

Multifunctional catalysis by Pd-polyoxometalate: one-step conversion of acetone to methyl isobutyl ketone

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Received (in Cambridge, UK) 28th October 2005, Accepted 14th December 2005

First published as an Advance Article on the web 6th January 2006

DOI: 10.1039/b515325e

Pd metal supported on $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ is an efficient bifunctional catalyst for the one-step conversion of acetone to methyl isobutyl ketone in gas and liquid phase.

The development of one-pot cascade processes without intermediate separation steps using multifunctional catalysts is an important strategy to carry out sustainable organic synthesis with a high atom and energy efficiency.¹

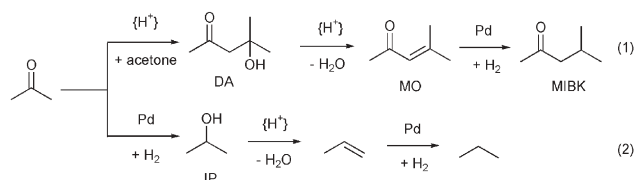
Polyoxometalates that found numerous applications as catalysts³ are inherently multifunctional compounds, possessing considerable structural mobility.^{2,3} Keggin-type heteropoly acids $\text{H}_n[\text{XM}_{12}\text{O}_{40}]$ (HPA), where $\text{X} = \text{Si}^{4+}$, P^{5+} and $\text{M} = \text{Mo}^{6+}$, W^{6+} , V^{5+} , etc., are the most common polyoxometalates. These are strong Brønsted acids as well as efficient redox agents. Their acid and redox properties can be tuned by varying polyanion composition, while the HPA molecular (primary) structure remains unchanged. Solid HPA allow a broad alteration of their texture (secondary structure) in a controlled manner and can be chemically modified to introduce a metal function, Lewis acidity, basicity, and so on.^{2,3} The potential of polyoxometalates as multifunctional catalysts has long been recognised. Thus solid HPA doped with Pd and Pt have been found efficient bifunctional catalysts for alkane isomerisation.^{4a} Pd-doped HPA catalyst is used in the Showa-Denko process for manufacturing acetic acid by oxidation of ethene.^{4b} However, little research on the use of HPA as multifunctional catalysts for cascade organic synthesis has been done so far. Here we report a Pd-doped acidic heteropoly salt, $\text{Cs}_{2.5}\text{H}_{0.5}[\text{PW}_{12}\text{O}_{40}]$ (CsPW),[†] as a very efficient bifunctional catalyst for the one-step conversion of acetone to MIBK in gas and liquid phase. CsPW is well known as a strong Brønsted solid acid and a versatile acid catalyst.^{2,3}

Methyl isobutyl ketone (MIBK) is one of the most widely used aliphatic ketones and is mainly employed as a solvent for paint and extraction.⁵ Diisobutyl ketone (DIBK), a by-product in the synthesis of MIBK, is a good solvent for a variety of natural and synthetic resins. Traditionally MIBK is manufactured *via* a three-step process: base-catalysed aldol condensation of acetone to diacetone alcohol (DA); acid-catalysed dehydration of DA to mesityl oxide (MO); and metal-catalysed hydrogenation of MO to MIBK.⁶ One-step processes operating at 120–200 °C and 20–50 bar H_2 pressure in liquid phase have been developed, employing bifunctional acid/redox catalysts comprising acidic resins, zeolites, or zirconium phosphate with addition of platinum group metals, usually palladium.^{6–8} Although high selectivity to MIBK (80–95%

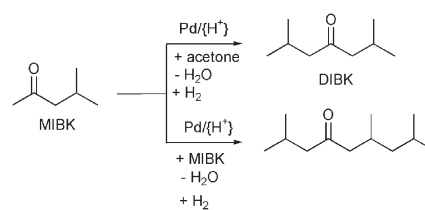
at 30–50% conversion) has been obtained, the high pressure is a disadvantage. Since the one-step process is simpler and more economically attractive, there is a great interest in finding new, improved catalyst systems operating at lower pressures. One-step synthesis of MIBK in the gas phase is also attractive. Usually it is carried out at 140–340 °C and ambient pressure, however, the MIBK selectivity is generally lower than in the liquid-phase reaction and catalyst deactivation may be a problem.^{6–8}

