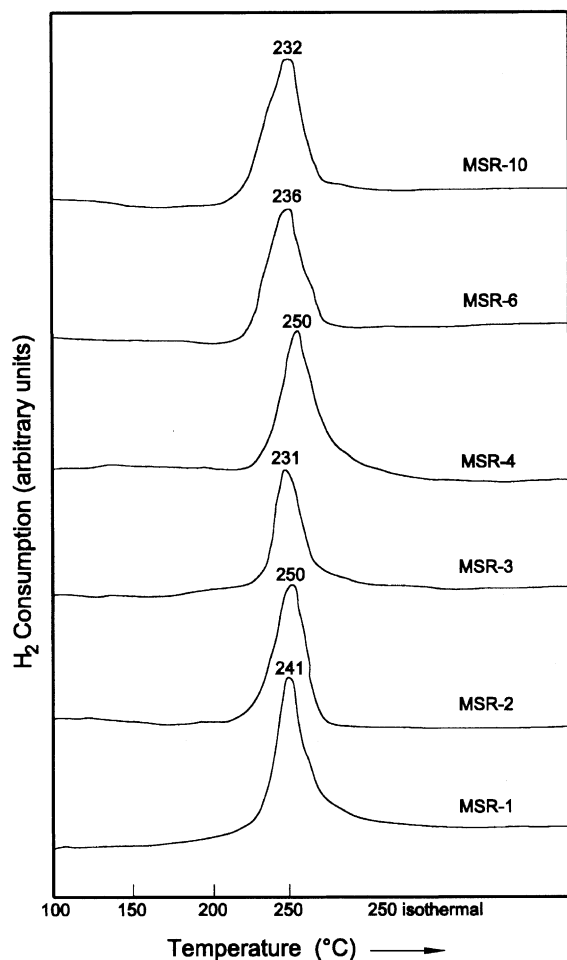


Fig. 1. TPR profiles of CuO/ZnO/Al₂O₃ catalysts. MSR-1 Cu–Zn–Al precipitated by build up pH 8; MSR-2 Cu–Zn–Al precipitated at constant pH 7; MSR-3 Cu–Zn precipitated at constant pH 7 and Al at pH 8 admixed; MSR-4, 6, 10 repetition of MSR-2.

may show that the catalyst reproducibility is critical in this method of preparation. This is also clearly evidenced while studying the time on stream activity of these catalysts. A catalyst with low temperature reducibility is showing stable methanol steam reforming activity.

3.3. Methanol steam reforming activity of Cu–Zn–Al–O catalysts vs time

Cu–Zn–Al–O catalysts prepared under different conditions are studied for steam reforming of

methanol as described in the experimental section and their time on stream activity is shown in Fig. 2. All the catalysts prepared under different conditions are showing initially 100% methanol conversion at 250 °C except MSR-1 (co-precipitated with build up pH to 8). The activity of MSR-1 declined slowly from 96% to 85% methanol conversion in 73 h and it is restored by increasing the temperature to 270 °C. Whereas Cu–Zn–Al–O catalyst co-precipitated at constant pH 7 is showing decline in the activity from 100% to 85% methanol conversion in 25 h (MSR-2). This system is prepared in several batches to check the reproducibility and effect of preparative conditions on stable activity. Thus MSR-4, MSR-6 and MSR-10 are repetition of MSR-2. A decline in the activity is observed on MSR-6 and MSR-10 after 50 h and it is relatively slow compared to MSR-2. The activity of these catalysts is seen restored when the temperature is increased to 270 °C. The stable activity of 100% methanol conversion is observed on MSR-3 at 250 °C for period of 100 h as shown in Fig. 2. A comparison of activity with time on stream of MSR-1, MSR-2 and MSR-3 catalysts prepared under different conditions indicate that the method of precipitation is affecting the stable

