

# The Role of Alkali Metal Exchanged Phosphomolybdic Acid Catalysts in the Solvent Free Oxidation of Styrene to Benzaldehyde at Room Temperature

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## Abstract

A series of alkali metal exchanged phosphomolybdic acid catalysts were synthesized by ion exchange, characterized by various physico-chemical techniques and used in the solvent free oxidation of styrene to benzaldehyde. XRD and infrared results showed that the primary structure of the Keggin ion usually present in phosphomolybdic acid is retained after metal exchange. HR-TEM analysis show a well-constructed spherical morphology of the materials with a lower degree of crystalinity. Type IV isotherms with mesoporous structure are observed from nitrogen adsorption–desorption isotherm studies and ex situ pyridine adsorption experiments reveal that Brønsted acidic sites increased after metal exchange. The K exchanged phosphomolybdic acid catalysts was K > Rb > Cs. Insight into the reaction pathway by investigating the oxidation styrene oxide was obtained. The results show that phenyl acetaldehyde together with benzaldehyde are produced, providing some evidence that styrene oxidation proceeds via C=C cleavage to selectively produce benzaldehyde. The catalyst was easily recovered and was reused for up to three cycles showing stable activity.

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#### **Graphical Abstract**



Keywords Oxidation · Styrene · Benzaldehyde · Alkali metal-PMA · Acidity

# 1 Introduction

Solvent free oxidation of styrene to the benzaldehyde and styrene oxide has shown great importance in basic and applied research due to its extensive applications in industrial chemical processes and also in academia. Benzaldehyde is the versatile aromatic carbonyl compound used in perfumery, cosmetics and agrochemical industries, while styrene oxide is used a starting material in the manufacture of epoxy resin, absorbents and flavoring agents [1, 2]. The oxidation of styrene was initially carried out using homogeneous catalysts containing components such as permanganates, chromates and hypochlorites. In addition to these formulations being toxic, poor selectivity was obtained in all reactions and the inherent use of solvents is a disadvantage with regards to environmental concerns [3]. Transition metal complexes have been used as catalysts. Although reasonable activities were obtained, a major drawback was recyclability and problems associated with separation of the product stream [4, 5]. As a result, extensive research into more viable and environmentally friendly catalysts for these type of reactions has been undertaken. Among these are the metal oxide systems, metal complex systems and solid acid catalysts [5–13]. Solid heteropolyacid (HPA) catalysts are recognized one of the more efficient catalytic systems for styrene oxidation, due to their tunable acidic and oxidation functionalities and they are also environmentally friendly and recyclable [14-29]. It has also been established that metal containing heteropolyacids produce excellent results for the oxidation of styrene [6-13]. The research has been focused on metals such as Mn, Co and Ni. On further investigation, it has been found that the catalytic properties can be greatly tuned by considering the use of alkali metals and recently there has been a growing interest in the study of alkali metals such K, Rb and Cs containing materials as catalysts in various catalytic transformations [30-44]. Pure heteropolyacid catalysts shows low yields of benzaldehyde during styrene oxidation, probably due to its low surface area. However when protons are exchanged with alkali metal species such as K, Rb and Cs into the Keggin ion of heteropolyacids, an improvement in the surface area is achieved, also altering the acidity is accomplished to the benefit of the oxidation reaction. Recently, the oxidation of toluene over Cs exchanged phosphomolybdic acid (PMA) catalysts was reported. In this study, it was clear that the acidity and mesoporous nature of catalysts influenced the activity as well as the selectivity [21]. The oxidation of styrene was studied using oxidants such as air,  $H_2O_2$  and TBHP [5–13]. Of the oxidants employed, TBHP showed the highest selectivity towards the desired product although there was moderate conversion of the substrate [45].

In the present work, the liquid phase solvent free oxidation of styrene to benzaldehyde was studied over alkali metal exchanged heteropolyacid catalysts to assess the effect of the different alkali metals.

## 2 Experimental

## 2.1 Catalyst Synthesis

A series of alkali metal exchanged phosphomolybdic acid catalysts with different metal loadings, ranging from 1 to 3 wt% were synthesized by ion exchange according to a method reported previously [21]. In a typical synthesis, for a 1 wt% K loading, 0.138 g of  $K_2CO_3$  (Sigma Aldrich, SA) was dissolved in 10 mL of double distilled water. This solution was added drop wise to a solution of 3.65 g 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 then washed repeatedly with double distilled water. The solid was dried at 200 °C for 10 h. This catalyst with the theoretical formula,  $K_{1.0}PMo_{12}O_{40}$ , was denoted as 1KPMA. The other catalysts were prepared using the method described and were denoted in a similar manner to 1KPMA.

