

OXIDATION OF STYRENE WITH HYDROGEN PEROXIDE OVER Cu/SBA-15 CATALYST

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Abstract

SBA-15 type silica was loaded with different amounts of copper species prepared via the isothermal treatment method. The obtained solids were characterized by XRD, BET, SEM, TEM techniques. All samples are mesoporous structure, large surface area, uniform pore size, good dispersion of copper species. All Cu/SBA-15 materials exhibited high activity in catalyzing the liquid phase oxidation of styrene with H₂O₂ solution. The conversion of styrene is about 10-40% with high selectivity to benzaldehyde. Thus, the high catalytic activity for these Cu/SBA-15 catalysts can be attributed to high dispersion of the active sites throughout the support.

Keywords. Benzaldehyde, styrene, SBA-15, copper, oxidation.

1. INTRODUCTION

The catalytic oxidation of styrene to produce oxygenated compounds is an important industrial reaction in the manufacturing of fine chemicals since its products are valuable chemicals in organic synthesis [1, 2]. For a long time, the oxidation of alkenes has been performed with H₂O₂ [3, 4] or molecular oxygen [5-7] because these oxidants are friendly agents in view point of environment and economic consideration as well. Among the products, benzaldehyde is an important intermediate in the production of a number of pharmaceuticals. Conventionally, this aldehyde is produced by reacting alkylaromatic with peracid in stoichiometric amounts [1, 2]. The use of peracid always yields a huge waste due to formation of undesirable products. Moreover, peracids are very expensive, corrosive, hazardous to operate and also non-selective for the styrene oxide formation. Thus, water soluble simple compounds of transition metals such as tungstate, molybdate, cobaltate, and vanadate... have been replaced and played as homogeneous catalyst in the oxidation of olefinic compounds [1, 2, 8, 9]. In the latter case, the separation and recycling of the homogeneous catalysts are very difficult. Another promising way is to search for a simply separable catalyst having both high activity and selectivity for the epoxidation. Recently, a vast number of works have been reported for a greener oxidation of styrene, using easily separable and reusable transition metal oxides,

such as NiO, CoO, TiO₂, or MnO₂[10-15]. In other ways, molecular sieve materials as heterogeneous catalysts have also been a subject of growing interests in the oxidation of alkenes in the last two decades [5, 10, 12, 13]. The selective oxidation of alkenes over Fe-MCM-41[4], Co-TUD-1 [15], Cu-SBA-15 [16, 17], V-SBA-15 [18] is recently published. The main reason of the usage of such porous materials is to obtain high dispersion of the metal oxide species which are the most important factors in determining the catalytic activity and selectivity. The nature of the metal precursor, the preparation method, and metal loading are also known to affect the morphology and dispersion of the metal oxide species on the support [2, 15].

Following on this trend, we recently investigated the effect of cobalt oxides dispersed on the bentonite clay [19] or Cu-intra lattice of hydrotalcite for the oxidation of unsaturated hydrocarbons [20]. This study reported the distribution of copper species on mesoporous silicate SBA-15 for the oxidation of styrene.

2. EXPERIMENTAL

2.1 Preparation and characterization of the catalysts

Siliceous SBA-15 template was prepared using tetraethyl orthosilicate (TEOS) and Pluronic P-123 as a structure-directing agent. A quantity of 4.0 grams of P123 was added into a 500 mL – flask

containing 130 mL of distilled water and 20 mL of 36.5 wt.% HCl. The solution was stirred at 35 °C for 2 hours. Then, 9.0 mL of TEOS is slowly added to the homogenous mixture beaker. The synthetic solution was sealed at 35 °C with stirring for 24 hours; then aged at 75 °C in oven for 48 hours. After cooling to room temperature, the precipitate was filtered and washed with distilled water. The filter cake was dried in air at room temperature overnight before calcination at 550 °C for 6 hours in air at a ramp of 2 °C/min.

In a typical synthesis, a given quantity of copper powder and SBA-15 was added into 10 mL of distilled water with stirring. Then, 60 mL of 30% H₂O₂ and 2 mL HCOOH 85 wt.% was added dropwise and the reaction stirred for 3 hours. The mixture was placed in a 100-mL autoclave with a Teflon liner. The autoclave was maintained at 80 °C for 2 days and then air-cooled to room temperature. The resulting precipitates were collected and washed with distilled water several times and then dried at 80 °C for 12 hours.

