

Research Article

Selective Oxidation of Styrene to Benzaldehyde by Co-Ag Codoped ZnO Catalyst and H₂O₂ as Oxidant

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Various ratio of Co-Ag supported on ZnO have been evaluated in the selective catalytic oxidation of styrene to benzaldehyde, using H₂O₂ as an oxidant. The catalysts were prepared by a sol-gel process and were characterized using XRD, FT-IR, TG-DTG, BET, and SEM/EDX. The performance of the prepared catalyst was investigated under different parameters such as solvent, temperature, substrate/oxidant molar ratios, reaction time, and doping percent. The Zn_{1-x-y}Ag_xCo_yO catalysts exhibit a good activity and a high selectivity towards benzaldehyde (95%) with the formation of only 5% of acetophenone.

1. Introduction

Benzaldehyde is an important intermediate in the industrial fine chemical synthesis for fragrances, flavorings, pharmaceuticals, and in the organic synthesis [1, 2]. Conventional preparation of benzaldehyde is based on the hydrolysis of benzyl chloride, and it can be obtained as an intermediate of the oxidation of toluene to benzoic acid [3, 4]. This process was not environmentally friendly because of using organic solvents and producing traces of chlorine [5]. The development of recyclable catalysts, to simply separate from the reaction mixture, has attracted an economic and ecological interest [6]. In this context, there are two categories of catalysts: transition metal immobilized or constituted molecular sieves, such as NbCo-MCM-41 [7], VSB-5 [8], and Co-ZSM-5 [9], and application of metal oxides or complexes, such as Mg_xFe_{3-x}O₄ [1] and TiO₂/SiO₂ [10]. Recently, Long et al. [11] have developed magnetic microparticles immobilizing palladium acetate as heterogeneous coordination catalysts for selective oxidation of styrene allowing mainly to prepare acetophenone. Earlier, it was shown that

in the presence of activated carbon (AC) and H₂O₂ as the oxidant, the styrene was selectively converted to benzaldehyde [12].

The main objective of this work was the preparation of heterogeneous supported catalysts (Zn_{1-x-y}Ag_xCo_yO) by a sol-gel method and their evaluation in the oxidation of styrene to benzaldehyde (supplementary data 1).

2. Experimental Details

2.1. Materials. Zinc acetate dihydrate (Zn(CH₃COO)₂·2H₂O), cobalt nitrate hexahydrate (Co(NO₃)₂·6H₂O), silver nitrate (Ag(NO₃)), citric acid (HOC(COOH)(CH₂COOH)₂), hydrogen peroxide (H₂O₂ 30 wt.%), ethanol, styrene, acetonitrile, acetone, and methanol were purchased from Sigma-Aldrich chemical reagent grade and used as received.

2.2. Characterization. Thermogravimetric analysis (TGA) was recorded on a TA Instrument Q500 apparatus in flowing air at a heating rate of 10°C·min⁻¹. BET specific surface areas and average pore diameter of the prepared catalyst were

