

One-step synthesis of methyl isobutyl ketone from acetone catalysed by Pd supported on Zn^{II}–Cr^{III} mixed oxide

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Abstract

Pd metal (0.1–1 wt%) supported on Zn^{II}–Cr^{III} (1:10) mixed oxide was found to be an efficient bifunctional catalyst for the one-step synthesis of methyl isobutyl ketone (MIBK) from acetone and H₂ in gas- and liquid-phase processes. The reaction involves the acid-catalysed condensation of acetone to form mesityl oxide, followed by its hydrogenation to MIBK. The gas-phase reaction produces MIBK with a selectivity up to 78% at 40–66% acetone conversion (200–350 °C, ambient pressure). Diisobutyl ketone (DIBK) is the main byproduct, with a total MIBK + DIBK selectivity of up to 93%. The catalyst reaches a steady state in ca. 1 h and shows constant activity and selectivity for at least 50 h on stream. The liquid-phase reaction yields MIBK with up to 83% selectivity and total selectivity to MIBK + DIBK up to 9 at 56% acetone conversion (200 °C, 5 bar H₂ pressure). As a catalyst support, the amorphous Zn–Cr oxide calcined at 300 °C provides higher catalytic activity than the crystalline Zn–Cr oxide calcined at 400 °C, probably due to the lower surface area of the crystalline oxide. XRD of 0.3–1%Pd/Zn–Cr oxide showed no pattern of Pd metal, indicating a fine dispersion of Pd particles in the catalyst.

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Keywords: Acetone; Methyl isobutyl ketone; One-step process; Palladium; Zn–Cr mixed oxide; Bifunctional catalysis

1. Introduction

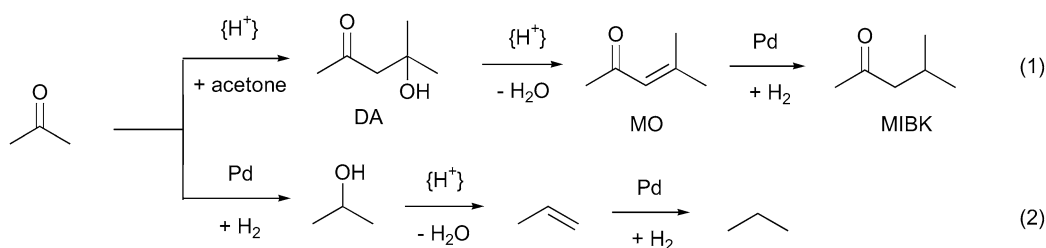
Methyl isobutyl ketone (MIBK) is one of the most widely used aliphatic ketones. Its primary uses included as a solvent for paint and protective coatings, an extracting agent for the production of antibiotics and commercial lubricating oils, a reagent for the separation and purification of metal ions, and an initiator for polymerisation [1]. Diisobutyl ketone (DIBK), a consecutive product in the synthesis of MIBK, is an exceptionally good solvent for a wide variety of natural and synthetic resins. It is also used in pharmaceutical and mining industries. Traditionally, MIBK is manufactured via a three-step process: (1) base-catalysed aldol condensation of acetone to diacetone alcohol (DA), (2) acid-catalysed dehydration of DA to mesityl oxide (MO), and (3) metal-catalysed hydrogenation of MO to MIBK [2]. One-step processes operating at 120–200 °C and 20–50 bar H₂ pressure in liquid phase have been developed using bifunctional acid–base/redox catalysts comprising

acidic cation-exchangers, zeolites, or zirconium phosphate with added platinum group metals, generally palladium. In one-step processes, the three steps occur simultaneously to yield MIBK in an exothermic reaction ($\Delta H = -117$ kJ/mol) [2]. Although high selectivity to MIBK (80–95% at 30–50% conversion) has been obtained, the high pressure is a disadvantage. Because 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, this 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 in this process.

The proposed general mechanism of the one-step synthesis of MIBK on a bifunctional catalyst Pd/{H⁺} is shown in Scheme 1 [3]. MIBK forms in three steps (route 1): (1) acetone condensation to DA over acid sites, (2) acid-catalysed dehydration of DA to MO, and (3) selective hydrogenation of the C=C bond of MO on Pd sites to yield MIBK [4]. Concurrently, the Pd-catalysed hydrogenation of the C=O group of acetone yields isopropanol (IP), which can further be dehydrated on

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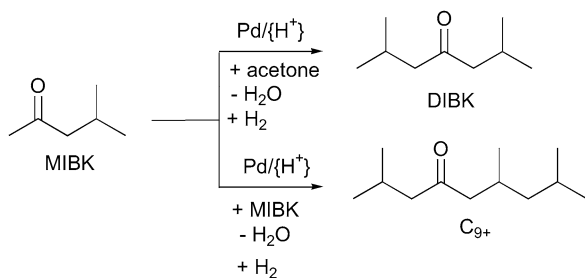


Scheme 1.

