Solvent free transformation of benzyl alcohol to benzaldehyde over copper and zinc modified phosphomolybdic acid catalysts at room temperature

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Copper and zinc exchanged heteropolyacid catalysts were synthesised and characterised by various techniques such as X-ray diffraction, infrared spectroscopy, pyridine adsorbed infrared spectroscopy, BET surface studies, ^{31}P NMR spectroscopy and inductively coupled plasma-optical emission spectroscopy to investigate its physico-chemical properties. Powder X-ray diffractograms showed that crystallites of the Keggin ion of the heteropolyacid were present and were retained after metal modification. Pyridine adsorbed infrared indicated that the Brønsted/Lewis acid site ratio increased in the metal exchanged phosphomolybdic acid catalysts, whereas there was a decrease in this ratio for the modified phosphotungstic acid catalysts. ^{31}P NMR spectra showed that the metal was successfully exchanged with protons and was not incorporated in the primary structure of heteropolyacid catalyst, thus maintaining the Keggin ion. In the oxidation of benzyl alcohol over metal exchanged catalysts, the Zn exchanged phosphomolybdic acid catalysts showed higher oxidation activity and correlated well with the acidity of the catalysts.

Keywords: PMA, PTA, benzyl alcohol, benzaldehyde, TBHP

Oplosmiddelvrye-transformasie van bensielalkohol na bensaldehied oor koper- en sink-gemodifiseerde fosfomolibdeensuur-katalisators by kamertemperatuur: Koper- en sinkuitgeruilde heteropolisuurkatalisators is gesintetiseer en gekarakteriseer deur verskeie tegnieke soos X-straaldiffraksie (XSD), infrarooispektroskopie (IR), piridien-geadsorbeerde infrarooispektroskopie, BET-oppervlakanalise, ^{31}P KMR-spektroskopie en Induktief Gekoppelde Plasma Optiese Emissiespektroskopie (IGP-OES) om die fisies-chemiese eienskappe daarvan te ondersoek. Poeier-X-straaldiffraktogramme het getoon dat kristalliete van die Keggin-ioon van die heteropolisuur teenwoordig was en dat dit behoue gebly het na metaalmodifikasie. Piridien-geadsorbeerde infrarooispektroskopie het aangedui dat die Brønsted/Lewis-suurplekverhouding toegeneem het in die metaaluitgeruilde fosfomolibdeensuur-katalisators, terwyl daar 'n afname was in hierdie verhouding vir die gemodifiseerde fosfowolframsuurkatalisators. ^{31}P NMR-spektra het getoon dat die metaal suksesvol met protone uitgeruil is en nie geïnkorporeer is in die primêre struktuur van heteropolisuurkatalisator nie; dus is die Keggin-ioon behou. In die oksidasie van bensielalkohol deur metaaluitgeruilde katalisators, het die Zn-uitgeruilde fosfomolibdeensuur-katalisators hoër oksidasie-aktiwiteit getoon wat goed gekorreleer het met die suurheid van die katalisators.

Trefwoorde: PMA, PTA, bensielalkohol, bensaldehied, TBHP

Introduction

The conversion of benzyl alcohol to benzaldehyde under eco-friendly conditions remains attractive and a challenge to both the academic sector and the chemical industry, due to the importance of benzaldehyde in basic and applied research (Fey et al., 2001; Franz et al., 1991; Regen and Koteel, 1977; Sheldon, 1991; Xia et al., 2005). Benzaldehyde is a versatile aromatic carbonyl compound that is used in the perfumery, cosmetics and agrochemical industries. Several catalytic materials have been developed to produce benzaldehyde from benzyl alcohol through homogeneous and heterogeneous oxidation catalysis (Bordoloi et al., 2008; Chen et al., 2014; Farsani et al., 2014; Nadealian et al., 2012; Nikbakht et al., 2015; Pathan and Patel, 2104;

Tundo et al., 2010). In homogeneous catalysis, difficulty in retrieving the catalyst is encountered and large amounts of solvents are required which is expensive and not eco-friendly. As a result, solvent free heterogeneous catalysts have received more attention because of easy recovery and recyclability. Among the various materials studied, solid acid catalytic materials such as heteropolyacids have gained popularity due to their bifunctional acidic and redox character (Choi et al., 2014; Choudhary et al., 2009; Fan et al., 2016; Farhadi and Zaidi, 2009; Haimov and Neumann, 2002; Hasannia and Yadollahi, 2015; Ma et al., 2017; Palermo et al., 2014; Park et al., 2015; Zhao et al., 2013). In addition, a major advantage is that its acid-base and redox properties can be tuned by the simple exchange of protons with metals.

