

Article



Selective Oxidation of Alcohols and Alkenes with Molecular Oxygen Catalyzed by Highly Dispersed Cobalt (II) Decorated 12-Tungstosilicic Acid-Modified Zirconia

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Abstract: Traditional procedures for oxidation processes suffer from a lack of selectivity, the use of organic solvents, the toxicity of the reagents, and waste production. As a cleaner alternative, highly dispersed Co over 12-tungstosilicicacid modified zirconia was synthesized and used for the selective oxidation of benzyl alcohol and styrene with molecular oxygen to carbonyl compounds under environmentally benign solvent-free conditions. The supremacy of the present catalyst lies in achieving excellent selectivity (>90%) for products with a very high turnover number. The catalytic activity of the recycled catalysts was also explored under optimized conditions to confirm sustainability. Further, the viability of the catalyst was studied via oxidation of various alcohols and alkenes under optimized conditions as well as superiority by comparison with the reported catalysts.

Keywords: cobalt; 12-tungstosilicicacid; heterogeneous catalysis; oxidation; carbonyl compounds

1. Introduction

Keggin heteropolyacids (HPAs; $H_a[XM_{12}O_{40}]$; X = P, Si; M = W, Mo etc.) have been gaining importance due to their numerous advantages, including tunable acidic and redox properties of the HPAs, making them sustainable alternatives as catalysts for vital organic transformations [1,2]. Further, the replacement of protons in the secondary structure of HPAs with different cations facilitates the development of catalysts with modified physic-ochemical properties such as acidity, redox, solubility, porosity, and thermal stability for the desired applications [1,3]. In the last decade, various metal-exchange HPAs (M'_yH_a-y[XM₁₂O₄₀]; M' = Cs, Co, Zr, Al, Fe, Cr, Sn, Cu, Zn, Pd) have been developed for oxidation [4,5], esterification-transesterification [6–8], oxidative esterification [9], acetylation [10], Friedel–Crafts acylation [11], etherification [12], dehydration [13], and hydrogenation reaction [14]. The reported M'yHa-y[XM₁₂O₄₀] with altered properties often demonstrated better catalytic activities as compared with the parent HPAs.

Towards the same, our group has contributed significantly to "metal exchangedsupported HPA" catalytic systems, e.g., synthesis of Co- [15], Pd- [16–18], Ni- [19], and Fe-exchange HPAs [20] and their applications for oxidation, C–C coupling, oxidative esterification, and hydrogenation. The reports suggested that these materials possess additional advantages such as freedom to exchange/incorporate metal in the range of 0.1 to 10 wt% of supported HPAs depending on the requirement of the reaction and nature of supports, improved dispersion of exchanged metal, chemical stability (i.e., leaching resistance), and decrease in cluster size, subsequently resulting in better performance of the catalysts. Among the transition metals, cobalt-containing catalytic systems [21,22] have been proven as efficient substitutes of stoichiometric metal- based-oxidants [23] for oxidation reactions



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). with air or molecular oxygen as an oxidant. A literature survey shows that number of studies on Co-incorporated polymers [22], zeolites [24–26], MOFs [27,28], silica [29], and other supports [30,31], catalyzed oxidation of alkenes and alcohols are reported. To the best of our knowledge, only one research paper on Co-exchanged supported HPAs has been reported and that was from our group only [15]. Despite the superiority of Co as well as supported HPAs, no reports on Co-exchanged supported HPAs are available in the literature since 2010. Further, in oxidation chemistry, air or O_2 as an oxidant is considered one of the sustainable alternatives in the context of cost and environmental factors [32]. Thus, it would be of interest to develop highly dispersed Co over supported HPAs for oxidation of alcohols and alkenes with O_2 as an oxidant.

