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# Use of tetraethylammonium bicarbonate as a precipitation agent on the preparation of coprecipitated Cu/ZnO catalysts

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#### **Graphical Abstract**



#### **Research Highlights**

- Cu/ZnO catalysts prepared using tetraethylammonium bicarbonate (TEA<sup>+</sup>HCO<sub>3</sub><sup>-</sup>) show comparable methanol synthesis activities to Na<sup>+</sup>-based analogues even though Cu,Zn precursor is not fully washed.
- The negative effects of sodium ion on the methanol synthesis activity are absent or lessened when  $TEA^{+}HCO_{3}^{-}$  is used as a precipitation agent for coprecipitation.
- The Na<sup>+</sup>-free preparation approach is worth being studied to overcome the drawbacks of the conventional Na<sup>+</sup>-based coprecipitation.

#### Abstract

Cu/ZnO catalysts were prepared by coprecipitation using tetraethylammonium bicarbonate  $(TEA^{+}HCO_{3}^{-})$ , and their properties and methanol synthesis activities were compared to those of the catalysts prepared using Na<sup>+</sup>HCO<sub>3</sub><sup>-</sup> usually employed for commercial Cu/ZnO/(Al<sub>2</sub>O<sub>3</sub>) catalysts. When washed fully, TEA<sup>+</sup>- and Na<sup>+</sup>-based precursors showed typical zincian malachite (zM) without any other structures, and both catalysts obtained after calcination and H<sub>2</sub> reduction exhibited the similar specific copper surface area and, in turn, the similar methanol productivity. Since this result explains that TEA<sup>+</sup> does not affect zM structure if Cu,Zn precipitate is fully washed, no washed and less washed TEA<sup>+</sup>- and Na<sup>+</sup>-based precursors were prepared. It was interesting that all TEA<sup>+</sup>-based catalysts exhibited the similar methanol productivity irrespective of the washing efficiency whereas Na<sup>+</sup>-based catalyst containing more residual Na<sup>+</sup> showed the smaller copper surface area and lower methanol productivity (i.e., linear correlation between the two parameters). This resulted from the inhibiting effect of  $Na^+$  on the degree of  $Cu^{2+}$  substitution by  $Zn^{2+}$  and the formation of high-temperature carbonate, consequently leading to a lower catalytic activity. These negative effects of Na<sup>+</sup> were absent or lessened when TEA<sup>+</sup>HCO<sub>3</sub><sup>-</sup> was used as a precipitation agent, which is effective in preparing an active methanol synthesis catalyst.

## *Keywords*: Methanol synthesis; Cu/ZnO; Coprecipitation; Tetraethylammonium bicarbonate; Residual sodium

#### **1. Introduction**

Coprecipitation method is one of the most important catalyst preparation methods in industrial and academic research [1]. However, this method is often considered difficult and hard to make a desired catalyst because it includes multiple steps in each of which the small change of a parameter influences the physicochemical property and catalytic performance (which is called "chemical memory") [2]. The most widely studied catalyst prepared by coprecipitation is an industrial Cu/ZnO/(Al<sub>2</sub>O<sub>3</sub>) catalyst in methanol synthesis. While the preparation variables are largely determined by empirical optimization, a great deal of effort has been made so far in elucidating the effect of synthesis parameters on the properties and activities of a final catalyst [3–13].

Coprecipitation starts from mixing an acidic metal solution with a basic precipitating agent solution (usually, Na<sub>2</sub>CO<sub>3</sub> and NaHCO<sub>3</sub>), inducing primary nuclei particles. Extensive works have been conducted to optimize main coprecipitation parameters such as temperature, pH and metal composition [2–5]. Suggested by a large set of experiments, the optimal pH and temperature range in 6–7 and > 333 K, respectively, for a high methanol synthesis activity [5]. Also, the effect of Cu:Zn composition has been investigated: Cu<sup>2+</sup> substitution by Zn<sup>2+</sup> in malachite (Cu<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub>, pure Cu precursor phase) and Zn<sup>2+</sup> substitution by Cu<sup>2+</sup> in hydrozincite (Zn<sub>5</sub>(OH)<sub>6</sub>(CO<sub>3</sub>)<sub>2</sub>, pure Zn precursor phase) happen in Cu-rich and Zn-rich precursor systems, respectively [2,4]. In a recent report of Behrens *et al.* [7], zincian malachite ((Cu<sub>1-x</sub>Zn<sub>x</sub>)<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub>, *x* = 0.3) is prepared at the Cu:Zn ratio of 70:30 and, after calcination and reduction, it shows the largest Cu surface area and the highest methanol productivity. Additionally, high-temperature carbonate (HT-CO<sub>3</sub>), which is known as an intermediate phase in the decomposition of Cu,Zn precursor [2–4,8], is developed when the substitution level of Cu<sup>2+</sup> or Zn<sup>2+</sup> is high in the Cu content range from 20% to 80% [2–4].

In the next ageing step, amorphous primary particles of initial precipitate are transformed into crystallite particles through dissolution, re-precipitation and ion exchange take place [7,9]. Whittle *et al.* [10] reported that the full ageing is necessary for preparing an active CO oxidation catalyst. The aged precursor is washed repeatedly with distilled water and filtered for complete removal of unnecessary ions including Na<sup>+</sup> and NO<sub>3</sub><sup>-</sup> [1]. The subsequent steps are thermal treatment such as drying, calcination and reduction producing a final Cu/ZnO-based catalyst. The kinetic works for the decomposition of dried Cu,Zn precursors [11] as well as the reduction of CuO/ZnO [8,12] revealed that the heating rate needs to be controlled well in order to prepare a good methanol synthesis catalyst [13].

