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As a cleaner alternative to traditional two steps procedures, one pot oxidative esterification of benzaldehyde to methyl ester was carried out over supported Cs salt of mono nickel substituted phosphotungstates ($CsPW_{11}Ni$). $CsPW_{11}Ni$ was supported on to ZrO_2 and characterized by various physico-chemical techniques. The influence of reaction parameters such as molar ratio of substrate to H_2O_2 , amount of the catalyst, reaction time, and reaction temperature on oxidative esterification reaction was investigated. Moreover, the catalyst could be recovered and reused upto three cycles without a significant loss in their selectivity. The present heterogeneous catalytic system was found efficient not only in terms of activity (63%) but also in selectivity (79%) of the desire product.

Introduction

Esters are valuable chemical products those have widespread applications such as in fragrance industry, flavoring agents, solvent extract-ants, diluents and intermediates. Traditionally two steps synthesis of ester from aldehydes generally suffer from generation of vast amount wastes, by-products and use of toxic reagents.¹ From the viewpoint of demands as well as significance of acid and oxidation reactions, it would be more beneficial to develop bifunctional catalytic systems for single step oxidative esterification reactions. Till, considerable efforts have been devoted to develop process for direct synthesis of esters from the oxidative esterification of aldehydes with alcohols using different catalysts based on Gold-Nickel Oxide (AuNiOx),² TS-1,³ gold nanoparticle Au/TiO2,⁴ Pb and Mg doping in Al_2O_3 -supported Pd,⁵ ionic liquid BmimBF₄, manganese phthalocyanine immobilized on silica gel.⁷ In the same context, polyoxometalates (POMs) based materials have been well explored for the said reaction.⁸⁻¹⁰ Recently, a subgroup of POMs. transition metal substituted polyoxometalates (TMSPOMs), are gaining remarkable attention in field of catalysis.¹¹⁻¹⁴ Among the various TMSPOMs ($[XW_{11}M(L)O_{39}]^{5-}$; X = P, Si; M = transition metal), the nickel-substituted POMs are of considerable interest because of their redox properties and variable oxidation states, which makes them important for various catalytic processes. 15-17

In 2004, Y. Yang and group prepared TiO_2 -APS-PW₁₁M (M = Ni/Co) and explored its catalytic performance for organochlorine pesticide and dyes.¹⁸ Preparation and detailed characterization of Na₅[PW₁₁O₃₉M], (M= Ni²⁺, Co²⁺, Cu²⁺, or

Zn²⁺) supported onto carbon was carried out by Pizzio and coworkers in 2007.¹⁹ The catalytic activity of the synthesized materials was also evaluated for isopropyl alcohol dehydration by them. Synthesis and photocatalytic activity of aminefunctionalized mesoporous silica/anatase titania impregnated with TMSPOMs $([M(H_2O)PW_{11}O_{39}]^{5-}-APS-TiO_2, M=Co/Ni)$ was reported by Guo et al. in 2007.²⁰ Hu and co-workers in 2009, carried out study of $K_{10-n}X^{n+}MW_{11}O_{39}$ -Schiff-SBA-15, (X = P/Si, M = Co/Ni/Cu/Mn) and its catalytic behaviour was evaluated for oxidation of styrene to benzaldehyde.²¹ In 2012, Li et al. prepared MCM-41 incorporated (PW₁₁O₃₉M1)⁵⁻(M1–POM, M1 = Ni^{2+} , Co^{2+} or Cu^{2+}) and its catalytic performance in esterification was investigated.²² Recently, R. A. Frenzel et al. reported use of transition metal-modified polyoxometalates $[PW_{11}O_{39}M(H_2O)]^{5-}$, where M= Ni²⁺, Co²⁺, Cu²⁺ or Zn²⁺ supported on carbon as a catalyst in 2-(methylthio)benzothiazole sulfoxidation.²³ Thus, the literature survey shows that there are no reports on oxidative esterification of aldehyde, an important industrial organic transformation, using supported Ni substituted phosphotungstate.

Recently we have reported one pot oxidative esterification over Cs salt of mono nickel substituted phosphotungstate (CsPW₁₁Ni), although the catalyst was homogeneous it could be recycled upto two cycles without any degradation and modification of the structure, so as an extension of that work we explored heterogeneous behavior of the catalyst by supporting it onto zirconia. As we mentioned in our report,²⁴ we have been working for the same since last six months and succeeded to develop heterogeneous catalyst comprising CsPW₁₁Ni and hydrous Zirconia.