Powder X-ray diffraction (XRD) patterns were recorded on a D8 Advance-Bruker instrument using CuK_α radiation ($\lambda = 1.59 \text{ \AA}$). Scanning Electron Microscopy was recorded on Hitachi S-4500 (Japan) with the magnification of 200,000 times. TEM images were collected on a Japan Jeol. Jem.1010. Nitrogen physisorption was measured at 77 K on an Autochem II 2920 (USA).

2.2. Catalytic performance

The catalytic oxidation process of styrene was carried out in a 100 mL three-neck glass flask fitted with a reflux condenser. For a typical run, 3.12 grams of styrene, 10 ml of solvent (N,N'-dimethylamide,

ethanol) and 0.2 grams of catalyst were loaded into the flask. After the reaction mixture was magnetically stirred and heated to the desired temperature, hydrogen peroxide solution (H₂O₂, 30 %) was dropped into stirred reaction mixture and the reaction was initiated. The three-neck glass flask was quenched to room temperature and then catalyst was filtered off after the reaction. The filtrate was quantitatively analyzed by a GC-MS (HP-6890 Plus).

3. RESULTS AND DISCUSSION

3.1. Textural Properties of Cu/SBA-15

Figure 1 presents XRD patterns for SBA-15 at low angle and larger angles. For the SBA-15 pattern, a well-resolved peak at 2-theta of 0.84, and two lower intensity peaks at that of 1.45, 1.68° corresponding to (hkl) planes of (100), (110), (200) are observable. This reflects the presence of highly ordered hexagonal mesoporous structure SBA-15 silica [16, 18]. Therefore, it is suggested that mesoporous silica SBA-15 was successfully fabricated using the TEOS and triblock copolymer as directing-structure agent. This mesoporous silica was further used for the loading of copper to prepare Cu/SBA-15 catalysts.

Figure 1B displays the X-ray diffraction patterns of both SBA-15 and Cu-SBA-15 samples for comparison. Two samples SBA-15 and 5.0 wt.% Cu/SBA-15 show no reflection signals at large angles (Fig. 1B). The reflection signals for metallic copper phase was only appeared in sample 10 wt.% Cu/SBA-15 while no peaks are observed in sample having a lower copper content, indicating a fine distribution of copper on the mesoporous silica

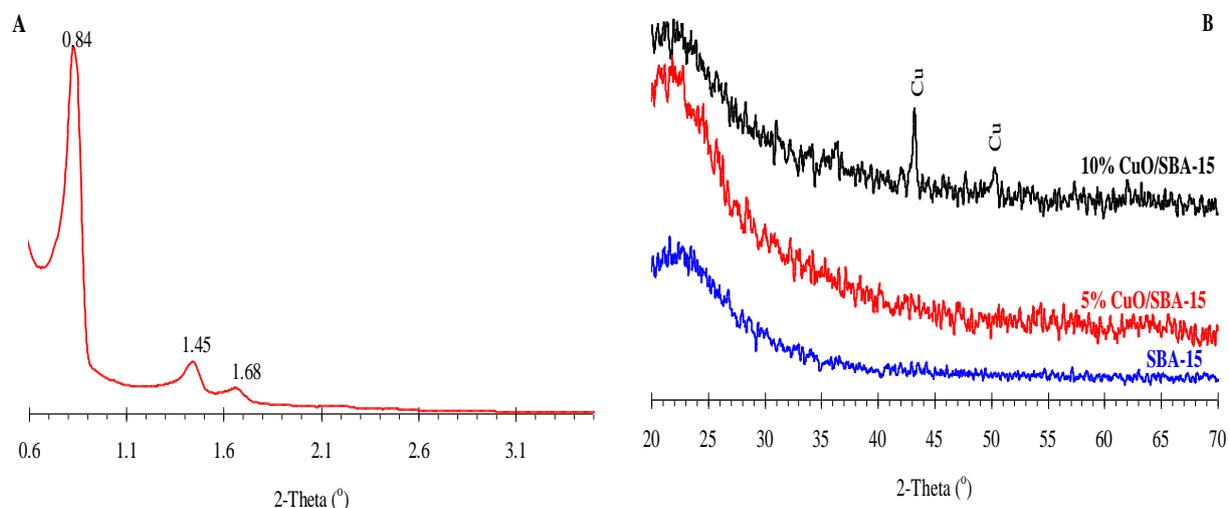


Figure 1: XRD patterns for SBA-15 at low angles (A) and all samples at large angles (B)

