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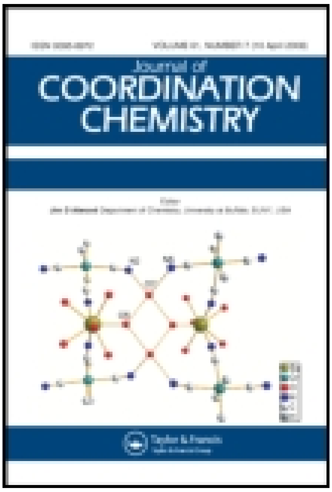

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Keggin-type mono lacunary silicotungstate supported onto zirconia: synthesis, characterization, and esterification reaction

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A solid acid catalyst comprising of lacunary silicotungstate and zirconia was synthesized and characterized by physicochemical techniques. Surface morphologies of support and catalyst were studied by scanning electron microscopy. Catalytic properties were evaluated for the esterification of *n*-butanol with acetic acid. Esterifications of sec-butanol and isobutanol with acetic acid as well as the esterification of *n*-butanol with different acids such as formic acid and propionic acid were carried out under optimized conditions. Catalytic activities for calcined as well as recycled catalysts were also evaluated for the esterification under optimized condition.

Keywords: Lacunary silicotungstate; Keggin; Heterogeneous catalysis; Esterification

1. Introduction

Lacunary polyoxometalates (LPOMs) represent an important class of compounds due to their unique structural as well as chemical properties. LPOMs can be obtained by removing one or two of the MO units from the fully occupied polyoxometalates (POMs), $[XM^{VI}_{12}O_{40}]^{n-}$, giving rise to mono- and di-lacunary POMs, $[XM^{VI}_{11}O_{39}]^{(n+4)-}$ and $[XM^{VI}_{10}O_{36}]^{(n+5)-}$, respectively [1]. LPOMs can be used for applications in medicinal chemistry [2], solid-state chemistry [3], electrocatalysis [4], and catalysis [5–7].

Among LPOMs, lacunary silicotungstate has been well explored by various groups [8–14]. The catalytic activity of the LPOMs including monolacunary silicotungstate has been reported by Hill and co-workers [5], who reported catalytic systems for the effective and selective aerobic oxidation of H_2S to S. Detailed studies have been carried out on oxidation reactions using dilacunary silicotungstates by a number of groups [15–21]. Acid catalysis over divacant silicotungstates was also reported by Yoshida *et al.* [20].

Few reports are available on the incorporated lacunary silicotungstates. Hu *et al.* [22] reported the synthesis, characterization, and photochemical properties of ordered

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macroporous hybrid silica materials based on mono-vacant silicotungstate. Guo *et al.* [23] reported the catalytic oxidation of styrene with H_2O_2 by the SBA-15-incorporated divacant Keggin $[(n\text{-}C_4H_9)_4N]_4[\gamma\text{-}SiW_{10}O_{34}(H_2O)_2]$.

No report is available on the study of mono-lacunary silicotungstate supported on metal oxides. Recently, our group reported detailed study on supported mono-lacunary phosphotungstate [24, 25]. The obtained results, especially for acid-catalyzed reactions, are superior, encouraging us to extend our work for lacunary silicotungstate.

In this article we report the synthesis, characterization, and catalytic evaluation of lacunary silicotungstates supported on to zirconia. A series of catalysts containing 10–40% loading of lacunary silicotungstates onto ZrO_2 were synthesized and characterized by various physicochemical techniques, such as chemical stability, elemental analysis, thermo-gravimetric analysis (TGA), differential scanning calorimetry (DSC), Fourier transform infrared (FT-IR), diffuse reflectance spectroscopy (DRS), and surface area measurement (BET method). Further, the surface morphologies of support and catalyst were studied by scanning electron microscopy (SEM). Their catalytic properties were evaluated for the esterification of *n*-butanol with acetic acid. The esterifications of sec-butanol and isobutanol with acetic acid as well as the esterification of *n*-butanol with different acids were carried out under optimized conditions. Further, the selected material was calcined at 200°C, 300°C, and 400°C. Catalytic properties for calcined as well as recycled catalysts were evaluated for esterification under optimized condition.

2. Experimental

2.1. *Materials*

All chemicals used were of A.R. grade. Sodium silicate (Loba chemie, Mumbai), sodium tungstate (S.D. Fine Chem, Mumbai), and zirconium oxychloride (Loba chemie, Mumbai) were used as received. Ethanol, *n*-butanol, sec-butanol, isobutanol, formic acid, glacial acetic acid, propionic acid, and liquid ammonia were obtained from Merck and used as received.