Zn and Cu exchanged heteropolyacid catalysts were studied for several reactions such as the Knoevenagel condensation reaction, oxidation reactions and acid catalysed organic transformations (Jagadeeswaraiah et al., 2014; Patil et al., 2014; Rao et al., 2012; Pope, 1991; Viswanadham et al., 2016). Khabazzadeh et al. (2009) developed $Cu_{1.5}PMo_{12}O_{40}$ and $Cu_{1.5}PW_{12}O_{40}$ reusable and efficient catalysts for the preparation of 1-amidoalkyl-2-naphthols, while Patil et al. (2014) studied the low temperature activation of methane over a Zn exchanged heteropolyacid resulting in the selective formation of methanol and acetic acid during the reaction. Jagadeeswaraiah et al. (2014) showed that the addition of Zn^{2+} ions into the secondary structure of heteropolyacids was efficient during glycerol carbonate synthesis from glycerol and urea, whereas Rao et al. (2012) who prepared niobia supported on Zn exchanged phosphotungstic acid, observed that the catalysts exhibited good activity during the conversion of furfuryl alcohol to butyl levulinate and related this to the acidic sites of catalysts. In a study conducted using Cu exchanged phosphomolybdic acid (Cu–PMA), the authors found that the Cu catalyst showed better catalytic performance than the blank, i.e. phosphomolybdic acid (PMA). This significant increase in the activity of the catalyst was correlated to its structural and acidic properties.

The objective of this investigation is to develop several Cu and Zn exchanged heteropolyacid catalysts for the oxidation of benzyl alcohol and to understand the influence of various reaction parameters such as reaction temperature, catalyst loading, mole ratio of reactant to oxidant, various oxidants, time-on-stream and regeneration studies for this reaction.

Experimental
Catalyst preparation

$H_3PMo_{12}O_{40}$ and $H_3PW_{12}O_{40}$, zinc sulphate hydrate, copper sulphate hydrate and barium hydroxide were procured from Sigma-Aldrich (RSA). The Zn and Cu exchanged catalysts were synthesised according to a method described previously (Pope, 1991). In a typical synthesis, 0.10 M of barium hydroxide was added to an aqueous mixture of 0.22 M of phosphomolybdic acid in 5 mL distilled water. Thereafter, 0.15 M of $CuSO_4.5H_2O$ was added to replace barium with copper by precipitating the barium as $BaSO_4$. The $Cu_{1.5}PMo_{12}O_{40}$ solid was recovered by centrifugation and dried 100°C for 10 h in an oven. The catalyst was denoted as Cu-PMA. Similarly, the other catalysts, viz. $Cu_{1.5}PW_{12}O_{40}$, $Zn_{1.5}PMo_{12}O_{40}$ and $Zn_{1.5}PW_{12}O_{40}$, denoted as Cu-PTA, Zn-PMA and Zn-PTA, respectively, were synthesised.

Catalyst characterisation

Powder X-ray diffraction patterns of selected catalysts were obtained using a Bruker D8 Advance diffractometer coupled with a Lynxeye detector, equipped with a Cu Kα radiation source (λ = 1.5406Å) 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 5 to 40°. The surface area was determined using N_2 adsorption isotherms at -196°C by the multipoint BET method taking 0.162 nm^2 as the cross-sectional area. Prior to these experiments, the materials were degassed under helium flow overnight at 200°C using a Micrometrics Flow Prep 060 degasser and all experiments were carried out at a relative pressure range (P/Po) 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 analysed using Spectrum 100 software. Ex-situ pyridine adsorbed FT-IR experiments were carried out 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. The metal content was determined by ICP-OES analysis using a PerkinElmer Optima 5300 DV spectrometer, while ^{31}P NMR spectra were recorded on a Bruker Advance 400 MHz spectrometer where chemical shifts were reported relative to 85% H_3PO_4 in D_2O, used as an external standard at 298 K.

