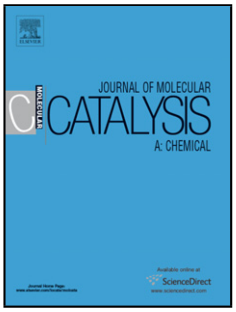

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Tuning Surface Composition of Cs Exchanged Phosphomolybdic Acid Catalysts in C-H Bond Activation of Toluene to Benzaldehyde at Room Temperature

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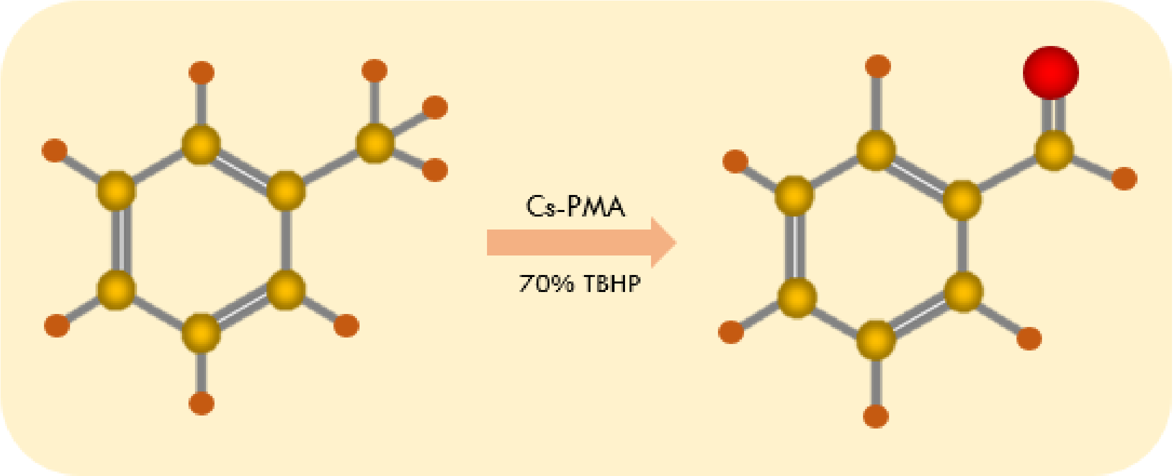
Graphical abstract



Highlights:

- Cs exchanged phosphomolybdic materials were synthesised by ion exchange method
- CsPMA-2 exhibits higher surface area and Brønsted acidity
- CsPMA-2 is highly selective and more active than the PMA and other Cs exchanged catalysts in C-H bond activation
- Regenerated CsPMA- catalyst exhibits stable activity during reaction

Abstract

A series of Cs exchanged phosphomolybdic (PMA) catalysts were synthesised by the ion exchange method. The prepared materials were characterized by various physico-chemical techniques such as X-ray diffraction, FT-IR, Raman spectroscopy, pyridine adsorbed FT-IR spectroscopy, ^{31}P NMR, BET surface area, nitrogen isotherms, TEM and STEM analysis. XRD results show crystallites of the Keggin ion of heteropolyacid catalysts. FT-IR and Raman spectra data reveal that the Keggin structure of PMA catalyst is maintained even after the exchange of the protons with Cs ions. Pyridine adsorbed FT-IR spectra show that available Brønsted acidic sites increases after Cs is incorporated in PMA. TEM analysis shows that the spherical shape remains intact after Cs exchange and STEM analysis shows a uniform distribution of elements in the Cs exchanged PMA catalyst. Nitrogen isotherms studies reveal a type IV isotherms for the Cs exchanged catalyst. The Cs exchanged phosphomolybdic acid (CsPMA) showed better catalytic performance than the phosphomolybdic acid (PMA) catalyst when evaluated for the C-H bond activation of toluene to benzaldehyde. The catalyst was easily recovered and reused for five cycles with stable activity.

Keywords: Cesium, phosphomolybdic acid, ion-exchange, C-H bond activation, Brønsted Acidity.

1. Introduction

Polyoxometalates (POMs) or heteropolyacids (HPAs) are well known solid acid catalysts due to their tunable bi-functional acid and redox properties for various acid and oxidation reactions, respectively [1, 2]. Recently, HPAs have been received considerable attention in many acid catalyzed and oxidation reactions with industrial applications [3-15]. HPAs are well known strong Brønsted acidity materials, however one of its major drawbacks is the low surface area which may impact on its catalytic performance. This can be resolved, to a certain extent, by modifying the textural properties and acidic functionalities of the compound, simply by exchanging or replacing the protons of HPA, specifically PMA with a large cation such as cesium Cs. Cs exchanged PMA catalysts are water tolerant solid acid catalysts which possess a higher surface area than the PMA catalysts and were studied in number of reactions including carbonylation, dehydration, condensation, alkylation, acylation, isomerization of *n*-

butane, hydration of olefins and biodiesel synthesis [16-22]. In the view of several organic transformations carried out over Cs containing Keggin HPA catalysts, we proceeded to investigate the selective C-H bond activation of toluene to to produce benzaldehyde at room temperature over Cs exchanged phosphomolybdic acid catalysts.

The catalytic selective oxidation of toluene to the benzaldehyde has great importance in both basic and applied research due to its extensive applications in academic and industrial chemistry. Benzaldehyde is a versatile aromatic carbonyl compound used in the perfumery, cosmetics and agrochemical industries. It is currently produced by liquid phase chlorination of toluene followed by hydrolysis [21,22] and also by the partial oxidation of toluene [23]. Among the two processes, oxidation of toluene is the more preferable route since chlorination of toluene followed by hydrolysis is a non-eco-friendly method. However, the oxidation of toluene in the gas phase leads to the formation of carbon oxides instead of benzaldehyde as the major product. Liquid phase oxidation or activation of toluene to benzaldehyde at room temperature could address these problems and at the same time, promote the selective synthesis of benzaldehyde as an eco-friendly process. Various studies involve the synthesis of benzaldehyde from toluene at room temperature and among them, heteropolyacid (HPA) has received considerable attention due to its eco-friendly and bi-functional nature [24-28]. Liu et al. [24] synthesized a tripodal tridentate copper(II) complex, CuImph (Imph = bis(4-imidazolyl methyl)benzylamine) to mimic the active site of copper enzymes that mediate the oxidation of aliphatic C–H bonds under mild conditions. Their results show high reactivity and selectivity toward toluene aliphatic C–H bond oxidation, converting the toluene initially to benzyl alcohol and subsequently to benzaldehyde as the major product in a kinetic consecutive reaction. No evidence for benzoic acid is obtained. Wurtele et al. [26], on the other hand used copper peroxo complexes which they found to be stable at room temperature for the aliphatic C-H bond oxidation of toluene. To test the potential of these complexes, they reacted four peroxo complexes with toluene at room temperature under air and observed the formation of benzaldehyde in yields of up to 20%, along with small amounts of benzyl alcohol.