Main efforts made so far are on the precipitation, ageing, calcination and reduction processes; however, the washing step has been much less studied. When the cation of precipitating agent and the anion of metal precursor remain in the catalyst, undesired structures including NaNO<sub>3</sub> or gerhardtite (Cu<sub>2</sub>(OH)<sub>3</sub>NO<sub>3</sub>) can be formed sometimes resulting in Cu sintering and, consequently, a lower activity [2]. Also, it was reported that residual Na<sup>+</sup> acts as a catalyst poison to decrease the catalytic activity due to particle agglomeration at the calcination stage [14]. To prevent these negative effects, thorough washing is generally employed. Otherwise, Na<sup>+</sup>-free preparation method would be developed; for instance, Kondrat et al. reported the CO<sub>2</sub> supercritical antisolvent (SAS) precipitation to synthesize amorphous zincian georgeite exhibiting enhanced methanol synthesis performance compared to typical co-precipitated Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst [15]. Furthermore, the effect of sodium species on the physical and catalytic properties of Cu/ZnO catalysts derived from zincian georgeite was investigated [16]. In this regard, we herein attempt to use tetraethylammonium bicarbonate (TEA<sup>+</sup>HCO<sub>3</sub><sup>-</sup>) as a Na<sup>+</sup>-free precipitating agent. Note that the bicarbonate anion is selected because of the need of HT-CO<sub>3</sub> presence and the ionic radius of TEA<sup>+</sup> (0.385 nm) is larger than the one of Na<sup>+</sup> (0.116 nm) [17,18].

Tetraalkylammonium compounds have been often used as a structure directing agent (SDA) for the synthesis of zeolite materials [19]. In the initial stage of zeolite synthesis, the use of different SDAs is a key factor in the formation of different silicate oligomers [19]. Compared to small counter ions including Na<sup>+</sup>, organic tetraalkylammonium cations (behaving as a hydrophobic solute) lead to electrostatic interaction with the silicates, which finally yields a well-defined hydrogen bond structure of the water molecules with negatively charged silicate oxygen [20]. Recently, tetraalkylammonium compounds are used in the preparation of precipitation-derived materials. For magnetic Fe<sub>3</sub>O<sub>4</sub> nanoparticles, tetramethylammonium hydroxide was added for strengthening repulsive stabilization forces of nanoparticles after precipitation by ammonium hydroxide [21]. Also, the use of tetraethylammonium hydroxide as an additive in sodium bicarbonate solution favored the formation of smaller Cu particles and improved the activity of Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst [22]. There is, however, no report to use TEA<sup>+</sup>HCO<sub>3</sub><sup>-</sup> itself as a precipitating agent for the synthesis of single or mixed metal oxides.

To investigate the effect of  $TEA^{+}HCO_{3}^{-}$  on the property and activity of a final Cu/ZnO catalyst, the Cu,Zn hydroxynate precursor with the Cu:Zn ratio of 70:30 were prepared by coprecipitation in  $TEA^{+}HCO_{3}^{-}$  solution. For comparison, the coprecipitation using Na<sup>+</sup>HCO<sub>3</sub><sup>-</sup> was conducted. The fully aged TEA<sup>+</sup>- and Na<sup>+</sup>-based precursors were washed by three different ways; *e.g.*, not washed, less washed and fully washed. The subsequent thermal treatments were conducted identically for all samples. The prepared materials of three different states were characterized for: 1) crystal structure and thermal stability of Cu,Zn precursors, 2) CuO reducibility, particle morphology, crystal structure, particle size and atomic composition of CuO/ZnO samples, 3) Cu surface area of Cu/ZnO catalysts. Through coupling these properties with the methanol synthesis activity, the effect of TEA<sup>+</sup> was discussed on the preparation of coprecipitated Cu/ZnO catalyst, compared to Na<sup>+</sup>.

#### 2. Experimental

#### 2.1. Synthesis of tetraethylammonium bicarbonate solution

 $CO_2$  was bubbled into an aqueous solution of tetraethylammonium hydroxide (TEA<sup>+</sup>OH<sup>-</sup>) in order to synthesize a tetraethylammonium bicarbonate solution. In detail, 40% TEA<sup>+</sup>OH<sup>-</sup> in H<sub>2</sub>O (Sigma-Aldrich, 208.96 g) was diluted to 1 M by adding deionized water (441.54 g), followed by CO<sub>2</sub> bubbling (2–3 L min<sup>-1</sup>) at room temperature. The solution pH approached *ca*. 7.16 after CO<sub>2</sub> bubbling of 17 min and was maintained (Fig. S1).

