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Covalent Immobilization of Polyoxotungstate on Alumina and Its Catalytic Generation of Sulfoxides

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Abstract: Structural and chemical stability of the immobilized polyoxometalates (POMs)-containing catalysts is one crucial factor for their industrial application. In this work, we discuss the preparation of a novel P$_2$W$_{15}$@Al$_2$O$_3$ catalyst using a facile condensation reaction between the tri-lacunary POM of Na$_{12}$[α-P$_2$W$_{15}$O$_{56}$]·24H$_2$O (P$_2$W$_{15}$) and the hydroxyl groups on the surface of the spherical γ-Al$_2$O$_3$ under acidic conditions. The heterogeneous catalyst was characterized by the $^{31}$P NMR, FT-IR, XRD, XPS, TG, Raman, HR-TEM and BET. The P$_2$W$_{15}$@Al$_2$O$_3$ catalyst showed excellent stability, highly efficient reactivity and selectivity for the oxygenation of thioethers to sulfoxides which are a very useful intermediate in organic synthesis and industrial preparation of drugs. The catalyst could be recycled and reused at least ten times without any observable loss of its catalytic efficiency, mainly due to the covalently grafted {P$_2$W$_{15}$} cluster and high dispersion onto the γ-Al$_2$O$_3$ surface.

Polyoxometalates (POMs) are a class of discrete anionic metal-oxides of V, Mo, W and Nb etc.\(^1\) in their highest oxidation states exhibiting unrivalled structural archetypes as well as a wide range of sizes, unique physical properties\(^2\) and applications\(^3\) in areas as diverse as catalysis, medicine, electrochemistry, photochromism and magnetism etc.\(^4\) Additionally, their solution processability due to their high solubility\(^1\) and low lattice energies\(^2\) due to generally weak interactions between the POMs clusters and the associated counterions (NH$_4^+$, K+, Na+ etc), render them ideal candidates and useful components for the design of functional materials such as catalysts. More specifically, studies on POM-based catalysis are mainly focused on the design of simplified routes for the preparation of heterogeneous systems due to catalyst recoverability,
reusability and excellent chemical, structural and thermal-stability.\textsuperscript{3}

Immobilization and solidification of POM species on various substrates are two widely applied approaches for the generation of multifunctional POM-based heterogeneous catalysts.\textsuperscript{3,4} Despite great efforts have been made for the efficient immobilization of POMs on supports such as SiO\textsubscript{2},\textsuperscript{5} Al\textsubscript{2}O\textsubscript{3},\textsuperscript{6} ZrO\textsubscript{2},\textsuperscript{7} zeolites\textsuperscript{8} and activated carbon\textsuperscript{9} materials, the produced composite materials generally suffer from various issues that need to be taken into consideration. For example, heterogeneous catalysts based on the electrostatic interactions developed between the POM species and the supports suffer from stability issues due to POM leaching.\textsuperscript{10-12} In the case of the heterogeneous catalysts produced under high temperature regimes (eg. calcination) usually leads to structural rearrangements and finally the compromise of the POMs’ structural integrity which greatly limits the offered opportunities to exploit the wide range of functionalities directly correlated to the POMs’ structural features.\textsuperscript{6,13,14} Therefore, utilization of robust support surfaces which preserve the POM’s structural integrity for the development of heterogeneous catalysts for a wide range of processes, is highly desirable.

Alumina-based particles exhibit remarkable properties, such as well-defined pore structure and high specific surface areas. The spherical γ-Al\textsubscript{2}O\textsubscript{3} exhibits good physical stability, high crush strength and great controllability. For these reasons, it is widely employed in the chemical and petrochemical industries.\textsuperscript{15-22} In this paper, we report the preparation of the P\textsubscript{2}W\textsubscript{15}@Al\textsubscript{2}O\textsubscript{3} composite material by immobilization of POMs onto spherical γ-Al\textsubscript{2}O\textsubscript{3} particles (Scheme 1) and we discuss its catalytic efficacy for the oxygenation of thioethers.