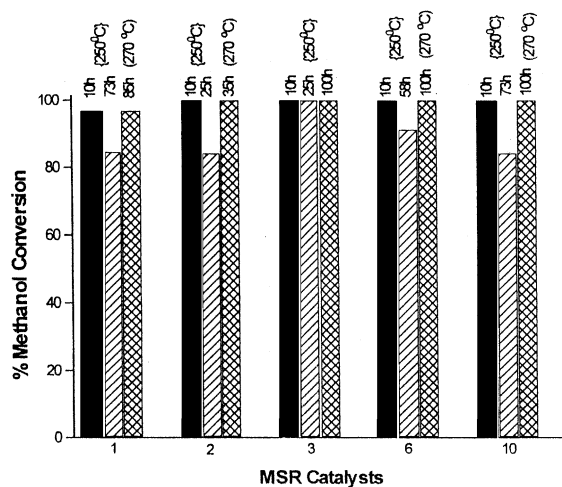


Fig. 2. Methanol steam reforming activity of CuO/ZnO/Al₂O₃ catalysts at 250 °C. MSR-1 Cu–Zn–Al precipitated by build up pH 8; MSR-2 Cu–Zn–Al precipitated at constant pH 7; MSR-3 Cu–Zn precipitated at constant pH 7 and Al at pH 8 admixed; MSR-4, 6, 10 repetition of MSR-2.

activity of methanol steam reforming catalysts and the stability is well maintained when alumina is precipitated separately and admixed (MSR-3). Admixing of alumina precipitated separately is seen resulting into active and stable catalysts and further studies on the role of Al_2O_3 are in progress.

3.4. Correlation of stable activity and Cu/Zn ratio derived by SEM–EDAX

It appears difficult to arrive at stable activity of methanol steam reforming catalysts merely by structural characterization and bulk composition. Hence an attempt has been made to determine the

Cu/Zn ratio of highly active and stable catalysts by SEM–EDAX (surface and sub-surface layers). We have chosen SEM–EDAX as a fast tool in the development of methanol reforming catalyst. The smooth surface of the pellet is used for the measurements. As SEM coupled EDAX microprobe analysis is semi-quantitative, analysis of several spots was carried out and finally for each system an average value is considered. In this process the analysis of white as well as gray spots of calcined, reduced and used catalysts is studied and the results of the representative samples are summarized in Table 2. The general understanding is that white spots are electron rich and gray spots are electron

Table 2
SEM-coupled microprobe analysis of steam reforming catalysts

Catalyst	Composition (wt%)			
	Cu	Zn	Al	Cu/Zn
MSR-3 (cal)	42.01	27.22	3.40	1.54
W	41.92	24.15	4.05	1.73
G	36.64	23.14	5.03	1.58
MSR-3 (red)	42.25	38.36	6.92	1.10
W	45.52	41.31	5.72	1.10
G	51.28	36.13	3.08	1.41
MSR-3 (used; 100 h)	35.55	22.50	5.97	1.58
W	41.39	29.04	4.32	1.42
G	50.69	37.27	2.26	1.36
MSR-6 (cal)	51.74	38.79	1.54	1.33
W	52.74	36.38	1.78	1.44
G	36.64	23.14	5.03	1.58
MSR-6 (red)	52.22	39.04	8.73	1.33
W	44.34	37.86	6.51	1.17
G	49.97	39.38	7.20	1.26
MSR-6 (used; 58 h)	31.60	15.67	5.16	2.01
W	35.42	17.28	3.82	2.00
G	36.21	20.25	6.67	1.77
MSR-10 (cal)	55.40	34.30	6.30	1.61
W	53.20	41.15	5.65	1.29
G	56.10	38.32	5.58	1.46
MSR-10 (red)	48.42	36.13	3.13	1.34
W	43.67	41.59	6.87	1.05
G	39.58	40.24	5.58	0.98
MSR-10 (used; 73 h)	52.37	32.92	3.04	1.59
W	56.01	30.71	4.12	1.82
G	54.24	39.61	1.79	1.36

Cal – calcined; red – reduced; W – white spot; G – gray spot.

deficient. The Cu/Zn ratio of white spots shows that it is difficult to conclude that white spots are electron rich through out the depth studied and the same is true with the gray spots. The Cu/Zn ratio of calcined catalysts by EDAX is falling in the same range (1.25–1.57) as used in the preparation. This ratio is changed on reduction and decreased to a lower value indicating changes in CuO phase on reduction. (Figs. 3(b) and (c)) The XRD pattern of reduced catalyst (Fig. 3(c)) shows the presence of metallic copper ($d = 2.091$). Whenever a decline in the activity in methanol steam reforming is observed, the catalysts samples are collected and subjected to EDAX analysis. The Cu/Zn ratio of used catalyst showing decline in the

activity (for example MSR-6) is increased and for a catalyst showing stable activity (MSR-3) with time the ratio is maintained in the same range as that of calcined catalyst (Table 2). This is strongly supporting the idea that Cu/Zn ratio of the surface and sub-surface is playing an important role in maintaining the activity of methanol steam reforming catalysts. When the Cu/Zn ratio of used catalyst is greater than the ratio of calcined catalyst (MSR-6) the catalyst is seen deactivating slowly and it is maintained only by increasing the temperature. The Cu/Zn ratio of calcined and used systems of MSR-3 and MSR-10 remained more or less in the same range and show a correlation with the observed activity and stability.