Thus, in the present study, synthesis of highly dispersed Co(II) on 12-tungstosilicic acid (TSA) modified zirconia (ZrO₂) was attempted. In order to derive thermal stability as well as the chemical and structural environment, various physico-chemical techniques were employed including thermo-gravimetric analysis (TGA), elemental analysis, Fourier Transform Infrared (FT-IR) spectroscopy, N₂-physisorption, and X-Ray Diffraction (XRD). Further, the presence of highly dispersed Co (along with other element) was also confirmed by TEM and elemental mapping. The catalytic activity was investigated for oxidation of benzyl alcohol and styrene as model reactions with O₂ as an oxidant and tert-Butyl hydroperoxide (TBHP) as an initiator under solvent-free conditions. The viability of heterogeneous Co/TSA-ZrO₂ was explored for different alcohols and alkene substrates under optimized conditions. Further, stability and recyclability studies were also carried out.

2. Results and Discussion

2.1. Characterization

The cobalt estimation analysis showed that the Co/TSA-ZrO₂ contains 1.29 wt% Co (and 1.38 wt% Co from TEM EDS), i.e., 12.9 mg/g of TSA-ZrO₂.

TSA-ZrO₂ exhibited (Figure 1) 11.5% weight loss up to 100 and 180 °C, respectively, due to the removal of adsorbed water as well as the water of crystallization. Similarly, Co/TSA-ZrO₂ (Figure 1) showed weight loss of 18% up to 180 °C for loss of water molecules. The additional weight loss of about 7% may be due to the loss of acetate ions. Both the materials showed minor weight loss (4%) in the region 200–500 °C indicating the synthesized materials are stable up to 500 °C.



Figure 1. TGA of TSA-ZrO₂ and Co/TSA-ZrO₂.

The FT-IR of TSA, TSA-ZrO₂, and Co/TSA-ZrO₂ are represented in Figure 2. All the synthesized materials showed a band in the region 3390–3370 cm⁻¹ for O–H stretching, and at around 1617 cm⁻¹ for H–O–H bending mode vibrations. TSA evinced major characteristic bands at 1017 cm⁻¹ v_{as} (Si-O_a), 976 cm⁻¹ v_{as} (W = O_b), 907 cm⁻¹ v_{as} (W–O_c–

W) and 742 cm⁻¹ v_{as} (W–O_d–W). The TSA-loaded ZrO₂. i.e., TSA/ZrO₂ showed identical peak values to TSA, suggesting the presence of unfragmented TSA on the surface of ZrO₂. A weak band at 592 cm⁻¹ was assigned to the Zr–O–H bending vibration. Similar to the counter components, Co/TSA–ZrO₂ also exhibited all the characteristic bands of TSA–ZrO₂. Besides, the new bands appearing at 1552, 1416 cm⁻¹ as well as 511 cm⁻¹ may correspond to the presence of acetate ion and Co–O vibration, respectively [33].



Figure 2. FT-IR of TSA, TSA-ZrO₂ and Co/TSA-ZrO₂.

Figure 3 represents the result of N₂-physisorption analysis of ZrO₂ and Co/TSA–ZrO₂. The nature of the N₂ adsorption–desorption isotherm curves for both the materials showed the Type II hysteresis, with a sharp uptake at p/p° - 0.4–0.9 related to unrestricted monolayer-multilayer adsorption in a wide range of meso-to-macropores [34]. The observed results were further confirmed by BJH pore size distribution (Figure 3 inset). The BET surface area value of Co/TSA-ZrO₂ (124 m²/g) was found lower as compared with ZrO₂ (170 m²/g). Additionally, a decrease in single-point adsorption pore volume for Co/TSA-ZrO₂ (0.046 cm³/g) as compared with ZrO₂ (0.071 cm³/g) suggested the incorporation of Co as well as TSA to ZrO₂. n-Butyl amine acidity values indicate that, as expected, acidity of TSA–ZrO₂ (1.13 mmole/g) was higher as compared with ZrO₂ (0.89 mmole/g), acidic. At the same time, Co/TSA–ZrO₂ (0.96 mmole/g) showed lower acidity as compared with TSA–ZrO₂, and this may be due to the exchange of available surface protons with Co(II).



Figure 3. Nitrogen physisorption analysis of ZrO₂ and Co/TSA-ZrO₂.