![Diagram](image_url)

\textbf{Scheme 1.} The synthetic process of P\textsubscript{2}W\textsubscript{15}@Al\textsubscript{2}O\textsubscript{3}.
Results

The P$_2$W$_{15}$@Al$_2$O$_3$ composite material was synthesized by immobilization of Na$_{12}$[α-P$_2$W$_{15}$O$_{56}$]-24H$_2$O clusters onto the surface of the spherical γ-Al$_2$O$_3$ particles under acidic conditions.$^{23,24}$ In an effort to optimize the immobilization conditions, we immobilized the POM clusters under various pH conditions ranging from 6 to 1 (Figure 1). The resultant solid was separated from the reaction mixture by filtration and washed with 0.3 M LiCl solution to remove the physically adsorbed {P$_2$W$_{15}$} clusters.$^{25}$

![Figure 1](image_url)

**Figure 1.** Solid state $^{31}$P NMR of (a) Na$_{12}$[α-P$_2$W$_{15}$O$_{56}$]-24H$_2$O and (b-f) P$_2$W$_{15}$@Al$_2$O$_3$ composite material prepared under different pH environments.

Figure 1a shows the solid state $^{31}$P NMR spectra of Na$_{12}$[α-P$_2$W$_{15}$O$_{56}$]-24H$_2$O, where the two observed signals located at -0.79 ppm and -15.77 ppm can be assigned to the non-equivalent phosphorus atoms, P1 and P2, respectively.$^{26}$ Upon decrease of the pH value from 6 to 1, the left shoulder peak centered at -0.79 ppm decreases and splits into several peaks in the range of -0.79 to -8.41 ppm, which is a potential indication of partial decomposition at specific pH values of the cluster prior to immobilization on the alumina surface. On the other hand, the signal located at -15.77 ppm, shifts gradually to -14.58 ppm due to the reaction between the {P$_2$W$_{15}$} anions and the γ-Al$_2$O$_3$ surface. According to the results obtained by the solid state $^{31}$P NMR, the optimum
conditions for the effective immobilization of the lacunary Dawson anions onto the alumina support takes place at pH = 1. This is in agreement with the Mulcahy’s report, where the positive net surface charge acquired at pH values below the isoelectric point (IEP) of the support, attracts and stabilizes the anionic species from the bulk solution. However, a simple electrostatic model cannot account for the adsorption of these anions. It is suggested that this is a two-step process where the electrostatic ion pairing occurs first as soon as the pH value is below the IEP = 8.6 of γ-Al₂O₃ (Figure S1), followed by a condensation reaction between the {P₂W₁₅} anions and the γ-Al₂O₃ surface according to the following equations:

\[
\text{Al} - \text{OH}_2^+ + P_2W_{15}O_{56}^{12-} \rightleftharpoons \text{Al} - \text{OH}_2^+P_2W_{15}O_{56}^{12-} \quad (1)
\]

\[
\text{Al} - \text{OH}_2^+P_2W_{15}O_{56}^{12-} \rightleftharpoons \text{Al} - O - P_2W_{15}O_{55}^{11-} + \text{H}_2\text{O} \quad (2)
\]

The W=O and W-O stretching and bending vibrations of the P₂W₁₅ generally occur below 1000 cm⁻¹ thus it is difficult to detect them by Fourier transform-infrared (FT-IR) due to the strong IR absorption of the γ-Al₂O₃ supports in this region (Figure S2). The XRD pattern of the P₂W₁₅@Al₂O₃ composite is similar to that of Al₂O₃, indicating no diffraction of the Na₁₂[α-P₂W₁₅O₅₆]·24H₂O due to poor crystallinity and co-existence of other crystalline phases (Figure S3). The Raman spectra of the P₂W₁₅@Al₂O₃ are presented in Figure 2a. It can be seen that the γ-Al₂O₃ support is not Raman active, allowing detection of all the W-O vibrations. The characteristic vibrations of bulk {P₂W₁₅} are located at 955, 871 and 827 cm⁻¹, respectively. The P₂W₁₅@Al₂O₃ exhibit Raman bands located at 980, 909 and 839 cm⁻¹, respectively, which can be assigned to the W=O stretch bands and W-O-W stretch modes of the immobilized cluster. The Raman shifts are due to the strong interactions between the tri-lacunary POM cluster and the γ-Al₂O₃ support, leading to the decrease of the cluster’s and/or the alumina’s local symmetry.
Figure 2. (a) Raman spectra of Al$_2$O$_3$, P$_2$W$_{15}$@Al$_2$O$_3$ and P$_2$W$_{15}$, respectively; (b) W$_{4f}$ XPS spectrum of P$_2$W$_{15}$@Al$_2$O$_3$.