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 [5]. Other products, such as DIBK and C_{9+} condensation products, may also form in further reactions of MIBK (Scheme 2) [6]. More about various products of this reaction can be found elsewhere [6]. The overall selectivity depends not only on the active sites in the catalyst, but also on the catalyst pore structure controlling the diffusion of reactants and products to and from the active sites [4].

Numerous bifunctional catalysts have been studied in the one-step synthesis of MIBK in both gas-phase and liquid-phase reactions [6–20]. These include Pt supported on gallosilicate and aluminosilicate [7], NaX, and CsX zeolites [8], Pd on ZSM-5 [9], SAPO-11 and AlPO-11 [10], zirconium phosphate [17], niobic acid and alumina [18,19], and Pd, Ni, Cu, or Pd–Cu supported on MgO, Mg/Al hydrotalcite, and alumina [6,11–16,20]. Here we report the one-step synthesis of MIBK in gas and liquid phase over a new catalyst: palladium supported on ZnO–Cr₂O₃ mixed oxide, Pd/Zn–Cr.

Zn–Cr oxide has long been used as a catalyst for various reactions of synthesis gas (CO + H₂), for example, the synthesis of methanol [21,22] and higher alcohols [23] and aliphatic and aromatic hydrocarbons [24]. It has also been used for the fluorination of hydrocarbons with HF [25,26], dehydrogenation of alcohols [27], hydrogenation of carboxylic acids [28], synthesis of quinoline from aniline and glycerol [29], and selective catalytic reduction of NO with NH₃ [30]. Pt/Zn–Cr has proven to be an effective catalyst for the low-temperature dehydrogenation of isobutane to isobutene [31]. To our knowledge, to date neither Zn–Cr oxide nor Pd/Zn–Cr has been used for the synthesis of MIBK. Zn–Cr oxide has been studied over a wide range of Zn/Cr atomic ratios [21,22,24]. Here we chose a Zn–Cr (1:10) oxide, which has a significant (Brønsted and Lewis) acidity, as evidenced by its high catalytic activity in acid-catalysed re-



Scheme 2.

Table 1
Catalyst characterisation

Entry	Catalyst	S_{BET} (m ² /g)	Pore size (Å)	Pore volume (cm ³ /g)	H ₂ O content ^a (wt%)
1	Zn–Cr (1:10) oxide ^b	169	39	0.16	8.3
2	Zn–Cr (1:10) oxide (cr) ^c	87	79	0.17	2.0
3	1%Pd/Zn–Cr	159	35	0.15	6.0
4	0.3%Pd/Zn–Cr	150	43	0.16	6.4
5	0.1%Pd/Zn–Cr	135	29	0.11	6.0
6	1%Pd/Zn–Cr (cr) ^d	84	67	0.14	2.2

^a From TGA as a weight loss in the temperature range of 30–700 °C.

^b Amorphous oxide calcined at 300 °C for 5 h under N₂; 8.4 wt% Zn and 63.0 wt% Cr content in anhydrous oxide (from ICP).

^c Crystalline oxide obtained from the amorphous oxide (entry 1) by calcination at 400 °C for 5 h under N₂.

^d Crystalline Zn–Cr (1:10) oxide as a support.

actions, such as hydrocarbon fluorination by HF [25,26]. We found that the Pd/Zn–Cr catalyst exhibits high activity and selectivity, as well as long durability, in the one-step synthesis of MIBK.

2. Experimental

2.1. Catalyst preparation

The Zn–Cr (1:10) mixed oxides (Zn/Cr atomic ratio of 1:10) were prepared via coprecipitation of Zn^{II} and Cr^{III} hydroxides using a procedure adapted from that reported elsewhere [22, 24,31]. The coprecipitation was carried out by adding 10 wt% aqueous ammonium hydroxide dropwise to a stirred 0.2 M aqueous solution of a mixture of Zn^{II} + Cr^{III} nitrates (1:10 molar ratio) at 70 °C until pH 7 was reached, followed by aging the suspension for 3 h at 70 °C. The precipitate was filtered off, washed with deionised water until ammonia-free, and dried in air at 100–110 °C overnight. The amorphous and crystalline Zn–Cr oxides were obtained by calcination of the mixed hydroxides under nitrogen flow for 5 h, the amorphous oxide at 300 °C and the crystalline oxide at 400 °C.

