Article

Liquid Phase Hydrogenation of MIBK over M/CsPW (M = Ag, Ru, Pt, and Pd)

Abdullah M. Alhanash ^{1,*} , Amal A. Atran ², Murad Eissa ¹, Mhamed Benaissa ¹
and Mohamed S. Hamdy ¹

¹ Catalysis Research Group (CRG), Chemistry Department, Science College, King Khalid University, P.O. Box 9004, Abha 61413, Saudi Arabia; meissa@kku.edu.sa (M.E.); mbenaissa@kku.edu.sa (M.B.); m.s.hamdy@gmail.com (M.S.H.)

² Chemistry Department, College of Science and Arts, Najran University, P.O. Box 1988, Najran 11001, Saudi Arabia; aaetran@nu.edu.sa

* Correspondence: alhnsh@kku.edu.sa; Tel.: +966-172417773

Received: 26 November 2018; Accepted: 2 January 2019; Published: 6 January 2019

Abstract: Four different metal nanoparticles (metal = Ag, Ru, Pt, or Rh) were impregnated on the acidic cesium salt of tungstophosphoric acid $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ (CsPW) with a loading amount of 2 wt%. The prepared catalysts were characterized by using X-ray diffraction (XRD), Fourier transform-infrared spectroscopy (FTIR), N_2 sorption measurements, scanning electron microscopy (SEM), and energy-dispersive X-ray spectroscopy (EDX). Results confirmed the formation of highly distributed metallic nanoparticle centres over the acidic CsPW. The catalytic activity of the prepared catalysts were evaluated in the liquid phase hydrogenation of methyl isobutyl ketone (MIBK) to 2-methylpentane (2-MP) at 453 K. Pd-CsPW showed the highest activity compared to other catalysts, where 10% conversion was obtained with 91% selectivity after 4 h's reaction time.

Keywords: heterogeneous catalysis; MIBK conversion; solvent-free; hydrogenation; 2-methylpentane; CsPW; MIBC

1. Introduction

Recent development in the production of fuels and chemicals from biomass resources has raised economic, environmental and health concerns due to the generation of large amounts of different by-products [1]. The conversion of these bio-based undesired by-products to valuable chemicals is an attractive target from both academic and industrial points of view [2]. As reported previously [3], almost 30% of undesired acetone is produced as a by-product in the conversion of sugar to biofuel (i.e., biobutanol). Therefore, it is a critical development to find new uses of acetone and its derivatives in the fuel sector. In a well-known industrial process, acetone is converted to methyl isobutyl ketone (MIBK), which is an important solvent in organic synthesis, paints, coatings, and resins. This process is carried out via aldol condensation in three different steps or in a one-pot system using bifunctional heterogeneous catalysts ([4–6] and references therein).

With new merging transformations of MIBK, it may be considered a platform chemical for a number of valuable commodity chemicals [7–9]. It can be hydrogenated (Scheme 1) to methyl isobutyl carbinol (MIBC) using metallic catalysts [8]. MIBC finds uses in organic synthesis, lubricant oil additive, and plasticizers etc. The dehydration of MIBC, followed by hydrogenation of the intermediates formed leads to the formation of 2-methylpentane (2-MP), which is an interesting additive in the fuel industry [9,10].

Multi-functional catalysis has become a promising approach in catalysis applications because the multiple active sites on a catalyst reduce the number of reaction steps and, hence, reduce the

costs of the chemical process and/or products. The catalytic conversion of MIBK to 2-MP is a typical two-catalytic step reaction where it requires two different active sites; metallic sites to catalyze the hydrogenation step, and acidic sites to catalyze the dehydration step (Scheme 1).

Scheme 1. The conversion of methyl isobutyl ketone (MIBK) to 2-methylpentane.