Thus, in the present paper, we report synthesis of Cs salt of mono nickel substituted phosphotungstate supported onto Zirconia, its characterization as well as catalytic activity for oxidative esterification of benzaldehyde to methyl benzoate was evaluated. Different reaction parameters including %

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loading of catalyst, mole ratio, amount of catalyst, time, temperature, and quantity of methanol were optimized for better result. The catalyst was recycled and regenerated upto three cycles.

Experimental

Materials

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All chemicals used were of A. R. grade. $ZrOCl_2.8H_2O$ (Loba Chemie), 12-Tungstophosphoric acid ($H_3PW_{12}O_{40}$), NaOH, NiCl₂·6H₂O, CsCl, liq. NH₃, C₆H₅CHO, CH₃OH, 30% H₂O₂, CH₂Cl₂ were obtained from Merck and used as received.

Synthesis of the support, ZrO₂

Hydrous zirconia was synthesized by the same method reported by us earlier.²⁵ In the typical method, aqueous ammonia solution was added to an aqueous solution of $ZrOCl_2.8H_2O$ up to pH 8.5, aged at 100 °C over a water bath for 1 h, filtered, washed with conductivity water until chloride free water was obtained and dried at 100 °C for 10 h. The obtained material is designated as ZrO_2 .

Synthesis of Cs salt of mono nickel substituted phosphotungstate²⁴

 $H_3PW_{12}O_{40}$ (2.88 g, 1 mmol) was dissolved in water (10 mL) and pH of the solution was adjusted to 4.8 using NaOH solution. NiCl₂·6H₂O (0.237 g, 1 mmol) dissolved in a minimum amount of water was mixed with the above hot solution. The final pH was adjusted to 4.8 and heated at 80°Cwith stirring for 2 h and filtered hot to which a saturated solution of CsCl was added. The obtained light green crystals were filtered, air dried and designated as CsPW₁₁Ni.

Synthesis of Cs salt of mono nickel substituted phosphotungstate supported to zirconia

A series of catalysts containing 10–40% of CsPW₁₁Ni supported onto ZrO₂ was synthesized using impregnation method. ZrO₂ (1 g) was impregnated with an aqueous solution of CsPW₁₁Ni (0.1/10–0.4/40 g mL⁻¹ of double distilled water) and dried at 100 °C for 10 h. The resulting materials were designated as 10% PW₁₁Ni/ZrO₂, 20% PW₁₁Ni/ZrO₂, 30% PW₁₁Ni/ZrO₂, and 40% PW₁₁Ni/ZrO₂ respectively.

Characterization

The acidity of catalyst was determined from n-butyl amine and potentiometric test. Thermo gravimetric analysis (TGA) was done using Mettler Toledo Star SW 7.01 up to 600°C. Adsorption–desorption isotherms were done through Micromeritics ASAP 2010 Surface area analyzer at -196 °C. Specific surface area was calculated using Brunauer-Emmett-Teller (BET method). Fourier transform infrared (FT-IR) spectroscopy was done using KBr pellets on a Perkin Elmer instrument. The Fourier Transform Raman (FT-Raman) spectra were recorded on a FT-Raman Spectrophotometer (Model Bruker FRA 106). Powder X-ray Diffraction (Powder XRD) was carried out using Philips Diffractometer (Model PW-1830). Electron spin resonance (ESR) spectra were recorded on a Varian E-line Century series X-band ESR spectrometer at low temperature and scanned from 2000 to 3200 gauss.

Catalyst acidity

n-Butyl amine acidity by titration

A 0.025 M solution of n-butyl amine in toluene was prepared for assessment of total acidity of the catalyst.²⁶ The 0.25 g catalyst was suspended in 0.025 M n-butyl amine solution for 24 h and the excess base was titrated against trichloroacetic acid using neutral red as an indicator. This test gives the total acidity of the material.

Acid sites determination using potentiometric titration

The type of acid sites was investigated by employing potentiometric titration with 0.05 N n-butylamine which helps in computing different acid sites.²⁷ 0.5 g of catalyst sample was suspended in 50 mL acetonitrile and the mixture was aged at 25 °C. 0.05 N n-butylamine (0.5 mL) in acetonitrile solution was added in equal time periods and the potential (mV) was recorded.