The Pd-doped catalysts were prepared by stirring a Zn–Cr oxide powder with 0.02 M solution of Pd(OAc)₂ in benzene at room temperature for 1 h, followed by slow evaporation of the solvent in a rotary evaporator. The material was then reduced under hydrogen flow (30–40 ml/min) at 250 °C for 2 h. The catalysts were ground into a powder (particle size ≤180 μm unless stated otherwise) and stored in a desiccator over P₂O₅. The density of the catalyst powder was 1.54 g/cm³. The Zn, Cr,

and Pd content of the catalysts thus prepared were determined by ICP. Catalyst characterisation is given in Table 1.

2.2. Techniques

The BET surface area and porosity of Zn–Cr oxides and Pd/Zn–Cr catalysts were measured by nitrogen physisorption at 77 K on a Micromeritics ASAP 2000 instrument. Before the analysis, the samples were evacuated at 250 °C for 4–6 h. Water content in the catalysts was measured by thermogravimetric analysis (TGA) under nitrogen flow using a Perkin-Elmer TGA 7 instrument. The amount of coke deposited on the used catalysts was measured by TGA under air as described elsewhere [32]. Powder X-ray diffraction (XRD) spectra of catalysts (phase analysis) were recorded on a Stoe Stadi-P diffractometer with a monochromatic $\text{Cu-K}\alpha_1$ radiation from a germanium monochromator in the angular range $20^\circ \leq 2\theta \leq 70^\circ$, with a step width of 0.04° and count time of 5 s per step. XRD patterns were attributed using the JCPDS database. Ammonia adsorption onto the catalysts was measured in a flow system using a Setaram TG-DSC 111 differential scanning calorimeter as described elsewhere [33]. ICP analysis was carried out on a Spectro Ciros emission spectrometer.

2.3. Catalyst testing for MIBK synthesis

2.3.1. Gas-phase process

The catalytic tests were performed under atmospheric pressure in a Pyrex glass fixed-bed microreactor (9 mm i.d.) with on-line GC analysis (Varian Star 3400 CX gas chromatograph equipped with a 30 m \times 0.25 mm BP5 capillary column and flame ionisation detector). The reactor was placed in a vertical tubular furnace. The catalyst bed containing 0.1–0.5 g of a catalyst powder ($\leq 180 \mu\text{m}$ particle size; 1.54 g/cm^3 density) was placed in the reactor between two layers of Pyrex glass wool. The temperature in the reactor was controlled with a Eurotherm controller using a thermocouple placed at the top of the catalyst bed. The gas feed was fed into the reactor from the top. Acetone was supplied to the gas flow by bubbling a flow of H_2 or an H_2/N_2 mixture (typically 10–20 ml/min, controlled by Brooks mass flow controllers) through a stainless steel saturator containing acetone, maintained at a certain temperature to maintain the chosen acetone vapour pressure. All gas lines were made of stainless steel. The downstream lines and sampling valves were heated at 150 °C to prevent product condensation. Before reaction, the catalysts were pretreated with hydrogen (10 ml/min) at 300 °C for 1 h. At regular time intervals, the downstream gas flow was analysed by on-line GC. The liquid products were collected in an ice trap and also analysed by off-line GC using a 30 m \times 0.25 mm HP-INNOWAX capillary column (Agilent Technologies). The products were identified by GC and GC-MS using authentic samples.

2.3.2. Liquid-phase process

The liquid-phase synthesis of MIBK was carried out in a 45-ml Parr 4714 stainless steel autoclave equipped with a pressure gauge and a magnetic stirrer. Typically, the reaction mixture

