Synthesis and Catalytic Performance of SBA-15 Supported Catalysts for Oxidation of Styrene

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Abstract- Cu(II) and Mn(II) anchored on SBA-15 were synthesized by incipient wet impregnation technique. The support and catalysts were characterized by using TEM, SEM and BET techniques. Further, the effect of SBA-15 supported Cu(II) and Mn(II) catalysts were analyzed for the oxidation of styrene at different reaction conditions such as styrene to TBHP mole ratio, temperature and catalyst amount using TBHP (tertiary-butyl-hydro-peroxide) as effective oxidizing agent. Styrene oxide and benzaldehyde were observed as the main reaction products. Maximum conversion of styrene (98.9 %) was obtained at styrene to TBHP mole ratio of 1:4, temperature 80 ^{0}C with 20 mg of catalyst.

Index Terms- Benzaldehyde, catalytic activity, oxidation, SBA-15, styrene, styrene oxide, supports

1 INTRODUCTION

The catalytic oxidation of styrene is a significant reaction from both academic and industrial point of view due to formation of styrene oxide and benzaldehyde. These are important valuable intermediates for the production of variety of fine chemicals and pharmaceuticals [1], [2], [3]. Styrene oxide, in particular is a commercially important oxide for producing epoxy resins, diluting and flavoring agents and valuable intermediate for organic synthesis and pharmachemistry. In conventional process, epoxides are produced through the reaction of styrene with organic peracids and permanganate as the oxidizing agent with some limitations such as poor selectivity of products, high cost, corrosivity of peracid and formation of undesirable waste products. Therefore, it is advantageous to replace the conventional scheme with ecofriendly process with uncontaminated oxidants and little waste.

Various transition metal compounds such as Ni, Cu, Mn, Co, Fe and V have been identified as homogeneous catalysts for styrene oxidation using H_2O_2, molecular oxygen and tert-butyl hydroperoxide (TBHP)oxidants at mild reaction conditions [4],[5].In spite of high selectivity of homogeneous catalysts, major problem associated with these catalysts is the recovery and recycling of the catalyst. Therefore to overcome these issues, more efficient and environment friendly heterogeneous catalysts have been developed for styrene oxidation. A large variety of supports have been used, which include inorganic supports such as molecular sieves, silica, alumina, zeolites and organic supports such as polymers [6], [7], [8]. The discovery of ordered mesoporous materials by Mobil Corporation scientists in 1992 have opened many new possibilities in the field of heterogeneous catalysts due to their high surface area, well defined pore structure, large pore size and high thermal and hydrothermal stability [9].

In last one decade, ordered mesoporous materials i.e. MCM-41, MCM-48, MCM-50 andSBA-15 have shown tremendous growth as catalytic supports for various oxidation reactions [10],[11],[12].Among various mesostructured silica materials, SBA-15 is a promising support owing to its very high surface areas (>700 m^2/g), uniform pore size distributions with high active-site accessibility, large tunable pore size (4-30 nm), thick framework wall (3.2-6.4 nm) and large pore diameter for easy diffusion of reactant molecules [13], [14].

In present work, we report the synthesis and characterization of Cu(II) and Mn(II) catalysts supported on SBA-15, prepared by incipient wet impregnation method. These catalysts were investigated for the liquid phase oxidation of styrene with TBHP as oxidant. All the catalysts have shown very high selectivity for styrene oxide.

2. EXPERIMENTAL

Synthesis of SBA-15

The mesoporous SBA-15 was synthesized according to the procedure described by Zhao et al

[15] using P 123 ($EO_{20}PO_{70}EO_{20}$, Sigma-Aldrich, M_w = 5800) as template [15]. In a typical synthesis, 4 g of Pluronic P123 was dissolved in 30 g of distilled water and 120 g of 2M HCl. After 3 hrs of stirring (600-700 rpm) at 30 °C, 8.5 g of TEOS (Alfa Aesar) was added and continued to stirring at the same temperature for 24 hrs. The final molar ratio of mixture solution was TEOS: HCl: H_2O: P123:: 1:80.58: 40.85: 0.0169.A solid product was obtained after aging at 80°C for 48 hrs without stirring and then recovered by filtration and washed with distilled water and ethanol (ethanol: water =1:1). The solid was first air dried at room temperature for 8 hrs and then in oven at 90°C for 6 hrs and finally calcined in a muffle furnace at 550°C under air for 4 hrs.