The synthesized TEA<sup>+</sup>HCO<sub>3</sub><sup>-</sup> solution is compared to the commercially available one (Sigma-Aldrich) by <sup>13</sup>C-NMR and <sup>1</sup>H-NMR using a D<sub>2</sub>O solvent. As shown in Figs. S2 and S3, the spectra of the two samples are very identical [23–25]. When the synthesized and commercial TEA<sup>+</sup>HCO<sub>3</sub><sup>-</sup> of the same concentration are analyzed by ATR-IR (Fig. S4), the spectra are almost same as follows: 1636 (C=O stretching of CO<sub>3</sub><sup>2-</sup>), 1487, 1459, 1443 and 1396 (C–O stretching of HCO<sub>3</sub><sup>-</sup>), 1356 (C–O stretching of CO<sub>3</sub><sup>2-</sup>), 1186 (C–OH in plane bending of HCO<sub>3</sub><sup>-</sup>) and 1174 (N–H bending) [26].

#### 2.2. Catalyst preparation

A series of Cu/ZnO catalysts were prepared by coprecipitation using  $TEA^+HCO_3^-$  ( $TEA^+$ -based precipitation) or Na<sup>+</sup>HCO<sub>3</sub><sup>-</sup> (Na<sup>+</sup>-based precipitation) as a precipitating agent. The precipitation details are similar to the two reports [4,27].

For preparing TEA<sup>+</sup>-based samples, an aqueous solution (totally 1.2 M and 28.5 mL) containing  $Cu(NO_3)_2 \cdot 3H_2O$  (5.84 g) and  $Zn(NO_3)_2 \cdot 6H_2O$  (3.11 g) was added dropwise (2 mL min<sup>-1</sup>) into TEA<sup>+</sup>HCO<sub>3</sub><sup>-</sup> solution (0.1 M, 684 mL) at 343 K for *ca*. 10 min under vigorous stirring. After complete addition, the resulting suspension was aged at 343 K for 90 min. The pH value was recorded at the precipitation and ageing steps (Fig. S5). After the aged

precipitate was filtered, the washing was conducted in three different modes. 1) The first precipitate was dried at 378 K overnight without washing, affording the precursor TEA-Nw. 2) The first precipitate was stirred with deionized water (ca. 1 L) for 30 min. This suspension was filtered again and dried at 378 K, affording the precursor TEA-Mw. 3) The washing with deionized water (ca. 1 L) and filtration were repeated four times. The final filtrate was dried at 378 K, affording the precursor TEA-Fw.

For preparing Na<sup>+</sup>-based samples, the concentrations of metal ion solution (totally 1.2 M) and Na<sup>+</sup>HCO<sub>3</sub><sup>-</sup> solution (0.1 M) are same as for TEA<sup>+</sup>-based precipitation. In detail, an aqueous solution (totally 1.2 M and 175 mL) containing Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (35.87 g) and Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (19.12 g) was added dropwise (14 mL min<sup>-1</sup>) into Na<sup>+</sup>HCO<sub>3</sub><sup>-</sup> solution (0.1 M, 4.2 L) at 343 K for *ca*. 10 min under vigorous stirring. Then, the resulting suspension was aged at 343 K for 90 min and then filtered. This Na<sup>+</sup>-based precipitate was washed differently, similar to TEA<sup>+</sup>-based precursor samples. 1) The first precipitate was dried at 378 K overnight without washing, referred to as Na-Nw. 2) The first precipitate was added to deionized water (ca. 100 mL) and stirred for 30 min. This suspension was filtered again and dried at 378 K, referred to as Na-Mw. 3) Similar to TEA-Fw, the washing with deionized water (ca. 3 L) and filtration were repeated four times. The final filtrate was dried at 378 K, referred to as Na-Fw.

All the prepared precursor samples are crushed and sieved to the size smaller than 200  $\mu$ m, followed by calcination in a muffle furnace at 603 K (2 K min<sup>-1</sup>) for 3 h.

#### 2.3. Characterization

Powder X-ray diffraction (PXRD) analysis was conducted in a Bruker D8 Discover with GADDS diffractometer using a Cu Kα radiation source (40 kV and 40 mA). For reduced samples, a MiniFlex 600 instrument (Rigaku) using a Cu Kα radiation source (40 kV and 15

mA) was used, where the sample (0.1 g) was prepared by H<sub>2</sub> reduction in the methanol synthesis reactor under the same condition as for the activity test.

Thermogravimetric (TG) profiles were obtained in a NETZSCH TG209F1 as the sample was heated to 1073 K at a rate of 10 K min<sup>-1</sup> in an air flow (100 sccm). ATR-IR spectroscopy (Thermo Scientific IS50 spectrometer) with a scan number of 32 and a resolution of  $4 \text{ cm}^{-1}$  was used to monitor functional groups of precursor samples. Scanning electron microscopy (SEM) images were taken in a FEI Nova NanoSEM 450 microscope operated in 18 kV after the sample was coated by Pt. The Brunauer-Emmett-Teller (BET) surface area of the sample (0.1 g) was measured in a Micromeritics 3Flex after pretreatment at 373 K for 2 h under vacuum. The metal composition of precursor and oxide samples was measured by inductively coupled plasma mass spectroscopy (ICP-MS) using a NexION300 (PerkinElmer) and X-Ray Photoelectron Spectroscopy (XPS) using PHI Quantera II (Ulvac-PHI) with a monochromatic Al Ka radiation. All XPS spectra were calibrated using a standard C 1s binding energy of 248.6 eV as reference. C, H, and N compositions of precursor samples were measured by 2400 Series II (Perkin Elmer). Temperatureprogrammed reduction (TPR) experiment was conducted in a Micromeritics AutoChem 2910. As the sample (50 mg) was heated at a rate of 2.5 K min<sup>-1</sup> using 10% H<sub>2</sub> in Ar (50 sccm), the effluent gas was measured by a quadruple mass spectroscope (Balzers Prisma QME 200).