Hydrogenation of a wide range of ketones to alkanes was successfully applied using a metal-acid bifunctional approach. Mizuno et al. have examined the hydrogenation (hydrodeoxygenation) of ketones, phenols, and ethers in the liquid phase, using a bifunctional catalyst (Pt/Cs_{2.5}H_{0.5}PW₁₂O₄₀) at 120 °C and 5 bar H₂ pressure [11]. Kozhevnikov et al. have investigated the gas phase conversion of selected ketones to alkanes using the same bifunctional catalyst at 100 °C and 1 bar H₂ pressure [12]. Only a few papers have reported the gas phase conversion of MIBK to 2-MP, and high conversion of MIBK and high selectivity towards 2-MP was obtained using Pt/H-ZSM-5 at 200 °C and 1 bar H₂ pressure [9,10]. However, a very limited number of publications reported the liquid phase and solvent-free hydrogenation of MIBK. Therefore, more work is needed to explore this process in the liquid phase. It is worth mentioning that the direct conversion of the liquid MIBK without using any solvents would be more favorable as it increases the economic value and reduces the environmental impact of the overall industrial process. Recently, our group reported the conversion of MIBK over the bi-functional catalyst Pt-Al-TUD-1 for the first time under liquid-phase, solvent-free conditions [13], and the results obtained were promising and motivated the team to investigate further the catalytic conversion of MIBK over different bi-functional catalysts, with more acidic support aiming to increase the overall conversion of MIBK.

The acidic heteropoly salt, cesium 12-tungstophosphate Cs_{2.5}H_{0.5}PW₁₂O₄₀ (CsPW) is well-known as a water-insoluble strong Brønsted acid and has been used successfully as a bi-functional catalyst for alkane isomerization [14–16], one-pot hydrogenation of acetone to MIBK [5], one-pot hydrogenolysis of glycerol to propanediols [17], and gas phase dehydration of glycerol to acrolein [18] among other reactions.

In the current study, the conversion of MIBK over metal-doped CsPW (metal = Ag, Pd, Pt, or Ru) was investigated for the first time under liquid phase, solvent-free conditions. The optimization of the hydrogenation process in terms of reaction temperature and operating pressure is reported. Moreover, the catalyst stability during the reaction is discussed as well.

2. Results

2.1. Characterization Results

The Brunauer–Emmett–Teller (BET) surface area of the prepared CsPW was approximately 140 m²/g. The pore volume of the prepared CsPW was about 0.065 cm³/g with a narrow pore size distribution of almost 2 nm. All the M-CsPW catalysts have high surface area (111–125 m²/g), uniform pore diameter ranging from 2.8 to 3.0 nm, and moderate pore volume of 0.06–0.09 cm³/g.

The result of powder X-ray diffraction (XRD) analysis of M-CsPW catalysts are shown in Figure 1. The patterns of M-CsPW catalysts shows only the patterns of the crystalline CsPW [19] which are consistent with its parent tungstophosphoric acid, H₃PW₁₂O₄₀ (HPW) and is well documented in other studies [20,21]. Moreover, the peaks of Pt, Pd, Ru and Ag nanoparticles did not appear. This is most likely due to the small size of the metal nanoparticles, in addition to their high dispersion onto the support. The peak intensity and location of all the peaks are almost identical, which means that the

doped metal did not affect the structure of CS-PW. More importantly, no more crystalline phase(s) was/were observed as an indication for the high purity of the prepared sample.

Figure 1. X-ray diffraction (XRD) patterns for Ru-CsPW, Pt-CsPW, Pd-CsPW, and Ag-CsPW.