support although the formation of a tiny amount of copper oxide highly dispersed on SBA-15 was not ruled out under reported catalyst preparation [21]. Thus, it is expected that Cu/SBA-15 may be an excellent catalyst candidate for the oxidation of styrene.

The surface morphology of Cu/SBA-15 sample is examined by SEM and TEM techniques. The scanning electron micrograph of 10 wt.% Cu/SBA-15 sample is represented in figure 2A. The sample is consisted of particles that are aggregated to form a rope-like macrostructure. Under large magnification level (not shown here), the particles are present in uniform shaped sphere. TEM image of the sample observed parallel to the direction of the channels

was shown in figure 2B. As TEM revealed, the Cu/SBA-15 sample exhibited the same morphological features as SBA-15 [16, 18], evidenced by the observation of uniform hexagonal channels. Interestingly, it is noteworthy that there was little contrast between the support and copper species inside the pores. Some dark spots well dispersed along the walls of the SBA-15 channels were observed. In other regions, some darker areas which can be referred to as copper rich domains were observed. Thus, TEM image indicates the distribution of copper species on both the internal and external surfaces of mesoporous silica SBA-15 at high loadings of copper of 10 wt.%.

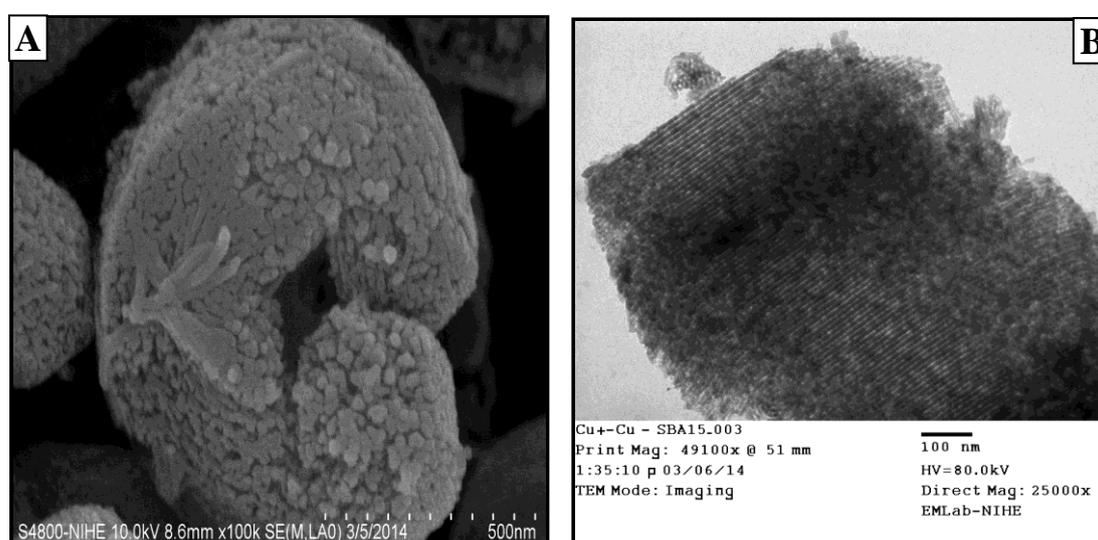


Figure 2: SEM micrograph (A) and TEM image (B) of sample 10 wt.% Cu/SBA-15

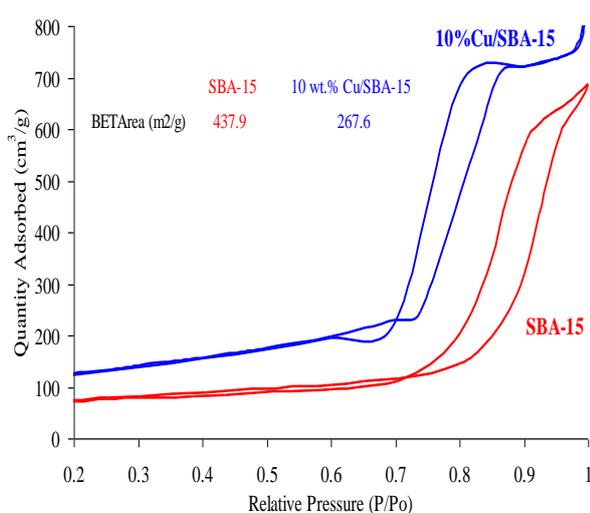


Figure 3: Nitrogen adsorption/desorption isotherms of the samples

Figure 3 displays nitrogen adsorption–desorption

isotherms of two representative SBA-15 and Cu/SBA-15 samples. The isotherms of these patterns were of identical shape to that of SBA-15, indicative of structural preservation of SBA-15 during catalyst preparation, in accordance with XRD analysis. However, the BET surface area of Cu/SBA-15 is much lower than that of SBA-15 mesoporous silica. As seen in Fig. 2B, it can be attributed to the presence of copper (and oxides) inside the pores, which appears to block a large fraction of both the micropores and mesopores [15, 18]. Indeed, as comparing with SBA-15, the isotherm of 10 wt.% Cu/SBA-15 exhibited capillary condensation in the range of $P/P_0 = 0.7-1.0$ that can be attributed to partial pore blockage due to the presence of the copper species [14, 15].