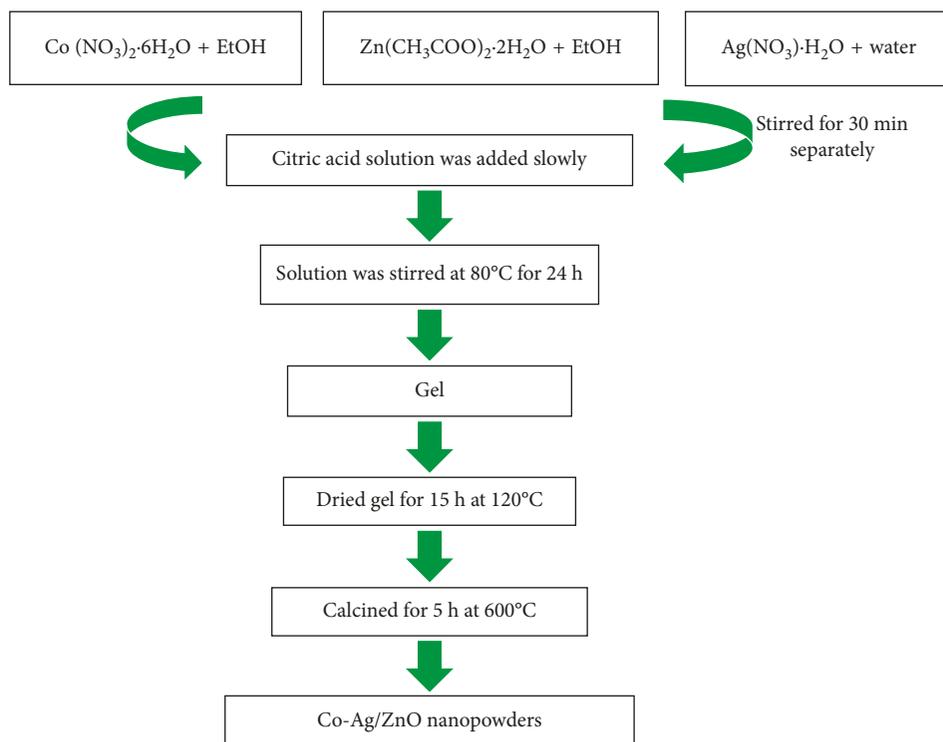


FIGURE 1: Flow chart for synthesis of Co-Ag/ZnO nanopowders by a sol-gel method.

measured by N_2 adsorption-desorption technique using a Micromeritics analyser P/N 05098-2.0 Rev A. The stretching vibration frequency of the catalyst was recorded by FT-IR spectroscopy in the range of $400\text{--}4000\text{ cm}^{-1}$ using a Bruker vertex 70 DTGS. Spectrometer XRD measurements were performed on a XPERT-MPD Philips diffractometer using $\text{Cu-K}\alpha$ radiation as the X-ray source in the 2θ range of $20^\circ\text{--}80^\circ$. The size and morphology of the microstructures were carried out on VEGA3 TESCAN microscope equipped with an energy dispersive X-ray spectrometer (EDAX TEAM).

2.3. Preparation of the Catalyst. Pure ZnO nanopowders were prepared by a sol-gel method. $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (50 mL, 0.5 M in ethanol) and citric acid (50 mL, 0.5 M in ethanol) were stirred separately for 30 min. Then, the citric acid solution was added slowly into the solution of zinc acetate. This hydroalcoholic solution was heated at 80°C for 24 h, giving an opaque white gel which was dried at 120°C overnight and calcined at 600°C for 5 hours under air to offer pure ZnO. The same procedure was used to prepare nanopowders of $\text{Zn}_{1-x-y}\text{Ag}_x\text{Co}_y\text{O}$ by adding the needed amount of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.5 M) and $\text{Ag}(\text{NO}_3)$ (0.5M) (Figure 1). Six samples were prepared: C1 (pure ZnO); C2 (1% mol Ag-doped ZnO); C3 (1% mol Co-doped ZnO); C4 (1% mol Co-1% mol Ag codoped ZnO); C5 (2.5% mol Co-2.5% mol Ag codoped ZnO), and C6 (5% mol Co-5% mol Ag codoped ZnO).

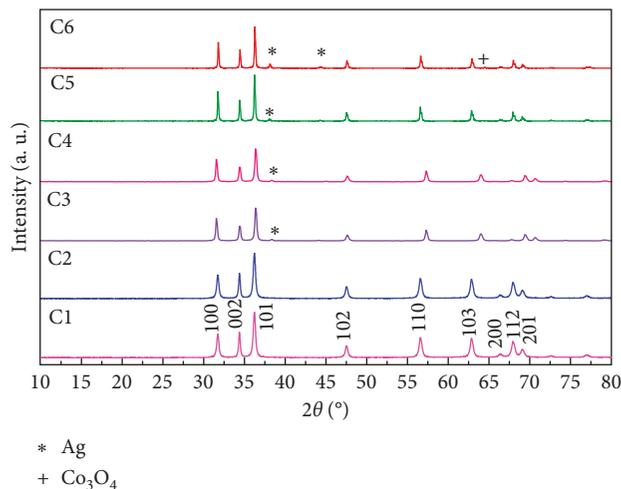
2.4. Catalytic Activity. The oxidation of styrene with hydrogen peroxide as the oxidant was carried out in a 50 mL