## 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 Å) at 40 kV and 30 mA. The measurements were recorded in steps of  $0.045^{\circ}$  with a count time of 0.5 s in the range of 5–40°. The surface area of catalysts was estimated using N<sub>2</sub> adsorption isotherms at – 196 °C by the multipoint BET method taking 0.162 nm<sup>2</sup> as its cross-sectional area. The pore size distribution was measured by N<sub>2</sub> adsorption-desorption isotherms using a Micrometrics ASAP 2020 multi-point BET surface area analyzer. Prior to N<sub>2</sub> gas sorption experiments, the materials were degassed under helium flow overnight at 200 °C using a Micrometrics Flow Prep 060 to remove adsorbed moisture or impurities from surface of the catalyst. The experiments were carried over a  $p/p^{\circ}$  pressure range of 0.05–0.9 by using nitrogen adsorption-desorption method. The surface area was calculated from adsorption isotherm points at relative nitrogen pressures  $(p/p^{\circ})$  between 0.05 and 0.3, while the pore size was calculated by BJH method. Infrared (IR) spectra were recorded on a Perkin Elmer Precisely equipped with a Universal ATR sampling accessory using a diamond crystal. All spectra generated were analyzed using Spectrum 100 software. Ex-situ pyridine adsorbed infrared 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 and the spectra were recorded on a PerkinElmer ATR spectrometer at room temperature. The surface morphology of the materials was obtained using scanning electron microscopy (SEM) utilizing a Leo 1450 Scanning Electron Microscope. Prior to SEM analysis, the samples were mounted on aluminium stubs using double sided carbon tape and subsequently gold spluttered using the Polaron E5100 coating unit. 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.

## 2.3 Catalytic Testing

Solvent free styrene oxidation experiments were conducted in a 50 mL round bottom flask at room temperature. In a typical run, 10 mmol of styrene, 10 mmol of tertiary butyl hydrogen peroxide (TBHP) and 0.1 g of the catalyst were placed in the flask, under stirring at room temperature and the reaction was constantly monitored by GC. The overall reaction is shown in Scheme 1. At the end of the reaction, the catalyst was removed, dried in an oven set at 200 °C and used for the same reaction.



## 3 Results and Discussion

#### 3.1 Catalyst Characterization

#### 3.1.1 X-ray Diffraction

X-ray diffraction patterns of the pure PMA and the K exchanged PMA catalysts are shown in Fig. 1a. Pure PMA shows the triclinic structure, whereas the cubic structure of the Keggin ion is observed for the K exchanged materials [21]. Sharp diffraction patterns were observed in the K exchanged PMA catalysts compared to pure PMA, revealing a more crystalline nature of the Keggin ion [21].



The XRD diffractograms of the 2 wt% loadings of K, Rb and Cs exchanged PMA catalysts, together with the pure PMA are shown in Fig. 1b. Similar profiles exhibited by the Rb and Cs exchanged catalysts to the K are observed and there is every indication that the Keggin ion is present.

#### 3.1.2 Infrared Spectroscopy

Infrared spectra of pure PMA and the modified KPMA catalysts show four well defined characteristic IR bands in the 500–1200 cm<sup>-1</sup> region (Fig. 2). These IR bands, in the case of pure PMA at 760, 889, 961 and 1058 cm<sup>-1</sup> are assigned to Mo–O<sub>c</sub>–Mo, Mo–O<sub>t</sub>–Mo, Mo=O and P–O bands, respectively [21]. In the modified catalysts, slight shifts in these bands are observed, probably implying exchange of the proton by the metal [21]. This was also true for the Rb and Cs exchanged catalysts as shown in Fig. S1, supplementary information.

The nature of acidic sites were examined by ex-situ pyridine adsorbed IR spectroscopy ( $1600-1400 \text{ cm}^{-1}$ ). The spectra of the parent PMA and K exchanged PMA catalysts are shown Fig. 3. The bands at 1539, 1487 and 1442 cm<sup>-1</sup> are attributed to Brønsted (B), Brønsted and Lewis (B+L) and Lewis (L) acidic sites, respectively [21]. The parent PMA contained more L acid sites that B acid sites. The Brønsted acidity increased when metal was incorporated and B acidity increase further with an increase in K loadings, but reached a maximum for the 2KPMA, thereafter showed a slight decrease for 3KPMA where Lewis acidity was dominant. The acidity of the Rb and Cs exchanged PMA-2 catalysts was also determined and compared with 2KPMA (Fig.



