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Efficient hydrodeoxygenation of biomass-derived ketones over bifunctional Pt-polyoxometalate catalyst†

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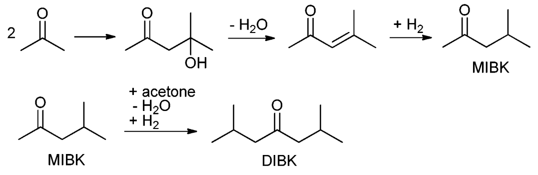
Acidic heteropoly salt $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ doped with Pt nanoparticles is a highly active and selective catalyst for one-step hydrogenation of methyl isobutyl and diisobutyl ketones to the corresponding alkanes in the gas phase at 100 °C with 97–99% yield *via* metal-acid bifunctional catalysis.

Efficient utilization of biomass resources is a major goal for academia and industry.[1] It is expected that biomass-based n-butanol will play a major role in the next generation of biofuels together with ethanol and biodiesel.[2] Biobutanol can be produced by acetone-butanol fermentation of carbohydrates and cellulosic raw materials using *Clostridium acetobutylicum* strain which yields butanol, acetone and ethanol in a weight ratio of 6 : 3 : 1.[3] Therefore, finding new outlets for acetone, preferably in the transportation fuel sector, would greatly improve the economy of biobutanol production. Acetone can be transformed into C_6, C_9 and larger organic molecules by aldol condensation. This is employed for the industrial synthesis of methyl isobutyl ketone (MIBK) and diisobutyl ketone (DIBK) (Scheme 1) that are used as solvents in paints. The synthesis can be carried as one-pot process using a bifunctional metal-acid catalyst, *e.g.*, Pd on an acidic support.[4] MIBK and DIBK could be hydrogenated to alkanes, 2-methylpentane (MP) and 2,6-dimethylheptane (DMH), which could be blended with gasoline and used through the existing fuel infrastructure. However, to the best of our knowledge, there is little data available on catalytic hydrogenation of MIBK and DIBK.

Here we report a very efficient gas-phase hydrogenation (hydrodeoxygenation) of MIBK and DIBK to MP and DMH, using heterogeneous bifunctional metal-acid catalysis.



Scheme 1 MIBK and DIBK production from acetone.

Table 1 Hydrogenation of MIBK[a]

Catalyst	Conversion [%]	Selectivity [%] MP	MP-ol	Other
0.5%Pt/SiO_2	64	14	86	0
10%Pt/C	95	6	93	1
10%Pt/C[b]	52	87	9	4
0.5%Pd/SiO_2	3	0	100	0
10%Pd/C	95	6	93	1
10%Pd/C[b]	84	94	5	1
5%Ru/C	96	2	95	3
5%Cu/SiO_2	<1	0	100	0
$2CuO\cdot Cr_2O_3$[c]	92	0	100	0

[a] At 100 °C, 0.20 g catalyst pretreated in H_2 at reaction temperature for 1 h, 3.6% MIBK in H_2 flow, 20 ml min^{-1} flow rate, 4 h time on stream. [b] At 300 °C. [c] Pre-reduced in H_2 at 400 °C for 2 h; exhibited XRD pattern of Cu metal (Supplementary Information).

First, we tested a number of conventional supported metal catalysts comprising Pd, Pt, Ru and Cu supported on silica and active carbon for MIBK hydrogenation in a continuous flow fixed bed reactor (9 mm internal diameter) in the temperature range 100–400 °C (for experimental details, see Supplementary Information†). Some representative results are shown in Table 1. At 100–200 °C, these catalysts were active for the hydrogenation of MIBK to 4-methyl-2-pentanol (MP-ol). Best results showed 10%Pt/C, 10%Pd/C, 5%Ru/C and copper chromite, with 93–100% MP-ol selectivity at 92–96% MIBK conversion at 100 °C. The selectivity to MP-ol decreased with increasing temperature due to formation of MP and hydrogenolysis of C–C bonds giving C_1–C_5 hydrocarbons. The highest MP selectivities 87–94% were observed for 10%Pt/C and 10%Pd/C catalysts at 52–84% conversion, but only at a temperature as high as 300 °C (Table 1), which indicates the difficulty of direct hydrogenation of MP-ol to MP.