The proposed general mechanism of the one-step synthesis of MIBK on a bifunctional catalyst Pd/{H⁺} is shown in Scheme 1.⁹ MIBK forms in three steps (route 1): acetone condensation to DA over acid sites; acid-catalysed dehydration of DA to MO; and selective hydrogenation of the C=C bond of MO on Pd sites to yield MIBK.¹⁰ Concurrently, the Pd-catalysed hydrogenation of the C=O group of acetone yields isopropanol (IP), which can further be dehydrated on the acid sites to propene, followed by the formation of propane *via* propene hydrogenation on Pd sites (route 2). Therefore, the selectivity to MIBK depends on the relative rates of routes (1) and (2) which can be varied by tuning the acid and hydrogenation properties of the bifunctional catalyst.¹¹ DIBK and C₉₊ condensation products may also form in further reactions of MIBK (Scheme 2).⁸

Representative results for the gas-phase reaction over Pd/CsPW are given in Table 1.‡ The reaction occurs at remarkably low temperatures of 80–100 °C which is probably due to the strong acidity of CsPW enhancing the first two steps in route (1) (Scheme 1). MIBK is the major reaction product, with DIBK also formed. Among by-products are propene and propane (C₃) and C₉₊ acetone condensation products (mainly the tetramer



Scheme 1



Scheme 2

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Table 1 Gas-phase synthesis of MIBK

Catalyst ^a	T/°C	Conversion (%)	Selectivity (%) ^b					
			MIBK	DIBK	C ₃	IP	MO	Other
CsPW	120	1.1	0	0	7.5	0	64.0	28.5
2.1%Pd/CsPW	80	11.0	62.5	6.0	16.0	5.0	0	10.5
1%Pd/CsPW	100	18.6	76.3	10.5	5.8	0.4	0	7.0
0.5%Pd/CsPW ^c	100	13.3	82.6	8.2	2.9	0.5	0.6	5.7
0.3%Pd/CsPW	100	12.9	80.2	8.3	3.7	0	0	7.7
0.3%Cu–0.3%Pd/CsPW	120	1.9	36.8	4.2	5.9	0	36.8	16.3
1%Pt/CsPW	120	77.7	1.2	0.2	83.4	2.5	0	12.7
0.3%Pt/CsPW	100	32.7	8.4	1.2	69.9	2.0	0.6	17.9

^a 0.20 g catalyst, 10 ml min⁻¹ H₂ flow rate, 0.36 s contact time, [acetone]/[H₂] = 1 : 2.3 mol/mol, 2 h time on stream; ^b C₃ is propene and propane, MO mesityl oxide, others mainly C₉₊ acetone condensation products (mostly 2,6,8-trimethylnonane-4-one); ^c [acetone]/[H₂] = 2 : 1 mol/mol; 5 ml min⁻¹ H₂.

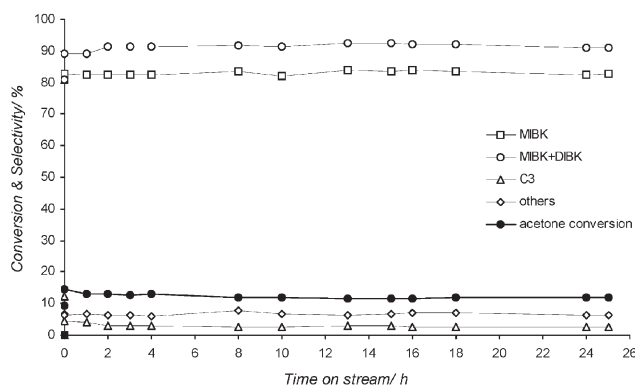


Fig. 1 Gas-phase acetone conversion and product selectivities vs. time on stream (0.20 g 0.5%Pd/CsPW, 7.5 ml min⁻¹ H₂ flow, [acetone]/[H₂] = 2 : 1, 100 °C).

2,6,8-trimethylnonane-4-one) together with small amounts of MO and IP. MIBK was obtained with up to 83% selectivity and 91% total selectivity to MIBK + DIBK. This compares well with the best results reported so far.^{7a-c} The reaction clearly requires both acid and redox catalysis which is provided by CsPW and Pd, respectively. When CsPW was used alone in the absence of Pd, MIBK was not observed, with MO, the product of acid-catalysed condensation of acetone, being major product. In contrast to Pd/CsPW, Pt/CsPW was very active in C=O hydrogenation *via* route (2) giving 83% selectivity to C₃ (*via* the dehydration of IP

and only 1.2% MIBK at 120 °C. Both Pt/CsPW and Pd/CsPW were found active in the dehydration of IP to propene. The Pd/CsPW catalyst exhibited very good durability in the synthesis of MIBK (Fig. 1). Catalyst deactivation was not observed after 25 hours continuous operation. The catalyst reached a steady state in *ca.* 1 h and then performed with a constant activity and selectivity.