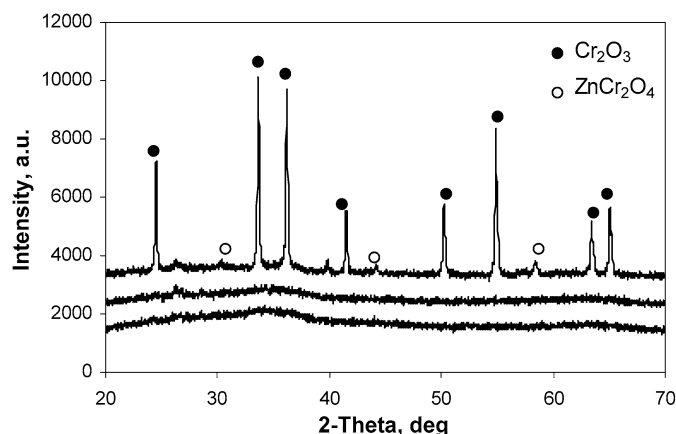


Fig. 1. XRD patterns from top to bottom: crystalline Zn–Cr oxide (Table 1, entry 2), amorphous Zn–Cr oxide (Table 1, entry 1), fresh 1%Pd/Zn–Cr (Table 1, entry 3).

contained 2.0 g of acetone, 0.30 g of decane (internal GC standard), and 0.20 g of catalyst. The autoclave was pressurised with H_2 and placed in an oil bath that was preheated to the reaction temperature. Judging from the resulting pressure, most of the acetone remained liquid under such conditions. After the completion of reaction (typically 2 h), the reactor was cooled to 0 °C, depressurised in a gas bag with a stopcock, and opened. The reaction mixture was taken out of the autoclave and separated from the catalyst by centrifugation. Products were identified by GC-MS and quantified by a gas chromatograph (Varian Star 3400 CX) equipped with a flame ionisation detector. A 30 m \times 0.25 mm BP5 capillary column was used to analyse gas products (collected in the gas bag), and a 30 m \times 0.25 mm HP-INNOWAX capillary column was used for liquid samples.

3. Results and discussion

3.1. Catalyst characterisation

The bifunctional acid–base/redox catalyst under study comprised Zn–Cr (1:10) mixed oxide as an acid–base component and Pd metal as a redox (hydrogenation) component. Depending on the calcination temperature, Zn–Cr oxide can be amorphous ($\leq 300^\circ\text{C}$) or crystalline ($>350^\circ\text{C}$), with the latter including, in general, ZnO, Cr_2O_3 , and ZnCr_2O_4 crystalline phases [22,24]. We used mostly the amorphous hydrous Zn–Cr (1:10) oxide calcined at 300 °C. It showed no crystallinity in its XRD spectrum (Fig. 1) and had a surface area of $169 \text{ m}^2/\text{g}$, an average pore size of 39 Å, and a water loss of 8.3 wt% on heating to 700 °C (Table 1, entry 1). The corresponding crystalline Zn–Cr (1:10) oxide obtained by calcination at 400 °C exhibited clear patterns of ZnCr_2O_4 spinel and Cr_2O_3 crystalline phases (Fig. 1), in agreement with the literature [22,24]. It had a surface area of $87 \text{ m}^2/\text{g}$, an average pore size of 79 Å, and a water content of 2.0 wt% (Table 1, entry 2).

The acidity of the amorphous Zn–Cr oxide was characterised by NH_3 adsorption at 100 °C using TG-DSC (Fig. 2). The oxide was pretreated at 300 °C for 2 h under N_2 (35 ml/min), followed by stabilisation at 100 °C for 1 h. Then it was brought

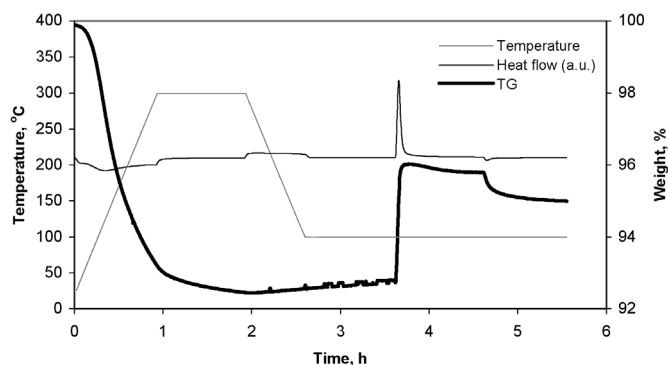


Fig. 2. TG-DSC for ammonia adsorption on the amorphous Zn–Cr oxide (Table 1, entry 1) at 100 °C.

in contact with a $\text{NH}_3 + \text{N}_2$ (1:1) gas flow (35 ml/min), which caused a sharp weight gain and heat release. After 1 h, the gas flow was switched to pure N_2 . The initial NH_3 adsorption under NH_3 flow on Brønsted and Lewis acid sites was 1.95 mmol/g_{cat}, and the enthalpy of adsorption was -117 kJ/mol NH_3 . After the gas flow was switched to N_2 , 1.52 mmol/g_{cat} ammonia remained adsorbed on the oxide, reflecting the number of stronger acid sites in the amorphous Zn–Cr oxide. Similarly, for the crystalline Zn–Cr oxide, the initial adsorption of NH_3 was 1.21 mmol/g_{cat}, and the enthalpy of adsorption was -127 kJ/mol NH_3 . This demonstrates that both oxides had acid sites of comparable strength, close to that of HY zeolite (115–130 kJ/mol) [34]. As expected, the crystalline oxide had a smaller density of acid sites due to its lower surface area.