The Fourier transform-infrared (FTIR) spectra of the four freshly prepared M-CsPW samples show the well-known spectrum of the Keggin structure of CsPW [22]. For simplification, the FTIR spectrum of Pt-CsPW is compared with the parent Cs-PW in Figure 2. The FTIR spectrum of Cs-PW is dominated by four main bands at around 1078, 986, 887, and 802 cm^{-1} . These bands can be assigned as $\nu_{\text{as}}(\text{P}-\text{O})$, $\nu_{\text{as}}(\text{W}-\text{O})$, $\nu_{\text{as}}(\text{W}-\text{O}_\text{c}-\text{W})$, and $\nu_{\text{as}}(\text{W}-\text{O}_\text{e}-\text{W})$, respectively [23]. These peaks were observed in all the FTIR spectra of M-CsPW as an indication that the doped metal atoms did not severely affect the Keggin structure of Cs-PW. This result agrees with the results of XRD analysis obtained. More importantly, the peaks of metallic nanoparticles did not appear in XRD due to the small loading and/or the very small size of these nanoparticles (most likely between 3–5 nm), which is located outside the limitation of the instrument.

Figure 2. Fourier transform-infrared (FTIR) spectra of Pt-CsPW and neat CsPW.

The morphological structure of the prepared samples were investigated by scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) analysis. The obtained micrographs and data are presented in Figure 3. SEM micrograph of Pd-CsPW shows the irregular shape of fine particles (with an average size pf 7–8 μm) characteristic of Cs-PW particles (Figure 3A).

The EDX analysis shows the main elements present in the sample, O, W, P, Cs, and Pd. No other atoms could be determined as an indication for the purity of the prepared samples (Figure 3B). In another SEM micrograph, the surface nature of Pd-CsPW was investigated (Figure 3C); the surface of the sample seems rough without extra-framework of PdO crystalline phase as an indication for total incorporation of Pd nanoparticles in the Keggin structure of Cs-PW. Finally, to investigate the dispersion of Pd nanoparticles, mapping of Pd was performed, and the micrograph obtained is shown in Figure 3D. The micrograph clearly shows the high dispersion of Pd nanoparticles throughout the CsPW without agglomeration.

Figure 3. (A) Scanning electron microscope (SEM) micrograph of Pd-CsPW particle, (B) The corresponding energy-dispersive X-ray spectroscopy (EDX) analysis of Pd-CsPW, (C) SEM micrograph of Pd-CsPW surface, and (D) Mapping of Pd nanoparticles throughout the Pd-CsPW surface.

2.2. Catalytic Activity

The catalytic activity of the prepared bi-functional catalytic series (M-CsPW) was investigated in the liquid phase reduction of MIBK to 2 MP. The reaction was performed at 170 °C, 10 bar H₂ pressure and 4 h reaction time. The obtained MIBK conversion % as well as the selectivity % of 2 MP are given in Figure 4. The results show that the CsPW catalyst could not catalyze the reaction: 0% conversion was obtained. This is expected in the absence of metallic active sites. Among various metals doped CsPW studied, Pd-CsPW showed the highest activity and selectivity towards MIBK conversion to 2 MP, with 10% conversion and 91% selectivity. The other products observed were 6.2% of 4-methylpentane-2-ol and negligible amount of the two intermediates, i.e., 4-methylpent-1-ene and 4-methylpent-2-ene. Other metals, Pt, Ru, Ag, exhibited lower activity for this reaction, with 8%, 5% and 2% conversion, respectively. From these results and previous results reported by our group and

others [10–13], we confirm that this is a truly bi-functional (metal/acid) system where both metallic and acidic active sites are essentially required to obtain the alkane product in liquid and gas phase.

Figure 4. Liquid phase hydrogenation of MIBK over M-CsPW (M = Pd, Pt, Ru, Ag). Reaction conditions: 443 K, 25 mL of MIBK (solvent free), 0.25 g catalyst, 2 wt% of metal, 10 bar H₂ pressure, stirring rate of 780 rpm.

For the optimization of reaction conditions, the reaction was studied under different temperatures and pressures, the results are presented in Figure 5. The conversion % of MIBK increases with increasing reaction temperature, reaching 10% at 170 °C. However, increasing hydrogen pressure above 10 bar negatively affected the conversion.

Figure 5. Left panel: effect of H₂ pressure on the MIBK conversion % at 170 °C over Pd-CsPW. Right panel: effect of reaction temperature on the conversion of MIBK over Pd-CsPW under 10 bar H₂.