2.2. *Synthesis of the catalyst*

Synthesis of the catalyst was carried out in three steps.

2.2.1. Synthesis of hydrous zirconia (ZrO_2). The first step involves the synthesis of the support, (ZrO_2), synthesized by the method reported by Bhatt and Patel [26].

2.2.2. Synthesis of lacunary silicotungstate ($Na_8[SiW_{11}O_{39}]\cdot 11H_2O$). The second step involves the synthesis of lacunary silicotungstate. Sodium tungstate (0.22 mol, 7.2 g) and sodium silicate (0.02 mol, 0.56 g) were dissolved in 150–200 mL of doubly-distilled water and heated to 80–90°C followed by the addition of concentrated nitric acid to adjust the pH to 4.8. The volume was then reduced to half by evaporation and the heteropoly anion was separated by liquid–liquid extraction with 80–100 mL of acetone.

The extraction was repeated until the acetone extract showed the absence of NO_3^- (ferrous sulfate test). The extracted sodium salt was dried in air. The resulting material is designated as SiW_{11}.

2.2.3. Supporting SiW_{11} onto ZrO_2. The third step involves the supporting of SiW_{11} onto ZrO_2. A series of catalysts containing 10–40% SiW_{11} were synthesized by impregnating 1 g of ZrO_2 with an aqueous solution of SiW_{11} (0.1–0.4 g/10–40 mL of doubly distilled water) and dried at 100°C for 10 h. The obtained materials were designated as $(SiW_{11})_1/ZrO_2$, $(SiW_{11})_2/ZrO_2$, $(SiW_{11})_3/ZrO_2$, and $(SiW_{11})_4/ZrO_2$. The best catalyst, $[(SiW_{11})_2/ZrO_2]$, was calcinated at 200, 300, and 400°C in air for 5 h and designated as $(SiW_{11})_{22}/ZrO_2$, $(SiW_{11})_{23}/ZrO_2$, and $(SiW_{11})_{24}/ZrO_2$, respectively.

2.3. *Characterization*

Different mineral acids and alcohols were used for checking the chemical stability of the material. The estimation of tungsten [27] as well as silicon [28] was carried out gravimetrically. TGA curve of the sample was obtained using the SEIKO Thermal Analysis System SS 5100 TG/DTA 32. Different mineral acids and alcohols were used for checking the chemical stability of the material. The DSC of the sample was performed on a METTLER STAR SW 8.10. The FT-IR spectrum of the sample was obtained using a KBr wafer on a Perkin-Elmer instrument. The UV-Vis-DR spectrum was recorded at ambient temperature on a Perkin-Elmer 35 LAMDA instrument using a 1 cm quartz cell. The adsorption–desorption isotherms of samples were recorded on a micrometics ASAP 2010 surface area analyzer at −196°C. From the adsorption–desorption isotherms, specific surface area was calculated using the BET method. The surface morphologies of the support and catalyst were studied by SEM using a Jeol SEM instrument (model-JSM-5610LV) with scanning electron electrode at 15 kV. Scanning was done at 1 mm range.

2.4. *Catalytic reaction*

The synthesized catalyst was evaluated for esterification reactions. The esterification reaction of *n*-butanol with acetic acid (mole ratio 1 : 4.4, 9.16 : 25.2 mL) was carried out in a 50 mL glass reactor provided with a double-walled air condenser, Dean–Stark apparatus, magnetic stirrer, and a guard tube. The resultant mixture was heated at 80°C for 4 h. Dean–Stark apparatus was attached to a round-bottom flask to separate the water formed during the reaction. Similar reactions were carried out with different % loading of SiW_{11} onto ZrO_2, different alcohol (*n*-butanol) to acid (acetic acid) ratio, and different amount of catalyst. Under optimized conditions, esterification was carried out for calcined as well as recycled catalysts. The esterification of sec-butanol (9.15 mL) and isobutanol (9.27 mL) with acetic acid (25.2 mL) as well as the esterification of *n*-butanol (9.16 mL) with formic acid (16.9 mL) and propionic acid (32.9 mL) were also carried out under optimized conditions. The product ester was analyzed on a (Nucon-5700) gas chromatograph using Carbowax 20 column.