Catalyst Preparation

The CuMn/SBA-15 catalyst was synthesized by incorporating copper and manganese metals into SBA-15 by incipient wet impregnation method using aqueous solutions of $Cu(NO_3)_2$. $3H_2O$ and $Mn(NO_3)_2.4H_2O$ as precursors. Initially, calculated pore volume (1 cm^3/g) of support SBA-15 was taken and after that 10 wt% metals precursors were dissolved in 2 ml distilled water. This solution was put in contact with 0.5 g SBA-15 support. The resulting powder was dried in oven for 6 hr at 80 °C and then calcined at 450 °C for 4 hr. Similarly Cu/SBA-15 and Mn/SBA-15 catalysts (10 wt %) were prepared by the same procedure.

Catalyst Characterization

The BET surface area of support and catalysts were determined by N_2 adsorption/desorption isotherms at -196 ^oC, using ASAP 2020 (Micromeritics, USA). The morphology of the samples was examined by Scanning Electron Microscopy (SEM) measurements, using SEM: EVO 18-20-45 system. The samples were sputtered with gold to minimize the charging effects. The micro and mesoporous particle shape was determined by Tunneling Electron Microscopy (TEM) measurements, using TECNAI 20G system.

Catalytic Activity Study

The liquid phase catalytic oxidation of styrene was carried out in a magnetically stirred three necked round bottom flask (50 ml) fitted with a thermometer and a reflux water condenser and the reaction mixture temperature was maintained using an oil bath. In a typical procedure, the catalyst (25 mg) was allowed to swell in 10 ml acetonitrile for 30 min. Styrene (1.04g, 10 mmol) was added to this reaction mixture followed by the addition of TBHP (0.90 g, 10 mmol). The reaction mixture was heated at 60 °C for 7 h with continuous stirring. The samples were withdrawn at every one hour time interval and were analyzed by gas chromatography (GC). The conversion and selectivity was calculated on the basis of mole percent of styrene. Iso-octane was used as the internal standard.

3 RESULTS AND DISCUSSION

The BET surface area, pore volume and pore diameter of SBA-15 support and catalysts are summarized in Table 1. The SBA-15 support shows a high surface area of 761.8 m^2/g and pore volume of 1.07cm^3/g. After impregnation of SBA-15 with copper and manganese metals, surface area gets reduced, this is attributed to clogging of pores by metal ions.

Table 1: Surface characteristics of support and catalysts

Compound	Specific surface area (m^2/g)	Pore volume (cm^3/g)	Pore size (nm)
SBA-15	761.8	1.07	5.62
CuMn/SBA-15	461.4	0.58	5.0
Cu/SBA-15	325.3	0.40	4.8
Mn/SBA-15	316.7	0.48	5.1

Scanning Electron Microscopy (SEM)

The surface morphology of SBA-15 support and various catalysts prepared by incipient wet impregnation was studied by using SEM as shown in Fig 1. SEM image of SBA-15 support (Fig 1(A)) shows a curved cylindrical structure that remained unaffected on immobilization of Cu(II) and Mn(II) metals (Fig 1(B), (C), (D)), thus confirming the retention of physical structure of mesoporous SBA-15.

Transmission Electron Microscopy (TEM)

TEM images of SBA-15 and supported catalysts are shown in Fig.2. The TEM image of SBA-15 (Fig 2(A)), illustrated ordered hexagonal array of uniform pores, which is characteristic of SBA-15. Fig 2(B), (C) and (D) revealed dark spots inside the mesoporous channels that may be due to well dispersion of metal ions inside the mesoporous channel.