Additionally, XPS spectroscopy was used in order to determine the oxidation centres of metal centres. More specifically, the XPS spectrum for W$_{4f}$ (Figure 2b) revealed two peaks located at 34.8$^{31}$, 36.2$^{32}$ eV in the energy region of W4f$_{7/2}$, 37.5, 39.5 eV$^{33,34}$ in the energy region of W4f$_{5/2}$, which are consistent with the W$^{VI}$ oxidation state. The thermogravimetric study of the P$_2$W$_{15}$@Al$_2$O$_3$ composite (see Figure S4) performed under nitrogen in the temperature range of 25 to 800 °C and revealed two main weight losses. The first one of 1.9% ranging from 25 to 207 °C can be attributed to the loss of the absorbed water and crystallization water molecules of the sample. The second weight loss of 1.4 % between 207 and 523 °C can be assigned to the loss of the constitutional water from P$_2$W$_{15}$@Al$_2$O$_3$.35

Figure 3. High-resolution-TEM images of Al$_2$O$_3$ (a-c) and P$_2$W$_{15}$@Al$_2$O$_3$ (d-e), respectively. f)
Energy dispersive spectroscopy of P$_2$W$_{15}$@Al$_2$O$_3$.

SEM images of the P$_2$W$_{15}$@Al$_2$O$_3$ composite material show sheet-like morphologies that are similar to that of the bare Al$_2$O$_3$ support (Fig. S5-S6). The HRTEM images of the P$_2$W$_{15}$@Al$_2$O$_3$ composite material revealed unambiguously the presence of {P$_2$W$_{15}$} clusters on the γ-Al$_2$O$_3$ support, in the form of dark dots of 1~2 nm size (Figure 3). In order to confirm further the covalent linkage between the {P$_2$W$_{15}$} clusters and the γ-Al$_2$O$_3$ support, we studied the stability of the P$_2$W$_{15}$@Al$_2$O$_3$ composite material in LiCl solution, according to previously reported procedure.$^{13}$ The P$_2$W$_{15}$@Al$_2$O$_3$ composite materials were dispersed in 0.3 M LiCl solution under vigorous stirring for 12 h, the solution was filtered and dried under vacuum. The procedure repeated three times; close examination of the HRTEM images (Fig S7) obtained from the collected and dried material showed that the POM clusters remained immobilized on the surface of γ-Al$_2$O$_3$ whilst ICP analysis on the collected filtrates showed that no W element was present. The experimental data strongly suggest that the {P$_2$W$_{15}$} clusters are not just physically adsorbed on the γ-Al$_2$O$_3$ since the presence of Li$^+$ counterions would have removed the clusters from the surface and extracted them into the solution. Examination of the elemental composition of the material by energy dispersive spectroscopy (EDS) showed that P and W atoms are present on the P$_2$W$_{15}$@Al$_2$O$_3$ composite material (Fig 3f) whilst X-ray fluorescence spectroscopy revealed that the loading of {P$_2$W$_{15}$} on the γ-Al$_2$O$_3$ support is approximately 9.98%.

As shown in Figure 4 and Table S1, the N$_2$ adsorption-desorption isotherms of γ-Al$_2$O$_3$ and P$_2$W$_{15}$@Al$_2$O$_3$ are classified as type IV with a clear H1-type hysteresis loop according to the IUPAC classification, indicating the presence of meso-porosity. The pore size distribution curves of γ-Al$_2$O$_3$ and P$_2$W$_{15}$@Al$_2$O$_3$ found to be 42.74 and 30.93 nm, respectively, indicating that the regular meso-porous channels of the γ-Al$_2$O$_3$ support are retained in the corresponding P$_2$W$_{15}$@Al$_2$O$_3$ catalysts. The pore size distribution curves of the P$_2$W$_{15}$@Al$_2$O$_3$ reduced with the P$_2$W$_{15}$ loading which can be explained by the fact that the pores are partially blocked by {P$_2$W$_{15}$} clusters.
Figure 4. The N₂ adsorption-desorption isotherm and the pore size distribution of (a) Al₂O₃, (b) P₂W₁₅@Al₂O₃.

Catalytic activity.