Fig. 1 a X-ray diffraction patterns of a PMA, b 1KPMA, c 2KPMA and d 3KPMA catalysts. b X-ray diffraction patterns of a PMA, b 2KPMA, c 2RbPMA and d 2CsPMA catalysts

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Fig. 2 IR spectra of a PMA, b 1KPMA, c 2KPMA, d 3KPMA and e regenerated 2KPMA catalysts



Fig. 3 Pyridine infrared spectra of a PMA, b 1KPMA, c 2KPMA, d 3KPMA and e regenerated 2KPMA catalysts

S2, supplementary information). 2KPMA contained more B acidic sites than both the 2RbPMA and 2CsPMA catalysts.

#### 3.1.3 Surface Studies

Surface properties of the catalysts such as surface area, pore volume and pore size of parent PMA and K-PMA catalysts were determined. The BET surface area of the catalysts increased with an increase in the metal loadings. However, this trend changed for all the catalysts with a loading of 3 wt% which showed a decrease in the surface area (Table 1). From the adsorption isotherms for PMA and the K exchanged catalysts, type IV isotherms with hysteresis loops

were obtained which indicated presence of mesoporous materials (Fig. S3, supplementary information). The high surface area 2KPMA which implies a lower Keggin anion density and this is reflected by lower crystalinity of the Keggin ion units obtained compared to other loadings. This result correlates well with the X-ray diffraction studies.

Comparing the isotherms of PMA and 2KPMA with its Rb and Cs counterparts (Fig. 4; Table 1), it can be seen clearly that all the materials possess mesoporous character in keeping with their type IV isotherms.

#### 3.1.4 Electron Microscopy

The surface morphology of PMA and metal exchanged PMA catalysts are shown in Fig. 5. The PMA shows bulk like morphology, whereas the metal exchanged catalysts exhibited a well-defined spherical morphology.

From HR-TEM images (Fig. 5), the metal exchanged catalysts display well defined particles with sizes ranging from 300 Å to 450 Å, whereas for the PMA, particles varied between 18,000 Å and 20,000 Å.

BF-STEM analysis of the metal exchanged PMA catalysts was carried out to map the structure and relative spatial distribution of the elements. Examples of some of these analyses for the K exchanged catalysts are shown in Fig. 6. In general, the metal content in the Keggin anion matches theoretical loadings (Table 1). These results are reinforced with data obtained by flame photometry and ICP analysis.

## 3.2 Catalytic Activity Studies

A detail study was performed on the oxidation of styrene to benzaldehyde to optimize the conditions at room temperature with various reaction parameters, such as, mole

Table 1 Elemental content and surface study data of PMA and metal exchanged catalysts

Catalyst	Surface area (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)	Pore diameter (Å)	Metal content calc. (wt%)	Metal content expt. (wt%) <sup>a</sup>	Metal content expt. (wt%) <sup>b</sup>	Keggin ion density (HPA/ nm <sup>2</sup> )
PMA	2.7	0.01	128	0	_	_	1.20
KPMA-1	66	0.02	81	1.0	1.1	0.9	0.0489
KPMA-2	133	0.05	46	2.0	2.0	1.8	0.0238
KPMA-3	101	0.03	43	3.0	3.0	2.7	0.0307
RbPMA-1	28	0.04	89	1.0	_	0.92	0.1126
RbPMA-2	181	0.07	40	2.0	1.9	1.89	0.0166
RbPMA-3	115	0.09	60	3.0	2.8	2.8	0.0252
CsPMA-1	25	0.03	80	1.0	0.9	0.95	0.1231
CsPMA-2	146	0.14	40	2.0	2.1	1.92	0.0197
CsPMA-3	80	0.08	50	3.0	2.9	3.0	0.0338