Catalytic Evaluation

The reaction of benzaldehyde (0.01 mol) with H_2O_2 (0.03 mol) and methanol was carried out in a 100 mL batch reactor provided with a double walled air condenser, magnetic stirrer, and a guard tube. The reaction mixture was refluxed at 80 °C for 6 h. The product was extracted with dichloromethane. The obtained products were analyzed on a gas chromatograph (Shimadzu-2014) using a capillary column (RTX-5). Each analysis was carried out three times and the associated % conversion values were found in the range of ±1.5 % which was calculated using the following eqn (1) of standard deviation for error analysis.

$$\sigma_x = \sqrt{\frac{1}{N} \sum (x_i - \bar{x})^2} \tag{1}$$

Leaching Test

The leaching of active species from the support makes the catalyst unattractive and unproductive, thus it is necessary to examine the stability as well as leaching of $PW_{11}Ni$ from the support. Polyoxometalates are quantitatively characterized by the heteropoly blue color, which is visible when it reacts with a mild reducing agent such as ascorbic acid. In the present study, reported method was used for determining the leaching of $PW_{11}Ni$ from the support.²⁸ The obtained results were further confirmed by atomic absorption spectroscopy (AAS).

Result and discussion

Characterization of Catalyst

Leaching test shows absence of blue color indicates no leaching of $PW_{11}Ni$ from support into reaction medium. Further, AAS analysis did not show presence of any metal content of $PW_{11}Ni$ suggested that absence of leaching or if any

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metal was present, it was below the detection limit, which corresponded to less than 1 ppm.

The total acidity of catalysts, 10-40% PW₁₁Ni loaded ZrO₂ was evaluated by n-butyl amine titration method and the results are presented in Table 1. It can be seen from Table 1 that with increase in % loading, total acidity increases up to 30% loading. Further increase in % loading leads to decrease in the acidity. A decrease in the acidic value can be attributed to the blocking of acidic sites for higher % loading.

Table 1 n-Butyl amine acidity values

Catalyst	Acidic sites mmol. of
·	n- Butyl amine/g
ZrO ₂	0.62
10% PW ₁₁ Ni/ZrO ₂	0.68
20% PW ₁₁ Ni/ZrO ₂	0.72
30% PW ₁₁ Ni/ZrO ₂	0.80
40% PW ₁₁ Ni/ZrO ₂	0.75

The types and strength of the acidic sites were further obtained by potentiometric titration method. The strength of acidic sites in terms of initial electrode potential is shown in Table 2.

Table 2	Acidity	determined	by	potentiometric	titratior

Catalyst	Acidic	Types	Types of acidic sites		
	stength		(meq.g ⁻¹)		no. of
	E _i (mV)	Very	Strong	Weak	acidic
		strong			sites
ZrO ₂	53	0	0.5	0.8	1.3
PW ₁₁ Ni	50	0	0.7	1.7	2.4
30% PW ₁₁ /ZrO ₂	58	0	0.5	1.0	1.5
10% PW ₁₁ Ni/ZrO ₂	55	0	1.2	1.6	2.8
20% PW ₁₁ Ni/ZrO ₂	70	0	1.2	1.8	3.0
30% PW ₁₁ Ni/ZrO ₂	110	0.2	1.3	2.2	3.7
40% PW ₁₁ Ni/ZrO ₂	75	0	1.4	2.5	3.9

It is seen from the Table 2 that the incorporation of $PW_{11}Ni$ increases the strength of the acid sites of catalysts to a great extent. It is interesting to note that 30% $PW_{11}Ni/ZrO_2$ shows highest acidic strength. For 40% loaded catalyst the total number of acidic sites is higher, however, acidic strength decreases due to blocking of acidic sited at higher loading. Hence 30% $PW_{11}Ni/ZrO_2$ was selected for detailed characterization studies.



Fig. 1. TGA of 30% PW₁₁Ni/ZrO₂

The TGA of 30% $PW_{11}Ni/ZrO_2$ (Fig. 1) shows initial weight loss of 8.8 % upto 180 °C indicating the loss of adsorbed water molecule. Further, about 2.2 % weight loss upto 300 °C was observed due to the loss of water of crystallization. Besides this, no significant weight loss was observed upto 550 °C, suggests higher thermal stability of synthesized catalyst.