rotaflo tube with magnetic stirring immersed in bath oil. The activity of the catalyst ($\text{Zn}_{1-x-y}\text{Ag}_x\text{Co}_y\text{O}$) was studied varying the following parameters: doping percents of $0 \leq x \leq 0.05$ and $0 \leq y \leq 0.05$, $\text{H}_2\text{O}_2/\text{styrene}$ molar ratios from 1.1 to 3, reaction temperatures range ($40^\circ\text{C}\text{--}120^\circ\text{C}$), and the amount of the catalyst (0.005–0.02 g) in aprotic and protic solvents. Aliquots samples from the reaction mixture were taken at regular intervals and were monitored by gas chromatography (GC) equipped with FID using Rtx-5 capillary column. Dodecane was used as an internal standard for the quantitative analysis of the reaction products. The conversion of styrene was based on the unreacted substrate.

3. Results and Discussion

3.1. Characterization of the Catalysts. Figure 2 shows XRD patterns of pure ZnO and $\text{Zn}_{1-x-y}\text{Ag}_x\text{Co}_y\text{O}$ nanopowders calcined at 600°C . According to pure ZnO reference (00-036-1451), the sample corresponding to C3 is highly crystallized and all diffraction peaks are well indexed to the diffraction pattern of hexagonal ZnO with the P63mc space group. However, the ZnO doped with 1% mol of Ag (C2) revealed new peaks with weak intensities at 38.20° and 44.62° , as it was reported by Zeferino et al. [13]. The doping concentration of 2% to 10% mole of Co-Ag (C5 and C6) can lead to the formation of Co_3O_4 with a corresponding trace at 64.66° [14].

Table 1 summarizes the position and the width at midheight (FWHM) of the main peaks, along with the lattice parameter values calculated from the XRD patterns of the pure and codoped ZnO nanopowders. The incorporation of Co-Ag on ZnO results in the decrease of the FWHM,

FIGURE 2: XRD patterns of $\text{Zn}_{1-x-y}\text{Ag}_x\text{Co}_y\text{O}$.TABLE 1: Position, FWHM, and the lattice parameters of $\text{Zn}_{1-x-y}\text{Ag}_x\text{Co}_y\text{O}$ nanopowders.

Nominal Ag-Co concentration	Position of the (101) peak	FWHM (degree)	Lattice parameters (Å)	
			<i>a</i>	<i>c</i>
0% mol	36.2583	0.2134	3.2498	5.2066
1% mol Ag	36.3177	0.082	3.24509	5.18829
1% mol Co	36.1927	0.325	3.25037	5.19644
1% mol Ag-1% mol Co	38.279	0.200	3.28825	5.23984
2.5% mol Ag-2.5% mol Co	36.4427	0.078	3.24454	5.19797
5% mol Ag-5% mol Co	36.3177	0.075	3.24016	5.21778

indicating an increase in crystallinity. A shift position of the diffraction peak (002) could be attributed to the incorporation of Ag^+ and Co^{2+} ions in the ZnO lattice sites. As it was shown earlier, Ag^+ ions in the ZnO lattice sites, probably substitute Zn^{2+} ions [13].

On the other hand, the peaks associated with the cobalt oxide or cobalt hydroxide phases such as CoO or $\text{Co}(\text{OH})_2$ were not detected as shown in the XRD patterns (Figure 2). According to Wojnarowicz et al. [15], some precipitation of Co_3O_4 was observed in the XRD investigation for the 10% mol Co-Ag sample in synthetic air.

TG/DTG curves of the prepared materials (supplementary data 2) reveal one thermal event at 162°C attributed to the loss of crystal water from the catalyst (2.42 wt.%).