Our present work is related to effect of Cs exchanged phosphomolybdic acid catalysts for the selective C-H bond activation of toluene to benzaldehyde at room temperature. These materials were characterized by various techniques to investigate its surface, structural and acidic functionalities and its correlation with the catalytic activity.

2. Experiential

2.1 Catalyst synthesis

A series of Cs exchanged phosphomolybdic acid catalysts with various Cs content, ranging from 1 to 3 wt% loadings were prepared by ion exchanged method. In a typical synthesis, for a 1 wt% loading, 0.326 g of Cs_2CO_3 (Sigma Aldrich, SA) was dissolved in 10 mL of double distilled water. This solution was added drop wise to a solution of 3.65g of $H_3PMo_{12}O_{40}$ (Sigma Aldrich, SA) made up in 15 mL of double distilled water. The resulting mixture was centrifuged to remove the precipitate which was the washed repeatedly with double distilled water. The solid was dried at 200°C for 10 h. These prepared catalysts which had the formulae, $Cs_{1.0}PMo_{12}O_{40}$, $Cs_{2.0}PMo_{12}O_{40}$ and $Cs_{3.0}PMo_{12}O_{40}$ were labelled as CsPMA-1, CsPMA-2 and CsPMA-3, respectively.

2.2 Catalyst characterization

Powder X-ray diffraction patterns of samples were obtained with a Bruker D8 Advance diffractometer, using a Cu Ka radiation source (1.5406 A˚) at 40 kV and 30 mA. The measurements were recorded in steps of 0.045° with a count time of 0.5 s in the range of 2-60°. The surface area of catalysts was determined using N_2 adsorption isotherms at -196^{o}C by the multipoint BET method taking 0.162 nm^2 as its cross-sectional area. The pore size distribution was measured by N_2 adsorption-desorption isotherms using a Micrometrics ASAP 2020 multi-point BET surface area analyzer. Prior to these experiments, the materials were degassed under helium flow overnight at 200°C using a Micrometrics Flow Prep 060 and all experiments were carried out at a relative pressure range (p/p°) of 0.05 to 0.9. Infrared (IR) spectra were recorded on a Perkin Elmer Precisely equipped with a Universal ATR sampling accessory using a diamond crystal. The powdered material was placed on the crystal and a force of 120 psi was applied to ensure proper contact between the material and the crystal. The spectra were analyzed using Spectrum 100 software. Ex-situ pyridine adsorbed FT-IR experiments were carried out to investigate the nature of acidity, such as Brønsted and/or Lewis acid sites present on the catalyst. The spectra were recorded on a Perkin-Elmer ATR spectrometer at room temperature. Prior to analysis, pyridine adsorption experiments were carried out by placing a drop of pyridine on a small amount of the catalyst, followed by evacuation in air for 1 h to remove the reversibly adsorbed pyridine. Raman spectra were collected using a Horbia-Jobin-Yvon LabRam high resolution spectrometer equipped with a confocal microscope with 2400/900 grooves/mm gratings and a notch filter. The visible laser excitation at 532 nm (visible/green) was supplied by a Yag double diode pumped laser (20mW). Transmission electron microscopy (TEM) images were obtained on a Jeol JEM-1010 electron microscope. The images were captured and analyzed using iTEM software. Distribution and chemical analysis of elements in the materials was examined by STEM analysis. ^{31}P NMR spectra of catalyst were recorded on a Bruker Advance 400 MHz spectrometer and chemical shifts were reported relative to 85 % H_3PO_4 in D_2O used as an external standard at 298K.

2.3 Catalytic testing

Solvent free liquid phase oxidation of toluene was carried out in a 10 mL round bottom flask at room temperature. In a typical run, 10 mmol of toluene, 2 mL of 70% TBHP and 4 mol %

of the catalyst were placed in the flask, under stirring (Scheme 1) and the reaction was constantly monitored by GC. The catalyst was then recycled and used for the same reaction.

3. Results & Discussion

3.1 Catalyst characterization

3.1.1 X-ray diffraction

X-ray diffraction patterns of pure PMA and synthesised Cs exchanged PMA catalysts are shown in Figure 1. These profiles indicate that PMA shows the triclinic structure, whereas the Cs exchanged PMA catalyst possesses the cubic structure of the Keggin ion of a heteropolyacid. The XRD profile also shows that in the pure PMA, the Keggin ion, usually found around a 2-thetha value of 9-10° is more pronounced when compared to the Cs exchanged PMA, consistent with findings in literature [29].

3.1.2 FT-IR spectroscopy

The FT-IR spectra of PMA and Cs-PMA catalysts shows four characteristic bands in the 500-1200 cm^{-1} region. The bands for the pure PMA at 760, 889, 961, 1058 cm^{-1} are attributed to Mo-Oc-Mo, Mo-O$_t$-Mo, Mo=O and P-O, respectively [3,4,6,7]. In Cs exchanged catalysts, a slight shift in the bands found at 754-767, 860, 960-962 and 1060-1061 are assigned to Mo-Oc-Mo, Mo-O$_t$-Mo, Mo=O and P-O, respectively. The shift of the peaks of about 2 to 7 cm^{-1} indicates that Cs successfully exchanges with protons in PMA, maintaining the characteristic Keggin ion of the heteropolyacid, even at higher loadings of cesium [30].

3.1.3 Raman spectroscopy

From Figure. 3, the characteristic Keggin ion band is present at 989-992 cm^{-1} for the PMA and the CsPMA catalysts. The more intense bands at 239, 600-603, 814 and 876-884 cm^{-1} are assigned to Mo-O$_a$, Mo-O$_c$-Mo, Mo-O$_b$-Mo and Mo-O$_t$, respectively [3,4,6,7]. It is also established that Keggin ion remains intact, even at higher loading of Cs. The findings in Raman spectroscopy complements the observations made in FT-IR spectroscopy.

3.1.4 Pyridine adsorbed FT-IR spectroscopy

The nature of the acidity in the catalysts was studied by *ex situ* pyridine FT-IR spectroscopy and the results are shown in Figure 4. The IR band at 1538 cm^{-1} is assigned to Brønsted acidic sites. The peak observed at 1486 cm^{-1} is due to both Brønsted and Lewis acidic sites, whereas the band is observed at 1441 cm^{-1} is attributed to Lewis acidic sites of the catalysts. From Figure 4, it is also apparent that Brønsted acidic sites increased slightly with an increase in the Cs content in PMA catalysts, but decreased considerably at higher Cs content. Lewis acidity is predominant at higher Cs content. A combination of both Brønsted and Lewis acidic sites decreased at higher Cs loadings.

Brønsted acidity is observed more in the case of CsPMA-2 catalyst rather than other loadings, which might be due to a large surface area exhibited by the CsPMA-2 catalyst, resulting in the availability of more protons on the surface area of catalyst.