3. Results and discussion

Leaching of the active species from the support makes the catalyst unattractive and hence it is necessary to study the stability as well as leaching of SiW_{11} from the support. HPA can be quantitatively characterized by the heteropoly blue color, which is observed when it reacted with a mild reducing agent such as ascorbic acid. In the present study, this method was used for determining the leaching of SiW_{11} from the support. Standard samples amounting to 1–5% of SiW_{11} in water were prepared. To 10 mL of the above samples, 1 mL of 10% ascorbic acid was added. The mixture was diluted to 25 mL. The resultant solution was scanned at a λ_{max} of $785\,cm^{-1}$ for its absorbance values. A standard calibration curve was obtained by plotting values of absorbance with percentage solution. One gram of $(SiW_{11})_2/ZrO_2$ with 10 mL *n*-butanol was refluxed for 4 h. Then 1 mL of the supernatant solution was treated with 10% ascorbic acid. No development of blue color indicates no leaching. The same procedure was repeated with water, isobutanol, sec-butanol, formic acid, acetic acid, propionic acid, and with the filtrate of the reaction mixture after reaction. The above procedure was followed for all catalysts and no leaching was found. The study indicates the presence of chemical interaction between the SiW_{11} and the ZrO_2, as well as the stability of resulting catalysts under reaction conditions.

The chemical stability of the materials has been checked in different mineral acids such as HCl, H_2SO_4, HNO_3 and bases such as NaOH, Na_2CO_3 up to $4\,mol\,L^{-1}$ concentration. The present material shows no changes in color or form, indicating their stability.

The sodium salt of lacunary silicotungstate has been analyzed for Si and W gravimetrically. The results obtained are in good agreement with theoretical values. Theoretical: W = 65.4%; Si = 0.91%; observed: W = 63.8%; Si = 0.89%. The number of water molecules, determined from TGA curve (figure S1), was 11.

From the elemental as well as the thermal analysis, the chemical formula of the isolated complex is proposed as $Na_8[SiW_{11}O_{39}]\cdot 11H_2O$. TGA shows that SiW_{11} is less stable (350°C) than $(SiW_{11})_2/ZrO_2$ (475°C). This shows that supporting of SiW_{11} on the surface of ZrO_2 increases the thermal stability of SiW_{11}. An increase in thermal stability indicates the presence of chemical interaction between SiW_{11} and ZrO_2.

The DSC thermogram of SiW_{11} shows an endothermic peak in the range of 80–180°C (figure S2), indicating loss of adsorbed water molecules. The DSC for the supported catalyst $[(SiW_{11})_2/ZrO_2]$ shows an endothermic peak at 50–100°C (figure S2), indicating loss of adsorbed water; the endothermic peak at 475°C indicates the decomposition of the supported species. The above study indicates that SiW_{11} is thermally stable to 475°C when supported onto ZrO_2.

The FT-IR spectra of ZrO_2 (figure S3) shows a broad band in the region of $3400\,cm^{-1}$, attributed to asymmetric hydroxo (–OH) and aquo (H_2O) stretches. Two types of bending vibrations at 1600 and $1370\,cm^{-1}$ are observed indicating the presence of (H–OH) and (O–H–O) bending, respectively. The FT-IR spectra of SiW_{11} (figure S3) shows bands at 886, 795, and $727\,cm^{-1}$ corresponding to W–O–W stretches and at $987\,cm^{-1}$ to Si–O stretches. The stretching vibration at $948\,cm^{-1}$ corresponds to W=O. These bands are in good agreement with those reported in [15]. These vibrational bands are also observed in the synthesized materials $[(SiW_{11})_2/ZrO_2]$ confirming the presence of these groups in the synthesized materials.

Table 1. Surface area for ZrO_2, $(SiW_{11})_1/ZrO_2$, $(SiW_{11})_2/ZrO_2$, $(SiW_{11})_3/ZrO_2$, and $(SiW_{11})_4/ZrO_2$.

Catalyst	Surface area ($m^2\,g^{-1}$)
ZrO_2	170
$(SiW_{11})_1/ZrO_2$	269
$(SiW_{11})_2/ZrO_2$	325
$(SiW_{11})_3/ZrO_2$	341
$(SiW_{11})_4/ZrO_2$	240

The DRS gives information about the non-reduced heteropoly anion due to charge transfer from oxygen to metal. DRS of SiW_{11} and $(SiW_{11})_2/ZrO_2$ (figure S4) show absorption maxima at 200–210 and 260–268 nm, attributed to oxygen–tungsten CT at W=O and W–O–W bonds, respectively. These values are in good agreement with values reported in [15], confirming the presence of the undegraded SiW_{11} in the catalyst.

The values for BET surface area measurements are shown in table 1. The larger surface area of all catalysts as compared to that of the support was because of the supporting of SiW_{11}, as expected. Initially the value for surface area increases with increase in loading from 10% to 30% while it decreases from 30% to 40%. This may be due to the formation of multilayers of active species, SiW_{11}, onto ZrO_2, which may cause blocking/stabilization of active sites on the monolayer.