To examine the heterogeneity of the system, a hot filtration technique was applied. In this experiment, the catalyst was hot-filtered after 2 h reaction time, then the reaction was allowed to proceed under the same conditions without the catalyst and the result is shown in Figure 6. It is concluded from this experiment that the system is truly heterogeneous as the conversion of MIBK did not proceed further after the removal of the catalyst because no leaching of active species took place.

Figure 6. The conversion % of MIBK with-/out the hot filtration experiment. Reaction conditions: 170 °C, 25 mL of MIBK (solvent free), 0.25 g catalyst, 2 wt% of metal, 10 bar H₂ pressure, stirring rate of 780 rpm.

3. Discussion

The results obtained clearly show that two different active sites are necessary to perform the conversion of MIBK to 2-MP. The use of only acidic catalyst CsPW could not activate the reaction (Figure 5), which was expected based on the initial results reported earlier [13]. The sequence of the reaction steps can be summarized as the following; (a) reduction of MIBK to 4-methylpentane-2-ol by metallic active sites and hydrogen gas, (b) dehydration of 4-methylpentane-2-ol to the alkenes intermediate by the acidic active sites, and finally (c) hydrogenation of the intermediate alkenes to form the desired product 2-methylpentane. Pd-CsPW possessing strong acidity with purely Brønsted sites has shown similar activity to Pt-Al-TUD-1 [13] which has moderate acidity and both Brønsted and Lewis sites. In a kinetic study conducted by Alharbi et al. [12], the first step in MIBK hydrogenation process to MP is the rate-determining step, which is the hydrogenation of the C=O group to the alcohol group. This probably explains why the acidity effect of the support was not significant in this step. It was also shown that the dehydration of alcohol intermediate to alkene is fast over CsPW support. Also, the hydrogenation of alkene intermediate over the metal site is fast [12]. It is interesting to mentioned that Pt incorporated TUD-1 catalyst [13], i.e., metallic nanoparticles only without acidic sites, was able to hydrogenate MIBK to 4-methylpentane-2-ol, and 0% of 2-MP was obtained, as an indication for the needs of the two different active sites to perform the conversion to the desired product 2-MP.

Moreover, the optimization of reaction temperature clearly shows that increasing temperature leads to a direct increase in the conversion% of MIBK. However, more experiments are needed to explore the conversion % in a temperature higher than 443 K. However, H₂ pressure optimization showed that the best MIBK conversion was achieved at 10 atm, while at H₂ pressure = 15 the obtained conversion decreased. This can be explained by to the blocking of the active sites at high H₂ pressure, as reported by Lemonidou and co-workers [24], and Holles and co-workers [25].

Our research team investigated earlier the conversion of MIBK over the bi-functional M-Al-TUD-1 series (M = Pd, Pt, Ru, and Ag) [13]. In this section, the activity difference between the two catalytic systems is discussed. Generally speaking, the obtained results of MIBK conversion to 2-methylpentane show that M-Al-TUD-1 samples exhibited better activity than the corresponding M-CsPW samples. Three main differences between the two catalytic systems can be observed. The first is the acidity, the second is the texture properties of the two supports, and finally the metallic active sites. The acidity in TUD-1 matrix was generated as a result of the incorporation of Al³⁺ tetrahedrally in the silica matrix.