TEM images (Figure 4) of Co/TSA-ZrO₂ confirmed the presence of Co, W, Zr, Si, and O in the synthesized catalyst. Further, mapping of W and Co showed absences of any agglomeration of W (even at 30% loading of TSA) and Co, indicating higher dispersion of metal centres throughout the matrix. The Co/TSA-ZrO₂ showed overall bulk morphology similar to typical ZrO₂ [35].



Figure 4. TEM and Elemental mapping of Co/TSA–ZrO₂.

2.2. Catalytic Activity

2.2.1. Oxidation of Alcohol

To optimize reaction conditions, oxidation of benzyl alcohol and styrene were selected as model reactions. Further to confirm the conversion of substrates is solely due to the activity of the Co/TSA–ZrO₂, all the reactions were carried out under catalyst-free conditions. The absence of major oxidation products of (1) benzyl alcohol, i.e., benzaldehyde and benzoic acid as well as (2) styrene, i.e., styrene oxide, benzaldehyde, phenylacetaldehyde, and 1-phenylethane-1,2-diol, confirmed that no oxidation occurred under catalyst-free conditions.

Oxidation of Benzyl Alcohol

The effect of various parameters such as reaction temperature, catalyst dosing, reaction, and time was studied comprehensively to achieve optimum activity $Co/TSA-ZrO_2$ with maximum selectivity of benzaldehyde.

Effect of temperature

The reaction temperature considerably affects the rate of the reaction and subsequently activity of the catalytic systems. Thus, the reaction progress was studied at 60, 70, 80, and 90 °C at constant catalyst amount (100 mg) and time (24 h). The data (Figure 5) showed that a significant increase in conversion of benzyl alcohol was achieved with an increase in reaction temperature and reached optimum at 90 °C. On other hand, an increase in temperature disfavored the selectivity of the benzyl alcohol. The decrease in selectivity of benzaldehyde from >99% to 90% is due to further oxidation to benzoic acid. It is also expected that the temperature higher than 90 °C would further reduce the selectivity of the carbonyl product. Thus, the temperature was fixed at 90 °C for further optimization.



Figure 5. Effect of temperature; Conversion is based on benzyl alcohol; benzyl alcohol (100 mmol); TBHP (0.15 mmol); amount of catalyst (100 mg); O₂ balloon 1 atm; TBHP (0.15 mmol); time (24 h); BzCHO—Benzaldehyde; BzCOOH—Benzoic acid.

Effect of catalyst amount

The effect of the amount of Co/TSA–ZrO₂ on the activity and selectivity was studied by carrying out the reaction at 90 °C, with 20, 40, 60, 80, and 100 mg of catalyst. From the results (Figure 6) it can be observed that with an increase in Co/TSA–ZrO₂ amount from 20 mg (0.258 mg Co; 4.6 mg TSA) to 100 mg (1.29 mg Co; 23 mg TSA), conversion increased from 29% to 41%. In other words, the higher TSA concentration has no substantial effect on the conversion of benzyl alcohol and the progression of the present catalytic reaction mainly depended on the Co content. However, the combined effect of Co and TSA cannot be ruled out and the role of TSA is explained in the control experiment. Further, catalysts particles at higher amount showed agglomeration under neat reaction conditions, resulting in blocking of active sites and insignificant increase in conversion was observed. Another reason for a relatively minor increase in activity may be due to mass transport limitations above 40% conversion. Thus, 100 mg Co/TSA–ZrO₂ with 41% conversion of benzyl alcohol and 90% selectivity of benzaldehyde was optimized for further studies.



Figure 6. Effect of catalyst amount; conversion is based on benzyl alcohol; benzyl alcohol (100 mmol); TBHP (0.15 mmol); temperature (90 °C); O₂ balloon 1 atm; time (24 h); BzCHO—Benzaldehyde; BzCOOH—Benzoic acid.