Next, we tested bifunctional metal-polyoxometalate catalysts comprising Pt, Pd, Ru, or Cu supported on Keggin heteropoly salt $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (CsPW). This salt is widely used as a solid acid catalyst. It is a strong Brønsted acid, almost as strong as the parent heteropoly acid $H_3PW_{12}O_{40}$, with the important advantage over the latter of having much larger surface area (111 m^2 g^{-1}) and a higher thermal stability (~500 °C decomposition temperature),[5] hence a longer lifetime.[6] Our idea was to explore bifunctional metal-acid catalysed pathway to achieve MIBK-to-MP hydrogenation in one step on a single catalyst bed. This pathway

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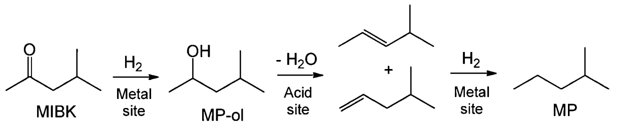


Scheme 2 Hydrodeoxygenation of MIBK *via* bifunctional metal-acid catalysis.

Table 2 Hydrogenation of MIBK over bifunctional metal-acid catalysts[a]

Catalyst	Conversion [%]	Selectivity [%]		
		MP	MP-ol	Other
0.5%Pt/CsPW	99	100	0	0
0.5%Pt/CsPW[b]	95	88	0	12
0.5%Pt/HZSM-5[c]	94	65	34	1
0.5%Pt/HZSM-5[b,c]	100	83	0	17
0.5%Pd/CsPW	7	34	0	66
0.5%Ru/CsPW	5	100	0	0
5%Ru/CsPW	99	100	0	0
5%Cu/CsPW	<1	100	0	0

[a] At 100 °C, 0.20 g catalyst pretreated in H_2 at reaction temperature for 1 h, 3.6% MIBK in H_2 flow, 20 ml min^{-1} flow rate, 4 h time on stream. [b] At 200 °C. [c] Atomic ratio Si/Al = 12.

would involve MIBK hydrogenation to MP-ol on metal sites followed by MP-ol dehydration on acid sites to form olefin and finally olefin hydrogenation to MP on metal sites (Scheme 2). Since dehydration of secondary alcohols on heteropoly acid catalysts is fast[7] and so is hydrogenation of $C{=}C$ bond on platinum metals, the bifunctional pathway was expected to be more efficient that the hydrogenation only pathway. Our study proved that this was indeed the case.

Representative results are shown in Table 2. It can be seen that amongst the bifunctional catalysts studied 0.5%Pt/CsPW clearly stands out yielding 99% MP at 100 °C, with 100% MP selectivity at $\geq$ 99% MIBK conversion (top entry). Importantly, no MP isomerisation was observed at this temperature, thus allowing synthetically viable complete transformation of ketone to alkane without carbon backbone alteration. At 200 °C, about 12% of MP isomerised to form n-hexane, 3-methylpentane and 2,3-dimethylbutane, in agreement with the literature.[8] 0.5%Ru/CsPW matched the Pt catalyst in MP selectivity, but had much lower activity per unit metal weight. About 5% Ru loading was required to match the activity of the 0.5% Pt catalyst. 0.5%Pd/CsPW was inferior to the Pt catalyst regarding both catalytic activity and MP selectivity, giving a large amount of heavy condensation products. Previously, Pd/CsPW has been found to be active bifunctional catalyst for the one-pot hydrocondensation of acetone to MIBK and further to DIBK.[4a] Finally, 5%Cu/CsPW practically did not show catalytic activity at 100 °C.

The Pt catalyst showed excellent performance stability. It reached steady state in about 1 h and operated without deactivation for at least 14 h (Fig. 1). It should be noted that to set in this run the conversion at about 80%, the amount of catalyst had to be reduced fourfold and the flow rate increased fivefold as compared to those in Table 2. Less than 1% of coke was found in the catalyst after reaction. Pt dispersion, *i.e.*, the fraction of exposed Pt atoms, which was 0.36 in the fresh 0.5%Pt/CsPW catalyst (from H_2 chemisorption), did not change after reaction, thus demonstrating high stability of Pt nanoparticles under reaction conditions.