3.1.5 Nitrogen adsorption-desorption isotherms

Textural properties of PMA and the synthesized Cs exchanged PMA catalysts are tabulated in Table 1. The surface area of the catalysts increases with an increase in Cs content up to the CsPMA-2 catalyst. All the Cs exchanged catalysts exhibits a type IV isotherm and a hysteresis loop associated with mesoporous materials [31]. At higher Cs loadings, the BET surface area decreased substantiantly with a slight increase in pore size, probably due to agglomeration. The high BET surface area of the CsPMA-2 catalyst results in a lower Keggin anion density as reflected by the lower crystallinity of Keggin ion units when compared to other Cs loadings. These results correlate well with X-ray diffraction studies which shows that pure PMA is more crystalline than the Cs exchanged PMA catalysts. The particle size obtained from sorption experiments shows large particle sizes for the PMA catalyst compared to the Cs exchanged PMA catalysts.

3.1.6 ^{31}P NMR spectroscopy

^{31}P NMR spectra of PMA and the Cs exchanged PMA catalysts were recorded in D_2O solvent (Figure 6). The pure PMA catalyst showed a chemical shift at -3.9 ppm, whereas in the case of Cs exchanged PMA catalysts, this peak disappears indicating that the Cs exchanged PMA is not soluble in the D_2O solvent, providing evidence that the Cs exchanged catalysts have no impurities such as the starting material which is PMA.

3.1.7 TEM analysis

The internal morphology of pure PMA and the CsPMA catalysts was studied by TEM analysis and the results are shown in Figure 7. There is every indication that the pure PMA has a spherical structure and this structure was maintained with the Cs exchanged compounds.

3.1.8 STEM analysis

BF-STEM imaging with chemical analysis of fresh and regenerated CsPMA-2 catalyst was conducted to map the structure and relative spatial distribution of the elements present in the catalysts (Figure 8) and to obtain the Cs content in the Keggin anion (Table 1).

3.2 Catalytic activity studies

The catalytic activation of C-H bond in toluene was studied over Cs exchanged PMA catalysts under nitrogen atmosphere and the results are tabulated in Table 2.

Initially, blank reactions were studied at same reaction conditions, however there was no activity recorded. The phosphomolybdic acid showed a 0.6% conversion and 53% towards benzaldehyde. Among the various Cs exchanged PMA catalysts, the CsPMA-2 catalyst showed the highest conversion with almost maximum selectivity towards benzaldehyde compared to the other Cs/P ratios, probably due to the larger number of available active sites as reflected by the high surface area of the catalyst. Surface acidity of the catalyst also plays a role. At a higher Cs loading, i.e. for CsPMA-3, the catalyst is more crystalline leading to a decrease in the surface acidity resulting in lower activity, similar to that observed for the CsPMA-1 and pure PMA catalyst. It is also interesting to note that the higher turnover number of CsPMA-2 leads to better activity compared to the other loadings and the PMA itself. The catalytic results are strongly associated with the nature of acidity of the catalyst. From pyridine adsorbed FT-IR studies, more surface Brønsted acidic sites are observed in the case of CsPMA-2 catalyst than the other Cs containing materials including the pure PMA catalyst. The mesoporous nature of CsPMA-2 catalyst with its high pore volume and surface area also favours formation of benzaldehyde compared other catalysts.

The oxidation of toluene over the CsPMA-2 catalyst was studied with various volumes of the oxidant, TBHP and the results are presented in Table 3. These results are show that the activity increases significantly when the volume of the oxidant is doubled from 1 mL to 2 mL. Thereafter, there is a slight increase in the activity as the volume of the oxidant increased. An increase in the concentration of TBHP results in the formation of benzoic acid at the expense of benzaldehyde.

The effect of amount of catalyst used on the activity was investigated and the results are given in Table 4. The conversion of toluene increased with an increase in the amount of the catalyst. Although the conversion increased with an increase of catalyst loadings, the selectivity towards benzaldehyde selectivity decreased substantiantly, probably be due to further oxidation of benzaldehyde to benzoic acid at higher concentration of the heteropolyacid at room temperature. The above findings also show that 0.1 g of catalyst is the optimum amount required.

We also studied effect of toluene concentration over the CsPMA-2 catalyst under similar reaction conditions (Table 5). These findings show that an increase in the concentration of reactant results in a decrease in the conversion but selectivity towards benzaldehyde increases significantly. The effect of various oxidants was studied and results are shown in Figure 9. TBHP is the most efficient oxidant that can activate the C-H bond in the presence of the heteropolyacid catalyst.

Time on stream experiments were conducted to investigate the influence of time on the activity of the CsPMA-2 catalyst. From Figure 10, at the outset, conversion of toluene and selectivity towards benzaldehyde is low, but increases significantly over time.

The catalyst was subjected to a number of cycles to study its stability (Figure 11). Before regeneration, the catalyst was separated, filtered and washed several times with organic solvent to remove any organic moiety on the surface of the catalyst and dried in an oven over night. The catalyst was characterized by FT-IR (Figure 2) to observe any structural changes and pyridine adsorbed FT-IR (Figure 4) to investigate any change in the surface acidity. STEM analysis was also conducted to observe any change in the Cs content of the regenerated catalyst. All these analyses showed no change in terms of structure, surface acidity and concentration in the regenerated CsPMA-2 catalyst as a result consistent results were obtained over the five cycles investigated.

The reaction was also studied a different temperatures various reaction temperatures and the results indicate that the formation of benzaldehyde increased with an increase in reaction temperature. However, as the temperature was increased to 120°C, the benzaldehyde selectivity decreased sharply and benzoic acid was observed as the major product. Brutchey et al. [32] studied toluene oxidation over Co supported SBA-15 using TBHP as oxidant showed a 8% conversion with a 64% selectivity towards benzaldehyde at 80°C. However, in our study, the Cs exchanged PMA catalyst achieved a 86% selectivity towards benzaldehyde for a 3.1 % conversion at 80°C, showing that the CsPMA-2 catalyst is highly selective towards benzaldehyde compared to Co-SBA-15 catalyst at a lower reaction temperature.

3.3 Proposed reaction mechanism

The selective synthesis of benzaldehyde over Cs-PMA catalysts could be due to the proposed pathways shown in Scheme 2 [33]. Initially, in path 1, the Cs-PMA catalyst reacts with TBHP to form tert-butyl peroxy and tert-butyloxy radicals. In path 2, these radicals react with toluene and produce benzaldehyde as the major product. However, the benzyl radical reacts with the catalyst to from the benzyl cation by a transfer of an electron to the catalyst which later reacts with the hydroxyl ion to form benzyl alcohol [33]. The formation of the benzaldehyde from benzyl alcohol over phosphomolybdic acid catalysts occurs through the transfer of two electrons and two protons from the benzyl alcohol to the catalyst to produce benzaldehyde [34].

4. Conclusion

In the present investigation, we have demonstrated an eco-friendly heterogeneous Cs exchanged phosphomolybdic acid catalysts exhibiting remarkable benzaldehyde selectivity and significant conversion than the pure PMA catalyst during C-H bond activation of toluene. BET surface area and pore size distribution studies shows that the mesoporous nature of CsPMA-2 catalyst results in higher selectivity towards desired product. FT-IR and Raman spectroscopy reveal that Keggin structure is maintained even after the exchange of Cs in PMA. ^{31}P NMR spectra strongly indicate the water tolerant nature of HPA catalysts, while pyridine FT-IR shows that surface acidity is related to the catalytic activity of the Cs exchanged catalysts. STEM images show an even spatial distribution of metals in both the fresh and regenerated CsPMA-2 catalyst. The catalyst maintains its structure and acidity even after recycling up to 5 times.

