

Influence of the Number of Washing on the Characteristic of Nanocrystalline Copper Oxide Powders

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ABSTRACT

The influence of the number of washing on the copper oxide physico-chemical properties was investigated by carrying out precipitation of copper (II) nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$) with an aqueous solution of sodium hydroxide. The structural evolution of the desired CuO phase, via an intermediate $\text{Cu}(\text{OH})_2$ phase, was investigated using XRD, FTIR, total surface area (BET method) and SEM. An investigation on the mobility of oxygen species was carried out using transient technique *i.e.* temperature programmed reduction (TPR). Results show that the BET surface area increased gradually with the number of washing from 8.5 to 15.9 $\text{m}^2 \text{g}^{-1}$. While, the total amount of oxygen atom being reduced is roughly the same. This indicates the ease of reducibility of the oxide when the precursor is washed several times. XRD pattern of these oxides gave well crystalline CuO with main peaks appeared at $2\theta = 35.5, 38.7$ and 48.7° . The powders obtained are of uniform size distribution, finely grained with an average size of 20 nm.

Keywords: copper oxide, nanocrystalline, precipitation, washing effect, temperature programmed reduction

1 INTRODUCTION

The catalytic properties of heterogeneous catalysts are strongly affected by every step of the preparation together with the quality of raw materials. The choice of a laboratory method for preparing a given catalyst depends on the physical and chemical characteristics desired in the final composition. Bulk catalysts are normally comprised of active substance is generally achieved by precipitation [1] with main purpose of formation of very small crystallite. Washing of the solids is then required to remove the mother liquor (usually water) completely, to eliminate impurities and to exchange certain undesirable or useless ions for others that are easily decomposable by calcinations.

This study was carried out with purpose to prepare catalysts for oxidation reaction especially propylene oxidation. As

been reported that the simple oxide Cu_2O [2] and supported mixed copper oxides [3] exhibit significant activity and selectivity in the partial oxidation of propylene to acrolein and has been chosen as a model catalysts for the determination of the involved reaction mechanisms. Thus, research focuses on the influence of number of washing on the copper oxide physico-chemical properties was investigated.

2 EXPERIMENTAL

Copper oxides were prepared using precipitation method under ambient temperature. An aqueous solution of NaOH (Analytical UNIVAR Reagent 97 %) was added continuously into aqueous solution of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (Hamburg Chemical GmbH 99 %) with constant stirring until a pH is reached at ~ 13.5 . The precipitate is allowed to age for 120 minutes. After ageing the precipitate was recovered by filtration and washed with 30 ml of cold distilled water. The washing process is repeated for 60, 90, 120, 150 and 180 ml of distilled water. All the samples were dried in oven at 373 K for 12 h. Six series of copper oxide catalysts were obtained and calcined in air at 723 K for 4 h and designated as CuO1, CuO2, CuO3, CuO4, CuO5 and CuO6, where number 1 to 6 indicating number of washing. The catalysts were then characterised by using XRD, FTIR, BET surface area measurement, SEM and TPR in H_2 .

3 RESULTS AND DISCUSSION

X-ray diffraction (XRD) patterns of the precursors prepared through this method showed that the precipitation occur mainly via $\text{Cu}(\text{OH})_2$ phase (Figure 1). Calcination of the synthesised samples at 723 K display a high and intense XRD patterns indicating that all the samples are highly crystalline (Figure 2). As the washing volume increases, the CuO phase peaks become apparent which consist of three main peaks appeared at $2\theta = 35.3, 38.7$ and 48.7° , correspond to $(\bar{1}11)$, (111) and (202) planes, respectively.