<sup>a</sup>Metal content obtained from STEM analysis

<sup>b</sup>Metal content obtained from Flame photometry and ICP analysis



Fig. 4 N<sub>2</sub> isotherms of a PMA, b 2KPMA, c 2RbPMA and d 2CsPMA catalysts

ratio of styrene to TBHP, amount of catalyst, various oxidants, reaction temperature, time on stream and recycling. Initially, blank reactions showed a 2% conversion with a 73 and 18% selectivity towards benzaldehyde and styrene, respectively, recorded at room temperature for 24 h. The pure phosphomolybdic acid showed a 4.5% conversion, with similar selectivity as the blank. Among the potassium exchanged catalysts, 2KPMA showed highest activity with an 80% selectivity towards benzaldehyde, probably attributed availability of active sites because of its large surface area and the surface acidity of the catalyst (Table 2). The results correlated well with the nature of acidic sites of the catalyst, in this case, Brønsted acidic sites [21]. From the pyridine infrared studies, 2KPMA had the highest surface Brønsted acidic sites than the other K exchanged PMA and PMA, itself. It is also possible that the mesoporous nature of the 2KPMA catalyst influences activity, since it has higher pore volume and surface area.

Styrene oxidation over the Rb and Cs exchanged PMA catalysts under similar reaction conditions indicate that the 2 wt% catalysts showed a similar activity trend to the 2KPMA catalyst, but not as efficient. The order of reactivity

of styrene oxidation follows the order, K > Rb > Cs, probably due to K being more efficient in generating TBHP radicals than Rb or Cs in the other catalysts.

Styrene oxidation was then conducted over the 2KPMA catalyst by varying the TBHP concentration. The results are tabulated in Table S1, supplementary information. These findings show that the activity increased initially with oxidant concentration. Thereafter, only a slight increase in the activity was observed, but the selectivity decreased marginally leading to the undesired diol. The catalytic reaction was also investigated using different amounts of the 2KPMA catalyst (Table S2, supplementary information). The styrene conversion increases with an increase in the catalyst amount, however, the selectivity towards benzaldehyde decreased significantly due to over oxidation of benzaldehyde to benzoic acid. It was also found that a lower concentration of reactant used gave higher activity and selectivity (Table S3, supplementary information). Of the various oxidants studied, TBHP is the only active oxidant at room temperature, producing a conversion of 8.5% and an 80% selectivity towards benzaldehyde. H<sub>2</sub>O<sub>2</sub> and air showed no activity at room temperature (Fig. S4, supplementary information).



Fig. 5 SEM and HR-TEM images of a PMA, b 2KPMA, c 2RbPMA and d 2CsPMA, respectively



Fig. 6 BF-STEM analysis of a 1KPMA, b 2KPMA and c 3KPMA catalysts

 
 Table 2
 Catalytic results over alkali metal exchanged phosphomolybdic acid catalysts

Catalyst	Conver-	Selectivity (%)			
	sion (%)	Benzaldehyde	Styrene oxide	Others <sup>a</sup>	
Blank	2.0	73	18	9	_
PMA	4.5	79	16	5	7.6
1KPMA	6.7	79	16	5	11.3
2KPMA	8.5	80	16	4	14.5
3KPMA	7.0	80	16	4	12.0
1RbPMA	6.2	79	15	6	10.5
2RbPMA	7.4	82	14	4	13.0
3RbPMA	6.3	80	15	5	10.8
1CsPMA	5.8	79	14	7	9.9
2CsPMA	6.5	80	15	5	11.1
3CsPMA	5.9	78	16	6	9.8

Reaction conditions: styrene (10 mmol), TBHP (10 mmol), catalyst=0.1 g, RT reaction temperature, reaction time=24 h

<sup>a</sup>Others: 1-phenylethane -1,2-diol, phenyl acetaldehyde;

<sup>b</sup>*TON* number of moles of product/number of moles of catalyst; reactions done in triplicate

A comparative study of the oxidation of styrene to other aromatic compounds such as benzyl alcohol and toluene was

	Table 3	Catalytic results over	KPMA-2 catalysts at	room temperature
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Substrate	Conversion (%)	Selectivity (%)			
		Benzalde- hyde	Styrene oxide	Others	
Toluene	1.2	99	0	1	
Styrene	8.5	80	16	4	
Benzyl alcohol	19.7	97	0	3	

Reaction conditions: substrate (10 mmol), TBHP (10 mmol), catalyst=0.1 g, reaction time=24 h

Others 1-phenylethane -1,2-diol, phenyl acetaldehyde, benzoic acid; reactions done in triplicate

conducted at room temperature over the 2KPMA catalyst (Table 3). Benzyl alcohol is more reactive than styrene and toluene. It is also highly selective towards benzaldehyde, probably due to the carbinol group being more reactive towards carbonyl compound than olefins and alkanes. A similar activity pattern was obtained with the 2RbPMA and 2CsPMA catalysts.