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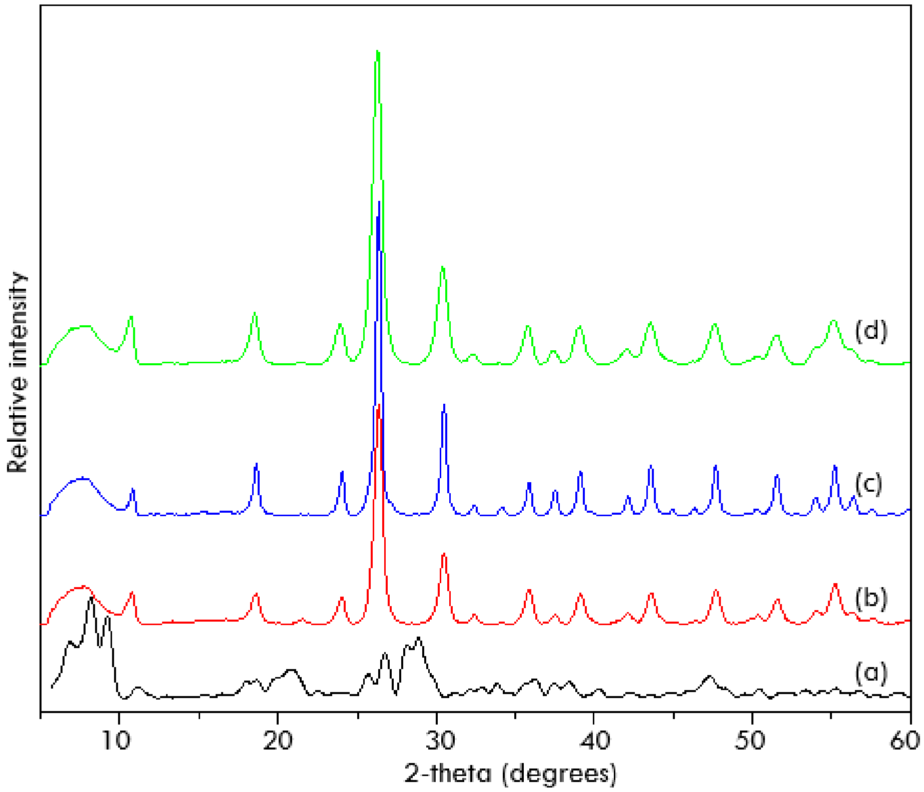


Figure 1. XRD profile of (a) PMA, (b) CsPMA-1, (c) CsPMA-2, (d) CsPMA-3 catalysts

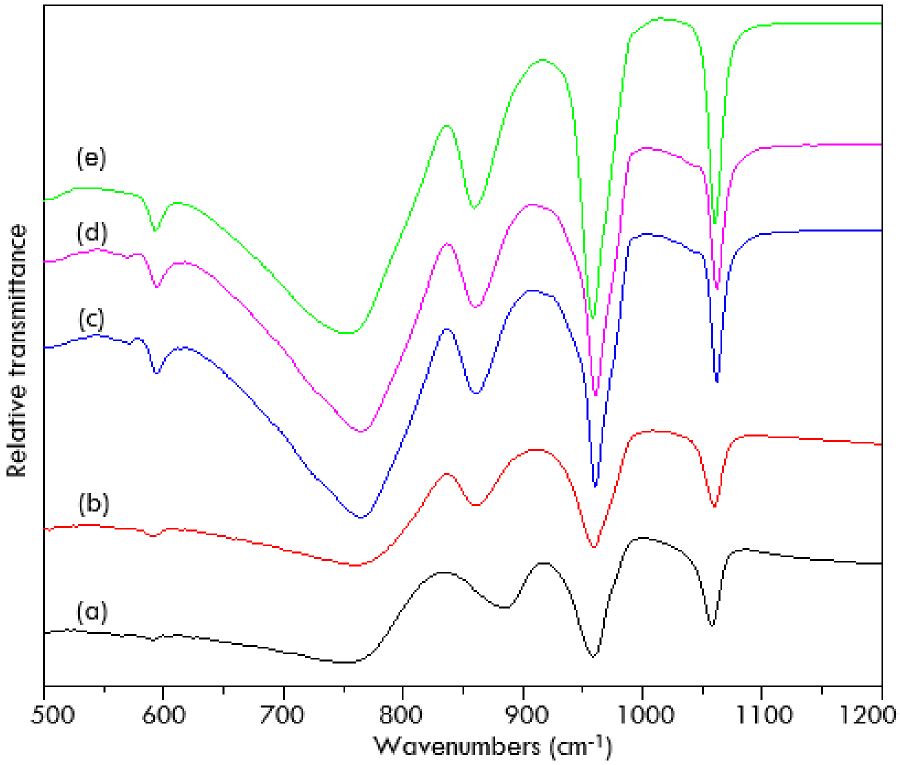


Figure 2: FT-IR spectra of (a) PMA, (b) CsPMA-1, (c) CsPMA-2, (d) Reg. CsPMA-2, (e) CsPMA-3 catalysts

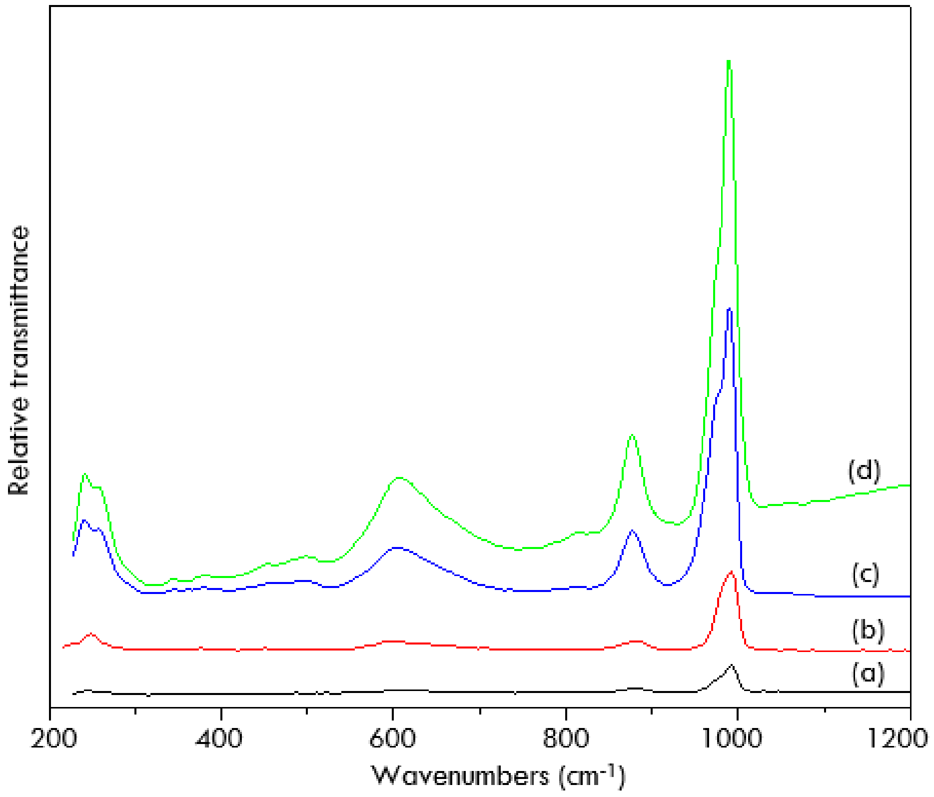


Figure 3: Raman spectra of (a) PMA, (b) CsPMA-1, (c) CsPMA-2, (d) CsPMA-3 catalysts