To investigate the specific areas and the porous nature of the C4 nanopowders, Brunauer–Emmett–Teller (BET) gas sorption measurements were performed. The nitrogen adsorption-desorption isotherm and the pore size distribution plots of the C4 sample are shown in supplementary data 3. The sample corresponds to type IV and V isotherm and type H3 hysteresis loop appearing which is attributed to the predominance of mesopores [16]. The determined surface area of the C4 sample was $5.90\text{ m}^2/\text{g}$, and the calculated BJH pores size was 5.42 nm.

FT-IR spectrum (supplementary data 4) of C4 nanopowder shows a strange band at 600 cm^{-1} and a relatively weak band at 500 cm^{-1} which could be assigned to the stretching modes of Zn–O [17]. The bands in the range

$910\text{--}1537\text{ cm}^{-1}$ may be attributed to the residual NO_3^- ions [18]. A weak band at 2375 cm^{-1} is attributed to the CO_2 present in air. The bands at 3400 cm^{-1} and 1630 cm^{-1} correspond to the stretching of hydroxyl groups due to the adsorption of water on the particles' surface [19].

The scanning electron microscopy (SEM) of the undoped and the Ag-Co codoped ZnO nanopowders are shown in Figure 3. Ag and Co do not bring significant change in the morphology. The EDX results confirmed that the products consist of zinc, cobalt, and silver elements in ZnO nanopowders, which are in good agreement with XRD patterns.

3.2. Catalytic Experiments. The oxidation reaction of styrene is influenced by several parameters. In an attempt to find out the suitable reaction conditions providing an optimum of conversion and yield, effects of different reaction conditions have been carried out.

3.2.1. Effect of Catalyst Loading. As shown in Table 2, when the loading amount of Co and Ag was increased from 2 to 10% mol, there was an obvious increase in styrene conversion from 61 to 80% (entries 5–7), but the selectivity of benzaldehyde decreases for more than 2% mol (entries 6–7). However, with 1% mol, either with Co or Ag, a similar result was obtained (entries 3–4). In the presence of pure ZnO or in the absence of the catalyst, no significant conversion was observed.