The liquid-phase reaction with Pd/CsPW (Table 2)§ generally gave the same products as the gas-phase one. At constant temperature, the catalyst activity and MIBK selectivity were almost independent of the Pd loading (0.1–1%). This may suggest that the Pd-catalysed hydrogenation of mesityl oxide is a fast step in the acetone conversion (Scheme 1). However, data on the Pd dispersion are needed to confirm this. Another possible explanation is that the hydrogenation step may be controlled by H₂ diffusion into the liquid phase. The best runs gave 92% MIBK selectivity and 95% total selectivity to MIBK + DIBK. This result is on a par with the best results reported so far.^{7b,7d,7e} It should be noted that the H₂ pressure is unprecedentedly low (5–7.5 bar)—typically about 20 bar or higher.^{7b,7d,7e} Doping the Pd/CsPW catalyst with Cu led to further increase in selectivity up to 95% MIBK and 98% MIBK + DIBK. Interestingly, the Cu-Pd/CsPW was a very poor catalyst for the gas-phase reaction (Table 1). In the liquid phase, Pt/CsPW, as in the gas phase, was very active to effect the reaction *via* route (2) giving 65% IP and 22% C₃, only 7% MIBK being formed. The Cu-Pd/CsPW catalyst could be reused simply after washing it with acetone, although it had a reduced

Table 2 Liquid-phase synthesis of MIBK (7.5 bar H₂ pressure, 2 h)

Catalyst	T/°C	Conversion (%)	Selectivity (%) ^a					
			MIBK	DIBK	C ₃	IP	MO	Other
CsPW ^b	160	26.4	0	0	4.2	0	52.7	43.1
1%Pd/CsPW	180	27.1	91.0	2.9	2.6	2.4	0	1.1
0.3%Pd/CsPW	140	21.5	91.6	2.8	2.3	1.6	0	1.7
0.3%Pd/CsPW	160	33.0	90.2	4.4	2.8	0	0	2.7
0.3%Pd/CsPW	180	42.0	87.0	6.6	2.8	0.6	0	3.0
0.1%Pd/CsPW	140	22.7	91.4	2.5	2.2	2.9	0	1.1
0.1%Pd/CsPW	180	42.1	89.8	4.3	0.9	2.1	0	2.9
0.1%Pd/CsPW ^c	180	40.0	84.0	5.6	3.0	0	0	7.4
0.3%Cu–0.3%Pd/CsPW	160	23.9	94.9	3.0	1.0	0	0	1.1
0.3%Cu–0.3%Pd/CsPW ^d	160	15.8	73.7	1.4	2.5	0	17.7	4.6
0.3%Pt/CsPW	140	49.7	7.2	0	22.0	64.8	0	6.0

^a C₃ is propene and propane, IP isopropanol, others mainly C₆₊ acetone condensation products. ^b Dark coloured product mixture in contrast to the uncoloured one with Pd/CsPW. ^c 5 bar H₂ pressure. ^d Reuse of the run above.

activity and gave less MIBK and DIBK and an increased amount of MO and C₉₊ compared to the first run (Table 2). This shows that the recovered catalyst partly lost its acidity and hydrogenation activity which may be regenerated by aerobic treatment at 350 °C, as described elsewhere.¹²

In conclusion, Pd/CsPW is an efficient bifunctional catalyst for the one-step synthesis of MIBK from acetone, both in the gas and liquid phase. The continuous gas-phase process and the batch liquid-phase process yield MIBK together with DIBK with a total selectivity of 91% and 98%, respectively. The gas-phase synthesis occurs effectively at a remarkably low temperature (80–100 °C), no catalyst deactivation is observed for at least 25 h on stream. In the liquid-phase reaction, the catalyst performs well at a very low H₂ pressure of 5 bar and can be reused. The selectivity of the polyoxometalate-based multifunctional catalyst can be dramatically changed by varying the metal function (*e.g.* by substituting Pt for Pd), which may find application in other cascade reactions. Work on catalyst characterisation and further process optimisation is in progress.

Thanks are due to Mr R. L. Al-Otaibi and Mr F. Al-Wadaani for their help with the experiments.

Notes and references

† CsPW and Pd/CsPW were prepared as described elsewhere.^{12,13} Cu and Pt catalysts were prepared by impregnating CsPW with Cu(acac)₂ in toluene and H₂PtCl₆ in water followed by reduction by H₂ at 250 °C for 2 h. The catalyst powders had ≤180 μm particle size, 2.26–2.31 g cm⁻³ density and S_{BET} = 110–130 m² g⁻¹.