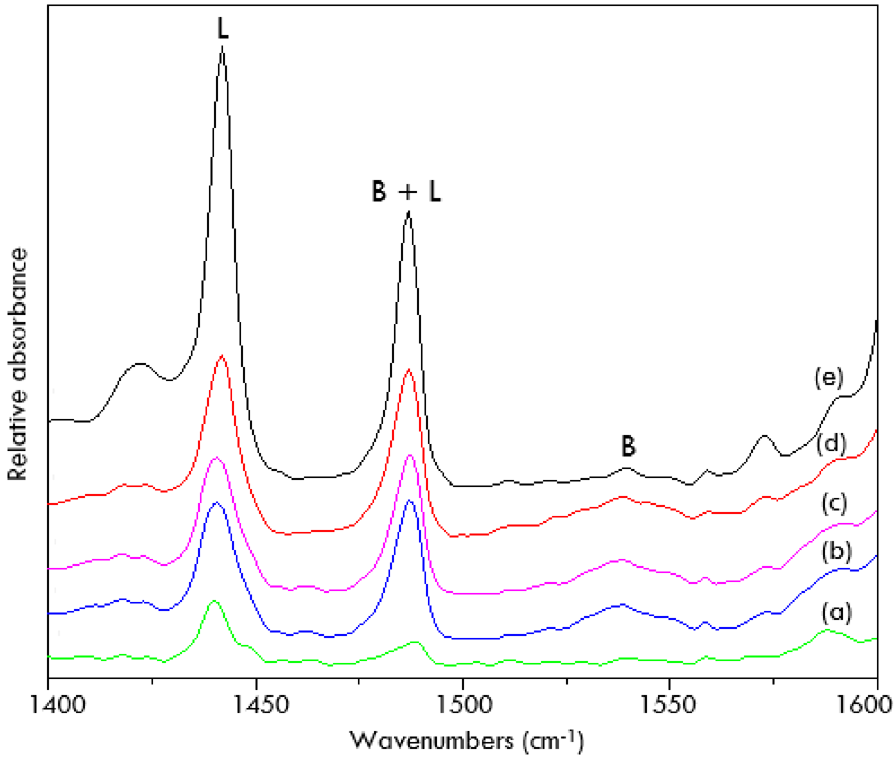


Figure 4: Pyridine adsorbed FT-IR spectra of (a) CsPMA-3, (b) CsPMA-2, (c) regenerated CsPMA-2, (d) CsPMA-1, (e) PMA catalysts

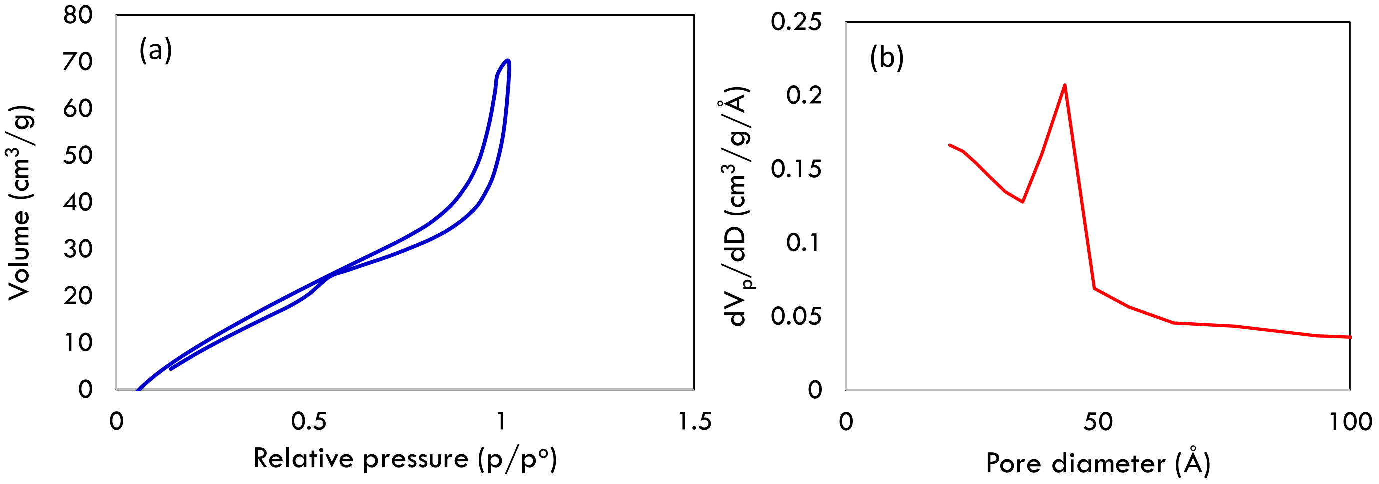


Figure 5 Nitrogen adsorption-desorption isotherm (a) and BJH pore size distribution (b) of the CsPMA-2 catalyst