3.2. Catalytic activity

The oxidation of styrene with aqueous hydrogen

peroxide solution was performed in atmospheric pressure in the temperature range of 40-80 °C. The product mixture includes benzaldehyde, styrene oxide, and some other heavy oxygenates [3, 6, 18]. In order to investigate the role of copper in the oxidation of styrene, the reaction has been carried out in the presence of catalyst with the Cu loadings of 0-10 wt.%. Figure 4 displays the correlation between catalytic activity and the copper loadings on SBA-15 support. It is noteworthy that the SBA-15 sample shows a null activity in the oxidation of styrene. As copper was loaded on SBA-15 support, styrene conversion gradually increases, but the product distribution varies with the conversion [17, 20]. For sample 5 wt.% Cu/SBA-15, there is only benzaldehyde detected at a modest conversion of 12.8 %. This suggests that more catalytically active species may be accessible for the reactants in 5 wt.% Cu/SBA-15 sample. At a higher copper loading of 10 wt.%, styrene oxide is detected in the liquid mixture in addition to a small amount of some other products such as benzoic acid, acetophenone, phenyl-acetaldehyde, styrene glycol. The explanation in the latter case is attributed to the presence of various active sites in both the internal and external surfaces of mesoporous silicate SBA-15. The copper (and oxides) sites inside the pores are suggested to be active for the conversion of styrene into benzaldehyde as observed on sample 5.0 wt.% Cu/SAB-15 while the copper species located on the external surfaces produces styrene oxide, a reactive compound which may initiate some secondary reactions resulting in the formation of several byproducts [2, 7, 6, 18, 19].

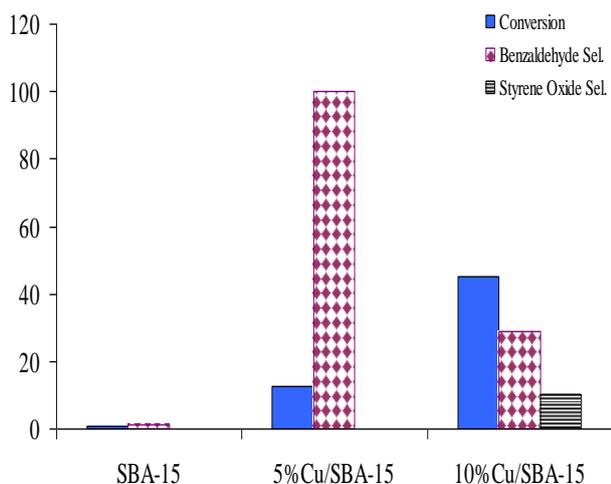


Figure 4: Catalytic activity of sample Cu/SBA-15 at 55 °C, 4hours, DMF solvent in the oxidation of styrene with H₂O₂

Indeed, total selectivity to byproducts is about 61% under reported reaction conditions over 10 wt% Cu/SBA-15. Although styrene oxide is a valuable product that deserves to be interested in improving the selectivity, but the catalyst exhibits a less selectivity to the desired products at higher copper contents. Thus, we are interested in sample 5 wt.% Cu/SBA-15 on target to the conversion of styrene into benzaldehyde.