3.1 Catalytic Oxidation of Styrene

Catalytic oxidation of styrene was carried out using TBHP oxidant and CuMn/SBA-15 as catalyst. The effect of various parameters such as styrene to TBHP mole ratio, reaction temperature and catalyst amount were quantified in terms of conversion and selectivity of different products.

Effect of Styrene to TBHP Mole Ratio

The effect of styrene to TBHP mole ratio was investigated by varying the mole ratio from 1:1 to 1:4. The conversion of styrene gradually increases with an increase in the amount of TBHP and time. The conversion of styrene was almost constant 92.7 % at 1:3 and 1:4 mole ratios at 70 ^{0}C after a reaction time of 7 h. Initially benzaldehyde was found as the major product and the selectivity of benzaldehyde was tending to decrease with increase in TBHP ratio and reaction time. After 7 h, styrene oxide was found as major reaction product with maximum yield of 76.7% at 1:4 mole ratios. Therefore, all other catalytic parameters were evaluated at the styrene to TBHP mole ratio of 1.

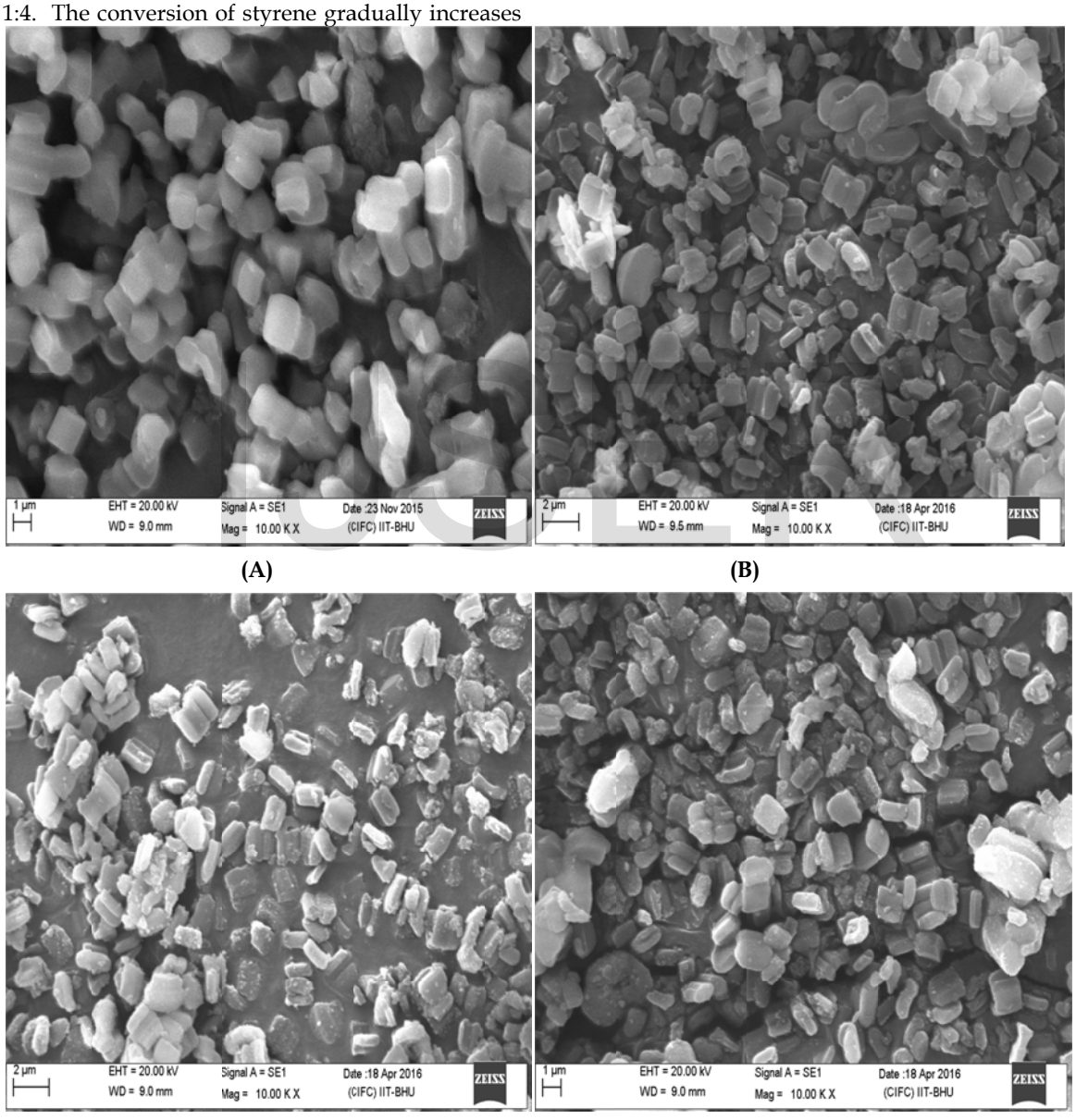

Fig. 1. Scanning Electron Microscopy (SEM) analysis of (A) SBA-15 support, (B) Cu/SBA-15, (C) Mn/SBA-15 and (D) CuMn/SBA-15