Scheme 2. Selective oxidation of sulfides to sulfoxides by using the P₂W₁₅@Al₂O₃ composite materials.

Catalytic oxidations of organic compounds under mild conditions are of both considerable intellectual interest and potential utility.³⁶,³⁷ Catalytic oxidation of organic sulfides remains a topical interest due to the versatile utility of both sulfoxides and sulfones in organic synthesis.³⁸-⁴⁰ While a mass of oxygen donors are available, utilization of H₂O₂ as “green” oxygen donor has become increasingly prominent.⁴¹-⁴⁴ In this work, catalytic oxidation of thioanisole in the presence of P₂W₁₅@Al₂O₃ as catalyst and H₂O₂ as oxidant has been carried out (Scheme 2). The selectivity of sulfoxide products and the conversion of the initial sulfides have been quantified using gas chromatography (GC) (Figure S8, S9) and ¹H.NMR of the reactant (thioanisole) and the product upon completion of the reaction (Figure 5). Table S2 summarizes the reactivity data for the oxidation of thioanisole in CH₃OH at 25 °C in the presence of the {P₂W₁₅}, P₂W₁₅@Al₂O₃ and in
the absence of the P$_2$W$_{15}$@Al$_2$O$_3$. In the presence of the P$_2$W$_{15}$@Al$_2$O$_3$ as a catalyst, the conversion and selectivity were improved considerably. This indicates that the P$_2$W$_{15}$@Al$_2$O$_3$ is an effective catalyst for the oxygenation of thioanisole by H$_2$O$_2$. In an effort to optimize the reaction conditions, various solvents, reaction times, amounts of H$_2$O$_2$ and catalyst were investigated (Figure S10-S12, and Table S3). The determined optimal conditions found to be the following: thioanisole = 1 mmol, H$_2$O$_2$ = 82 μL, CH$_3$OH = 200 μL. Thus, the experiments for the determination of the kinetic parameters for the catalytic oxidation of thioanisole, were carried out using the optimized conditions.

Experimental conditions: thioanisole = 1 mmol, H$_2$O$_2$ = 1 mmol, catalyst = 2.5 μmol, CH$_3$OH = 200 μL, T=25 °C, t = 35 min.

Reaction kinetics for the oxidation of thioanisole are presented in Figure 6, where the (C$_t$/C$_0$) is plotted against the reaction time. The C$_0$ and C$_t$ are the initial thioanisole concentration and thioanisole concentration at time t, respectively. The rate constant k of the oxidation reaction is determined to be -0.082 min$^{-1}$ on the basis of Equations (1) and (2). The oxidation of thioanisole and subsequent conversion to the product (sulfoxide) can be completed in about 35 min.

\[
\frac{-dC_t}{dt} = kC_t \quad (1)
\]
\[
\ln \frac{C_0}{C_t} = kt \quad (2)
\]

As such, the catalyst shows high catalytic efficiency for the oxidation of sulfides to sulfoxides, and the catalytic reaction exhibits pseudo-first-order kinetics for the oxidation of thioanisole with a 99% selectivity for sulfoxides \((R^2 = 0.99)\). In an effort to confirm that the catalyst is truly heterogeneous, we removed the catalyst from the reaction mixture when the conversion reached a value of 60% after 15 min. Real time monitoring of the reaction mixture by GC showed that the substrate catalytic conversion stopped immediately. The addition of the catalyst back to the reaction mixture restarted the reaction as shown in Figure S13.

![Figure 6. The catalytic conversion of thioanisole and \(\ln (C_t/C_0)\) as functions of reaction time.](image)

Reaction conditions: thioanisole = 1 mmol, \(H_2O_2 = 1\) mmol, \(CH_3OH = 200\) μL, \(T = r.t., t = 35\) min.

After confirming the stability and efficiency of the composite material we investigated the general applicability and selectivity of the as-prepared catalyst of \(P_2W_{15}@Al_2O_3\), we utilized a series of thioether-based compounds as substrates in catalytic oxygenation reactions under the same conditions (Table 1). The results revealed that alkyl-aryl thioethers and 4-Pentamethylene sulfides can be selectively fully converted to the desired product. However, 2-Bromothioanisole showed a relatively low conversion, which might be due to increased steric hindrance and/or electrophilic effect (Entry 4). Interestingly, the phenylallyl thioether gave a conversion of 63% to the desired sulfoxide along with an unknown by-product (Entry 6).
Table 1 Oxidation of various sulfides to the corresponding sulfoxides by using 30% H₂O₂ and P₂W₁₅@Al₂O₃.