The BET surface area of 30% $PW_{11}Ni/ZrO_2$ was found to be 229 m²/g whereas of zirconia is 170 m²/g.²⁵ The surface area of 30% $PW_{11}Ni/ZrO_2$ was observed to be higher as compared to that of the support zirconia because of supporting of $PW_{11}Ni$ as expected. The pore size distribution curve (Fig. 2) exhibits average pore diameter of 30.9 Å (3.09 nm).



Fig. 2 Nitrogen adsorption–desorption isotherm and pore size distribution of 30% PW₁₁Ni/ZrO₂.

The FT-IR spectra of ZrO_2 (Table 3) shows broadband in the region of 3400, 1600 and 1370, and 600 cm⁻¹ attributed to O-H asymmetric stretches, H–O–H and O–H–O bending, and Zr-O-H bending respectively.²⁵ FT-IR data of CsPW₁₁Ni (Table 3) exhibits bands at 1062; 961; and 885, 810 cm⁻¹ corresponding to P-O, W=O, and W-O-W asymmetric stretching frequencies respectively, also a band at 490cm⁻¹ is observed which is attributed to Ni-O vibration, indicating the inclusion of metal ion into the Keggin framework. In case of CsPW₁₁Ni the splitting value (Δu) for P–O is 0cm⁻¹ which is in good agreement with the literature.²⁹

|--|

Catalyst	Frequencies (cm ⁻¹)						
	O-H	H–O–H	Zr–O–H	P-O	W=O	W-0-	Ni-O
		0-H-0				W	
ZrO ₂	3400	1600	600	-	-	-	-
		1370					
CsPW ₁₁ Ni	3447	1624	-	1062	961	885,	490
						810	
30%	3255	1624	682	1064	938	852	453
PW ₁₁ Ni/ZrO ₂		1375					

FT-IR data of 30% $PW_{11}Ni/ZrO_2$ shows similar bands as CsPW₁₁Ni at 1064; 938; 852 453; cm⁻¹ indicating P-O; W=O; W-O-W and Ni-O respectively (Fig. 4). In addition, peaks at 3255; 1624 and 1375; and 682 cm⁻¹ attributed to O-H stretches, H–

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O–H and O–H–O bending, and Zr-OH bending respectively. The shift in the band positions of supported catalyst as compared to $CsPW_{11}Ni$ is observed due to the interaction of terminal oxygen of $CsPW_{11}Ni$ with hydrogen from surface -OH of zirconia. The Thus, it can be seen that the characteristic bands of active species in supported catalyst are retained even after the heterogenization.

CsPW₁₁Ni due to the substitution of metal ion into the lacuna. The diffraction peaks corresponding to crystalline phase CsPW₁₁Ni are absent in XRD pattern of 30% PW₁₁Ni/ZrO₂ confirming the well dispersion of PW₁₁Ni onto the support.



Fig. 3 Raman Spectra of (a) ZrO₂, (b) CsPW₁₁Ni and (c) 30% PW₁₁Ni/ZrO₂

Raman spectra of ZrO₂ (Fig. 3) shows broad peaks in the region from 100 to 800 cm⁻¹, which are associated with long-range disordering arrangement in amorphous state.³⁰ Raman spectra of CsPW₁₁Ni (Fig. 3) shows bands at 993, 976, 895, 506, and 225 cm⁻¹, corresponding to υ_s (W=O_d), υ_{as} (W-O_d), υ_{as} (W-O_b-W), υ_s (W-O_c-W), and υ_s (W-O_a) respectively. An additional band in the range of 400-500 cm⁻¹ is attributed to Ni-O stretching confirming the presence of nickel in the CsPW₁₁Ni. The spectrum of 30% PW₁₁Ni/ZrO₂ displays bands at 992, 975, 942, 522, 213 corresponding to υ_s (W=O_d), υ_{as} (W-O_d), υ_{as} (W-O_b-W), υ_s (W-O_c-W), and υ_s (W-O_a) respectively. The presence of all the bands of PW₁₁Ni in 30% PW₁₁Ni/ZrO₂ confirms that structure of CsPW₁₁Ni remains intact even after supporting on to ZrO₂. Observed significant shift in the bands is due to the interaction of CsPW₁₁Ni with surface hydroxyl groups of ZrO₂.