Hanefeld and coworkers [26] reported that the tetrahedral incorporation of Al^{3+} in the silica matrix can generate Brønsted sites as well as Lewis acidic sites. On the other hand, Kozhevnikov [15,16,23] reported that the type of acidic site in CsPW is only Brønsted acidity. In another word, Al-TUD-1 possesses two different types of acidity which most likely has a positive effect on intermediate formation through the dehydration step. The texture properties of the two catalytic systems show that TUD-1 is mesoporous three-dimensional with a pore size > 4 nm, moreover, the surface area of TUD-1 samples is >600 m^2/g . On the other hand, CsPW possess a micropore system with a pore size of 0.62–0.75 nm [27] with a surface area around 120 m^2/g . Hence, again the texture properties of TUD-1 provide more advantages related to the accessibility of the reactants/products to/from the active sites. Finally, the metal active sites functionalization in the two catalytic system was different: metal nanoparticles were incorporated in TUD-1 during the synthesis (i.e., one-pot synthesis), and by the impregnation technique in CsPW salt. Here, the impregnation technique has an advantage related to the operating temperature. CsPW was impregnated at room temperature and dried at 333 K, while the synthesis of M-Al-TUD-1 was calcined at 600 °C for 10 h, i.e., the energy required to prepare the catalysts are preference in the side of M-CsWP. One more point can be considered in the side of CsPW, which is the number of metals whom can activate the hydrogenation step. In Al-TUD-1 matrix, Pt and Ru nanoparticles were able to catalyze the hydrogenation step, while, Pd and Ag nanoparticles were not [13]. In Cs-WP, the four incorporated metals were able to catalyze hydrogenation step. The reason for the deactivation of two metals in the Al-TUD-1 system is still under investigation, but at least it is known now that number of metals, which can catalyze the hydrogenation step in the MIBK conversion is higher over CsPW system. To conclude, the two catalytic systems have some advantages and some disadvantages, however, the two catalytic systems were able to convert MIBK to 2-methylpropane in liquid phase, solvent free condition, which is reported—to the best of our knowledge—for the first time.

4. Materials and Methods

4.1. Chemicals

The following chemicals were purchased for the current research and they were used without any further treatment/modification: cesium carbonate (Cs_2CO_3 , 99.5% Acros Organics, Geel–Belgium), phosphotungstic acid hydrate ($\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 18\text{H}_2\text{O}$, 97% Sigma Aldrich, St. Louis, MO, USA), chloroplatinic acid hexahydrate ($\text{H}_2\text{Cl}_6\text{Pt} \cdot 6\text{H}_2\text{O}$, 98%, Sigma Aldrich, St. Louis, MO, USA), ruthenium chloride trihydrate ($\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$, 98%, Aldrich, St. Louis, MO, USA), palladium chloride (PdCl_2 , 99%, Sigma Aldrich, St. Louis, MO, USA), and silver nitrate (AgNO_3 , 99%, Sigma, St. Louis, MO, USA).

4.2. Synthesis of CsPW ($\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$)

CsPW was prepared as described elsewhere [27]. Cesium carbonate was dissolved in distilled water to prepare a solution with a concentration of 0.47 M. Then Phosphotungstic acid hydrate was dissolved in demi-water to prepare another solution with concentration 0.75 M. An aqueous solution of Cs_2CO_3 was added dropwise to an aqueous solution of $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 18\text{H}_2\text{O}$ while stirring continuously at 40 °C. The mixture formed was aged at room temperature for 24 h and dried in a rotary evaporator at 60 °C. Finally, the solid formed was calcined in the vacuum drying oven at temperature of 150 °C and pressure of 0.07 kPa for 2 h.

4.3. Synthesis of Metal (Pt, Pd, Ru or Ag) Supported on $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$

Four materials of 2 wt% metal (M = Pt, Pd, Ru or Ag) supported on CsPW were prepared by the impregnation technique. The calculated amount of the desired metal salts was dissolved in demi-water with concentration to form a solution of 0.1 M. The prepared solid of CsPW was gently grinded and added slowly into the salt solution during stirring. Then, the mixture formed was aged at room

temperature for 24 h and dried in a rotary evaporator at 60 °C. Finally, all prepared catalysts were reduced in a tube furnace at 300 °C for 2 h under hydrogen gas flow at 10 mL/min.