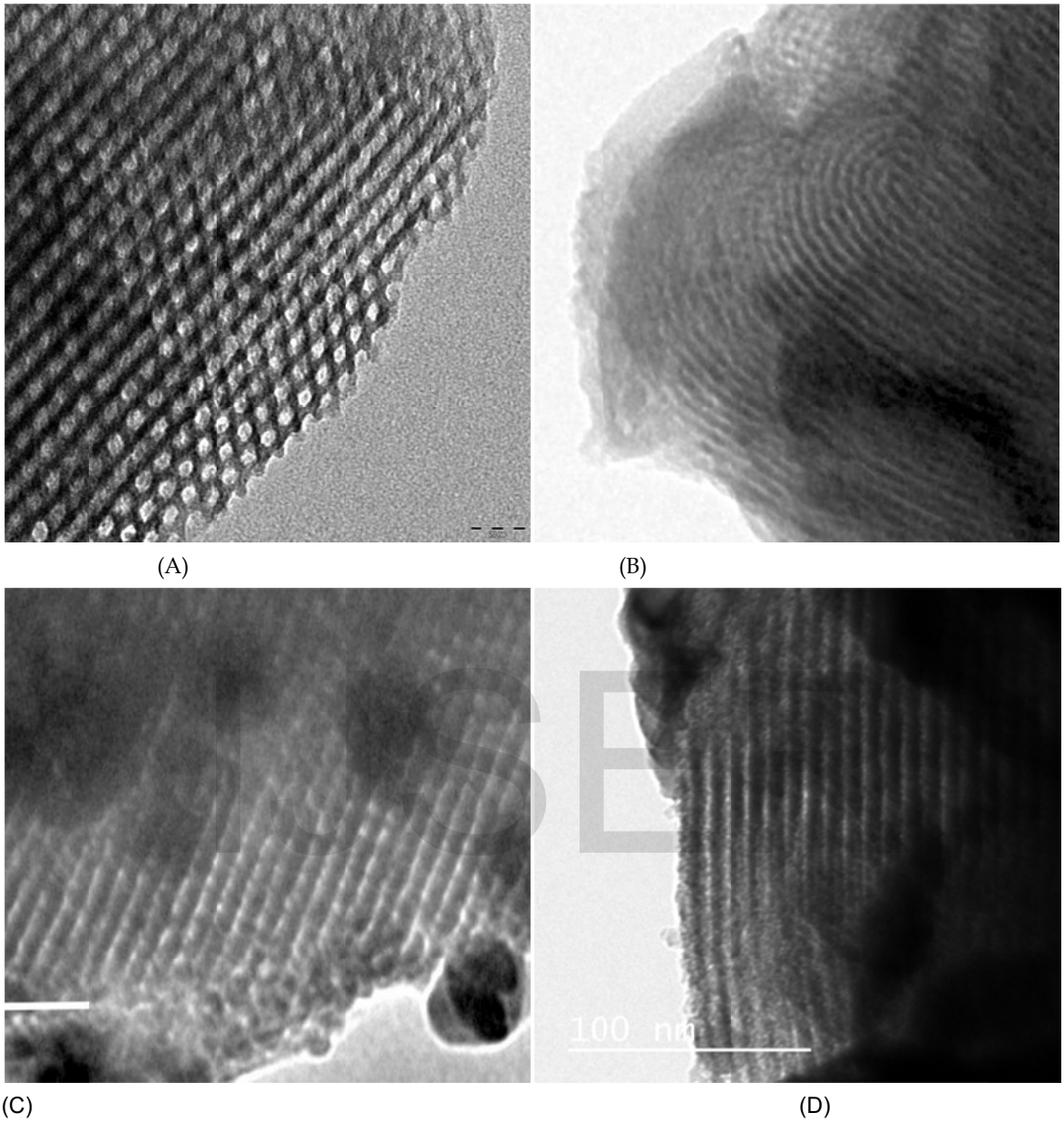

Fig.2. Transmission Electron Microscopy of (A) SBA-15 support, (B) Cu/SBA-15, (C) Mn/SBA-15 and (D) CuMn/SBA-15

Table 2 Optimized Reaction Conditions for Styrene Oxidation

Catalyst	Reaction Conditions	Conversion (%)	Styrene Oxide yield* (%)	Benzaldehyde yield (%)
CuMn/SBA-15	Styrene: 10 mmol TBHP: 40 mmol Catalyst: 20 mg Temperature: 80°C Acetonitrile: 10 ml	98.9	80.0	18.8
Cu/SBA-15		96.3	64.5	31.8
Mn/SBA-15		74.7	20.4	54.3

* Yield = conversion x selectivity

Effect of Temperature

Reaction temperature is an important parameter, which has a significant effect on styrene conversion and yield of different products. The influence of reaction temperature on styrene oxidation was studied in a temperature range of 50-80 ^{0}C while all other reaction parameters were kept constant. The analysis showed that conversion of styrene increased with increase in reaction temperature. The maximum conversion of 98.9 % was obtained at 80 ^{0}C. The results indicated that with increase in temperature yield of styrene oxide increased and maximum yield of 80 % was obtained at 80 ^{0}C. Therefore, 80 ^{0}C was chosen as reaction temperature for further studies.

Effect of Catalyst Amount