The SEM of ZrO_2 and $(SiW_{11})_2/ZrO_2$ are shown in figure S5. The surface of the support is distinctly altered, exhibiting considerable surface shining after supporting of the SiW_{11} (figure S5c). Picture taken at higher magnification (figure S5d, 500×) clearly shows the alternation and shining of the surface.

3.1. *Catalytic study*

Esterification is a straightforward reaction subjected to general Bronsted acid catalysis. The esterification reactions of different alcohols with acetic acid and different acids with *n*-butanol have been carried out. The yields can be increased by increasing the concentration of either alcohol or acid. In practical situation when one wants to prepare an ester in maximum yield, the reactant that is less expensive of the two is taken in excess.

3.1.1. Effect of % loading of SiW_{11} onto ZrO_2. The esterification reaction was carried out with unsupported SiW_{11} (active amount 25 mg) as well as with catalysts having different % loading of SiW_{11} onto ZrO_2. Results are shown in figure 1. The % yield increases with increase in the % loading of SiW_{11} from 10% to 30%. Further increase in the % loading from 30% to 40% decreases the % yield. The decrease in % yield may be correlated with the values of surface area (table 1). Hence, a decrease in % yield of *n*-butyl acetate is as expected. The catalyst containing 20% loading [$(SiW_{11})_2/ZrO_2$] was used for detailed study.

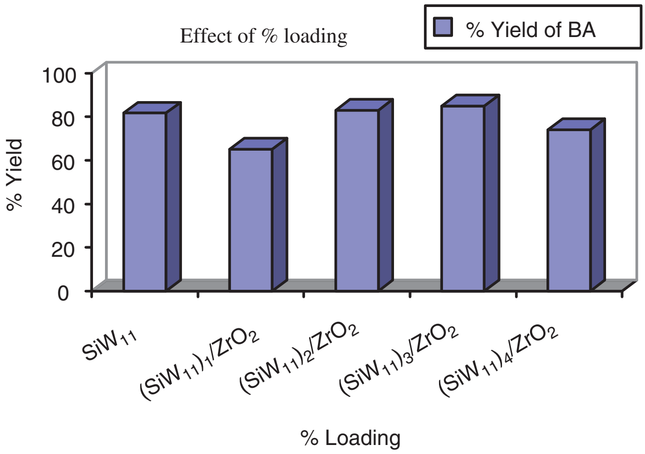

Figure 1. Effect of % loading of SiW_{11} onto ZrO_2 on the esterification of *n*-butanol; reaction time: 4 h; temperature: 80°C; amount of catalyst: 0.15 g; 1 : 4.4 mole ratio.

Table 2. Effect of mole ratio on % yield using $(SiW_{11})_2/ZrO_2$ as catalyst.

Mole ratio of alcohol to acid	% Yield
1 : 2	63
1 : 4.4	83

Amount of catalyst: 0.15 g; reaction time: 4 h; temperature: 80°C; 1 : 4.4 mole ratio.

3.1.2. Effect of mole ratio of alcohol and acid. The reaction was carried out by varying mole ratio of *n*-butanol to acetic acid, with 0.15 g of the catalyst for 4 h at 80°C. It is observed from the table 2 that with the increase in the concentration of acid the % yields of products increase. So all reactions are carried out in 1 : 4.4 molar ratio of reactants.

3.1.3. Effect of amount of catalyst. The reaction was carried out by varying the amount of catalyst and the % yields are shown in figure 2. The activity increases with an increase in the amount of catalyst from 0.10 to 0.25 g. For further increase in the amount of catalyst, the % yield decreases and then remains almost the same. This may also be due to the blocking of the active sites as after achieving a certain amount, the catalyst may behave as a bulk.

The optimum conditions for maximum yield of butyl acetate were with the mole ratio of *n*-butanol to acetic acid as 1 : 4.4, with 0.15 g of catalyst and 4 h reaction time at 80°C.