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</table>

Experimental conditions: substrate = 1 mmol, H₂O₂ = 1 mmol, catalyst = 2.5 μmol, CH₃OH = 200 μL, T=25 °C, t = 35 min.

The main advantage of using heterogeneous catalysts in a liquid-phase reaction is the ease of separation and recycling of the catalyst. In order to confirm in our case that there are no catalyst leaching issues, we filtered off the catalyst after each cycle, washed with acetone, dried and then added into a fresh reaction mixture. It has been demonstrated that the solid state ³¹P NMR (Figure 7a), Raman (Figure 7b), and HR-TEM (Figure 7c) results for the recovered catalyst are almost the same as those of the fresh one, indicating the stability and chemical composition of the catalyst. The aged P₂W₁₅@Al₂O₃ catalytic system can be reused for the oxidation of thioanisole, promoting the oxidation of sulfides to sulfoxides at least ten times without significant decrease of its catalytic efficiency (Figure 7d). Previously reported examples of catalytic oxidative efficiencies using sulfide substrates of various catalytic systems are summarized in Table S4. It is worth noting that the high efficiency and selectivity of the P₂W₁₅@Al₂O₃ catalyst along with the easy preparation in a single step, in less time and lower consumption of H₂O₂ during the catalytic conversion of the substrates (Table S4, entry 14) renders it an ideal candidate for larger scale applications.
Figure 7. a) Solid state $^{31}$P NMR, b) Raman spectra, and c) HRTEM images of the fresh P$_2$W$_{15}$@Al$_2$O$_3$ and the recycled P$_2$W$_{15}$@Al$_2$O$_3$. d) The recycling experiments for selective oxidation of sulfides to sulfoxides using the P$_2$W$_{15}$@Al$_2$O$_3$ as catalyst at 25 °C. Experimental conditions: thioanisole = 1 mmol, H$_2$O$_2$ = 1 mmol, catalyst = 2.5 μmol, CH$_3$OH = 200 μL, T = 25 °C, t = 35 min.

**Conclusions**

The immobilization of {P$_2$W$_{15}$} onto spherical γ-Al$_2$O$_3$ particles results in the formation of a new heterogeneous catalyst, P$_2$W$_{15}$@Al$_2$O$_3$, where the strong covalent bond are formed between the [α-P$_2$W$_{15}$O$_{56}$]$^{12-}$ clusters and the hydroxyl groups of the spherical γ-Al$_2$O$_3$ support inducing exceptional stability to the catalytic system. Moreover, the {P$_2$W$_{15}$} is distributed uniformly onto the γ-Al$_2$O$_3$ surface as evidenced by HRTEM studies. Highly efficient oxygenation of thioethers can be achieved by the P$_2$W$_{15}$@Al$_2$O$_3$ in the presence of H$_2$O$_2$ with 99% selectivity of sulfoxides and 94% conversion in 35 min. The P$_2$W$_{15}$@Al$_2$O$_3$ can be separated easily by filtration and reused at least ten times without obvious decrease of the catalytic efficiency. The facile preparation, reusability, and efficacy of the heterogeneous P$_2$W$_{15}$@Al$_2$O$_3$ catalyst provides great potential for
industrial applications. Finally, the straightforward covalent attachment of the appropriate choice of the polyoxometalate core (architecture and composition) opens the door for further exploration and design of multi-functional catalytic materials tailored for specific applications. Our current research effort is focused on exploring the potential of the family of POM@Al₂O₃ catalysts for the development of chiral sulfoxides.