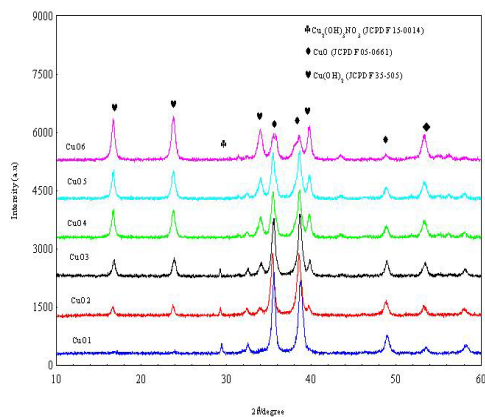


Figure 1: XRD patterns of CuO precursors

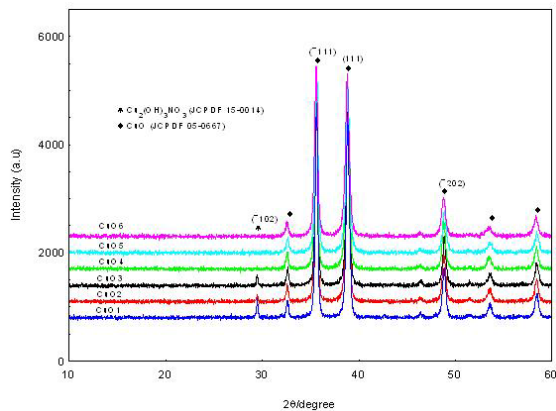


Figure 2: XRD patterns of CuO catalysts

Catalysts	FWHM ₋₁₁₁	FWHM ₁₁₁	$t_{-111}^a / (\text{Å})$	$t_{111}^a / (\text{Å})$
CuO1	0.3003	0.3618	275.32	230.70
CuO2	0.3191	0.3768	259.08	221.51
CuO3	0.3121	0.3805	264.91	219.37
CuO4	0.3309	0.3890	249.83	214.55
CuO5	0.3605	0.4260	229.35	195.94
CuO6	0.3696	0.4478	223.66	186.37

a crystallite size by means of Scherrer's formula: $t (\text{Å}) = (0.89 \times \lambda) / \beta_{hkl} \cos \theta_{hkl}$

Table 1: XRD data of CuO Catalysts

The Fourier transform infrared spectroscopy (FTIR) spectra of CuO catalysts were also recorded (Figure 3). Main feature recorded in samples CuO1, CuO2 and CuO3 show sharp band at 1384 cm^{-1} which is referred to as copper hydroxynitrate band [4]. This is probably due to insufficient decomposition of nitrate during calcinations. Few times of washing is also thought to contribute to the above observations. This occurrence may be avoided when using a

large amount of water to wash the precipitates, thereby the suspension may thoroughly mix to remove the impurities [5]. The band at region 1636 cm^{-1} is associated with the bending mode of OH groups of adsorbed water. The CuO vibration bands which are found to appear at $575, 500$ and 460 cm^{-1} cannot be observed clearly because it is shifted due to the existence of OH group.