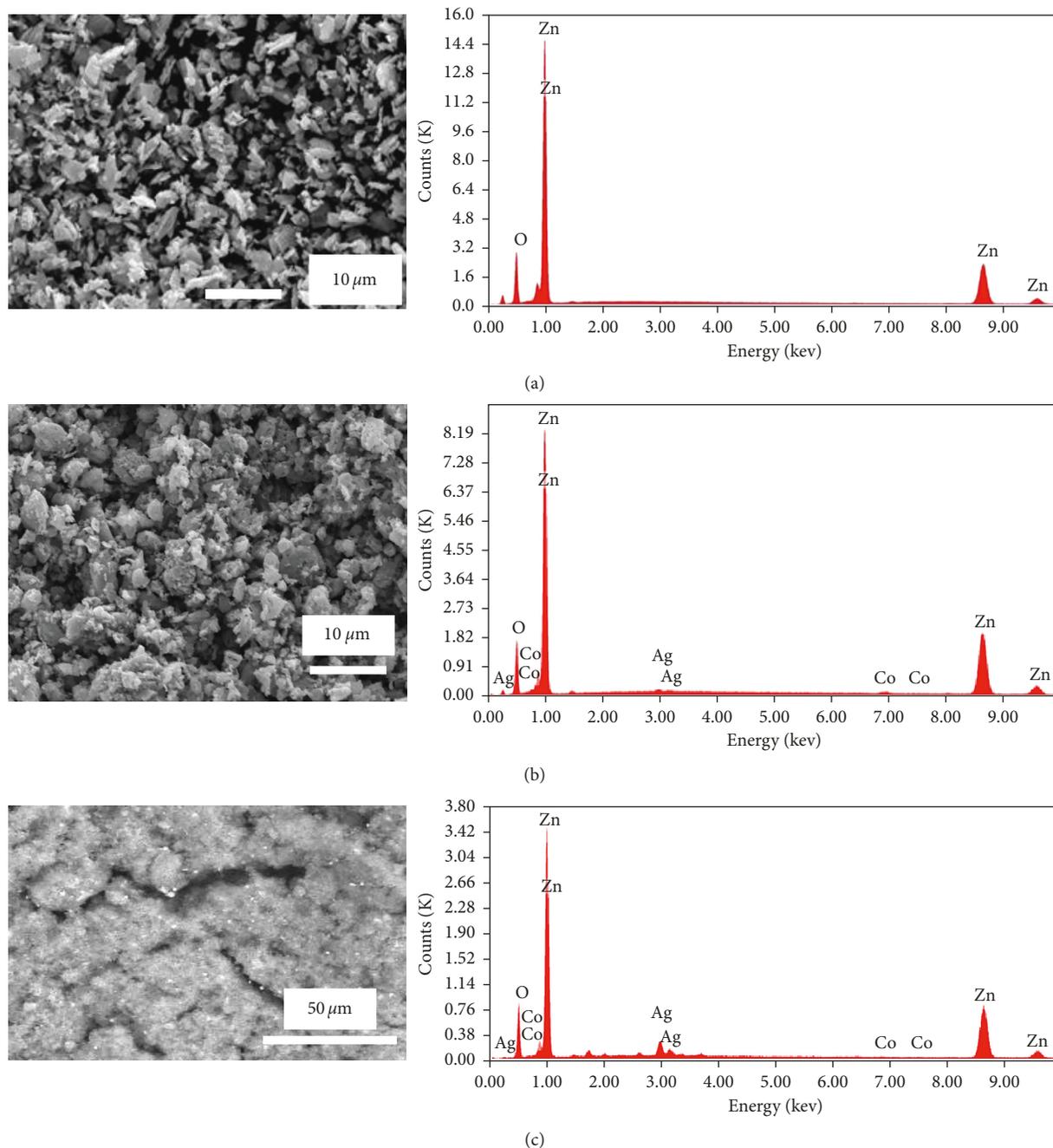


FIGURE 3: SEM images and EDX spectra of (a) C1, (b) C4 before used, and (c) C4 after the 4th cycles.

3.2.2. Effect of Catalyst Amount. To investigate the catalyst amount effect on the oxidation reaction, different amounts of the C4 catalyst have been studied. As shown in Table 2, the optimal catalyst amount was found to be 0.02g with high selectivity of benzaldehyde (95%).

3.2.3. Effect of the Reaction Time. In order to shed more light on this point, a kinetic study was carried out with 0.02 g of C4 catalyst using GC to determine the conversion and product distribution (Figure 4). As depicted, the evolution of styrene versus time shows that benzaldehyde

was formed as the major product. This compound reached a maximum after 24 hours with 61% in conversion and 95% in selectivity.

3.2.4. Effect of Molar Ratio H_2O_2 /Styrene. The catalytic oxidation of styrene using the C4 catalyst was performed by varying the molar ratio of the H_2O_2 /styrene. The increase in molar ratio from 1:1 to 1:2.5 resulted in a significant increase in the conversion. The yield of benzaldehyde increased from 57% to 72% mol. However, the selectivity of benzaldehyde slightly decreases (Table 3).

TABLE 2: Effect of the catalyst's amount and loading.

Entry	Catalyst	Amount of catalyst (g)	Styrene conversion	Yield ^a (% mol)	
				Benzaldehyde	Acetophenone
1	Without	—	1	1	0
2	C1	0.02	5	5	0
3	C2	0.02	30	30	0
4	C3	0.02	25	25	0
5	C4	0.02	61	58	3
6	C5	0.02	75	45	33
7	C6	0.02	80	48	16
8	C4	0.005	30	30	0
9	C4	0.01	50	50	0
10	C4	0.015	53	53	0

Reaction conditions: H₂O₂/styrene, 1; temperature, 80°C; solvent, acetonitrile; reaction time, 24 h; ^ayields determined by GC using dodecane as an internal standard.