**Methods**

**Chemicals and Materials:** All chemicals were of analytical grade and were used as received without any further purification. Thioether compounds were purchased from Alfa Aesar. LiCl, HCl, KNO₃, HNO₃ and NaOH were purchased from Beijing Chemical Reagent Company (Beijing, China). Acetone, methanol, ethanol, acetonitrile and ethyl acetate were purchased from J&K Chemical Ltd. The spherical γ-Al₂O₃ was purchased from Shandong Benten Chemical Corporation. The deionized water from a Millipore water purification system was used throughout the experiments. Na₁₂[α-P₂W₁₅O₅₆]-24H₂O (P₂W₁₅) was prepared according to the published procedure.²⁵

**Instruments:** Solid state NMR experiments were carried out at 10 kHz for ³¹P on a Bruker Avance 300M solid-state spectrometer equipped with a commercial 5mm MAS NMR probe. FT-IR spectra were collected in transmission mode using a JASCO FT-IR 410 spectrometer or a JASCO FT-IR 4100 spectrometer (wavenumbers (ν) are given in cm⁻¹; intensities are denoted as wk = weak, sh = sharp, m = medium, br = broad, s = strong). XRD measurements were performed in JCN UltimaIII X-ray diffraction. XPS data was received from the Thermo-Fisher scientific ESCALAB 250 X-ray photoelectron spectroscopy. TGA data was obtained using a DTG-60A analyzer of Shimadzu Corporation. TGA measurements were performed under Nitrogen atmosphere with a temperature increase of 10°C/min between 25 and 800°C. Laser Raman spectroscopy were obtained using a LabRAM ARAMIS Raman spectrometer. Scanning emission microscope (SEM) images were collected on a Zeiss Supra 55 VP field-emission scanning electron microscope. High-resolution transmission electron microscopy (HR-TEM) images were obtained with a JEOL JEM-3010 microscope operated at 300 kV. BET data were obtained using a Bei Shi De 3H-2000PS2 specific surface area and pore size analyzer. X-Ray Fluorescence
Spectrometer data were obtained using a XRF-1800 with 20 degree/min. The content of sulfides and sulfoxides were analyzed on an Agilent 7820A GC system using a 30 m 5% phenylmethyl silicone capillary column with an ID of 0.32 mm and 0.25 mm coating (HP-5).

**Synthesis of P$_2$W$_{15}$@Al$_2$O$_3$:** The spherical γ-Al$_2$O$_3$ was activated at 900°C under atmospheric pressure for 24 h, then cooled down to room temperature in accordance to Cargnello et al. In a reaction vessel, 1.66 × 10$^{-4}$ mol of Na$_{12}$[α-P$_2$W$_{15}$O$_{56}$]·24H$_2$O were dissolved as a clear solution in 50 mL deionized water without CO$_2$; and then 1 g of spherical γ-Al$_2$O$_3$ was added to the solution. The pH of the solution was adjusted to 1.00 carefully by dropwise addition of 4 M HCl (aq). The reaction mixture was kept under stirring at room temperature for 1 hour and then heated at 90 °C for three hours. The reaction mixture was cooled down to room temperature and the product was filtered and washed by 0.3 M of LiCl solution (100 mL × 3). The product was obtained after drying under vacuum oven at 60 °C for 24h.

**Determination of IEP:** The IEP (isoelectric points) value of γ-Al$_2$O$_3$ support was determined by a batch equilibration method as described in the literature. 25 mg of spherical γ-Al$_2$O$_3$ support was dispersed in 25 ml of 0.1 M KNO$_3$ aqueous solution with vigorous stirring for 60 min. Six bottles of above solution were prepared and initial pH of each bottle was adjusted to 3, 4, 5, 6, 7, 8, 9, 10 and 11 using aqueous solution of HNO$_3$ or NaOH. The zeta potential of the solution was measured. The zeta potential value is plotted as a function of pH as presented in Figure S1. Finally, the pH$_{IEP}$ value (ca. 8.6) of γ-Al$_2$O$_3$ support was determined at the point of Zeta Potential = 0.

**Catalytic test:** The oxidation reaction was carried out in a 25mL flask with magnetic stirring. The typical optimized procedure was the following: Thioanisole (1 mmol), H$_2$O$_2$ (1 mmol), CH$_3$OH (200 μL), P$_2$W$_{15}$@Al$_2$O$_3$ (2.5 μmol, the loading of P$_2$W$_{15}$ on Al$_2$O$_3$: 9.98%) were added to the flask. The reaction time was counted after the addition of the catalyst (T = 25 °C, t = 35 min). The resulting products were extracted with diethyl ether and analyzed by GC. The yield was determined using reference standards. After completion of the reaction, the catalyst was recovered by filtration, washed with the acetone and dried in the oven.


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**Additional Information**

Supplementary information accompanies this paper at http://www.nature.com/scientificreports