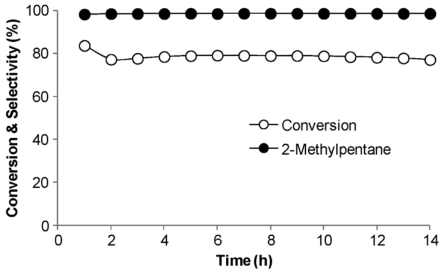


Fig. 1 Time course for MIBK hydrogenation over 0.5%Pt/CsPW (0.05 g) at 100 °C (3.6% MIBK in H_2 flow, 100 ml min^{-1} flow rate, the catalyst diluted with 0.15 g SiO_2).

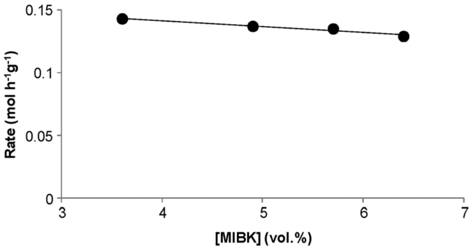


Fig. 2 Effect of MIBK concentration on the rate of MIBK hydrogenation over 0.5%Pt/CsPW (0.025 g) at 100 °C (100 ml min^{-1} H_2 flow rate, the catalyst diluted with 0.175 g SiO_2).

The reaction rate practically did not change with MIBK concentration in the gas feed (Fig. 2), which means that the order in MIBK was close to zero. Therefore, MIBK conversion is equivalent to the rate of MIBK consumption in our system. The order in the catalyst was close to one, as shown in Fig. 3. The apparent activation energy was found to be 50 kJ mol^{-1} in the temperature range 60–100 °C, which indicates that the reaction occurred under kinetic control. From these results, the turnover frequency (TOF) was estimated to be 160 h^{-1} per exposed Pt atom at 100 °C.

Further, to prove the bifunctional mechanism (Scheme 2), we tested the dehydration of MP-ol on 0.5%Pt/CsPW catalyst. This was carried out at 100 °C under the conditions applied for MIBK hydrogenation (Table 2), except with N_2 (20 ml min^{-1}) instead of H_2. As expected, the reaction was very fast, yielding two olefins, 4-methylpentene-1 and 4-methylpentene-2, in about 1 : 1 ratio at 100% conversion (eqn (1)). The same reaction under H_2 gave MP in a 100% yield (eqn (2)). These results,

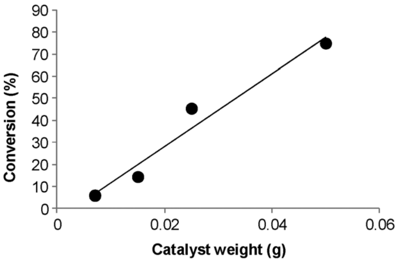


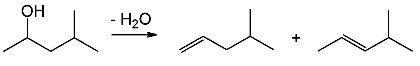
Fig. 3 Effect of catalyst weight on conversion for MIBK hydrogenation over 0.5%Pt/CsPW at 100 °C (3.6% MIBK in H_2 flow, 100 ml min^{-1} flow rate, 0.5%Pt/CsPW + SiO_2 = 0.20 g).

Table 3 Effect of Pt loading in Pt/CsPW on MIBK hydrogenation[a]

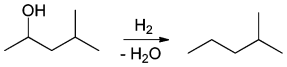
Pt loading [wt%]	Conversion [%]	MP selectivity [%]
0.25	30	93
0.50	78	98
1.0	100	100

[a] Catalyst mixture 0.05 g Pt/CsPW + 0.15 g SiO_2, 100 °C, 3.6% MIBK in H_2 flow, 100 ml min^{-1} flow rate, 4 h time on stream.

therefore, support the bifunctional mechanism for MIBK hydrogenation over 0.5%Pt/CsPW catalyst.