Effect of reaction time

The progress of reaction at different time from 4 h to 24 h with 4 h interval was monitored, and the effect on conversion and selectivity was investigated (Figure 7). From Figure 7 it can be observed that with the time (up to 20 h) conversion of alcohol increased

significantly with a slight decrease in selectivity in the later stage (after 16 h). The minor increase in conversion was observed at 24 h, suggesting the catalytic system reached near the equilibrium. Further, the reaction time promoted over-oxidation of benzaldehyde to benzoic acid was also observed. Thus, the optimized condition for benzyl alcohol conversion (>41%) with >90% selectivity of benzaldehyde is: 100 mg Co/TSA–ZrO₂, time: 24 h, and temperature: 90 °C.





Scope and Limitations for Oxidation of Various Alcohols

To explore the viability of the present catalyst Co/TSA–ZrO₂, a reaction was carried out for various alcohols under the optimized conditions (Figure 8). From Figure 8, it is observed that in all the cases excellent selectivity (90%–99%) for desired carbonyl products was obtained. Further, it is clear that oxidation of benzylic alcohol was comparatively facile compared with secondary and aliphatic alcohols. Despite this, secondary alcohol showed significantly higher conversion than aliphatic alcohols. Almost all the substrates conversion showed good to excellent TON with the present catalytic system. The activation of long-chain aliphatic alcohols over Co/TSA-ZrO₂ is still a challenging objective and requires efforts in studies related to experimental designs, chemometrics, etc.



Figure 8. Scope and limitations with turn over number (TON, in parentheses TOF h^{-1}); conversion is based on substrate; substrate (100 mmol); TBHP (0.15 mmol); temperature (90 °C); O₂ balloon 1 atm; amount of catalyst (100 mg); time (24 h).

2.2.2. Oxidation of Alkenes

Optimization was also performed for oxidation alkenes (styrene as a model substrate) by varying reaction parameters under solvent-free conditions using environmentally benign oxidant O_2 (Figure 9a–c), similar to oxidation of benzyl alcohol. The reported oxidation

of styrene reaction follows oxidative cleavage of C=C rather than epoxidation, and thus benzaldehyde was observed as a major product (>92%), and styrene oxide and benzoic acid minor products (<8%). In addition to this, similar trends were observed for effect of time, amount of catalysts, and temperature. However, the oxidation of styrene was found quite susceptible to temperature over 80 °C and time beyond 4 h. for both the cases decrease in the selectivity of carbonyl product was found due to the formation of unidentified sticky side-products. Thus, the optimized condition for styrene conversion (>48%) with >92% selectivity of benzaldehyde is as follows: styrene (100 mmole); Catalyst amount (150 mg); reaction time (4 h); temperature (80 °C).



Figure 9. (**a**–**c**) Optimization of reaction conditions for styrene oxidation. (**d**) Scope and limitations with turn over number (TON, in parenthesis TOF h^{-1}); conversion is based on substrate; substrate (100 mmol); TBHP (0.15 mmol); temperature (80 °C); O₂ balloon 1 atm; amount of catalyst (150 mg); time (4 h) BzCHO—Benzaldehyde.

Depending on the reaction conditions, the alkenes typically oxidized to their epoxides either as a product or an intermediate product. However, in the present cases (Figure 9d), styrene derivatives transformed to stable product carbonyl compounds with excellent selectivity and high TON and TOF were observed as major products via (i) direct oxidative cleavage of C=C and/or (ii) conversion of epoxides to carbonyl compounds. It is well known that the catalytic transformation involved TBHP and metal based active centers prefer to follow an oxidative cleavage route over epoxidation [36]. further, the obtained results are in good agreement with the reported oxidation reactions under similar reaction conditions [37]. However, in the case of cyclohexene, very low conversion (<6%) with epoxidation product was observed. This could be attributed to the stability of the cyclic structure as well as lower reactivity of Co/TSA–ZrO₂ towards cyclic olefins. Thus, the reported catalytic system is not pertinent to the oxidation of cyclic olefins.