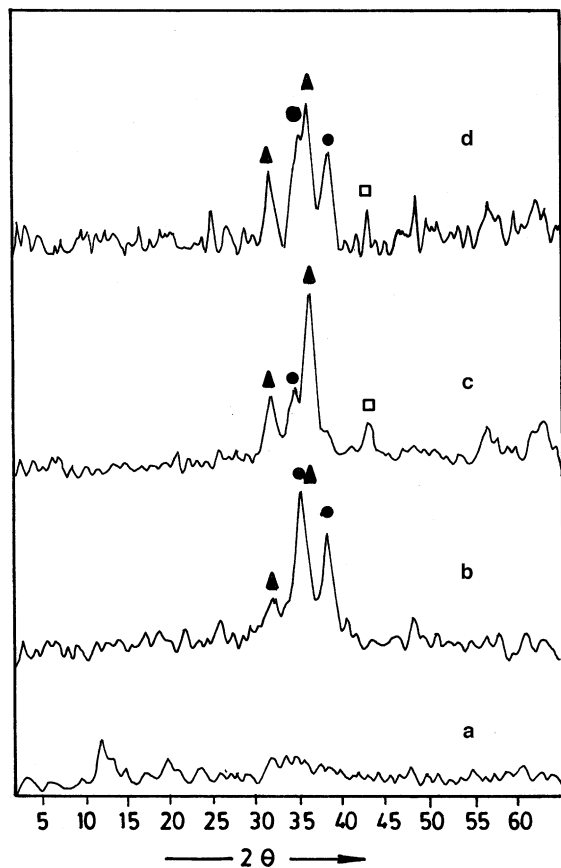


Fig. 3. XRD patterns of methanol steam reforming catalyst: (a) uncalcined; (b) calcined; (c) reduced; (d) used. (●) CuO ($d = 2.52, 2.32, 2.53$); (▲) ZnO ($d = 2.47, 2.81, 2.602$); (□) metallic Cu ($d = 2.09, 1.81, 1.28$).

3.5. Comparison of pre- and post-characterization of Cu–Zn–Al–O methanol steam reforming catalysts

The XRD patterns of calcined, reduced and used methanol steam reforming catalysts are shown in Fig. 3. Calcined catalyst shows both CuO and ZnO phases and on reduction CuO phase is seen reduced and ZnO is predominant along with metallic copper ($d = 2.091$). The XRD pattern of used catalyst after passivation in air clearly shows the appearance of CuO phase along with metallic copper (Fig. 3(d)).

The SEM photographs of calcined, reduced and used MSR catalyst shown in Fig. 4 indicate no change in the morphology and small crystallites observed in calcined and reduced (Figs. 4(a) and (b)) are more pronounced in used sample (Fig. 3(c)).

TPR profiles of used catalysts are also studied to find out the changes in the reducibility of the catalysts and compared with TPR profiles of the fresh catalysts as shown in Table 3 (TPR 1). It is clear from the table that catalyst showing stable activity (MSR 3) shows almost the same H_2 consumption even after 100 h use. The reversibility of the structure of these systems is checked by passivating the reduced catalyst from TPR 1 as described in the experimental and subjected to TPR 2. The consistency in H_2 consumptions (TPR1 & TPR 2) of these systems show the presence of reversibly oxidizable species that are stable under the conditions of our operation.