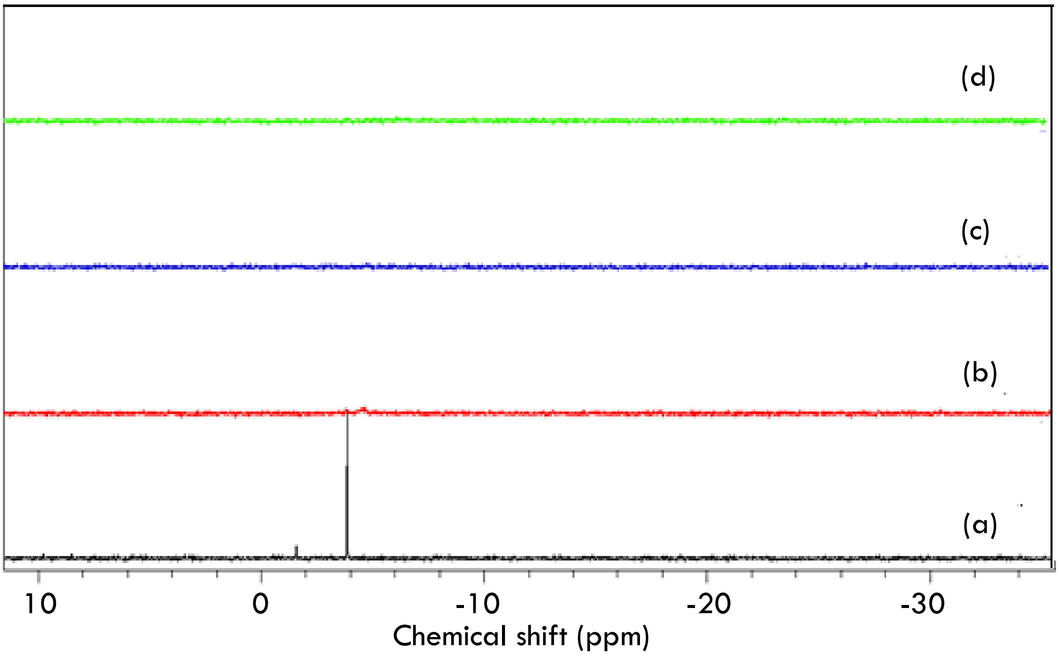


Figure 6: ^{31}P NMR of (a) PMA, (b) CsPMA-1, (c) CsPMA-2, (d) CsPMA-3 catalysts

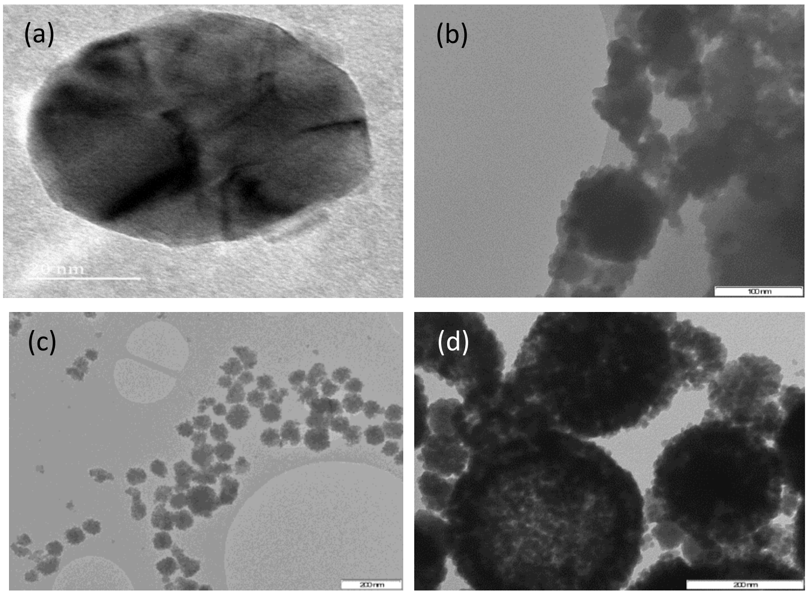


Figure 7 TEM images of (a) PMA (b) CsPMA-1, (c) CsPMA-2 and (d) CsPMA-3 catalysts

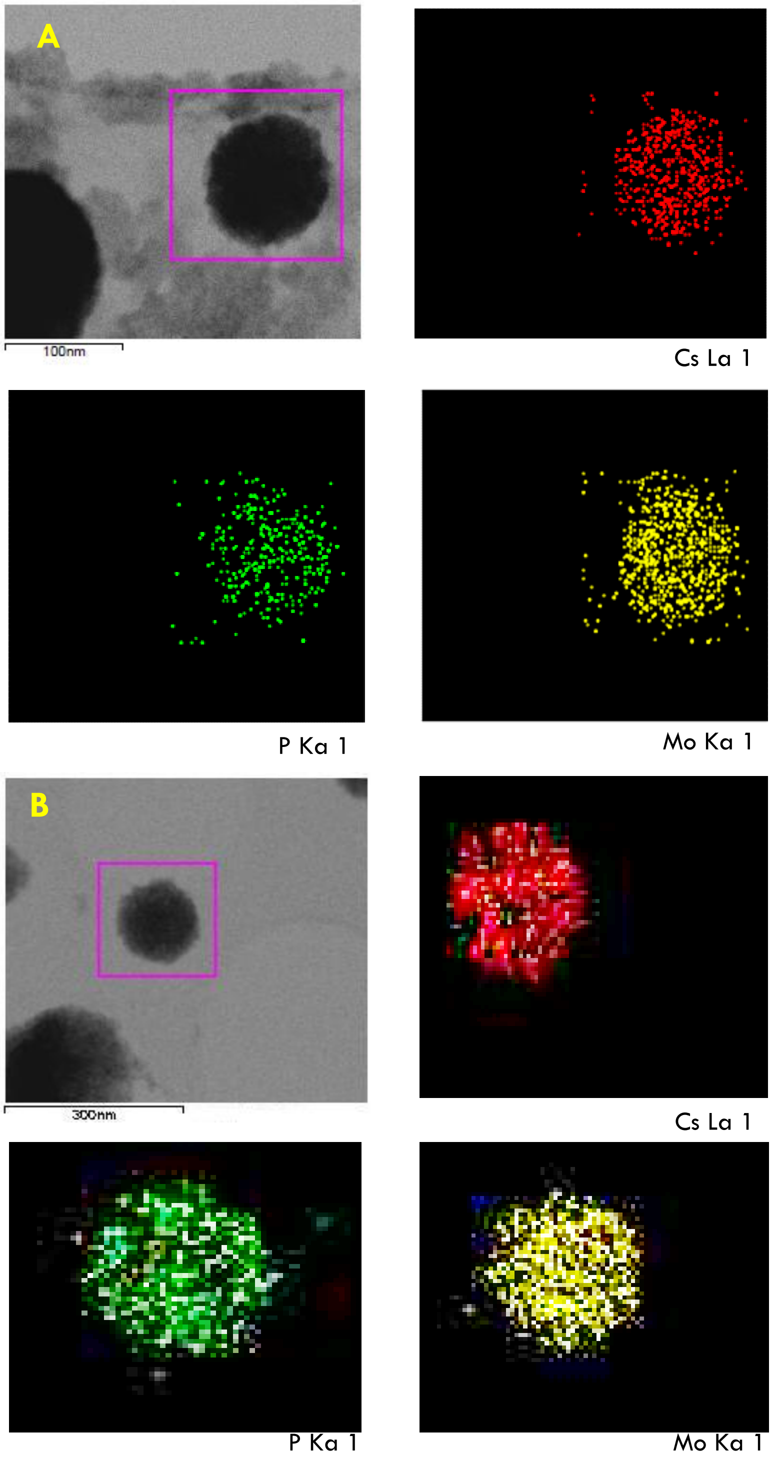


Figure 8 STEM images of (A) fresh and (B) regenerated CsPMA-2 catalyst

These findings show that theoretical Cs loadings are well correlated with experimental atomic % data obtained from STEM chemical analysis. The fresh and regenerated CsPMA-2 shows uniform spatial distribution of all the elements and shows a 2.1 Cs atomic % of the catalyst.