For N<sub>2</sub>O reactive frontal chromatography (N<sub>2</sub>O-RFC) experiment to measure copper surface area (S<sub>Cu</sub>), the calcined sample (0.1 g) was reduced at 523 K for 1 h (1 K min<sup>-1</sup>) using 10% H<sub>2</sub> in Ar (30 sccm) in a BELCAT-B (BEL Japan, Inc.). After cooling to 313 K in He, 1% N<sub>2</sub>O in He (5 sccm) was introduced and product gas (N<sub>2</sub>, m/z = 28) was measured by a BEL-Mass (BEL Japan, Inc.). It was assumed that the reaction stoichiometry between copper and oxygen is two (Cu/O = 2/1) and the copper surface density is  $1.46 \times 10^{19}$  Cu atom m<sup>-2</sup>. Although N<sub>2</sub>O-RFC result cannot be directly related to only the exposed Cu surface

due to oxidation of reduced Zn species by  $N_2O$  studied in a recent report [28,29], the measured copper surface area (SA<sub>Cu</sub>) still remains the best indicator for the catalytic performance of Cu/ZnO-based catalysts.

#### 2.4. Activity test

Prior to methanol synthesis experiment, the calcined CuO/ZnO sample (0.1 g) was reduced at 523 K for 3 h (1 K min<sup>-1</sup>) using 20% H<sub>2</sub> in N<sub>2</sub> (100 sccm) in a stainless-steel reactor. After cooling to 503 K, the reaction gas (H<sub>2</sub>/CO/CO<sub>2</sub>/N<sub>2</sub>/He = 59.5/6/8/4/balance) was fed to the reactor and pressurized to 30 bar (GHSV 60,000 L kg<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>) that is similar to the condition reported by Schumann *et al.* [30]. Methanol synthesis rate was monitored when the reaction is under steady state (after ca. 35 h). Note that the conversions of CO and CO<sub>2</sub> are below 5% that is near a differential condition.

#### 3. Results

The fully washed Cu,Zn precursors, Na-Fw and TEA-Fw, were characterized by PXRD, TG-MS and ATR-IR. The PXRD patterns of the two precursors display the typical reflections of zincian malachite (zM) at 14.65°, 17.47°, 24.08° and ca. 32.3° for (110), (120), (220) and (20–1) reflections, respectively (Fig. 1). Among these, the most important is (20–1) reflection of which the  $2\theta$  shift from 31.24° to a higher angle indicates Cu<sup>2+</sup> substitution by Zn<sup>2+</sup> in the malachite [6]. The  $2\theta$  value of (20–1) reflection is 32.38° for Na-Fw and 32.30° for TEA-Fw, where the corresponding *d*-spacing value is 2.765 and 2.771 Å, respectively. This very little difference indicates that the precursor structure of Na-Fw is almost identical to that of TEA-Fw. On the other hand, any reflections of crystal structure related to Na<sup>+</sup> and TEA<sup>+</sup> are not detected in the PXRD patterns, suggesting that Na<sup>+</sup> and TEA<sup>+</sup> are very little in Na-Fw and TEA-Fw precursors, respectively, possibly by full washing.

Since it is known that  $Cu^{2+}$  substitution by  $Zn^{2+}$  in malachite affects the thermal stability of Cu/Zn precursor [2–4], TG-MS experiments were conducted as shown in Fig. 2. The first DTG peaks of Na-Fw and TEA-Fw precursors around 640 K originate from dehydroxylation and decarbonylation events, supported by evolved gas analysis for H<sub>2</sub>O (*m*/*z* = 18) and CO<sub>2</sub> (*m*/*z* = 44). The latter DTG peak at 728 K (Na-Fw) and 724 K (TEA-Fw) involves release of CO<sub>2</sub> by decomposition of high-temperature carbonate (HT-CO<sub>3</sub>) [2]. It was reported that HT-CO<sub>3</sub> exists in Cu/Zn precursors above 10% and below 90% Zn/(Cu+Zn) in which Cu<sup>2+</sup> and Zn<sup>2+</sup> are intermixed in particles [2–4]. Therefore, the presence of HT-CO<sub>3</sub> in both TEA-Fw and Na-Fw precursors explains that the Cu/Zn precursor precipitated by TEA<sup>+</sup>HCO<sub>3</sub><sup>-</sup> solution shows the similar thermal stability to the one prepared using the conventional NaHCO<sub>3</sub> solution.

CuO/ZnO samples calcined at 603 K were conducted by TPR experiments to observe the reducibility of CuO particles. In Fig. 3, Na-Fw and TEA-Fw oxides show the sharp TPR peaks at 440 and 442 K, respectively, with the shoulder peak around 446–448 K. When Na-Fw oxide is reduced by H<sub>2</sub> flow, the small amount of CO<sub>2</sub> is also evolved due to decomposition of residual carbonate present in the oxide. Though CO<sub>2</sub> evolution is little in TEA-Fw oxide, the overall H<sub>2</sub> consumption curve is similar to that of Na-Fw oxide. In detail, only a difference of 2 K in terms of the temperature at maximum reduction ( $T_{max}$ ) indicates that CuO reduction is almost same for Na-Fw and TEA-Fw CuO/ZnO samples.