The Powder XRD of $PW_{11}Ni$ is shown in Fig. 4. The peaks ranging from 15° to 30° 2Theta value indicating the presence of characteristic peaks of parent Keggin ion are shifted in case of



Fig. 4 Powder XRD of a) CsPW₁₁Ni b) ZrO₂ and c) 30% PW₁₁Ni/ZrO₂.

The full range (3200–2000 G) X-band liquid nitrogen temperature ESR spectra for CsPW₁₁Ni (Fig. 5a) and 30% PW₁₁Ni/ZrO₂ (Fig. 5b) was recorded. The obtained g value for CsPW₁₁Ni (g ~ 2.07) is in good agreement with reported one,³¹ indicates the presence of Ni(II) in octahedral or distorted octahedral environment. Similarly, ESR spectra of 30% PW₁₁Ni/ZrO₂ shows signal at g ~ 2.0 confirm undegraded CsPMo₁₁Ni on the surface of ZrO₂. In other words, the Keggin structure remains unaltered after supporting it on ZrO₂.



Fig. 5 ESR Spectra of a) CsPW₁₁Ni b) 30% PW₁₁Ni/ZrO₂

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Catalytic Activity Catalyst $MeOH, H_2O_2$ Benzaldehyde Methyl Benzoate Methyl BenzoateMenzoic acid

Scheme 1 Oxidative Esterification of Benzaldehyde.

In order to evaluate the efficiency of the catalyst, for the direct conversion of aldehydes into their corresponding esters reaction of benzaldehyde with methanol in the presence of hydrogen peroxide as an oxidant was carried out as shown in Scheme 1. The effect of different reaction variables such as benzaldehyde/H₂O₂ mole ratio, amount of catalyst, reaction time and temperature were studied to optimize the conditions for maximum conversion.

Effect of % loading

The reaction was carried out by varying % loading of the active species (10-40%) onto the support with 10 mg of catalysts for 6 h at 80 °C. The results are presented in Fig. 6, which shows, conversion and selectivity increases with increase in % loading from 10% to 30% $PW_{11}Ni/ZrO_2$.



Fig. 6 Mole ratio (benzaldehyde/ H_2O_2) (1:3), amount of catalyst (10 mg), temperature (80 °C), time (6 h), amount of methanol (5 ml).

However, further increase in loading from 30% to 40% results decrease in conversion and selectivity. This may be due to faster decomposition of H_2O_2 in presence of excess of active centers in case of 40% $PW_{11}Ni/ZrO_2$, results decrease in conversion of benzaldehyde. The obtained results may be due to the blocking of acidic sites in the catalysts (Table 1 and 2). Thus, 30% $PW_{11}Ni/ZrO_2$ catalyst was selected for detailed catalytic study.

Effect of Mole Ratio

The effect of H_2O_2 on the catalytic activity was studied by varying mole ratio from 1:1 to 1:4 for benzaldehyde: $H_2O_2.$ As

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Fig. 7 Amount of catalyst (10 mg), temperature (80 °C), time (6 h), amount of methanol (5 ml).

The increase in conversion may be due to rise in concentration of H_2O_2 . A decrease in the conversion and selectivity is observed in case of 1:4. Therefore, 1:3 mole ratio of benzaldehyde: H_2O_2 was optimized which gave 63% conversion and 79% ester.

Effect of amount of 30% $\rm PW_{11}Ni/ZrO_2$

In order to determine the optimum amount of catalyst, the reaction was investigated at five different amounts of catalysts, keeping other parameters fixed (1: 3 mole ratio of benzaldehyde to H_2O_2 for 6 h at 80 °C and 5 ml of methanol) and result is presented in Fig. 8.



Fig. 8 Mole ratio (benzaldehyde/ $H_2O_2)$ (1:3), temperature (80 $^\circ C$), time (6 h), amount of methanol (5 ml).