2.2.3. Control Experiment

Under the optimized reaction conditions, ZrO_2 was found inactive for both the oxidation processes. Besides, TSA–ZrO₂ showed very lowered activity for oxidation of benzyl alcohol as well as styrene (up to 8%) as compared with Co/TSA–ZrO₂ (>40%) (Table 1). Cobalt acetate was also found active for oxidation of both the substrate. However, unsupported Co-acetate exhibited significantly less conversion and selectivity. Further, with reaction progress, Cobalt acetate particles agglomerated to form a sticky mass at the wall of the reaction vessel. As a result, decrease in activity was seen. On the other hand, highly dispersed Co on TSA modified ZrO_2 , i.e., Co/TSA–ZrO₂, was found excellent in terms of activity and selectivity under present reaction conditions. The results also indicated that Co has major contribution in the catalytic transformation to carbonyl products.

Sr.	Catalysts	% % Selectivity		tivity	TON
		Conversion	Benzaldehyde	Other	
1.	ZrO ₂	-/-	-	-	-
2.	TSA-ZrO ₂	8 ^a /7 ^b	>99 ^a />99 ^b	-	-
3	Co-acetate ^c	24 ^a /34 ^b	>86 ^a />84 ^b	14 ^a /16 ^b	-
4.	Co/TSA-ZrO ₂	41 ^a /48 ^b	90 ^a /92 ^b	10 ^a /8 ^b	1872 ^a /1461 ^b
5.	Co/TSA-ZrO ₂ d	<2 ^a /3 ^b	>99 ^a />99 ^b	-	-
6.	Without catalyst ^e	-/-	-	-	-

Table 1. Control experiments and effect of HPAs.

Conversion is based on substrate; substrate: benzyl alcohol ^a; styrene ^b (100 mmol); TBHP (0.15 mmol); temperature (^a 90 °C/^b 80 °C); O₂ balloon 1 atm; amount of Co/TSA-ZrO₂ (^a 100 mg (1.29 mg Co)/^b 150 mg (1.93 mg Co); ^c amount of Co-acetate (^a 5.46 mg/^b 8.16 mg); time (^a 24 h/^b 4 h); ^d Without O₂; ^e Without O₂ and catalyst.

In order to examine role of TBHP, reactions without O_2 as well as without (O_2 + catalyst) were also carried out (Table 1; Entry 5,6). In both the cases, no significant conversion of substrates was observed, indicating that O_2 acts as the sole oxidant and TBHP as an initiator, which is in good agreement with the reported POMs-catalyzed aerobic oxidation reactions [38]. The reactions with different solvents were also carried out and results are presented in Table S1. From the data, it is clear that water as a solvent was found incongruous and showed drastic reduction in activity of the catalyst. At the same time, the use of organic solvents such as hexane and toluene showed similar activity with better selectivity of benzaldehyde as compared with solvent-free conditions. Despite this fact, solvent-free conditions seem a more environmentally benign alternative to avoid the use of organic solvent, product separation, and solvent recovery.

2.3. Heterogeneity Test

Co/TSA–ZrO₂ was subjected to a leaching test, and it showed negative results, i.e., no leaching of Co was found or it was <1 ppm. These remarks indicated that the Co/TSA–ZrO₂ is truly heterogeneous in nature. Heterogeneity test was carried out, in which the catalyst was filtered from the reaction mass at the desired time and the filtrate was allowed to react up to the completion of the reaction. The reaction mass before and after completion of the reaction was analyzed by gas chromatography and the result is presented in Figure 10. From the data, it is concluded that after filtration of catalysts, no evidence in the progress of the reaction in terms of conversion was found, suggesting that no leaching of active metals occurred in the reaction mass and Co/TSA–ZrO₂ is truly heterogeneous.



Figure 10. Heterogeneity test for oxidation of (**a**) benzyl alcohol and (**b**) styrene Conversion is based on the substrate (benzyl alcohol/styrene); TBHP (0.15 mmol); temperature (90 °C/80 °C); O₂ balloon 1 atm; amount of Co/TSA-ZrO₂ (100 mg/150 mg).

At desired time, the reaction mass was extracted and the catalyst was recovered by centrifugation. The catalyst was washed with a small portion of CH₂Cl₂ and dried at 100 °C. The oxidation reaction under optimized conditions was carried out with a recycled catalyst and the results are represented in Figure 11.