The deposition of Pd on Zn–Cr oxide provides the catalyst with hydrogenation activity. This activity strongly depends on the dispersion of the Pd phase, because the size of Pd particles is a key parameter of the catalytic efficiency of the supported

metal [35]. A wide range of methods is used for supporting Pd nanoparticles, and the Pd particles obtained thusly vary considerably in size [35]. Here we used the impregnation of Zn–Cr oxide by a dilute (0.02 M) benzene solution of $\text{Pd}(\text{OAc})_2$, followed by evaporation of the solvent and reduction of Pd^{II} to Pd^0 by a H_2 flow under relatively mild conditions (250 °C). Note that the size of the deposited Pd particles increased with increasing temperature of Pd^{II} reduction [36]. To estimate the dispersion of the Pd phase on Zn–Cr oxide, we used XRD, which can measure the average size of Pd particles [35,36]; however, XRD of 0.3–1% Pd/Zn–Cr, both fresh and used, revealed no patterns of Pd metal. Thus the most intense 111 diffraction peak of the Pd phase at $2\theta = 40.1^\circ$ was not seen (Fig. 1), indicating a very fine dispersion of Pd in the Pd/Zn–Cr catalysts. This may be one reason for the high efficiency of these catalysts (see below). Loading Pd (0.1–1 wt%) on Zn–Cr oxides slightly decreased the surface area and porosity of the catalysts (Table 1), as expected. Note that we were unable to accurately measure the NH_3 adsorption on Pd/Zn–Cr, because TGA showed an adsorption peak rather than a plateau, which could be caused by the base-catalysed loss of water from the oxide [33].

3.2. Gas-phase synthesis of MIBK

The gas-phase reaction was studied in a fixed-bed flow reactor under the following conditions: 200–350 °C, ambient pressure, GHSV of 6500–18,000 h⁻¹, 9–50 vol% acetone, and 23–70 vol% H_2 in the gas feed (N_2 balance). The Pd loading on the amorphous Zn–Cr oxide varied from 0.1 to 1 wt%. Representative results at 300 °C are given in Table 2. MIBK was the major reaction product, and a significant amount of DIBK also formed. Byproducts included C_{9+} acetone condensation products (mainly the tetramer 2,6,8-trimethylnonane-4-one) and small amounts ($\leq 1\%$ selectivity) of propene and

Table 2
Gas-phase synthesis of methyl isobutyl ketone over Pd/Zn–Cr catalysts^a

Entry	Catalyst	GHSV (h ⁻¹)	Conversion (%)	Selectivity ^b (%)				
				MIBK	DIBK	C ₃	MO	Others
1	Zn–Cr oxide	12,900	16.7	15.3	9.4	0.2	63.2	12.0
2	1% Pd/Zn–Cr	12,900	40.7	69.4	22.9	0.8	0.1	6.8
3	1% Pd/Zn–Cr	6500	57.3	64.1	25.4	0.3	0.1	10.2
4	1% Pd/Zn–Cr ^c	6500	42.0	77.6	14.9	0.8	0.2	6.5
5	1% Pd/Zn–Cr ^d	6500	66.4	43.8	33.7	1.1	0.1	21.4
6	1% Pd/Zn–Cr(cr)	6500	48.7	55.8	30.1	0.1	0.3	13.7
7	0.3% Pd/Zn–Cr	6500	41.6	60.9	17.6	0.6	1.0	19.8
8	0.3% Pd/Zn–Cr ^c	6500	36.9	65.9	23.2	0.3	0.3	10.3
9	0.1% Pd/Zn–Cr	6500	36.1	61.3	20.6	0.3	2.3	15.5
10	1% Pd/Zn–Cr ^e	18,000	32.1	44.3	20.6	0.3	1.0	33.8
11	1% Pd/Zn–Cr ^f	10,200	52.5	40.5	25.6	1.4	0.1	32.4
12	1% Pd/Zn–Cr ^{f,g}	10,200	37.9	41.9	14.9	0.7	1.4	41.0

^a Reaction conditions: 300 °C, acetone/ H_2 = 30:70 (vol.), 0.1–0.2 g catalyst powder of ≤ 180 μm particle size and 1.54 g/cm³ density, 2 h time on stream.