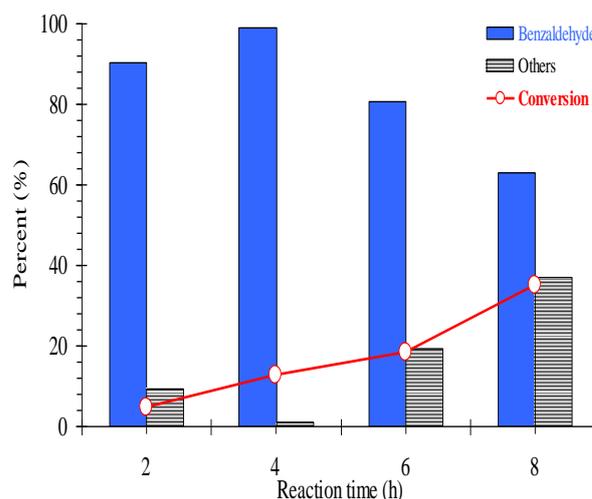


Figure 5: Effect of reaction time on catalytic activity of sample 5%Cu/SBA-15 at 55 °C, H₂O₂/styrene = 3.3, DMF solvent

Therefore, another set of experiments have been carried out on 5%Cu/SBA-15 at 55 °C, H₂O₂/styrene = 3.3, DMF solvent and maintain for different reaction times. The changes in conversion of styrene were monitored and plotted with respect to time; the reaction results are displayed in Fig. 5. It was seen that the conversion of styrene increases continuously until 34.9 % as time increases, the selectivity of benzaldehyde decreases after 2 hours, which was relative to the over-oxidation of benzaldehyde, however, it dropped observably to 62.9 % at 8 h, therefore duration about 4 h was the proper reaction time [6, 18, 20].

Analysis of liquid products obtained showed a mixture of oxygenates of phenyl derivatives including benzaldehyde, benzoic acid, acetophenone, phenyl-acetaldehyde, styrene oxide, styrene glycol, suggesting that the styrene oxidation at the side chain can lead to various reaction products, depending on the catalyst and reaction conditions. In the present work, it is suggested that two major reactions take place on Cu/SBA-15 catalysts to undergo the oxidative C=C cleavage into benzaldehyde and epoxide [2, 6, 18, 20]. However,

under the present catalysis conditions, the major oxidation product obtained was benzaldehyde. This may be related from the direct oxidative cleavage of C=C of styrene and the fast oxidation of styrene oxide to benzaldehyde. This is in good consistent with the literature [16-18, 20] which proves that benzaldehyde formed through only the direct oxidative cleavage of the C=C bond of styrene. Thus, Cu loaded on SBA-15 are thus found to have the special property of stimulating direct oxidative cleavage of C=C in order to convert styrene to benzaldehyde as the major product [18, 20].

4. CONCLUSION

SBA-15 supported catalysts with two different Cu-loadings were prepared by the isothermal pretreatment. The mesoporous structure of the support, SBA-15, was preserved as Cu was added under oxidative-hydrothermal conditions. Under preparation conditions, a major component of metallic copper is founded on SBA-15 carrier. SEM and TEM images showed parallel channels and the location of copper species both inside pores and outside surface of the SBA-15 support. The Cu/SBA-15 showed a good ability to conversion of styrene into benzaldehyde. The catalytic activity is dependant on the reaction conditions, copper loading amounts, the location of copper sites in the SBA-15 support. The catalyst with the lowest Cu-loading exhibited the highest selectivity to benzaldehyde. The styrene conversion varies from 12 to 45 % while the product selectivity depends on the conversion values and location of copper sites. The highest selectivity to benzaldehyde is 99 %.

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