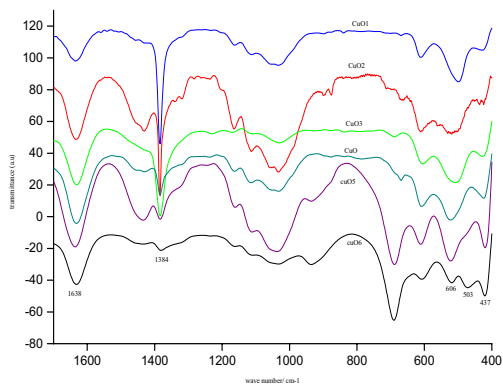


Figure 3: FTIR Spectra of CuO Catalysts

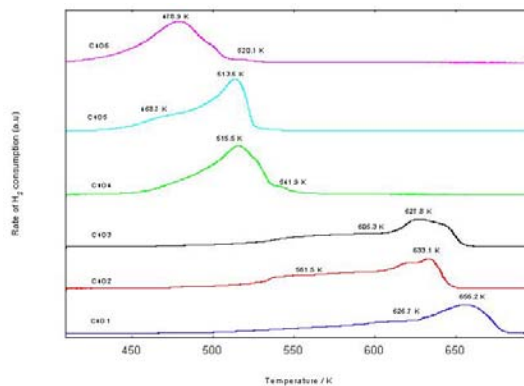


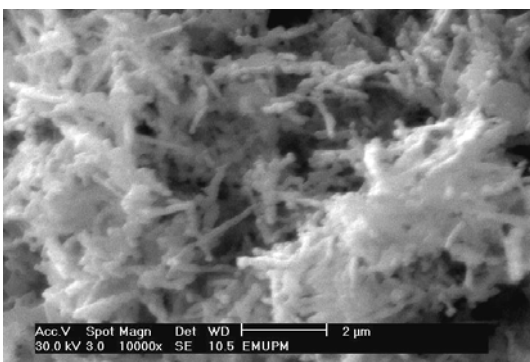
Figure 4: TPR Profile of CuO Catalysts

Peaks ^a	T _{ONSET} / K	T _{MAX} / K	Reduction activation energy, E _r /kJ mol ⁻¹	Oxygen atom removed from catalysts (mol g ⁻¹)	Oxygen atom removed from catalysts (atom g ⁻¹)	Coverage (atom cm ⁻²)
<u>CuO1</u>						
1	445	626.8	104.81	4.81 x 10 ⁻³	2.90 x 10 ²¹	3.41 x 10 ¹⁶
2		656.2	109.72	6.18 x 10 ⁻³	3.72 x 10 ²¹	4.38 x 10 ¹⁶
Total oxygen atom removed				1.04 x 10⁻²	6.62 x 10²¹	7.79 x 10¹⁶
<u>CuO2</u>						
1	425	561.5	93.89	2.73 x 10 ⁻³	1.64 x 10 ²¹	1.39 x 10 ¹⁶
2		633.1	105.87	8.71 x 10 ⁻³	1.24 x 10 ²¹	4.44 x 10 ¹⁶
Total oxygen atom removed				1.14 x 10⁻²	6.88 x 10²¹	5.83 x 10¹⁶
<u>CuO3</u>						
1	444	605.3	101.22	5.07 x 10 ⁻³	3.05 x 10 ²¹	2.70 x 10 ¹⁶
2		627.8	104.98	5.53 x 10 ⁻³	3.33 x 10 ²¹	2.95 x 10 ¹⁶
Total oxygen atom removed				1.06 x 10⁻²	6.38 x 10²¹	5.65 x 10¹⁶
<u>CuO4</u>						
1	424	515.6	86.21	9.67 x 10 ⁻³	5.83 x 10 ²¹	4.79 x 10 ¹⁶
2		541.9	90.61	6.93 x 10 ⁻⁴	4.17 x 10 ²⁰	3.42 x 10 ¹⁵
Total oxygen atom removed				1.04 x 10⁻²	6.25 x 10²¹	5.13 x 10¹⁶
<u>CuO5</u>						
1	415	468.7	80.50	3.13 x 10 ⁻³	1.88 x 10 ²¹	1.28 x 10 ¹⁶
2		513.5	85.86	6.15 x 10 ⁻³	3.70 x 10 ²¹	2.52 x 10 ¹⁶
Total oxygen atom removed				9.28 x 10⁻³	5.58 x 10²¹	3.80 x 10¹⁶
<u>CuO6</u>						
1	370	478.9	80.08	8.78 x 10 ⁻³	5.29 x 10 ²¹	3.34 x 10 ¹⁶
2		520.1	86.97	3.13 x 10 ⁻⁴	1.89 x 10 ²⁰	1.19 x 10 ¹⁵
Total oxygen atom removed				9.09 x 10⁻³	5.48 x 10²¹	3.46 x 10¹⁶

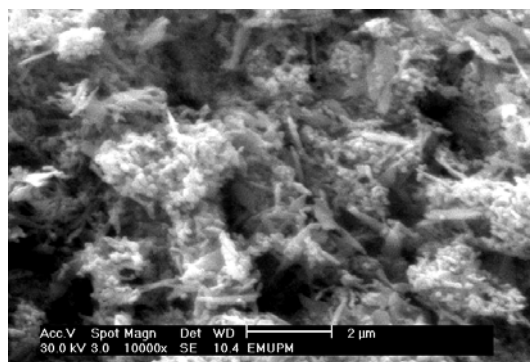
Table 2: Temperature Programmed Reduction (TPR)
Total number of O₂ removed from the copper oxide catalysts by reduction in H₂/Ar stream (5% H₂)

The oxides have also been characterised by TPR with hydrogen as the reducing gas (5 % H₂-Ar). See Figure 4. The figure show that the first peak maximum of the reduction profile is significantly reduced from ~ 650 to 470 K as the number of washing is increased. The total amount of oxygen atom being reduced was calculated and listed in Table 2. As the number of washing increases, the total amount of oxygen atom being removed is also increase.

This result shows the increment of ease of reducibility of the oxides as the number of washing is increases. Meanwhile, the total surface area of the CuO catalysts is found climbing with the increasing number of washing. This result is suggested due to the smaller crystallite size synthesised. The crystallite size is calculated from the Scherrer's formula (Table 1).



(a)



(b)

Figure 5: SEM Images for (a) CuO1 and (b) CuO6

Figure 5 display scanning electron micrograph (SEM) of two of the calcined samples, i.e CuO1 and CuO6. Both images show needle-like structure. The type of morphologies for the crystallites could be detected from the XRD is triclinic crystallite (tenorite).

4 CONCLUSION

The CuO oxides were demonstrated to have enhanced in surface area, thus smaller crystallite size when it were washed several times. From the XRD and FTIR spectrums, there is still small amount of nitrate remain in the samples probably due to insufficient amount of water used to wash the precipitate. On the other hand, TPR profiles showed that the peak of the reduction temperature shifted to lower temperature indicating the ease of reducibility of the oxide as the number of washing increases.

5 ACKNOWLEDGEMENTS

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