(1)



(2)

To determine the rate-limiting step in this mechanism, we looked at the effect of Pt loading in Pt/CsPW catalyst on MIBK hydrogenation (Table 3). As can be seen, MIBK conversion increases from 30 to 100% with increasing Pt loading from 0.25 to 1%. In contrast, the MP selectivity practically does not change with Pt loading, being in the range of 93–100%. This clearly shows that the reaction is limited by the first step–hydrogenation of MIBK to MP-ol on Pt sites (Scheme 2). Subsequent dehydration and hydrogenation steps are fast under the chosen conditions. The fast dehydration of MP-ol over Pt/CsPW can be explained by the strong acidity of CsPW. Its acid strength corresponds to 164 kJ mol^{-1} in terms of the differential heat of NH_3 adsorption.[7b] In this respect it was interesting to test a Pt catalyst with weaker acid sites. As such we tested 0.5%Pt/HZSM-5 with zeolite HZSM-5 as an acidic support, possessing acid sites with a heat of NH_3 adsorption of 145–150 kJ mol^{-1}.[9] This catalyst at 100 °C gave MIBK conversion close to that of 0.5%Pt/CsPW, but its MP selectivity (65%) was lower than for Pt/CsPW due to incomplete dehydration of MP-ol on the weaker acid HZSM-5 (Table 2). This shows that the strong acidity of CsPW is essential for the high efficiency of the Pt/CsPW catalyst in hydrodeoxygenation of MIBK. At 200 °C, Pt/HZSM-5 matched the performance of Pt/CsPW, but at this temperature considerable isomerisation of MP took place (Table 2).

Finally, we tested 0.5%Pt/CsPW catalyst for DIBK hydrogenation (Table 4). For comparison, copper chromite was also tested. The Pt catalyst again showed excellent performance under the conditions similar to those applied for MIBK hydrogenation. At 100 °C, it gave 97% selectivity to DMH at 100% conversion, with 3% of C_9 alkane isomers also formed. No 2,6-dimethyl-4-heptanol (DMH-ol) was found amongst the reaction products. Copper chromite, possessing weak acidity, performed differently like in the case of MIBK reaction. At 100–200 °C, it gave DMH-ol as the main product (90–92% selectivity at 74–80% conversion). At 300 °C, it effected complete hydrogenation to give DMH with 92% selectivity at 96% conversion, with 8% selectivity to other C_9 alkane isomers. Both catalysts, Pt/CsPW at 100 °C (Fig. 4) and copper chromite at 300 °C, exhibited very good durability, operating without deactivation for at least 14 h. As determined with Pt/CsPW catalyst, the reactivity of DIBK was 8 times lower than that of MIBK at 100 °C. This can be explained by greater steric hindrance in the case of DIBK hydrogenation.

Table 4 Hydrogenation of DIBK[a]

			Selectivity [%]		
Catalyst	T/°C	Conversion [%]	DMH	DMH-ol	Other[b]
0.5%Pt/CsPW	100	100	97	0	3
$2CuO{\cdot}Cr_2O_3$[c]	300	96	92	0	8

[a] 0.20 g catalyst, 1.7% DIBK in H_2 flow, 20 ml min^{-1} flow rate, 4 h time on stream. [b] Other products: C_9 alkane isomers. [c] Pre-reduced in H_2 at 400 °C for 2 h; exhibited XRD pattern of Cu metal.

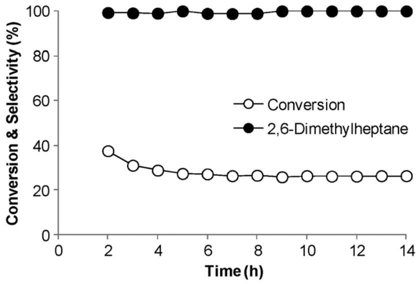


Fig. 4 Time course for DIBK hydrogenation over 0.5%Pt/CsPW (0.05 g) at 100 °C (1.7% DIBK in H_2 flow, 80 ml min^{-1} flow rate, the catalyst diluted with 0.15 g SiO_2).

In conclusion, we developed a very efficient catalyst Pt/CsPW for selective one-step hydrodeoxygenation of biomass-derived aliphatic ketones MIBK and DIBK under mild conditions without isomerisation of carbon backbone *via* metal-acid bifunctional mechanism.

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