SEM images of Na-Fw and TEA-Fw oxides are examined. It was reported that pure CuO consists of elongated cuboid-like particles and as the Cu/Zn ratio decreases from 100/0 to 70/30, individual cuboids are split into smaller needles [4]. As depicted in Fig. 4, the morphology of TEA-Fw oxide resembles that of Na-Fw oxide like needle-like particles of the similar size. The similar particle size is supported by the similar BET surface area (SA<sub>BET</sub>) values of 50 and 56 m<sup>2</sup> g<sub>cat</sub><sup>-1</sup> for TEA-Fw and Na-Fw oxides, respectively (Table 1).

After reduction at 523 K, the specific Cu surface area (SA<sub>Cu</sub>) and methanol productivity ( $r_{MeOH}$ ) of Na-Fw and TEA-Fw Cu/ZnO catalysts were measured by the N<sub>2</sub>O-RFC experiment and activity test. There is negligible difference in the SA<sub>Cu</sub> and  $r_{MeOH}$  values of TEA-Fw and Na-Fw catalysts (Table 1). Since it is well known that SA<sub>Cu</sub> is correlated well with  $r_{MeOH}$  [5,31], the similar copper surface area is responsible for the similar catalytic activity of Na-Fw and TEA-Fw Cu/ZnO catalysts.

#### 4. Discussion

The results reveal that Na-Fw and TEA-Fw samples of the different states (precursor, calcined and reduced states) show no significant difference in the physicochemical properties and catalytic performance. This means that the pH difference in the synthesis, shown in Fig. S5, is not a critical issue in this work, although this difference was reported to affect precursor properties and catalytic performance [5,9]. Based on our finding and the discussion of Bems *et al.* [2], it can be inferred that zM structure is similarly developed in the ageing step irrespective of TEA<sup>+</sup>HCO<sub>3</sub><sup>-</sup> and Na<sup>+</sup>HCO<sub>3</sub><sup>-</sup> as a precipitation agent. Once the well-developed zM structure is fully washed, the effect of the precipitating agent on the preparation of a final Cu/ZnO catalyst is likely to be minimal. Thus, the washing step needs to be examined in order to unveil the effect of TEA<sup>+</sup>HCO<sub>3</sub><sup>-</sup>. It is worth noting here that thorough washing is very required when a precipitation agent containing Na<sup>+</sup> ion is used [1,2]. Aside from the full washed precursors, no washed (Na-Nw and TEA-Nw) and less washed (Na-Mw and TEA-Mw) Cu,Zn precursors are prepared and then subjected to the same thermal treatment condition as for Na-Fw and TEA-Fw catalysts.

In Table 1, the methanol productivity of Na-Nw catalyst is almost half (134.3 g kg<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>) compared to Na-Fw catalyst (260.5 g kg<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>) and Na-Mw catalyst still shows a lower activity (197.8 g kg<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>). This is the corroborating evidence that the removal of Na<sup>+</sup>

from Cu,Zn precursor is absolutely critical in preparing an active Cu/ZnO catalyst. In contrast, the methanol productivities of TEA-Nw and TEA-Mw catalysts are 253.0 and 248.6 g kg<sub>cat</sub><sup>-1</sup> h<sup>-1</sup> almost similar to that of TEA-Fw catalyst (243.0 g kg<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>). Such findings are similarly observed for bulk TOF and surface TOF values. When the methanol productivity was plotted against the time on stream (TOS), the degrees of deactivation were almost similar for all Cu/ZnO catalysts (Fig. S6). The activity results are supported by N<sub>2</sub>O-RFC results such that TEA-Nw and TEA-Mw (27.9 m<sup>2</sup> g<sub>cat</sub><sup>-1</sup> for both) show the almost similar SA<sub>Cu</sub> values to TEA-Fw and even Na-Fw catalysts. Note that Na-Nw and Na-Mw catalysts show the smaller SA<sub>Cu</sub> values of 19.6 and 22.6 m<sup>2</sup> g<sub>cat</sub><sup>-1</sup>, respectively. When r<sub>MeOH</sub> is plotted against SA<sub>Cu</sub>, linear correlation with the R<sup>2</sup> value of 0.94 is obtained for all data points excluding the data point of Na-Nw catalyst (Fig. 5). The first data point being out of the regression line is due to inhibiting effect of Na<sup>+</sup>. Another finding is that the data points for all TEA<sup>+</sup>-based catalysts are rarely scattered.

This suggests that when  $\text{TEA}^{+}\text{HCO}_{3}^{-}$  is used as a precipitation agent, the efficiency of washing is not a critical issue in preparing an active Cu/ZnO catalyst, very different from the case when  $\text{Na}^{+}\text{HCO}_{3}^{-}$  is used. Prieto et al. investigated the washing effect in Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalysts prepared by Na<sub>2</sub>CO<sub>3</sub> and (NH<sub>4</sub>)HCO<sub>3</sub> [14]. The latter precipitating agent, which is Na<sup>+</sup>-free, showed higher methanol yield and prevented metal agglomeration. However, no-washed NH<sub>4</sub><sup>+</sup>-based catalyst was less active than full washed Na<sup>+</sup>- or NH<sub>4</sub><sup>+</sup>-based catalysts. In contrast, TEA-Nw catalyst showed the comparable methanol productivity to Na-Fw and TEA-Fw catalysts. This means that TEA<sup>+</sup>HCO<sub>3</sub><sup>-</sup> can be a good candidate of precipitating agent.