^b C₃ is propene and propane, MO mesityl oxide, others are mainly C_{9+} acetone condensation products (mostly 2,6,8-trimethylnonane-4-one) and ca. 1% isopropanol.

^c Gas feed diluted with N_2 ; acetone/ H_2 / N_2 = 30:35:35 (vol.).

^d Catalyst particle size ≤ 90 μm .

^e Acetone/ H_2 = 50:50 (vol.).

^f Acetone/ H_2 = 9:91 (vol.).

^g Gas feed diluted with N_2 ; acetone/ H_2 / N_2 = 9:23:68 (vol.).

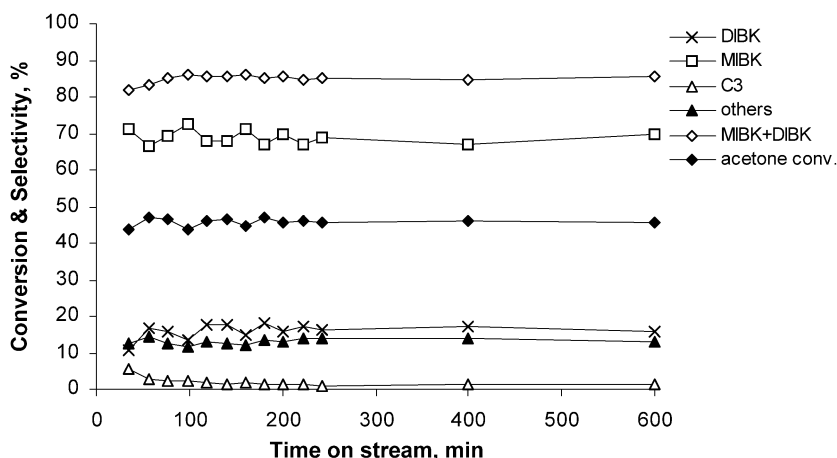


Fig. 3. Acetone conversion and product selectivities vs. time on stream (0.2 g 1%Pd/Zn–Cr, 10 ml/min H₂ flow, acetone/H₂ = 30:70 (vol.), GHSV = 6500 h⁻¹, 300 °C).

propane, mesityl oxide, and isopropanol. MIBK was obtained with up to 78% selectivity and 93% total selectivity to MIBK + DIBK at 42% acetone conversion (39% yield) (Table 2, entry 4). This compares well with the best results reported to date [9,15,18,20]. The highest MIBK + DIBK yield of 51% was obtained at 64% MIBK selectivity and 57.3% acetone conversion (entry 3). These results were obtained at 300 °C, GHSV of 6500 h⁻¹, 30 vol% acetone in the gas feed, and an acetone/H₂ volume ratio of 0.5–1. At higher or lower acetone/H₂ ratios, lower conversions and/or MIBK selectivities were observed (entries 10–12).

The reaction clearly requires both acid–base and redox catalysis, which are provided by Zn–Cr oxide and Pd, respectively. When Zn–Cr oxide was used in the absence of Pd, mesityl oxide (the product of acid-catalysed condensation of acetone) was the major product, whereas the selectivity to MIBK was only 15% (entry 1). This shows that the Zn–Cr oxide itself acts mainly as an acid catalyst, with weak hydrogenation activity. The conversion of acetone increased with increasing Pd loading from 0.1% to 1% (cf. entries 3, 7, and 9). This finding may suggest that the Pd-catalysed hydrogenation of mesityl oxide is a slow step in acetone conversion (Scheme 1); however, data on Pd dispersion are needed to confirm this.

Using the crystalline Zn–Cr oxide (Table 1, entry 2) as a support resulted in a lower catalytic activity compared with that of the amorphous Zn–Cr oxide (cf. entries 3 and 6, Table 2). This may be explained by the lower surface area of the crystalline oxide, which can affect both the acidity and the Pd dispersion of the catalyst.

The Pd/Zn–Cr catalyst exhibited very good stability (Fig. 3). No catalyst deactivation was observed during at least 10 h of continuous operation and 50 h of discontinuous operation with overnight breaks. The catalyst reached a steady state in ca. 1 h and after that performed with constant activity and selectivity. Carbonaceous deposits lay on the catalyst during the reaction (4.6 wt% in 10 h at 300 °C) but did not affect catalyst performance.