‡ The gas-phase reaction was performed under atmospheric pressure in a Pyrex glass fixed-bed microreactor (9 mm internal diameter, 0.20 g catalyst bed, 10 ml min⁻¹ H₂ flow rate, 0.36 s contact time, [acetone]/[H₂] = 1 : 2.3 mol/mol, 2 h time on stream) with on-line GC analysis (30 m × 0.25 mm HP-INNOWAX capillary column, flame ionisation detector). All gas lines were made of stainless steel. The downstream lines and sampling valves were heated at 150 °C to prevent product condensation. Prior to reaction, the catalysts were pre-treated with hydrogen at 250 °C for 1 h.

§ The liquid-phase synthesis of MIBK was carried out in a 45 ml Parr 4714 stainless steel autoclave equipped with a magnetic stirrer. The reaction mixture contained 2.0 g of acetone, 0.30 g decane (GC standard) and 0.20 g

catalyst. The autoclave was pressurised with H₂ and placed in the oil bath, preheated to the reaction temperature (140–180 °C). The resulting pressure indicated that the acetone remained liquid under such conditions. After reaction completion, the reactor was cooled to 0 °C, depressurised in a gas bag and opened. The catalyst was separated by centrifugation. Products were identified by GC-MS and quantified by GC equipped with flame ionisation detector. A 30 m × 0.25 mm BP5 capillary column was used to analyse gas products (collected in the gas bag) and a 30 m × 0.25 mm HP-INNOWAX capillary column was used for liquid samples.

- 1 J.-C. Wasilke, S. J. Obrey, R. T. Baker and G. C. Bazan, *Chem. Rev.*, 2005, **105**, 1001; A. Bruggink, R. Schoevart and T. Kieboom, *Org. Process Res. Dev.*, 2003, **7**, 622; H. van Bekkum and H. W. Kouwenhoven, *Stud. Surf. Sci. Catal.*, 2005, **157**, 311.
- 2 T. Okuhara, N. Mizuno and M. Misono, *Adv. Catal.*, 1996, **41**, 113; I. V. Kozhevnikov, *Chem. Rev.*, 1998, **98**, 171; M. Misono, *Chem. Commun.*, 2001, 1141.
- 3 I. V. Kozhevnikov, *Catalysts for Fine Chemicals. Vol. 2. Catalysis by Polyoxometalates*, Wiley, Chichester, England, 2002.
- 4 (a) T. Baba, Y. Hasada, M. Nomura, Y. Ohno and Y. Ono, *J. Mol. Catal. A: Chem.*, 1996, **114**, 247; K. Na, T. Okuhara and M. Misono, *J. Chem. Soc., Chem. Commun.*, 1993, 1422; T. Okuhara, *Appl. Catal., A*, 2003, **256**, 213; (b) K. Sano, H. Uchida and S. Wakabayashi, *Catal. Surv. Jpn.*, 1999, **3**, 55.
- 5 W. F. Hoelderich, *Stud. Surf. Sci. Catal.*, 1988, **41**, 83.
- 6 K. Weissmehl and H.-J. Arpe, *Industrial Organic Chemistry*, 3rd edn., Wiley, Weinheim, 1997, p. 280.
- 7 (a) V. Chikán, Á. Molnár and K. Baláznik, *J. Catal.*, 1999, **184**, 134; (b) Y. Higashio and T. Nakayama, *Catal. Today*, 1996, **28**, 127; (c) S. Narayanan and R. Unnikrishnan, *Appl. Catal., A*, 1996, **145**, 231; (d) S.-M. Yang and Y. M. Wu, *Appl. Catal., A*, 2000, **192**, 211; (e) Y. Z. Chen, B. J. Liaw, H. R. Tan and K. L. Shen, *Appl. Catal., A*, 2001, **205**, 61; (f) Y. Diaz, L. Melo, M. Mediavilla, A. Albornoz and J. L. Brito, *J. Mol. Catal. A: Chem.*, 2005, **227**, 7.
- 8 M. Martínez-Ortiz, D. Tichit, P. Gonzalez and B. Coq, *J. Mol. Catal. A: Chem.*, 2003, **201**, 199.
- 9 L. Melo, P. Magnoux, G. Giannetto, F. Alvarez and M. Guisnet, *J. Mol. Catal. A: Chem.*, 1997, **124**, 155.
- 10 R. Ruiz, C. Pesquera, F. González and C. Blanco, *Appl. Catal., A*, 2004, **257**, 165.
- 11 L. Melo, A. Llanos, L. García, P. Magnoux, F. Alvarez, M. Guisnet and G. Giannetto, *Catal. Lett.*, 1998, **51**, 207.
- 12 E. F. Kozhevnikova, E. Rafiee and I. V. Kozhevnikov, *Appl. Catal., A*, 2004, **260**, 25.
- 13 Y. Izumi, M. Ono, M. Kitagawa, M. Yoshida and K. Urabe, *Microporous Mater.*, 1995, **5**, 255.