The results showed that no substantial variation in conversion and selectivity was detected for up to five cycles. The comparative FT-IR spectra of the fresh and the regenerated catalysts are represented in Figure 12. The recycled catalyst (after the fifth cycle) showed all the bands with no significant shifting in the wavenumber similar to fresh Co/TSA-ZrO₂ indicating no alalteration in chemical composition of the catalyst, i.e., the catalyst was stable and reusable even after five cycles.



Figure 12. FT-IR of Co/TSA–ZrO₂ and Co/TSA–ZrO₂-R.

2.5. Comparison with Reported Catalyst

Comparative catalytic data of the present catalyst for oxidation of benzyl alcohol and styrene using O₂ or air as an oxidant with the cobalt-based reported catalytic systems are summarized in Table 2. From the data, it is clear that all the efficient catalytic systems (Entry 1–4, 6) showed excellent conversion and selectivity of benzaldehyde. However, higher loading of Co-contents as well as a lower concentration of substrate resulted in poor TON. Despite this, the oxidation was carried out in various organic solvents. The reported

Co/TPA–ZrO₂ showed good-to-excellent conversion and selectivity with 623 TON, confirming the superiority of Co-HPAs based catalysts. Further, on comparing the present catalytic system with (12.9 gm Co/gm of catalyst) with Co/TPA–ZrO₂ (72 mg/gm of catalyst; Entry 5) [15], it was observed that lower loading of Co resulted in better dispersion of metal centers and subsequently provided the higher activity. Thus, the careful evaluation of the result revealed that the presence of HPA not only provides positive synergies but also assisted in higher dispersion of Co, eventually giving rise to higher activity of Co/TSA–ZrO₂.

Sr.	Catalysts	Conditions *	% Conversion	% Benzalde- hyde	TON	Remarks	Refs.				
Benzyl alcohol oxidation											
1	Co(II) salen complex@KCC—1	1:60:0.5:60	-	95 **	1.8	Isobutyraldehyde as co—substrate, HOAc—solvent	[29]				
2	Co ₃ O ₄ /Activated carbon	0.2:100:3:80	100	-	-	Very high catalyst:substrate	[39]				
3	CoAl-ELDH/GO	1:100:4:120	92.2	99.3	5	DMF—solvent	[40]				
4	Co ₃ O ₄ /MnO ₂	1:25:12:100	93	99	16	Air, 1,4—Dioxane- solvent	[41]				
5	Co/TSA–ZrO ₂	100:100:24:90	41	90	1872	TBHP—additive, solvent-free	Present work				
Styrene oxidation											
6	NaCoX96	10:200:4:100	100	67	16	DMF-solvent	[25]				
7	Co/TPA—ZrO ₂	100:100:4:80	76	>99	623	TBHP—additive, solvent-free	[15]				
8	Co/TSA—ZrO ₂	100:150:4:80	48	92	1461	TBHP—additive, solvent—free	Present work				

Table 2. Comparison of catalytic activity for aerobic oxidation of styrene with reported catalyst.

* Substrate (mmole): amount of catalyst (mg): t (h): Temperature (°C); ** Yield; Conversion is based on substrate; TBHP (0.15 mmol); O_2 balloon 1 atm.

3. Materials and Methods

3.1. Materials

All chemicals used were of A.R. grade. $Co(CH_3COO)_2 \cdot 4H_2O$, Benzyl alcohol, cyclopentanol, 1-Hexanol, 1-Octanol, Styrene, α -Methylstyrene, Cyclohaxene, 30% H_2O_2 , Trichloroacetic acid (TCA), and Dichloromethane were obtained from Merck (Mumbai, India) and used as received. ZrOCl₂.8H₂O and H₄[SiW₁₂O₄₀].xH₂O were obtained from Loba Chemie(Mumbai, India) and used as received. ZrO₂ and 30% TSA–ZrO₂ were synthesized using the reported literature [42].