The reaction temperature caused only a slight effect on acetone conversion, which increased from 29% at 200 °C to 48%

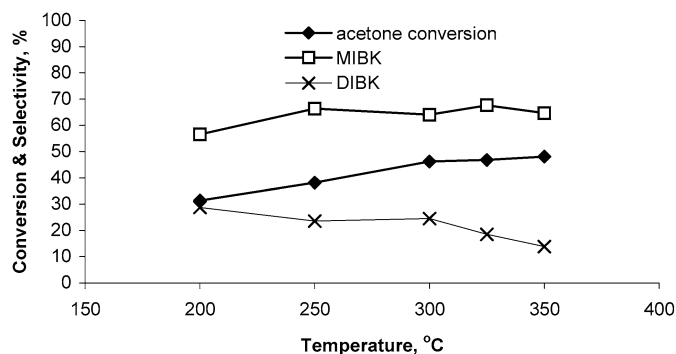


Fig. 4. Acetone conversion and selectivities to MIBK and DIBK vs. reaction temperature (0.2 g 1%Pd/Zn–Cr, 10 ml/min H₂ flow, acetone/H₂ = 30:70 (vol.), GHSV = 6500 h⁻¹, 2 h time on stream).

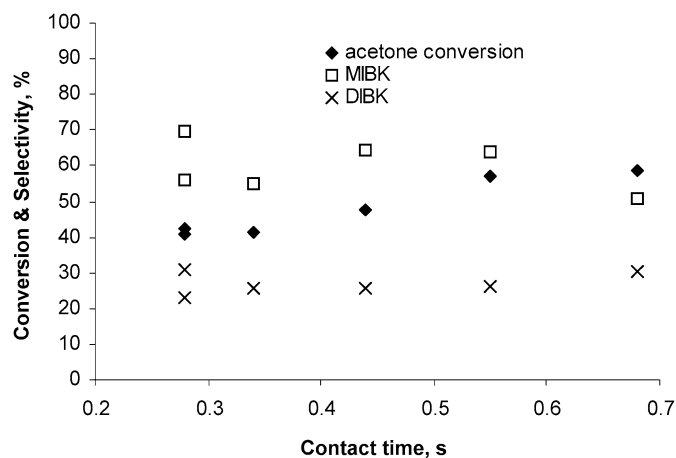


Fig. 5. Acetone conversion and selectivities to MIBK and DIBK vs. contact time (0.1–0.5 g 1%Pd/Zn–Cr, 10–40 ml/min H₂ flow, acetone/H₂ = 30:70 (vol.), 300 °C, 2 h time on stream).

at 350 °C (Fig. 4). With increasing reaction temperature, MIBK selectivity increased slightly and DIBK selectivity decreased considerably. Fig. 5 shows the effect of contact time (the reverse of GHSV) on acetone conversion and selectivity to MIBK and DIBK. Note that the reactor was operating under nondifferential conditions. The conversion increased with increasing contact

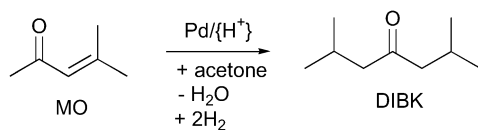
Table 3
Liquid-phase synthesis of methyl isobutyl ketone over Pd/Zn–Cr catalysts^a

Entry	Catalyst	<i>T</i> (°C)	<i>p</i> (H ₂) (bar)	Conversion (%)	Selectivity ^b (%)					
					MIBK	DIBK	C ₃	IP	MO	C ₉₊
1	1%Pd/Zn–Cr	200	20	83.0	22.3	2.9	1.0	64.8	8.1	0.9
2	1%Pd/Zn–Cr	200	7.5	53.6	70.6	13.4	0.7	9.1	1.6	4.6
3	1%Pd/Zn–Cr	200	5	55.6	83.1	10.2	1.3	1.1	0	4.3
4	1%Pd/Zn–Cr(cr)	200	7.5	52.8	57.2	7.2	1.1	27.0	3.0	4.4
5	1%Pd/Zn–Cr	160	20	48.5	26.8	1.0	1.4	68.5	1.9	0.4
6	1%Pd/Zn–Cr	160	7.5	28.5	80.4	4.6	1.1	11.2	0.4	2.3
7	1%Pd/Zn–Cr ^c	160	5	26.7	78.7	3.4	2.6	13.1	0	2.2
8	0.3%Pd/Zn–Cr	200	7.5	52.4	77.1	15.5	0	2.5	0.4	4.5
9	0.3%Pd/Zn–Cr	200	5	49.5	76.0	13.5	0.4	0.6	1.8	7.7
10	0.3%Pd/Zn–Cr	160	5	33.3	72.1	4.5	0.6	19.8	0.9	2.1
11	0.1%Pd/Zn–Cr	200	7.5	53.8	76.5	15.4	0.7	1.4	0.2	5.7
12	0.1%Pd/Zn–Cr	200	5	46.3	79.0	13.1	0.6	3.2	0.4	3.7