3.1.4. Esterification of 1° and 2° alcohols with acetic acid and esterification of various acids with *n*-butanol using $(SiW_{11})_2/ZrO_2$ as catalyst. The reactions were carried out under optimized conditions described earlier and the % yields of various esters, *n*-butyl

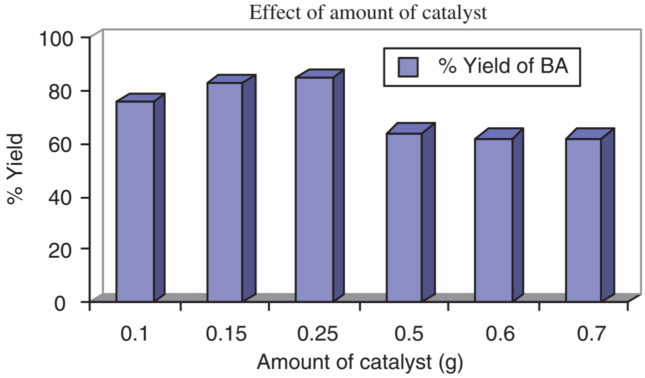

Figure 2. Effect of the amount of catalyst on the esterification of *n*-butanol; reaction time: 4 h; temperature: 80°C; 1 : 4.4 mole ratio.

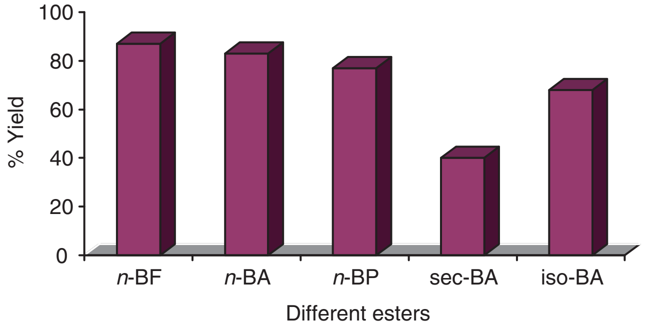

Figure 3. % Yields of different esters; amount of catalyst: 0.15 g; reaction time: 4 h; temperature: 80°C; 1 : 4.4 mole ratio.

formate (*n*-BF), *n*-butyl acetate (*n*-BA), *n*-butyl propionate (*n*-BP), sec-butyl acetate (sec-BA), and isobutyl acetate (iso-BA), are shown in figure 3.

3.2. *Effect of calcination temperature on [$(SiW_{11})_2$/ZrO_2]*

The esterification of *n*-butanol was carried out with different calcinated samples under optimized conditions. The results are shown in table S1. On calcination, there was no appreciable change in % yield of butyl acetate, indicating that the catalyst is stable up to 400°C. From this, it can be concluded that the catalyst was stable and its catalytic activity is unaltered even on calcinations. The catalyst can be used up to 400°C.

3.3. *Heterogeneity test*

For rigorous proof of heterogeneity, a test [29] was carried out by filtering catalyst from the reaction mixture at 80°C, after 1 h, and allowing the filtrate to react up to 4 h, that

Table 3. Heterogeneity test.

Catalyst	% Yield (*n*-Butyl acetate)
$(SiW_{11})_2/ZrO_2$ (1 h)	19.4
Filtrate (4 h)	19.0

Amount of catalyst: 0.15 g; temperature: 80°C; 1 : 4.4 mole ratio.

Table 4. % yield of *n*-butyl acetate with recycled catalyst.

Cycle	% Yield (*n*-Butyl acetate)	TON
Fresh	83	10246
1	79	9752
2	79	9752

Amount of catalyst: 0.15 g; reaction time: 4 h; temperature: 80°C; 1 : 4.4 mole ratio.

is, completion of the reaction. The reaction mixture of 1 h and filtrate were analyzed by gas chromatogram. No change in the % yield was found (table 3), indicating that the present catalyst falls into category C [29]. On the basis of these results, it can be concluded that there is no leaching of SiW_{11} from the support and the present catalysts are truly heterogeneous.

3.4. *Regeneration/recycling of the catalyst*

In order to investigate the details of the deactivation, repeated use of the catalyst was examined. The catalyst was separated from the reaction mixture by simple filtration, washed with conductivity water till filtrate is free from acid, dried at 100°C in an oven for 5 h and the recovered catalyst was charged for further run. The results obtained are shown in table 4; in the regenerated sample, the yield decreased by 4% and becomes constant on further regeneration.

4. Conclusion

FT-IR and DRS spectra show that lacunary silicotungstate keeps its Keggin-type structure when supported on ZrO_2. Thermal studies show that catalyst is stable up to 475°C. A SEM study shows uniform dispersion of heteropoly anion onto the surface of ZrO_2. The catalysts are successful in the esterification of different alcohols with acetic acid as well as the esterification of *n*-butanol with different acids under mild conditions as compared with traditional liquid acid catalysts. In all reactions, removal of the catalyst consists of single filtration and catalyst can be re-used after a simple work-up. No structural change takes place in reused catalysts, indicating stability. Thus the present catalysts are promising alternatives to the traditional acid catalysts for liquid-phase-acid-catalyzed reactions.

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