Since the difference in  $SA_{Cu}$  and  $r_{MeOH}$  of final Cu/ZnO catalysts would be related to the properties of the corresponding calcined samples [4,32], several characterization works were conducted for Na-Nw, Na-Mw, TEA-Nw and TEA-Mw CuO/ZnO samples. There is no big

difference in PXRD patterns of all the prepared oxides such that the major reflections are detected at  $32.51^{\circ}$ ,  $35.54^{\circ}$  and  $38.71^{\circ}$  that are for tenorite (CuO), while small shoulder reflections related to zincite (ZnO) are at  $34.42^{\circ}$  and  $36.25^{\circ}$  (Fig. S7). SEM images of these four oxides also show the similar morphology to the fully washed samples (needle-like particles), but Na-Nw appears to consist of bigger particles compared to the other three oxides (Fig. S8). This is consistent with the BET results that as the precursor gets more washed, the SA<sub>BET</sub> value increases from 28 (Na-Nw) to 56 m<sup>2</sup> g<sub>cat</sub><sup>-1</sup> for Na<sup>+</sup>-based samples whereas all TEA<sup>+</sup>-based oxides exhibit the similar SA<sub>BET</sub> values of 46–50 m<sup>2</sup> g<sub>cat</sub><sup>-1</sup> (Table 1). The similar finding is noticed in the TPR profiles displaying the similar H<sub>2</sub> reduction process of the other oxides except Na-Nw (Fig. 6). Moreover, the reduced Cu/ZnO samples were characterized by PXRD analysis (cf. raw PXRD patterns in Fig. S9). The Cu(111) crystallite sizes of Na-Mw, Na-FW, and all TEA<sup>+</sup>-based catalysts are similar (10.6–11.4 nm), whereas that of Na-Nw catalyst is a little larger (12.6 nm) due to strong Cu(111) reflection (Table 1). This is also in accordance with BET and TPR results.

The slow and broad reduction of Na-Nw oxide is caused by Na<sup>+</sup> present in the oxide. It was reported that alkali-doped Cu-based catalysts are reduced at higher temperatures compared to alkali-free ones [33]. The compositions of metal elements for all CuO/ZnO samples were thus characterized by ICP-MS and XPS works. As summarized in Table 2, sodium in the bulk is detected by ICP-MS for only Na-Nw (0.8%) and Na-Mw (0.2%) samples, although surface sodium is not detectable for all samples due to a XPS detection limit of < 0.1%. Therefore, we believe that the lower methanol productivities of Na-Nw and Na-Mw catalysts originate from the negative effect of Na<sup>+</sup> even if its measured content is low, and that all TEA<sup>+</sup>-based catalysts are free of Na<sup>+</sup> and, in turn, show the similar activity in methanol synthesis. On the other hand, ICP-MS and XPS results confirm that the bulk Cu/Zn ratio and also the surface Cu/Zn ratio, which is calculated by XPS Cu 2p and Zn 2p

spectra (Fig. S10), are close to the target ratio of 70%/30% for all samples.

Fig. 7 displays the PXRD patterns of Na-Mw, Na-Nw, TEA-Mw and TEA-Nw precursors. Even though the prepared precursors are not or less washed, zM structure is only observed without any  $Na^+$  and  $NO_3^-$  related structures. Note that  $Na^+$  was found only in Na-Nw and Na-Mw precursors, which is similar to the results obtained in CuO/ZnO samples (Table 2). According to the results of elemental analysis (Table 2), N element is detected only for Na-Nw precursor (0.08%) among Na<sup>+</sup>-based precursors, whereas it is detected for all TEA<sup>+</sup>based precursors and its amount decreases from 0.29% (TEA-Nw) to 0.06% (TEA-Fw) by more washing. It is worth noting here that a source of N element is  $NO_3^-$  for Na<sup>+</sup>-based precursors, whereas it would be  $NO_3^-$  and/or TEA<sup>+</sup> for TEA<sup>+</sup>-based precursors. Thus, all precursors were characterized by ATR-IR. All spectra show the typical absorbance peaks of zM structure (Fig. S11): O–H stretching vibration in the range 4000–2500 cm<sup>-1</sup>, asymmetric C–O stretching vibration of the carbonate anions in the range  $1700-1100 \text{ cm}^{-1}$ , and O–H deformation and additional carbonate vibrations (out-of-plane and asymmetric O-C-O bending) in the region 1200–600 cm<sup>-1</sup> [34]. For TEA<sup>+</sup>-based precursors, C–H stretching vibration were not distinctly observed, which means that a likely form that N is present in is not TEA<sup>+</sup> but NO<sub>3</sub><sup>-</sup>. However, NO<sub>3</sub><sup>-</sup> related absorbance, usually found at ca. 1380 cm<sup>-1</sup> [35], was hardly detected for all precursors, due to overlapping of strong zM-related absorbance at 1388 cm<sup>-1</sup>. Therefore, it is considered that the amount of N element is too low for all precursor samples even if present.