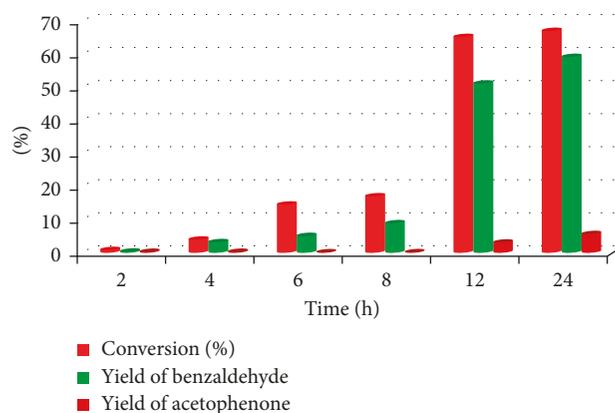


FIGURE 4: Effect of reaction time on the oxidation of styrene. Reaction conditions: H₂O₂/styrene, 1; temperature, 80°C; solvent, acetonitrile. Yields are determined by GC using dodecane as an internal standard.

TABLE 3: Effect of styrene, H₂O₂ molar ratio, temperature, and solvent.

Entry	H ₂ O ₂ /Styrene	Solvent	Temperature (°C)	Styrene conversion	Yield ^a (% mol)	
					Benzaldehyde	Acetophenone
1	1.1	Acetonitrile	80	61	57	3
2	1.5	Acetonitrile	80	66	62	3
3	2	Acetonitrile	80	70	67	3
4	2.5	Acetonitrile	80	81	72	3.5
5	3	Acetonitrile	80	95	73	5
6	2.5	Acetonitrile	40	10	10	0
7	2.5	Acetonitrile	70	50	50	0
8	2.5	Acetonitrile	100	94	60	4
9	2.5	Acetonitrile	120	98	50	9
10	2.5	Acetone	80	90	77	12
11	2.5	Water	80	12	12	0
12	2.5	Methanol	80	75	59	6
13	2.5	Ethanol	80	50	31	7

Reaction conditions: C4 catalyst (0.02 g); reaction time, 24 h; ^ayields determined by GC using dodecane as an internal standard.

3.2.5. *Effect of Reaction Temperature.* Table 3 depicts the influence of reaction temperature on the oxidation of styrene catalyzed by the C4 catalyst. The increase of the temperature from 40°C to 120°C results in the increased conversion from 10 to 98, indicating that the styrene conversion has a strong dependency on the reaction temperature. Hence, at high

temperature, the benzaldehyde selectivity decreases in competition with the formation of acetophenone and other products. This confirms that the cleavage of C=C bond is greater at lower temperatures and epoxidation participates more favorably against C=C cleavage to high temperatures [20, 21].

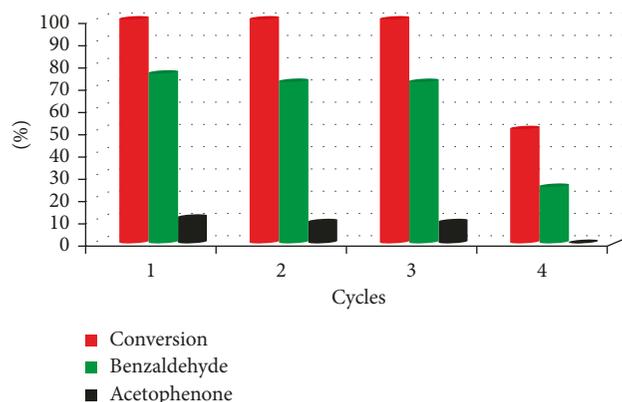


FIGURE 5: Reusability of the catalyst in oxidation of styrene. Reaction conditions: C4 catalyst (0.02 g); H_2O_2 /styrene, 2.5, temperature, $80^\circ C$; solvent, acetone; reaction time, 24 h. Yields are determined by GC using dodecane as an internal standard.

3.2.6. *Effect of the Solvent.* An examination of the effects of a variety of protic and aprotic solvents on the model reaction using C4 as the catalyst has been carried out (Table 3).