4.4. Characterization

XRD was performed by using Shimadzu 6000 DX instrument diffractometer (Shimadzu Corporation, Kyoto, Japan) equipped with a graphite monochromator using $\text{CuK}\alpha$ radiation ($\lambda = 0.1541 \text{ nm}$). Nitrogen adsorption/desorption isotherms were recorded on QuantaChrome NOVA 2000e instrument (Quantachrome Instruments, Boynton Beach, FL, USA). Nitrogen adsorption/desorption isotherm was recorded on a QuantaChrome NOVA 2000e instrument. Samples were degassed at 250 °C for 4 h. The BET method was used to calculate the surface area (S_{BET}) of the samples. FTIR spectra of the prepared M-CsPW samples were collected on Jasco FTIR 460 Plus instrument (JASCO, Easton, PA, USA) by using KBr. Infrared spectra for the prepared materials was recorded in the region from 400 to 4000 cm^{-1} . SEM study was carried out by using (Jeol Model 6360 LVSEM, JEOL Inc., Peabody, MA, USA), the micrographs were obtained after coating the samples by Au. Moreover, the microscope is equipped with an X-ray spectroscopy (EDAXS) unit which was used for elemental analyses and mapping.

4.5. Catalytic Performance Study

Liquid phase hydrogenation of MIBK was carried out in 300 mL semi-batch Parr reactor, with maximum temperature up to 180 °C whereas the maximum pressure was up to 21 atm. The equipment was provided with automatic temperature control and a pressure recording system. The temperature of the liquid in the reactor could be controlled within (± 1 °C). A fast and accurate pressure transducer (± 1 Psi) was used to measure the pressure. In a real reaction, 25 mL of MIBK and 0.25 g of the catalyst were placed inside the reactor and hydrogenated by 10 atm of H_2 gas pressure at 170 °C under stirring rate of 780 rpm for four hours. After reaction, the gas was released, and the reactor was cooled down to room temperature. The solution was filtrated, and finally analyzed by means of gas chromatography (GC) (SHIMADZU GC-17 instrument, Shimadzu Corporation, Kyoto Japan) with a RTX-5(G27) capillary column (30 m $\times$ 0.25 mm $\times$ 0.25 μm film thickness) equipped with a flame ionization detector (FID). Helium (He) gas was used as carrier gas while H_2 and air was used as FID gases.

Conversion % and selectivity % were calculated according on the following equations:

$$\text{Conversion}(\%) = \frac{[A_o] - [A_t]}{[A_o]} \times 100$$

where $[A_o]$ is the initial MIBK concentration, $[A_t]$ is the concentration of MIBK at time (t).

$$\text{Selectivity}(\%) = \frac{[2MP]}{\Sigma[\text{products}]} \times 100$$

where [product] is the concentration of 2-MP (in moles) after 4 h and $\Sigma[\text{products}]$ is the summation of concentrations of the entire products.

5. Conclusions

Here, we reported the liquid phase hydrogenation of methyl isobutyl ketone (MIBK) to 2-methylpentane (2-MP) at 170 °C. Pd-CsPW exhibited the highest activity compared to other M-CsPW (M = Pt, Ru, and Ag) catalysts, where 10% conversion was obtained with 91% selectivity after 4 h reaction time. The results confirm that Pd-CsPW is a bi-functional (metal/acid) catalytic system where both metallic and acidic active sites are essentially required to obtain the alkane product in liquid phase. There is no significant improvement in the activity of the catalyst over the use of CsPW as a

highly acidic support compared to TUD-1, and this is probably due to rate-determining step being the hydrogenation of ketone to alcohol.

Author Contributions: Conceptualization, A.M.A. and M.S.H.; methodology A.A.A. and M.E.; validation, M.B., A.M.A. and M.S.H.; formal analysis, A.M.A.; investigation, M.E. and M.B.; resources, A.M.A.; data curation, M.S.H.; writing—original draft preparation, A.M.A.; writing—review and editing, M.S.H.; supervision, A.M.A. and M.S.H.; project administration, A.M.A.; funding acquisition, A.M.A.

Funding: This research was funded by the Deanship of Scientific Research in King Khalid University, grant number R.G.P. 195-39.