Additionally, the  $2\theta$  value of (20-1) reflection for zM structure was examined. The (20-1) reflection is detected at  $32.21^{\circ}$  for Na-Nw and at  $32.34^{\circ}$  for Na-Mw, where the corresponding *d*-spacing values are 2.779 Å (Na-Nw) and 2.768 Å (Na-Mw). Recall that the  $2\theta$  value of the corresponding reflection for Na-Fw precursor is  $32.38^{\circ}$  (*d*-spacing: 2.765 Å). This shift is related to residual sodium ion because the  $2\theta$  value of (20-1) reflection for

TEA<sup>+</sup>-based precursors is in the range of  $32.27^{\circ}$ -  $32.32^{\circ}$ .

The prepared precursors were also characterized by TGA, as presented in Fig. 8. Na-Nw precursor shows only one DTG peak at 627 K accompanying the dehydroxylation and decarbonylation events. Along with this peak, Na-Mw precursor shows additional DTG peak at 694 K that is more developed for Na-Fw precursor. Similarly, two DTG peaks at 643 and 720 K are observed for TEA-Mw precursor. In case of TEA-Nw precursor, one more DTG peak at a lower temperature of 490 K is found. This is possibly due to decomposition of TEA<sup>+</sup>, evidenced by the fact that the peak intensity at 490 K decreases in the order of TEA-Nw > TEA-Mw > TEA-Fw. Therefore, it is believed from PXRD and TGA results that  $Zn^{2+}$  and  $CO_3^{2-}$  constituents in zM structure ( $(Cu_{1-x}Zn_x)_2(OH)_2CO_3$ ) are not affected by TEA<sup>+</sup> but significantly by Na<sup>+</sup>.

Consequently, the beneficial effect of  $\text{TEA}^+\text{HCO}_3^-$  is identified on the washing step; that is, thorough washing is not required for acquiring an active Cu/ZnO catalyst. This is very contrast to the case when the precipitation agent with sodium ion is used. On the basis of our results and the report of Bems *et al.* [2], Na<sup>+</sup> apparently lowers the degree of Cu<sup>2+</sup> substitution by Zn<sup>2+</sup> in zM structure and prevents the formation of HT-CO<sub>3</sub> in Cu.Zn precursor, which in turn inhibits CuO reduction and decreases active Cu sites finally resulting in a lower activity of final Cu/ZnO catalyst. A possible explanation for the negative effect of Na<sup>+</sup> is associated with the formation of sodium zinc carbonate that was observed in the ageing step when the precipitation agent containing Na<sup>+</sup> was used [9]. This phase was reported to play a role as a Zn-storage phase releasing Zn<sup>2+</sup> during precipitate dissolution and reprecipitation that can substitute Cu<sup>2+</sup> in malachite and thus produce zincian malachite. However, the formation of this intermediate structure would be suppressed in TEA<sup>+</sup>-based method, thereby leading to easy Cu<sup>2+</sup> substitution by Zn<sup>2+</sup>. The negative effects of Na<sup>+</sup>, therefore, come from its strong interaction with HT-CO<sub>3</sub> acting as a bridging anion between

 $Cu^{2+}$  and  $Zn^{2+}$  ions in precursor samples (furthermore acting as "glue" between Cu or CuO and ZnO particles [2]). In comparison, weak interaction between TEA<sup>+</sup> and HT-CO<sub>3</sub> in zM structure results in the similar properties of TEA<sup>+</sup>-based Cu,Zn precursors and CuO/ZnO samples as well as the similar methanol synthesis activity of TEA<sup>+</sup>-based Cu/ZnO catalysts irrespective of the washing efficiency.

#### 5. Conclusions

We have used  $TEA^{+}HCO_{3}^{-}$  as a precipitating agent in the preparation of final Cu/ZnO catalyst for methanol synthesis. Irrespective of the washing efficiency, all TEA<sup>+</sup>-based precursors show zM structure with the similar  $Zn^{2+}$  replacement and HT-CO<sub>3</sub> presence, resulting in the similar copper surface area and methanol productivity of all TEA<sup>+</sup>-based Cu/ZnO catalysts. This indicates that TEA<sup>+</sup>, even if present in the precursor, does not influence zM structure developed by full ageing, which is very different from the case when the precipitating agent containing Na<sup>+</sup> is used because a lower catalytic activity is obtained for a less washed Na<sup>+</sup>-based catalyst. Inhibited formation of HT-CO<sub>3</sub> and lowered Cu<sup>2+</sup> substitution by  $Zn^{2+}$  explain that the residual Na<sup>+</sup> in the precursor affects well-developed zM structure. Therefore, washing is of prime importance to suppress these negative effects of Na<sup>+</sup> even if coprecipitation and ageing would be conducted in a well optimized manner. The consequence of using  $TEA^{+}HCO_{3}^{-}$  is that it is possible to prepare an active Cu/ZnO catalyst for methanol synthesis without thorough washing of the precursor. From this lesson, we can suggest that the catalyst synthesis approach needs to be studied to use a precipitation agent with an organic cation composed of N, H and/or C atoms for the preparation of a methanol synthesis catalyst.

