Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Catalysis 238 (2006) 286–292

JOURNAL OF CATALYSIS

www.elsevier.com/locate/jcat

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

Elena F. Kozhevnikova, Ivan V. Kozhevnikov [*]

[a] *Department of Chemistry, University of Liverpool, Liverpool L69 7ZD, UK*

Received 19 September 2005; revised 7 November 2005; accepted 21 November 2005

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 H_2 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 H_2 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.

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

1. Introduction

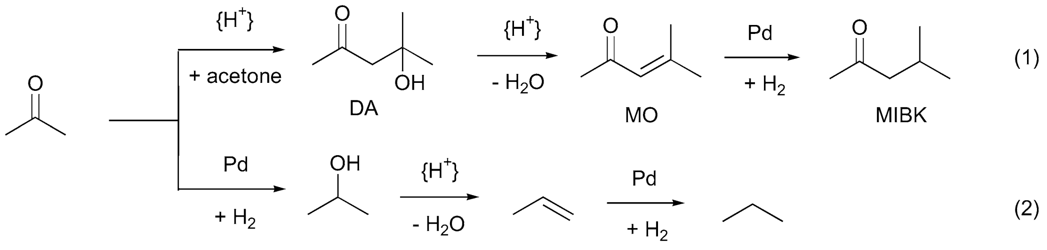
Methyl isobutyl ketone (MIBK) is one of the most widely used aliphatic ketones. Its primary uses included as a solvent for paint and protective coatings, an extracting agent for the production of antibiotics and commercial lubricating oils, a reagent for the separation and purification of metal ions, 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 H_2 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

---

[*] Corresponding author. Fax: +44 151 794 3589.
E-mail address: kozhev@liverpool.ac.uk (I.V. Kozhevnikov).

0021-9517/$ – see front matter © 2005 Elsevier Inc. All rights reserved.
doi:10.1016/j.jcat.2005.11.028

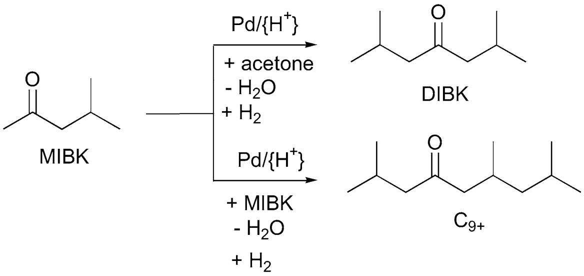


Scheme 1.

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 alumosilicate [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 $ZnO–Cr_2O_3$ mixed oxide, Pd/Zn–Cr.

Zn–Cr oxide has long been used as a catalyst for various reactions of synthesis gas ($CO + H_2$), 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 NH_3 [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 reactions, 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.



Scheme 2.

Table 1
Catalyst characterisation

Entry	Catalyst	S_{BET} (m^2/g)	Pore size (Å)	Pore volume (cm^3/g)	H_2O 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 N_2; 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 N_2.

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

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 P_2O_5. The density of the catalyst powder was 1.54 g/cm^3. The Zn, Cr,