The effect of catalyst amount on styrene oxidation was investigated by changing the catalyst amount from 10 to 30 mg and keeping the temperature and styrene to TBHP mole ratio at 80 ^{0}C and 1:4 respectively. At 10 mg catalyst amount, conversion was 96.0% and further increased to 98.9% at 20 mg. At 30 mg, conversion was decreased to 94.5 %. The maximum yield of styrene oxide was 80.0 % at 20 mg catalyst amount.

Therefore optimum reaction conditions for styrene oxidation have been found at styrene to TBHP mole ratio of 1:4, temperature 80 ^{0}C with 20 mg of catalyst. The maximum conversion of styrene oxidation was 98.9 % in 7 h at these reaction conditions with styrene oxide yield of 80.0 % and benzaldehyde yield of 18.81% respectively. Under these optimized conditions, Cu/SBA-15 and Mn/SBA-15 catalysts were also analyzed for oxidation of styrene and their results are summarized in Table 2.

4 CONCLUSIONS

In summary, CuMn/SBA-15, Cu/SBA-15 and Mn/SBA-15 catalysts were synthesized by wet impregnation technique and characterized by BET, SEM and TEM analysis. These catalysts were investigated for oxidation of styrene using TBHP as oxidant. Among all the catalysts, CuMn/SBA-15 was found to be highly selective for styrene oxide.

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