The solvent free oxidation of benzyl alcohol was studied in a 10 mL round bottom flask at room temperature. In a typical experiment, 10 mmol of benzyl alcohol, 10 mmol of 70% TBHP and 0.05 g of the catalyst were placed in the flask, under stirring. The reaction was constantly monitored by a Perkin Elmer Auto gas chromatograph equipped with a flame ionisation detector (GC-FID), using TurboMatrix™ software. The catalyst was recycled and re-used for the reaction by repeating the procedure described.

Results and discussion

Characterisation of catalysts

X-ray diffraction profiles of the parent and the metal exchanged heteropolyacid catalysts are shown in Figure 1. The pure phosphomolybdic acid (PMA), Cu-PMA and Zn-PMA catalysts exhibit diffraction peaks at 2θ = 8.2°, 9.1°, 26.5° and 28.8° and represent characteristic diffraction peaks of the primary structure of a Keggin ion (Viswanadham et al., 2016). However, in the case PTA, Cu-PTA and Zn-PTA catalysts, the characteristic Keggin ion of the parent PTA remained intact after Cu and Zn loadings. Infrared spectroscopy also confirms the primary structure of the Keggin ion. Ex-situ pyridine studies were conducted to assess the relative acidity of the catalysts. The infrared bands located at 1529-1538, 1483-1487, 1439-1442 cm⁻¹ represents Brønsted (B), Brønsted + Lewis (B+L) and Lewis (L) acidic sites, respectively (Figure 2).

The B/L acidic sites ratio increased significantly for the metal exchanged-PMA catalysts, but decreased in the case of PTA
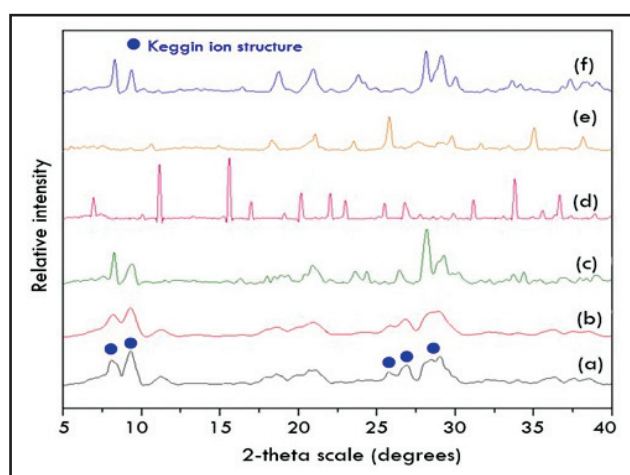

FIGURE 1: Powder XRD profile of (a) PMA, (b) Cu-PMA, (c) Zn-PMA, (d) PTA, (e) Cu-PTA, (f) Zn-PTA catalysts
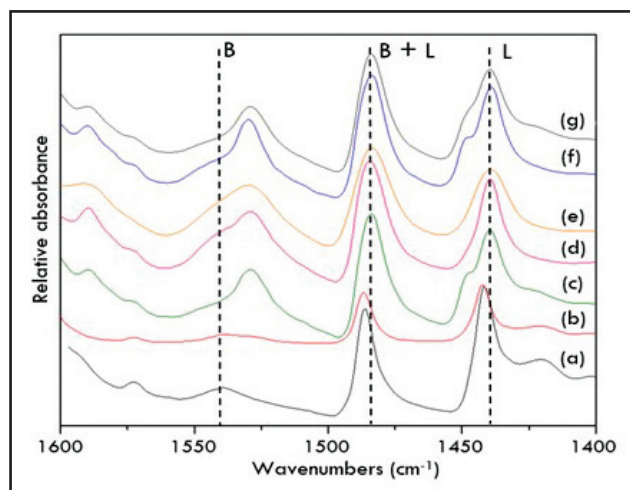