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	$SA_{BET}$ $(m^2 g_{out}^{-1})$	$Cu(111)^a$ (nm)	$SA_{Cu}$ $(m^2 g_{out}^{-1})$	$r_{MeOH}$ (g kg <sub>ent</sub> <sup>-1</sup> h <sup>-1</sup> )	Bulk TOF <sup>b</sup> $(h^{-1})$	Surface TOF <sup>c</sup> $(h^{-1})$
	(III Beat )	(1111)	(III Beat )	(g ngeat n )	(11)	(11)
Na-Nw	28	12.6	$19.6\pm2.5$	$134.3\pm3.4$	$0.47\pm0.01$	$8.8\pm0.2$
Na-Mw	42	10.8	$22.6\pm2.3$	$197.8\pm2.7$	$0.69\pm0.01$	$11.2\pm0.2$
Na-Fw	56	10.6	$27.9\pm2.3$	$260.5\pm23.7$	$0.90\pm0.08$	$11.9 \pm 1.1$
TEA-Nw	46	10.8	$27.9\pm2.1$	$253.0 \pm 15.9$	$0.88\pm0.06$	$11.6\pm0.7$
TEA-Mw	48	11.3	$27.9\pm2.7$	$248.6\pm9.8$	$0.87\pm0.03$	$11.4\pm0.4$
TEA-Fw	50	11.4	$26.3\pm2.1$	$243.0\pm12.9$	$0.83\pm0.04$	$11.8\pm0.6$

Table 1. BET surface area (SA<sub>BET</sub>) of CuO/ZnO samples, and Cu surface area (SA<sub>Cu</sub>), methanol productivity (r<sub>MeOH</sub>), bulk TOF, and surface TOF of Cu/ZnO catalysts

<sup>a</sup> calculated from the FWHM values of Cu(111) reflections (Fig. S9) using the Scherrer's equation <sup>b</sup> calculated by dividing  $r_{MEOH}$  values by the total Cu content measured by ICP-MS <sup>c</sup> calculated by dividing  $r_{MEOH}$  values by the surface Cu content measured by N<sub>2</sub>O-RFC

	Metal composition from ICP-MS (mol%)					Metal composition from XPS (mol%)		C, H, N percentage of precursors (%)			
	Cu,Zn precursor		CuO/Z	CuO/ZnO sample							
	Cu	Zn	Na	Cu	Zn	Na	Cu	Zn	С	Н	Ν
Na-Nw	66.9	32.4	0.7	71.7	27.5	0.8	67.5	32.5	5.17	1.16	0.08
Na-Mw	67.2	32.5	0.2	71.9	27.8	0.2	69.1	30.9	5.20	1.12	ND*
Na-Fw	68.7	31.2	ND*	72.7	27.3	ND*	69.0	31.0	5.26	1.00	ND*
TEA-Nw	66.7	33.2	ND*	71.7	28.3	ND*	69.4	30.6	6.17	1.38	0.29
TEA-Mw	66.7	33.3	ND*	71.6	28.4	ND*	67.8	32.2	5.17	1.06	0.11
TEA-Fw	68.0	32.0	ND*	73.0	27.0	ND*	67.2	32.8	5.12	1.02	0.06

XPS of CuO/ZnO samples, as well as C, H, N atomic percentages of the precursor samples

Table 2. Metal composition of precursor samples and CuO/ZnO samples by ICP-MS and

\*ND: Not detected

#### **Figure captions**

- **Figure 1.** PXRD patterns of Na-Fw and TEA-Fw precursors, where the reflections of malachite (marked as blue bars) are given at the bottom. The  $2\theta$  range in  $31-34^{\circ}$  is zoomed at the right-hand side in order to show a shift of (20–1) reflection.
- **Figure 2.** DTG curves and MS traces for  $H_2O$  (m/z = 18, blue) and  $CO_2$  (m/z = 44, red) evolved during TG experiments of Na-Fw and TEA-Fw precursors in the temperature range 320–1,000 K. The value indicates the mass loss of each precursor.
- **Figure 3.** TPR profiles and MS traces for  $H_2$  (m/z = 2, green) and  $CO_2$  (m/z = 44, red) of Na-Fw and TEA-Fw oxides.
- Figure 4. SEM images of Na-Fw and TEA-Fw oxides.
- **Figure 5.** Correlation between the specific Cu surface area and methanol productivity of Na<sup>+</sup>-based (black) and TEA<sup>+</sup>-based (red) Cu/ZnO catalysts. Dot line is linear regression of Cu/ZnO catalysts without Na-Nw catalyst. A dotted line represents linear regression of all data points excluding the point for Na-Nw catalyst, where R<sup>2</sup> is estimated to be 0.94.
- **Figure 6.** TPR profiles and MS traces of  $H_2$  (m/z = 2, green) and  $CO_2$  (m/z = 44, red) for Na-Nw, Na-Mw, TEA-Nw and TEA-Mw oxides.
- **Figure 7.** PXRD patterns of Na-Mw, Na-Nw, TEA-Mw and TEA-Nw precursors, where the reflections of malachite (marked as blue bars) are given at the bottom. The  $2\theta$  range in  $31-34^{\circ}$  is zoomed at the right-hand side in order to show a shift of (20–1) reflection.
- **Figure 8.** DTG curves and MS traces of  $H_2O$  (m/z = 18, blue) and  $CO_2$  (m/z = 44, red) evolved during TG experiments of Na-Mw, Na-Nw, TEA-Mw and TEA-Nw precursors in the temperature range 320–1,000 K. The value indicates the mass loss of each precursor.

Figure 1



Figure 2



#### Figure 3



Figure 4



Figure 5



Figure 6



Figure 7



Figure 8