According to Kumar [22], aprotic solvents are more favorable for the styrene oxidation than protic ones. The selectivity towards benzaldehyde with respect to percentage yield is in the following order: $CH_3CN > CH_3COCH_3 > CH_3OH > C_2H_5OH > H_2O$. The styrene conversion in acetone, methanol, ethanol, and water is, respectively, equal to 90% mol, 75% mol, 50% mol, and 12% mol, with 77% mol, 59% mol, 31% mol, and 12% mol yield of benzaldehyde, respectively. Among the solvents, acetonitrile appears to be the best one (entry 4).

3.2.7. *Recycling of Catalyst.* To investigate the reusability of C4, the catalytic activity of this catalyst was evaluated in four consecutive cycles (Figure 5). Before reusing the catalyst, it was separated from the reaction mixture by filtration, washed with water, and finally dried at $200^\circ C$ for 2 hours. As shown in Figure 5, the catalyst still exhibits a good catalytic activity in the first three reuse cycles. However, a noticeable drop in styrene conversion was observed after the fourth consecutive run due to agglomerated particles.

SEM image of C4 before and after four cycles of oxidation has been studied (Table 4). Before the catalytic test, SEM image of the Ag-Co codoped ZnO shows relatively dispersed nanoparticles (Figure 3(b)). However, SEM morphology of the catalyst after four cycles of oxidation showed agglomerated particles with the presence of smaller single particles (Figure 3(c)). Even by SEM, the physical change of the matrix is well visible due to probable decomposition during the reaction. In fact, EDX on various regions of the catalyst after 4 cycles confirmed the presence of Co and Ag elements without any significant variation. The analysis indicates a predominance of oxygen species, which comes mainly from the oxidation of Co and Ag species, leading to the deactivation of the catalyst.

4. Conclusion

In this study, the C4 catalyst was prepared by a sol-gel method, and its catalytic activity was investigated in the

TABLE 4: EDX analysis of C4 before using and at the 1st, 2nd, 3rd, and 4th cycles.

Elements	Wt.%	Atomic %	
As-prepared catalyst	OK	14.73	41.58
	AgL	1.88	0.76
	CoK	0.42	0.32
	ZnK	82.96	57.31
1st cycle	OK	18.05	47.58
	AgL	1.97	0.76
	CoK	0.45	0.32
	ZnK	79.54	51.31
2nd cycle	OK	20.80	52.01
	AgL	2.08	0.77
	CoK	0.44	0.30
	ZnK	76.68	46.92
3rd cycle	OK	25.54	58.63
	AgL	2.26	0.77
	CoK	0.43	0.27
	ZnK	71.77	40.32
4th cycle	OK	31.36	65.43
	AgL	2.49	0.77
	CoK	0.36	0.20
	ZnK	65.73	33.59

oxidation of styrene. Among all the catalysts examined, the C4 catalyst exhibited the best activity and provided 76% yield of benzaldehyde in the presence of H_2O_2 as an oxidant after 24 hours. The optimum reaction conditions was acetonitrile, temperature reaction $80^\circ C$, H_2O_2 /styrene molar ratio equal to 2.5, catalyst loading of 1% mol Ag-1% mol Co, and the catalyst amount of 0.02 g. Under the optimized conditions, the Co-Ag codoped ZnO shows a high degree of efficiency and selectivity towards the oxidation reactions.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Supplementary Materials

General scheme, SEM images, EDX, FT-IR spectra, and other analytical data are available free of charge via the

Internet in the Electronic Supporting Information (ESI). Supplementary data 1: catalytic oxidation of styrene. Supplementary data 2: TG and DTG curves of C4. Supplementary data 3: N₂ adsorption-desorption isotherm and BJH pore diameter distribution of C4. Supplementary data 4: FT-IR spectrum of C4. Supplementary data 5: SEM images and EDX spectra of (a) C1, (b) C2, (c) C3, (d) C4, (e) C5, (f) C6, (g) 1st cycle, (h) 2nd cycle, (i) 3th cycle, and (j) 4th cycle of the reused catalyst. (*Supplementary Materials*)

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