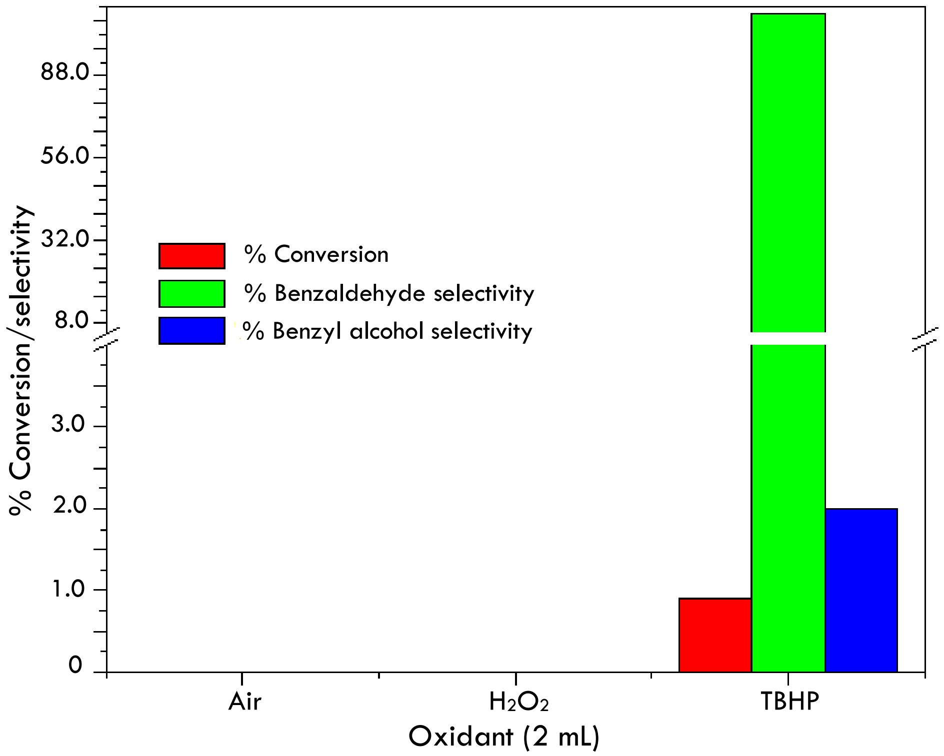


Figure 9: Catalytic results with various oxidants over CsPMA-2 catalyst

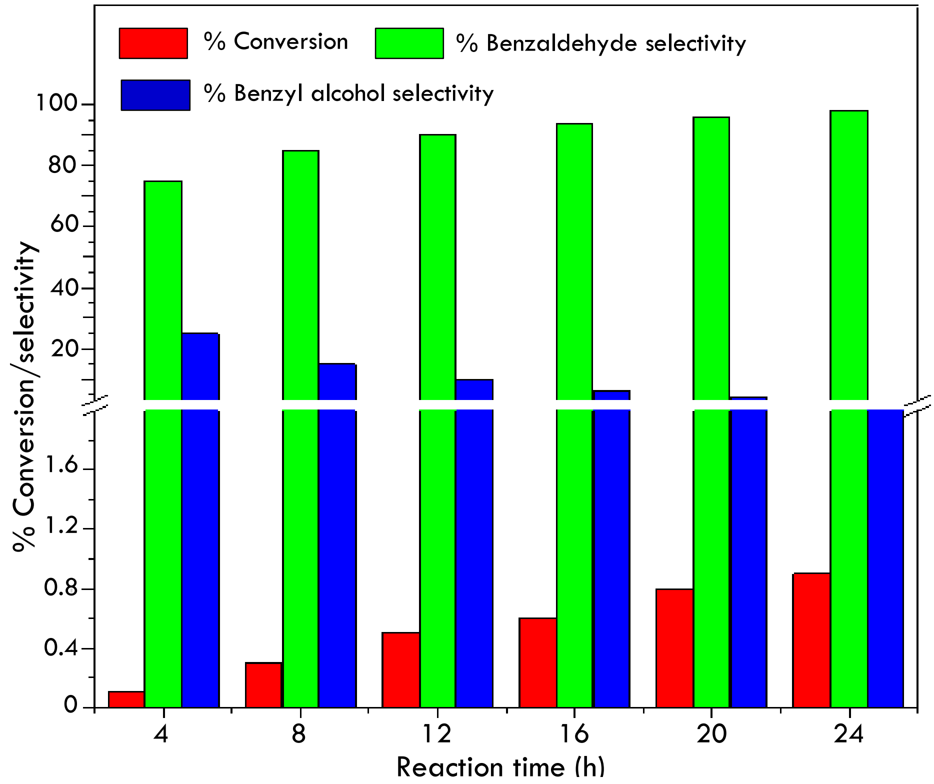


Figure 10 Time on stream studies over the CsPMA-2 catalyst

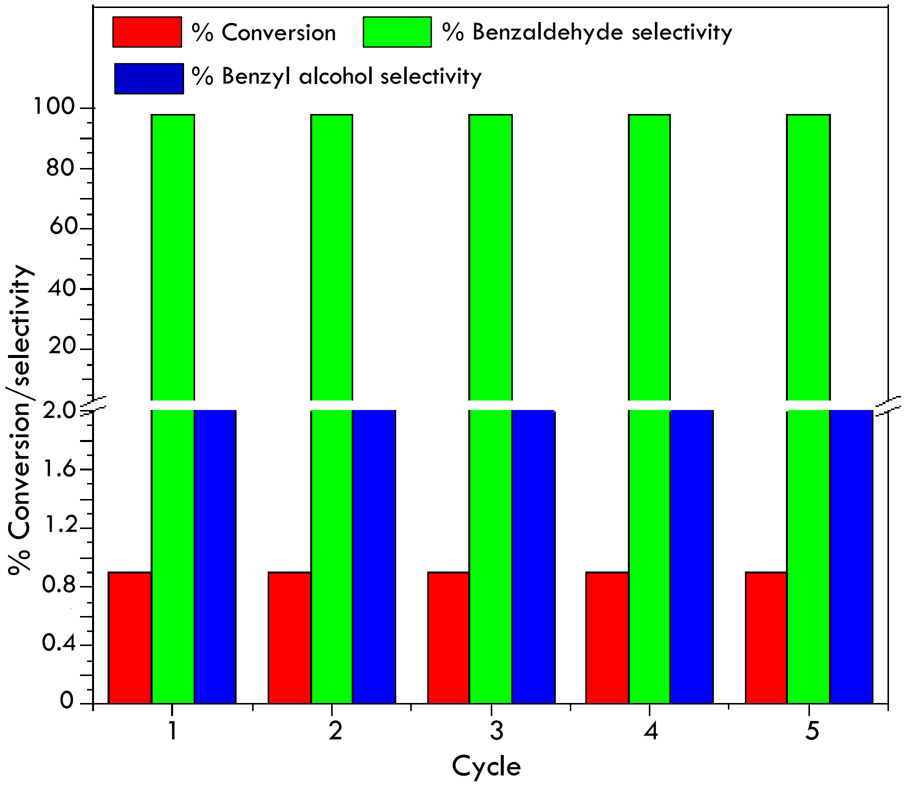
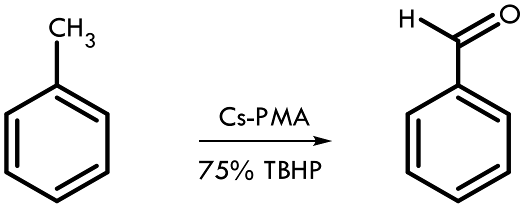
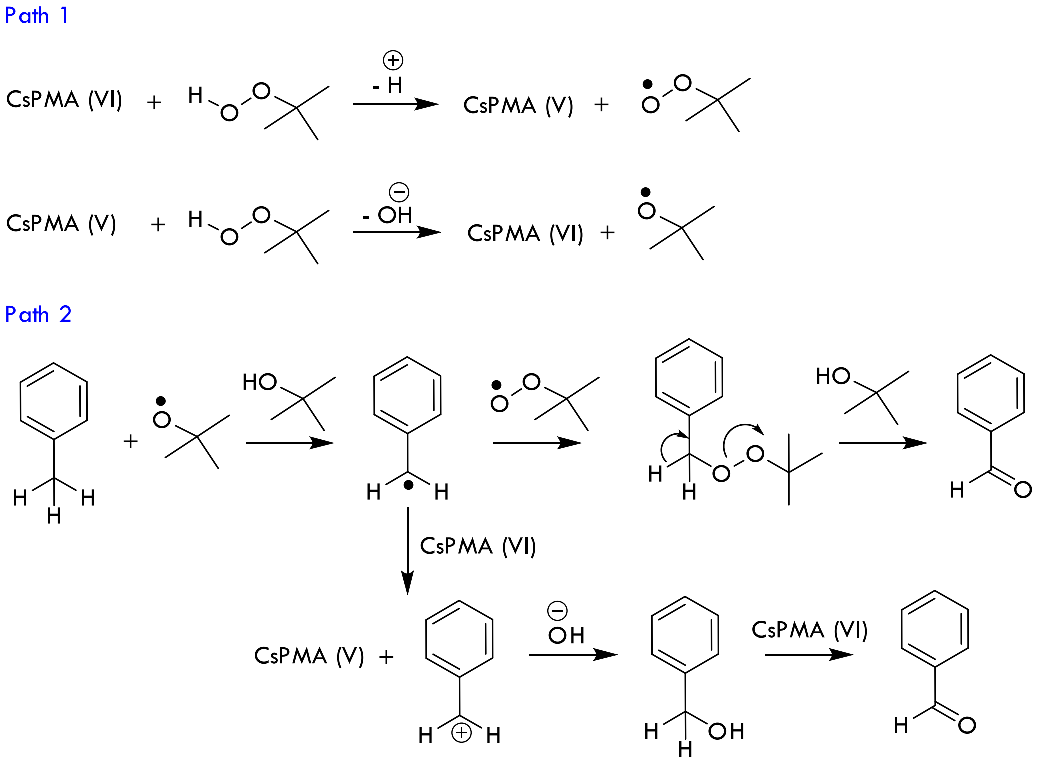


Figure 11 Conversion of toluene and selectivity towards benzaldehyde and benzyl alcohol over the CsPMA-2 catalyst for 5 cycles.



Scheme 1. Oxidation of toluene to benzaldehyde over Cs exchanged phosphomolybdic acid catalyst



Scheme 2 Proposed reaction mechanism of C-H bond activation of toluene to benzaldehyde over Cs exchanged phosphomolybdic acid (Cs-PMA) catalysts.

Table 1 Textural properties and Cs content of Cs-PMA catalysts

Catalyst	**BET surface area (m^2/g)**	**Pore volume (cm^3/g)**	**Pore diameter (Å)**	**Particle size (Å)**	**Cs content theoretical per Keggin ion (atomic %)**	**[a]Cs content practical per Keggin ion (atomic %)**	**Keggin anion density (HPA/nm^2)**
PMA	2.7	0.01	128	21662	--	--	1.2
CsPMA-1	25	0.03	80	1950	1.0	0.9	0.12
CsPMA-2	146	0.14	40	409	2.0	2.1	0.019
CsPMA-3	80	0.08	50	756	3.0	2.9	0.033

[a]Cs content obtained from STEM analysis

Table 2: Catalytic results over Cs exchanged phosphomolybdic acid catalysts[a]

Catalyst	**Conversion (%)**	**Selectivity (%)**		**[b]TON**
		Benzaldehyde	**Benzyl alcohol**	
Blank	--	--	--	--
PMA	0.6	53	47	1.09
CsPMA-1	0.7	85	15	1.37
CsPMA-2	0.9	98	2	1.88
CsPMA-3	0.5	78	22	1.10