3.2. Synthesis of Co(II) Supported TSA-ZrO₂ (Co/TSA-ZrO₂)

Synthesis of Co/TSA-ZrO₂ was carried out using previously reported procedure with minor modifications [15]. Briefly, TSA–ZrO₂ (1 g) was suspended in 0.5% aqueous solution of Co(CH₃COO)₂·4H₂O (25 mL) under the static condition at room temperature. Co⁺² from the aqueous solution was allowed to soak on TSA–ZrO₂ for 30 h without stirring. After 30 h, the powder was collected by simple filtration followed by washing to remove excess of cobalt. The obtained product was dried for 1 h at 100 °C. The resulting light pink powder was designated as Co/TSA–ZrO₂.

3.3. Analytical Techniques

Cobalt was estimated in the filtrate by UV–vis spectroscopy on Shimadzu, Uv-1900i (Kyoto, Japan). TGA of the samples was carried out on a Mettler Toledo Star SW 7.01 (Columbus, OH, USA) from 50 to 600 °C temperature with a ramp rate of 10 °C min⁻¹ under a nitrogen atmosphere (flow rate: 2 mL min⁻¹). N₂ adsorption–desorption isotherm of samples were recorded on a Micromeritics ASAP 2020 (Norcross, GA, USA) surface area

analyzer at -196 °C. The FTIR spectra of the samples were recorded on a Bruker (Alpha II) instrument (Karlsruhe, Germany) in the range of 4000–500 cm⁻¹. TEM analysis was carried out on FEI TEM instrument (model: Tecnai G2, F30, Eindhoven, Netherland) with an accelerating voltage of 300 kV. The samples were dispersed in ethanol and ultrasonicated for 5–10 min. A small drop of the sample was then taken in a carbon-coated copper grid and dried before viewing. The total acidity for all the materials has been determined by n-butylamine titration [43]. A solution of n-butylamine in toluene (0.025 M) was used for estimation, where 0.5 g material was suspended in the prepared solution for 24 h and excess of n-butylamine was titrated against TCA using neutral red as an indicator.

3.4. Oxidation Reactions

In three neck-round bottom flask charged with the magnetic needle bar, substrate (100 mmol), required amount of catalyst and TBHP (0.15 mmol) were charged at the desired temperature (80 °C for alkenes and 90 °C for alcohols). The reaction was initiated by the bubbling of O_2 from a balloon connected through the bend-glass tube. The process was optimized by varying the concentration of the catalyst, reaction time, and temperature. After the desired reaction time, the products were extracted with CH₂Cl₂, dried over MgSO₄ and analyzed on a gas chromatograph (Shimadzu 2014, Kyoto, Japan) with RTX-5 capillary column and flame ionization detector. Product identification was carried out by comparison with authentic samples. The conversion, selectivity, turn over number (TON) and turn over frequency (TOF) were calculated as per the equations below [44].

Conversion (%) = [(Initial mol%) – (Final mol%)]/(Initial mol%)

Selectivity (%) = [(moles of product formed)/(moles of substrate consumed)] \times 100

TON = moles of product/moles of catalyst

TOF = TON/unit time

4. Conclusions

In conclusion, Co- supported on TSA-modified ZrO₂ was synthesized via a soaking method using a diluted precursor solution. The characterization data, especially TEM mapping, confirmed the high-dispersion of Co in the synthesized Co/TSA–ZrO₂. The present catalytic system was found as competent in obtaining excellent selectivity and TON for the desired carbonyl products via (i) oxidation of alcohols and (2) oxidative cleavage of C=C of alkenes with environmentally benign oxidant. Despite limitations for cyclic olefins and long-chain alcohol, the Co/TSA–ZrO₂ was found viable for the oxidation various of alcohols and styrenes. The catalytic data showed that highly dispersed cobalt and the presence of HPA resulted in a positive synergistic effect. Further, comparing different classes of Co-based catalysts revealed that the present synergistic catalyst was found superior and able to offer exceptional TON/TOF with a very small amount (100–150 mg Co/TSA–ZrO₂; 1.2–1.9 mg of Co) under solvent-free sustainable reaction conditions. Moreover, simple work-up for reuse as well as recycling up to five cycles without substantial loss in conversion and selectivity makes the process captivating from the perspective of sustainability.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/catal12121622/s1. Table S1: Effect of Solvent on oxidation of benzyl alcohol over Co/TSA-ZrO₂.

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