It is seen from the Fig. 8 that the conversion initially increases with an increase in the amount of 30% $PW_{11}Ni/ZrO_2$ from 7.5 mg to 10 mg. However, on increasing catalysts amount from 10mg, decrease in conversion as well as selectivity for ester was observed. This drop in conversion with increase in

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amount of catalyst is due to rapid unproductive decomposition of H₂O₂ in presence of excess amount of catalyst. In order to confirm the obtained results, decomposition of H₂O₂ (SI-1) with different amount of catalysts were studied and results are presented in Table S1. From Table S1, it is clear that on increasing catalyst amount, percentage decomposition of H₂O₂ increases under identical time. The obtained result suggests that the best utilization of H₂O₂ was obtained in the case of 10 mg of catalysts whereas amount greater than 10 mg results in unproductive decomposition of H_2O_2 . Also, rapid decomposition of H₂O₂ generates relatively excess moles of water results decrease in selectivity of esterification process which is a reversible process in presence of water. The reaction carried out using 10 mg of catalyst gave 63 % conversion and 79 % selectivity for ester, which is guite good with such a minimal amount of catalyst.

Effect of Temperature



Fig. 9 Mole ratio (benzaldehyde/ H_2O_2) (1:3), amount of catalyst (10 mg), time (6 h), amount of methanol (5 ml).

Increase in temperature resulted increase in conversion as seen from the case of 60 °C and 80 °C. As observed from Fig. 9, at 60 °C good selectivity is observed. In case of 80 °C temperature, it gave better conversion and selectivity when compared with that of other varied temperatures. In case of 90 °C, conversion and selectivity for ester was decreased. This may be due fast thermal and catalytic decomposition of H_2O_2 at elevated temperature. Thus, as a result 80 °C was selected for the optimum reaction temperature.

Effect of time

For the optimization of reaction time (Fig. 10), reaction was carried out at various time duration, resulting good conversion in case of 6 h as compared to other cases. As shown in the Fig. 10 with increase in time of reaction, conversion was increased proficiently along with selectivity. But as the reaction time was increased no significant change in conversion and selectivity of ester was observed, due to attainment of equilibrium in the reaction. As a result, reaction was optimized for 6 h for better conversion and selectivity.



Fig. 10 Mole ratio (benzaldehyde/ H_2O_2) (1:3), amount of catalyst (10 mg), temp. (80 °C), amount of methanol (5 ml).

Effect of methanol quantity

The effect of volume of methanol was also studied for optimizing the reaction (Table 4). With 2 ml methanol it gave 67% with 35% selection of ester was observed.

Table 4 Effect of Methanol Quantity

Methanol quantity	% Conv.	%Sel.	
		Ester	Acid
2 ml	67	35	65
5 ml	63	79	21
8 ml	56.3	74.5	25.5

Mole ratio benzaldehyde to H_2O_2 1:3; reaction temperature, 80 °C; reaction time, 6 h.

But, as volume of methanol was increased to 5 ml, better conversion and selectivity was obtained. Further, it was observed that with an increase in the volume of methanol there was a decrease in conversion which may be due to less availability of hydrogen peroxide for the reaction and dilution of the reaction with increasing volume of methanol. Thus, 5 ml methanol was selected as an optimized parameter for the reaction.

Control Experiment

Table 5 Control experiments.

Entry	% Conv.	%Sel.	
		Ester	Acid
Without catalyst	3.0	-	100
30% PW ₁₁ /ZrO ₂	56.3	61.9	38.1
PW ₁₁ Ni ^a	59.4	62.3	37.7
30% PW ₁₁ Ni/ZrO ₂	63.0	79.0	21.0

Mole ratio, 1:3; reaction temperature, 80 $^{\circ}$ C; catalyst amount, 10 mg (a=2.3 mg); reaction time, 6 h; amount of methanol, 5ml.

The control experiment for present catalytic system was carried under optimized condition and results are shown in Table 5. Oxidative esterification of benzaldehyde was done without employing any of the catalyst which gave very

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negligible amount of conversion (3%) proving the need of an efficient catalyst to speed up the reaction. When supported lacunary counterpart 30% PW₁₁/ZrO₂ was employed as a catalyst, 56.3% conversion with 61.9% selectivity for ester was obtained. On comparing this result with present catalytic system, it clearly shows the 30% PW₁₁Ni/ZrO₂ is better catalysts in terms of both activity and selectivity. The control experiment was also carried out with unsupported CsPW₁₁Ni, which shows 59.4% conversion with 62.3% selectivity of ester. Further, by comparing the conversion and selectivity for homogeneous as well as supported systems, it can be observed that the 30% PW₁₁Ni/ZrO₂ shows relatively proficient amount of ester. The obtained data from the control experiments revealed the catalytic activity of the supported catalyst to be a good source to accelerate and precede the reaction to the desired level. On comparison the activity and selectivity of all catalysts, 30% PW₁₁Ni/ZrO₂ was found to be best catalyst, gives excellent conversion and selectivity with a very low catalyst amount.