[a]Reaction conditions: Toluene (10 mmol), TBHP (2 mL), Catalyst = 0.1 g, Reaction temperature = RT, Reaction time = 24 h, [b]TON = Number of moles of products/Number of moles of catalysts

Table 3 Catalytic results over CsPMA-2 catalysts with various amounts of TBHP[a]

TBHP (mL)	Conversion (%)	Selectivity (%)		
		Benzaldehyde	Benzyl alcohol	Benzoic acid
1	0.5	96	4	--
2	0.9	98	2	--
4	1.0	99	--	1
6	1.1	97	--	3

[a] Reaction conditions: Toluene (10 mmol), TBHP (1-6 mL), Catalyst = 0.1 g, Reaction temperature = RT, Reaction time = 24 h.

Table 4 Catalytic results over various loadings of CsPMA-2 catalysts[a]

Catalyst (g)	Conversion (%)	Selectivity (%)		
		Benzaldehyde	Benzyl alcohol	Benzoic acid
0.05	0.4	96	4	--
0.1	0.9	98	2	--
0.2	1.1	90	1	9
0.3	1.1	85	-	15

[a] Reaction conditions: Toluene (10 mmol), TBHP (2 mL), Catalyst = 0.05 – 0.3 g, Reaction temperature = RT, Reaction time = 24 h.

Table 5 Catalytic results over CsPMA-2 catalysts with different concentrations of toluene[a]

Concentration of toluene (mmol)	Conversion (%)	Selectivity (%)	
		Benzaldehyde	Benzyl alcohol
2	1.6	46	54
4	1.3	75	25
8	1.1	90	10
10	0.9	98	2

[a]Reaction conditions: Toluene (2-10 mmol), TBHP (2 mL), Catalyst = 0.1 g, Reaction temperature = RT, Reaction time = 24 h.

Table 6 Catalytic results over CsPMA-2 catalysts at various reaction temperature [a]

Temperature (°C)	Conversion (%)	Selectivity (%)		
		Benzaldehyde	Benzyl alcohol	Benzoic acid
RT	0.9	98	2	--
80	3.1	86	4	10
120	5.0	61	5	34

[a]Reaction conditions: Toluene (10 mmol), TBHP (2 mL), Catalyst = 0.1 g, Reaction time = 24 h