Time on stream studies was carried out to determine the influence of reaction time on conversion and selectivity



Fig. 7 Time on stream results for the oxidation of styrene over 2KPMA at room temperature

Table 4 Styrene oxide oxidation over 2KPMA catalyst

Reaction	Conversion (%)	Selectivity (%)			
time (h)		Phenyl acetalde- hyde	Benzaldehyde	Others	
1	97	71	22	7	
2	97.3	69	23	8	
3	97.9	68	24	8	
4	98	67	25	8	
5	98.1	66	26	8	

Reaction conditions: styrene oxide (10 mmol), TBHP (10 mmol), catalyst=0.1 g, *RT* reaction temperature

Others: 1-phenylethane -1,2-diol, benzoic acid; reactions done in triplicate

over the 2KPMA catalyst (Fig. 7). Initially, the selectivity towards benzaldehyde and styrene oxide was 77 and 28%, respectively. Over time, the selectivity towards benzaldehyde increased while there was a decrease in styrene oxide selectivity, indicating that the formation of benzaldehyde also occurs via styrene oxide. This result supports the assumption that there are most probably two pathways for benzaldehyde formation, one is C=C cleavage and the other is the cleavage of styrene oxide to produce benzaldehyde. To further gather evidence, the oxidation of styrene oxide was studied under present conditions. These results show that phenyl acetaldehyde together with benzaldehyde are produced (Table 4), providing some evidence that styrene oxidation proceeds via C=C cleavage to produce benzaldehyde.

Recycling experiments were carried out to investigate the stability of the 2KPMA catalyst (Figure S5, supplementary information). The catalyst was separated from aqueous layer, filtered and washed several times with organic solvent dichloromethane to remove any organic moiety on the surface of the catalyst and dried in an oven over night. It was then characterized by infrared spectroscopy (Figs. 2, 3) to observe any structural changes and any changes in the surface acidity. There was minimal change in structural and acidic properties of the catalysts. Although there was minimal change in the conversion, changes in the selectivity were evident. This could be due to the loss of metal after each cycle as corroborated by ICP analysis.

The mechanistic pathway for the synthesis of benzaldehyde from styrene is well known [21, 45]. For the selective synthesis of benzaldehyde from styrene over KPMA catalysts, the proposed path ways are shown in Scheme 2. Initially, the catalyst reacts with TBHP to produce *tert*-butyl peroxy and *tert*-butyloxy radicals. These radicals then react with styrene to produce benzaldehyde as major product and styrene oxide. Styrene oxide can undergo isomerization and hydrolysis to produce phenyl acetaldehyde and 1,2diol, respectively. Further oxidation of the diol produces benzaldehyde. Styrene also forms dioxitane and further cleavage results in the formation of benzaldehyde and formaldehyde.

## 4 Conclusion

Eco-friendly heterogeneous metal exchanged phosphomolybdic acid catalysts were efficient for the solvent free oxidation of styrene to benzaldehyde. The 2KPMA catalyst performed much better than its Rb and Cs counterparts in terms of selectivity towards benzaldehyde. The catalytic activity correlated well with the physical and chemical properties of the catalyst. The metal exchanged catalysts with a 2 wt% loading showed the highest surface areas ranging between 130 and 180 m<sup>2</sup> g<sup>-1</sup>, all of them exhibiting Type IV isotherms, clearly demonstrating their mesoporous nature. XRD patterns and infrared spectroscopy showed that the primary structure of the Keggin ion remains intact after incorporation of the metal, while pyridine adsorbed spectroscopy shows the existence of Brønsted as well as Lewis acid sites on the surface. The surface of all the catalysts possessed a uniform spherical morphology and from BF STEM analysis, an even distribution of metals in the catalysts were observed. The regenerated catalyst showed minimal change in structural and acidic properties, reflected in the catalytic results done up to three cycles.



Scheme 2 Proposed reaction mechanism of oxidation of styrene to benzaldehyde over KPMA catalysts

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## **Compliance with Ethical Standards**

**Conflict of interest** There is no conflict of interest by Jhansi Pedada, Holger B. Friedrich and Sooboo Singh.

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