FIGURE 2: Pyridine finger- print infrared spectra of (a) PMA, (b) Cu-PMA, (c) Zn-PMA, (d) PTA, (e) Cu-PTA, (f) Zn-PTA and (g) regenerated Zn-PMA catalysts (B = Brønsted, L = Lewis)

catalysts. ³¹P NMR spectra of the parent, Cu and Zn metal exchanged heteropolyacid catalysts show the presence of a single signal at -3.89 ppm due to the phosphorus atoms in the PMA, whereas for PTA it was observed at -15.20 ppm. After exchange of the Cu with Zn, the catalysts exhibit a slight shift in the peak, but have no significant effect in the phosphorus environment which is maintained. These results match well with studies conducted by other researchers (Rao et al., 2012; Viswanadham et al., 2016). ICP analysis and BET surface area of the metal exchanged heteropolyacid catalysts results are tabulated in Table 1. These findings show that theoretical metal loadings of the exchanged catalysts correlate well with experimental values. The regenerated catalyst shows minimal change in the metal content. There was an increase in the surface area of the copper exchanged catalysts compared to its parent, whereas a decrease was observed for the Zn catalysts, probably due to metal size.

The ³¹P NMR spectra of the parent, Cu and Zn metal exchanged heteropolyacid catalysts show the presence of single signal at -3.89 ppm due to the phosphorus atoms in the PMA, whereas for PTA it was observed at -15.20 ppm. After exchange with Cu and Zn, the catalysts exhibit slight shift in the peak, which has no effect in the phosphorus environment which is maintained and these results match well with studies conducted by other researchers (Rao et al., 2012; Viswanadham et al., 2016).
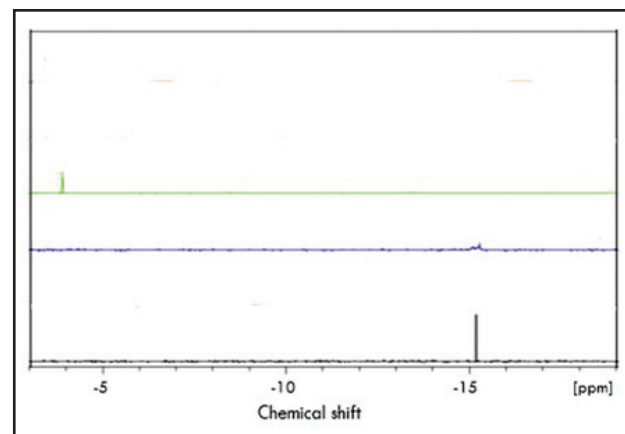

FIGURE 3: ³¹P NMR spectra of (a) PMA, (b) 0.5CuPTA and (c) PTA

TABLE 1: BET surface area, elemental composition and B/L acidic sites of Cu and Zn exchanged heteropolyacid catalysts

Catalyst	Surface area (m²/g)	Cu/Zn loadings Calc. (%)	Cu/Zn loadings Expt. (%)	B/L ratio
PMA	2.5	--	--	0.44
Cu-PMA	6.9	1.5	1.42	0.46
Zn-PMA	2.1	1.5	1.46	0.59
PTA	4.5	--	--	0.60
Cu-PTA	7.5	1.5	1.45	0.54
Zn-PTA	1.8	1.5	1.49	0.55
Zn-PMA (regen.)	2.0	1.5	1.44	0.58

B/L = Brønsted/Lewis

Catalytic testing

The catalytic properties were studied considering various reaction parameters such as nature of catalyst, catalyst loading, TBHP concentration, type of oxidant, concentration of reactant and reaction temperature. Time on stream and regeneration experiments were also conducted. The catalytic oxidation of benzyl alcohol was carried out over the Cu and Zn exchanged heteropolyacid catalysts under a nitrogen atmosphere and the results are presented in Table 2.