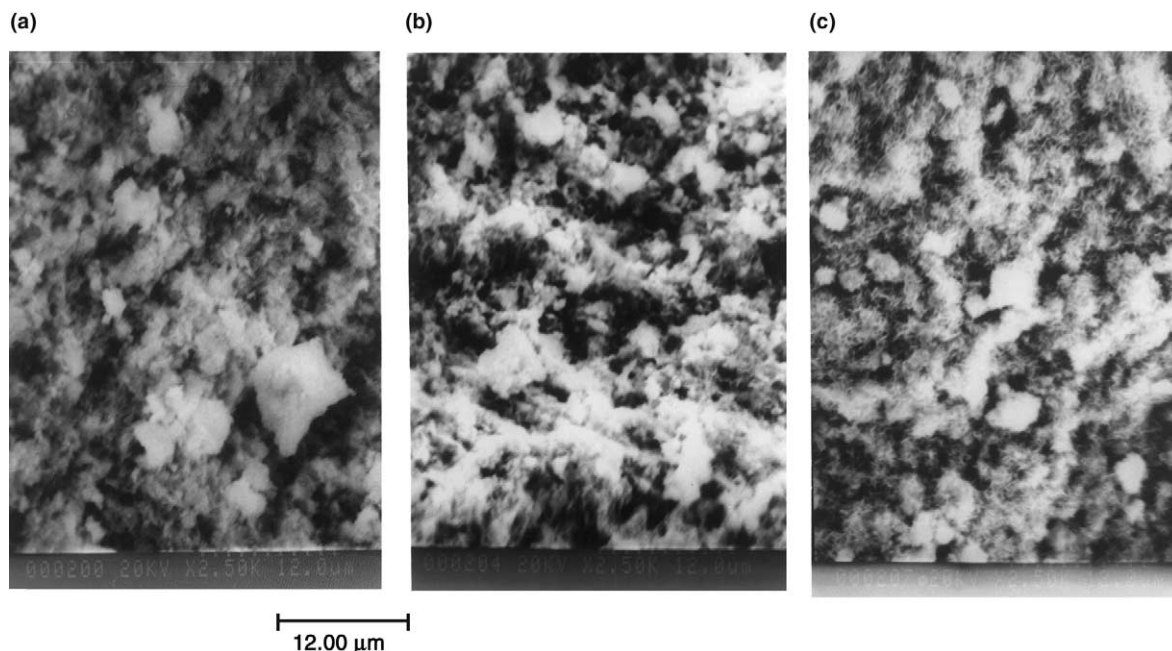


Fig. 4. SEM photographs of methanol steam reforming catalyst: (a) calcined; (b) reduced; (c) used catalysts.

Table 3
TPR results on methanol steam reforming catalysts

Catalyst	T_{\max} (red)	H_2 Consumption $mmol\ g^{-1}$ TPR1	% H_2 Consumption on passivation TPR 2
MSR-3 (fresh)	231	5.35	97.9
MSR-3 (used)	250	5.43	98.0
MSR-6 (fresh)	236	6.14	97.0
MSR-6 (used)	250	5.04	99.0
MSR-10 (fresh)	232	5.70	96.9
MSR-10 (used)	250	5.50	98.3

3.6. Active species in Cu/ZnO catalysts

The active sites in Cu/ZnO catalysts have long been studied, as Cu/ZnO based catalysts are generally used in methanol synthesis, an industrially important process. Many different views have been proposed regarding the nature of the surface active sites [15–18]. Fujitani and Nakamura [19, references therein] were working on the mechanism of Cu–ZnO catalyzed methanol synthesis since 1993 and proposed finally a model containing Cu–Zn site and Cu^0 as the active components of Cu/ZnO catalysts, because the state of a portion of Zn was

found not to be ZnO but a Cu–Zn alloy during the reaction [20]. Addition of a refractory oxide like Al_2O_3 to Cu/ZnO is well acknowledged to stabilize ZnO [21].

The characterization of Cu–Zn–Al–O methanol synthesis catalysts is extended by many workers to understand the system in steam reforming of methanol. Cu/ZnO catalysts are always prepared typically as mixed hydroxycarbonates. The best Cu–Zn–Al–O catalysts are prepared by precipitation around pH 7 and this is achieved by a precipitation procedure in which the acidic and alkaline solutions are mixed continuously. The

catalyst precursors prepared in the present investigation are X-ray amorphous as they are not allowed to age and amorphous precursors produced catalysts of high activity and stability. The stable activity observed with Cu–Zn–Al–O prepared in the present investigation may be resulting from the Cu–Zn hydroxycarbonates (wherein the copper is atomically mixed with zinc) admixed with alumina leading to the formation of active Cu/ZnO catalysts on calcination and reduction. An increase in the Cu/Zn ratio of the surface and sub-surface of methanol steam reforming catalysts during deactivation suggests that a Cu/Zn ratio ≈ 1.5 is required to obtain high activity and stability.

4. Conclusion

SEM–EDAX probing of MSR catalysts show that surface and sub-surface Cu/Zn composition in the range of 1.2–1.5 may produce catalysts with stable activity and the stable activity is also evidenced by the presence of reversibly oxidizable Cu species.

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