Acknowledgments: The authors extend their appreciation to the Deanship of Scientific Research at King Khalid University for funding this work through the research group program. The authors thank M. Shkir for the SEM study.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Corma, A.; Iborra, S.; Velty, A. Chemical routes for the transformation of biomass into chemicals. *Chem. Rev.* **2007**, *107*, 2411–2502. [[CrossRef](#)] [[PubMed](#)]
2. Liu, B.; Zhang, Z. Catalytic conversion of biomass into chemicals and fuels over magnetic catalysts. *ACS Catal.* **2015**, *6*, 326–338. [[CrossRef](#)]
3. Van der Wal, H.; Sperber, B.L.; Houweling-Tan, B.; Bakker, R.R.; Brandenburg, W.; López-Contreras, A.M. Production of acetone, butanol, and ethanol from biomass of the green seaweed *Ulva lactuca*. *Biores. Technol.* **2013**, *128*, 431–437. [[CrossRef](#)] [[PubMed](#)]
4. Rao, P.V.R.; Kumar, V.P.; Rao, G.S.; Chary, K.V. Vapor phase selective hydrogenation of acetone to methyl isobutyl ketone (MIBK) over Ni/CeO₂ catalysts. *Catal. Sci. Technol.* **2012**, *2*, 1665–1673. [[CrossRef](#)]
5. Hetterley, R.D.; Kozhevnikova, E.F.; Kozhevnikov, I.V. Multifunctional catalysis by Pd-polyoxometalate: One-step conversion of acetone to methyl isobutyl ketone. *Chem. Commun.* **2006**, *7*, 782–784. [[CrossRef](#)] [[PubMed](#)]
6. Al-Wadaani, F.; Kozhevnikova, E.F.; Kozhevnikov, I.V. Pd supported on ZnII–CrIII mixed oxide as a catalyst for one-step synthesis of methyl isobutyl ketone. *J. Catal.* **2008**, *257*, 199–205. [[CrossRef](#)]
7. Pholjaroen, B.; Li, N.; Yang, J.; Li, G.; Wang, W.; Wang, A.; Zhang, T. Production of renewable jet fuel range branched alkanes with xylose and methyl isobutyl ketone. *Ind. Eng. Chem. Res.* **2014**, *53*, 13618–13625. [[CrossRef](#)]
8. Liao, T.; He, G.X.; Yang, S.H.; Luo, G.H.; Xu, X.; Guo, X.Y.; Jin, H.B. Study on the catalytic performance of supported skeletal nickel catalyst for hydrogenation of MIBK. *Mod. Chem. Ind.* **2017**, *6*, 75–80.
9. Alotaibi, M.A.; Kozhevnikova, E.F.; Kozhevnikov, I.V. Efficient hydrodeoxygenation of biomass-derived ketones over bifunctional Pt-polyoxometalate catalyst. *Chem. Commun.* **2012**, *48*, 7194–7196. [[CrossRef](#)]
10. Alotaibi, M.A.; Kozhevnikova, E.F.; Kozhevnikov, I.V. Hydrogenation of methyl isobutyl ketone over bifunctional Pt–zeolite catalyst. *J. Catal.* **2012**, *293*, 141–144. [[CrossRef](#)]
11. Itagaki, S.; Matsushashi, N.; Taniguchi, K.; Yamaguchi, K.; Mizuno, N. Efficient Hydrodeoxygenation of Ketones, Phenols, and Ethers Promoted by Platinum–Heteropolyacid Bifunctional Catalysts. *Chem. Lett.* **2014**, *43*, 1086–1088. [[CrossRef](#)]
12. Alharbi, K.; Kozhevnikova, E.F.; Kozhevnikov, I.V. Hydrogenation of ketones over bifunctional Pt-heteropoly acid catalyst in the gas phase. *Appl. Catal. A* **2015**, *504*, 457–462. [[CrossRef](#)]
13. Eissa, M.; Alhanash, A.M.; Benaissa, M.; Hamdy, M.S. Pt-Al-TUD-1: A bifunctional catalyst for liquid phase hydrogenation of MIBK. *Catal. Commun.* **2016**, *86*, 27–31. [[CrossRef](#)]
14. Okuhara, T. Microporous heteropoly compounds and their shape selective catalysis. *Appl. Catal. A* **2003**, *256*, 213–224. [[CrossRef](#)]
15. Kozhevnikov, I.V. Catalysis by Heteropoly Acids and Multicomponent Polyoxometalates in Liquid-Phase Reactions. *Chem. Rev.* **1998**, *98*, 171–198. [[CrossRef](#)]
16. Corma, A. Inorganic Solid Acids and Their Use in Acid-Catalyzed Hydrocarbon Reactions. *Chem. Rev.* **1995**, *95*, 559–614. [[CrossRef](#)]
17. Alhanash, A.; Kozhevnikova, E.F.; Kozhevnikov, I.V. Hydrogenolysis of glycerol to propanediol over Ru: Polyoxometalate bifunctional catalyst. *Catal. Lett.* **2008**, *120*, 307–311. [[CrossRef](#)]