Blank experiments conducted under similar reaction conditions showed an 8.0% benzyl alcohol conversion with high selectivity towards benzaldehyde. The parent heteropolyacids, phosphomolybdic acid showed a 14.5% conversion, whereas phosphotungstic acid, a 13.5% conversion. In both cases, benzaldehyde was the major product obtained with very high selectivity. Among the Cu and Zn exchanged heteropolyacid catalysts, Zn-PMA catalysts performed slightly better compared to parent and other metal exchanged heteropolyacid catalysts, probably due to a slightly higher B/L acidic site ratio.

The catalytic properties of different amounts of Zn-PMA catalysts were studied and results are presented in Table 3.

These findings indicate that, as the loading increases from 0.025 to 0.05 g, the catalytic activity increased. Catalysts with higher loadings resulted in a slight increase in the catalytic activity. The optimum catalyst amount was 0.05 g and was used in subsequent studies involving other parameters. An increase in the TBHP concentration resulted in an increase in the oxidation activity, but a decrease in the selectivity

towards benzaldehyde. It was concluded that the optimum value of the TBHP was 10 mmol TBHP by considering both the conversion and selectivity towards benzaldehyde (Table 4).

The oxidation ability of various oxidants such air, H2O2 and TBHP for benzyl alcohol oxidation were assessed over Zn-PMA catalysts (Table 5).

These findings indicate that TBHP was most efficient during the oxidation reaction. However, air was more selective, although the activity was rather poor at room temperature. The effect of benzyl alcohol concentration over Zn-PMA catalysts was studied under the same reaction conditions and results are presented in Table 6. The conversion was highest for a 2% feedstock, however the selectivity towards benzaldehyde was low and more benzoic acid was observed.

There was a decrease in conversion at higher concentrations of benzyl alcohol, probably due to dilution. The effect of reaction time and catalyst recyclability was studied and the results are shown in Figure 4A and B, respectively. From the figure, the activity increased with an increase in reaction time, however there was a decrease in the selectivity towards benzaldehyde, probably due to over oxidation to benzoic acid which showed a relative increase over time. Once regenerated, the Zn-PMA catalyst was subjected to

TABLE 2: Catalytic results of the oxidation of benzyl alcohol over parent and metal exchanged heteropolyacid catalysts

Catalyst	Conversion (%)	Selectivity (%)		TON
		Benzaldehyde	Benzoic acid	
Blank	8	94	6	–
PMA	15	96	4	30
Cu-PMA	23	95	5	48
Zn-PMA	25	85	15	53
PTA	14	98	2	28
Cu-PTA	22	96	4	46
Zn-PTA	24	94	6	50

Reaction conditions: benzyl alcohol (10 mmol), TBHP (10 mmol), catalyst (0.1 g), reaction temperature = room temperature, reaction time = 24 h, TON = number of moles of products/number of moles of catalyst. (Experiments done in triplicate).

TABLE 3: Catalytic results of benzyl alcohol oxidation over various catalytic amounts of Zn exchanged PMA catalysts

Catalyst amount (g)	Conversion (%)	Selectivity (%)	
		Benzaldehyde	Benzoic acid
0,025	23	76	24
0,05	40	83	17
0.1	25	85	15
0.2	26	86	14

Reaction conditions: benzyl alcohol (10 mmol), TBHP (10 mmol), reaction temperature = room temperature, reaction time = 24 h. (Experiments done in triplicate).

TABLE 4: Catalytic results of benzyl alcohol oxidation with various amounts of TBHP over Zn exchanged PMA catalysts

TBHP (mmol)	Conversion (%)	Selectivity (%)	
		Benzaldehyde	Benzoic acid
5	22	98.0	2.0
10	40	83.5	16.5
20	47	76.0	24.0
30	50	74.0	26.0

Reaction conditions: benzyl alcohol (10 mmol), TBHP (5–30 mmol), catalyst (0.05 g), reaction temperature = room temperature, reaction time = 24 h. (Experiments done in triplicate).