^a Reactions in 45 ml-autoclave, 2.0 g acetone, 0.20 g catalyst powder of ≤180 μm particle size, 2 h.

^b C₃ is propene and propane, IP isopropanol, MO mesityl oxide, C₉₊ higher acetone condensation products.

^c Reuse of this run gave 17.2% conversion, 58.1% MIBK, 1.2% DIBK, 40.1% IP and 0.6% C₉₊.



time, as expected. The selectivity to MIBK and selectivity to DIBK were practically independent of the contact time; only at long contact times did MIBK selectivity decrease in favour of DIBK, as expected. The conversion did not depend on the gas flow rate at constant GHSV, but increased as the catalyst particle size decreased (cf. entries 3 and 5, Table 2). Unexpectedly, the DIBK/MIBK ratio increased with decreasing catalyst particle size. This result, together with the effect of contact time (Fig. 5), suggest that DIBK may be formed mainly in a parallel reaction from MO and acetone (Scheme 3) rather than from MIBK (Scheme 2).

3.3. Liquid-phase synthesis of MIBK

The reaction in the liquid phase was carried out at 160–200 °C and 5–20 bar H₂ pressure in the presence of Pd/Zn–Cr catalyst with 0.1–1 wt%Pd loading; the results are given in Table 3. The same products were generally observed in the liquid-phase reaction as in the gas-phase reaction, except with more isopropanol and less C₉₊ products formed in the liquid phase. The reaction was the most efficient at 200 °C and hydrogen pressure of 5–7.5 bar, almost independent of the Pd loading (entries 3, 8, 9, 11, and 12). The best run (entry 3) gave 83% MIBK selectivity and 93% total MIBK + DIBK selectivity at 56% acetone conversion (200 °C, 5 bar H₂ pressure). This result is on a par with the best results reported to date [10,18,19], and the H₂ pressure is unprecedentedly low (typically about 20 bar or higher [10,18,19]), which may be explained by the high dispersion of Pd in the catalyst. Increasing the H₂ pressure to 20 bar led to the predominant formation of isopropanol by hydrogenation of the C=O group of acetone (entries 1 and 5).

Similar to the gas-phase reaction, Pd supported on the crystalline Zn–Cr oxide was less active than the catalyst supported on the amorphous oxide (cf. entries 2 and 4). Pd/Zn–Cr(cr) gave less MIBK and DIBK but significantly more isopropanol.

The Pd/Zn–Cr catalyst could be reused simply after washing it with acetone, although with a reduced activity (entry 7). The second run gave less MIBK and DIBK and much more isopropanol, as compared to the first run. This shows that the recovered catalyst partly lost its acidity but retained its hydrogenation activity. Therefore, the regeneration of catalyst acidity is required to achieve better catalyst performance on reuse.

4. Conclusion

The present study has shown that palladium metal (0.1–1 wt%) supported on amorphous Zn–Cr (1:10) mixed oxide is an efficient bifunctional catalyst for the one-step synthesis of MIBK from acetone in both gas-phase and liquid-phase processes. The catalyst is easy to prepare by coprecipitation of Zn^{II} and Cr^{III} hydroxides, followed by calcination at 300 °C and palladium salt impregnation and reduction. Both the continuous gas-phase process (300 °C, ambient pressure) and the batch liquid-phase process (200 °C, 5 bar H₂ pressure) yield MIBK together with DIBK with a total selectivity of 93% at 56–57% acetone conversion, on a par with the best results reported to date. In the gas-phase synthesis, no catalyst deactivation is observed for at least 50 h on stream. In the liquid-phase reaction, the catalyst performs well at a very low H₂ pressure of 5 bar. It can be reused, although regeneration of its acidity is required. Further improvement may be achieved by catalyst and process optimisation over a broader range of Zn/Cr atomic ratios, as well as by better characterisation of the acid and metal sites in the catalyst.

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