18. Alhanash, A.; Kozhevnikova, E.F.; Kozhevnikov, I.V. Gas-phase dehydration of glycerol to acrolein catalysed by caesium heteropoly salt. *Appl. Catal. A* **2010**, *378*, 11–18. [\[CrossRef\]](#)
19. Okuhara, T.; Watanabe, H.; Nishimura, T.; Inumaru, K.; Misono, M. Microstructure of cesium hydrogen salts of 12-tungstophosphoric acid relevant to novel acid catalysis. *Chem. Mater.* **2000**, *12*, 2230–2238. [\[CrossRef\]](#)
20. Dias, J.A.; Caliman, E.; Dias, S.C.L. Effects of cesium ion exchange on acidity of 12-tungstophosphoric acid. *Microporous Mesoporous Mater.* **2004**, *76*, 221–232. [\[CrossRef\]](#)
21. Kozhevnikov, I.V. Heteropoly acids and related compounds as catalysts for fine chemical synthesis. *Catal. Rev.* **1995**, *37*, 311–352. [\[CrossRef\]](#)
22. Okuhara, T.; Mizuno, N.; Misono, M. Catalytic chemistry of heteropoly compounds. *Adv. Catal.* **1996**, *41*, 113–252.
23. Hashimoto, M.; Koyano, G.; Mizuno, N. In situ IR spectrum of 12-tungstophosphoric acid hexahydrate with planar $H_5O_2^+$. *J. Phys. Chem. B* **2004**, *108*, 12368–12374. [\[CrossRef\]](#)
24. Yfanti, V.L.; Vasiliadou, E.S.; Sklari, S.; Lemonidou, A.A. Hydrodeoxygenation of glycerol with in situ H_2 formation over Pt catalysts supported on Fe modified Al_2O_3 : Effect of Fe loading. *J. Chem. Technol. Biotechnol.* **2017**, *92*, 2236–2245. [\[CrossRef\]](#)
25. Zhang, C.; Lai, Q.; Holles, J.H. Ir@ Pt bimetallic overlayer catalysts for aqueous phase glycerol hydrodeoxygenation. *Appl. Catal. A* **2016**, *526*, 113–125. [\[CrossRef\]](#)
26. Telalović, S.; Karmee, S.K.; Ramanathan, A.; Hanefeld, U. Al-TUD-1: Introducing tetrahedral aluminium. *J. Mol. Catal. A* **2013**, *368*, 88–94. [\[CrossRef\]](#)
27. Izumi, Y.; Ono, M.; Kitagawa, M.; Yoshida, M.; Urabe, K. Silica-included heteropoly compounds as solid acid catalysts. *Microporous Mater.* **1995**, *5*, 255–262. [\[CrossRef\]](#)

© 2019 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).