TABLE 5: Catalytic results of benzyl alcohol oxidation using different oxidants over Zn exchanged PMA catalysts

Oxidant	Conversion (%)	Selectivity (%)	
		Benzaldehyde	Benzoic acid
Air	2	94.5	5.5
H_2O_2	6	58.5	41.5
TBHP	40	83.5	16.5

Reaction conditions: benzyl alcohol (10 mmol), catalyst (0.05 g), reaction temperature = room temperature, reaction time = 24 h. (Experiments done in triplicate).

TABLE 6: Catalytic oxidation results with various concentrations of benzyl alcohol over Zn exchanged PMA catalysts

Benzyl alcohol (mmol)	Conversion (%)	Selectivity (%)	
		Benzaldehyde	Benzoic acid
2	75	76.0	24.0
4	58	79.0	21.0
8	47	80.0	20.0
10	40	83.5	16.5

Reaction conditions: TBHP (10 mmol), catalyst (0.05g), reaction temperature = room temperature, reaction time = 24 h. (Experiments done in triplicate).
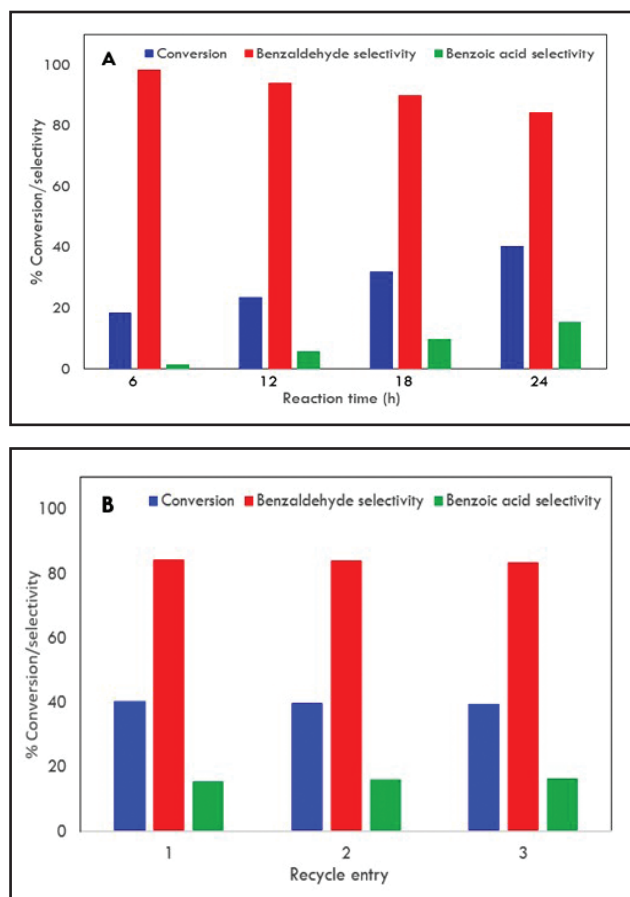
FIGURE 4: Oxidation of benzyl alcohol over Zn-PMA catalysts as a function of time (A) and over three cycles (B)

further studies. There is a slight decrease in the activity over three cycles which correlates with the acidity of used catalysts. Also, there is minimal change in Zn content after regeneration.

Conclusion

Zn exchanged heteropolyacid catalysts exhibit higher oxidation ability than Cu catalysts in the conversion of benzyl alcohol to benzaldehyde and this is related to the acidity of the catalysts. XRD and infrared results confirm that the primary structure of the Keggin ion is retained even after metals are incorporated in its structure, while pyridine adsorbed infrared spectroscopy showed that the incorporation of metal in PMA resulted in an increase in the B/L acidic sites ratio, whereas it decreased for the metal exchanged PTA catalysts. 31P NMR spectra clearly shows that the phosphorus environment is retained, indicating that metal successfully exchanged with protons but did not interfere with the primary structure of heteropolyacid. The Zn exchanged PMA catalysts produced a 97% conversion of benzyl alcohol with a 76% benzaldehyde selectivity.

Acknowledgments

Conflict of interest

The authors declare that there is no conflict of interest.

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