Thus, the optimum conditions are, mole ratio to benzaldehyde to H_2O_2 (1:3); catalyst amount 10 mg, temperature 80 °C, time 6 h, methanol 5 mL, resulting Turnover number (TON) to be 9690.

Heterogeneity Test

Accurate evidence of heterogeneity can be gained only by filtering the catalysts before completion of the reaction and analyzing the filtrate for % conversion.³² A test was performed by filtering the catalyst from the reaction mixture at 80 °C after 3h of the reaction, and the filtrate was allowed to react further.

Table 6 Heterogeneity test

Reaction time	% Conv.	% Ester	% Acid
3h	49.8	74.5	25.4
6h	49.6	73.9	26.0
			-

The reaction mixture and the filtrate (after 6h) were analysed by a gas chromatogram (Table 6). No significant change in the % conversion indicates role of catalyst in obtaining good yield and selectivity of desired product. The present catalyst falls into the category C,³² i.e. the active species does not leach and the observed catalysis is truly heterogeneous in nature.

Regeneration of the Catalyst

The catalyst was regenerated so as to examine its stability and recycled for investigating its activity. The catalyst after the reaction was separated, from the reaction mixture by simple centrifugation; washed using dichloromethane and then dried at 100 °C.

Characterization of regenerated catalyst

The regenerated catalyst was further characterized by powder XRD for confirmation of retention of the structure of catalyst.



Fig. 11 Powder XRD of a) 30% PW₁₁Ni/ZrO₂ b) R- 30% PW₁₁Ni/ZrO₂.

The reused catalyst was characterized by Powder XRD as shown in Fig. 11. There is no appreciable change in the XRD pattern of fresh 30% $PW_{11}Ni/ZrO_2$ and recycled R- 30% $PW_{11}Ni/ZrO_2$ indicating that the material remains unchanged even after regeneration.

Catalytic activity of recycled catalyst

Table 7 Recycling study of 30% PW₁₁Ni/ZrO₂

Cycle	Total no. of acidic sites (m _{eq} g ⁻¹)	% Conv.	% Selectivity		Turn over number (TON)	Turn over frequencies (TOFs) h ⁻¹
			Ester	Acid		
Fresh	3.7	63	79	21	9690	1615
1	3.2	63	62	38	9636	1606
2	3.2	63	64	36	9587	1598
3	3.1	61	63	37	9364	1560

Reaction conditions: mole ratio, 1:3; reaction temperature, 80 $^{\circ}\text{C};$ catalyst amount, 10 mg; reaction time, 6 h; amount of methanol, 5ml.

Recycling data (Table 7) shows almost same conversion for all the catalysts. However, remarkable decrease in selectivity of ester was observed, especially for the first cycle. After that, no significant change in selectivity was observed for subsequent cycles. The observed trend in selectivity can be explained on the basis of acidity of catalysts. From the Table 7; It is clearly seen that, for first cycle, total number of acidic sites decreased considerably as compare to fresh one which is responsible for drastic decrease in selectivity of ester. However, total number of acidic sites of successive recycled catalysts remained constant; as a result no significant change in selectivity of ester was observed.

Conclusion

The present contribution reports one pot oxidative esterification for the direct conversion of benzaldehyde to methyl benzoate over heterogeneous catalyst. The superiority of the catalyst lies in better conversion and excellent selectivity of the methyl benzoate with high TON (9690). The advantages of using a recyclable Ni based catalyst under mild reaction conditions instead of more expensive metals makes

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this methodology interesting from an economic and an ecological point of view.

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One pot oxidative esterification of benzaldehyde over supported Cs-salt of mono nickel substituted phosphotungstate

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• Table of Content Graphics:



• Synopsis:

The synthesized mono Ni(II)-substituted phosphotungstate supported on to zirconia was used as a catalyst for one pot oxidative esterification of benzaldehyde.