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Acetone condensation and selective hydrogenation to MIBK on Pd and Pt hydrotalcite-derived Mg–Al mixed oxide catalysts

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Abstract

The condensation and selective hydrogenation of acetone to methyl isobutyl ketone (MIBK) was studied on a directly comparable series of 0.1–1.5 wt% Pd and Pt catalysts supported on hydrotalcite (HT)-derived Mg–Al mixed-oxides in a liquid-phase batch micro-reactor at 99–153 °C and 400 psig. The support catalyzes the condensation of acetone to diacetone alcohol (DAA) and its subsequent dehydration to mesityl oxide (MO); Pd and Pt catalyze the selective hydrogenation of MO to MIBK. The net yield of MIBK is independent of metal type and loading, depending only on the wt% of exposed metal. However, the by-products are quite different-Pt/HT is more selective for the direct hydrogenation to isopropanol (IPA) while Pd/HT forms more of the intermediate diacetone alcohol (DAA). Among the Pd- and Pt-based catalysts examined, the 0.1 wt% Pd/HT gives the maximum MIBK yield of ~32%, with an unusually low selectivity to IPA, 0.6 mol% compared to 15 mol% for the next best catalyst. This appears to be due to its higher basicity, and (to a lesser extent) to its minimal concentration of metal sites. This metal loading is sufficient to fully hydrogenate mesityl oxide to MIBK, and it also shows minimal acetone hydrogenation to isopropanol. A study of physically mixed Pd/silica + HT versus Pd/HT shows that the acid/base and hydrogenation functions need not be molecularly close.

Keywords: Acetone; Aldol condensation; Diacetone Alcohol; Hydrotalcite; Mesityl oxide; Methyl isobutyl Ketone; Palladium; Platinum

1. Introduction

There are clear economic and environmental incentives to develop heterogeneous catalysts in order to replace conventional homogeneous catalysts in many industrial processes. The aldol condensation of alcohols, aldehydes, and ketones, which is practiced industrially for the synthesis of wide range of products, is one such process [1].

Of specific interest here is the liquid-phase condensation of acetone, which is an important industrial process for the synthesis of diacetone alcohol (DAA), mesityl oxide (MO) and methyl isobutyl ketone (MIBK) [1]. MIBK is extensively used as a solvent in paints, resins and coatings (mainly nitrocellulose, vinyl and acrylic), as well as an extracting agent in the production of antibiotics and lubricating oils [2–4]. The current annual production of MIBK is ca. 150 million pounds in the United States, ca. 120 million pounds in Europe, and ca. 80–100 million pounds in Asia [4].

The main reaction pathways for the synthesis of MIBK from acetone are given in Fig. 1 [1]. The first step is the self-condensation of acetone to diacetone alcohol (DAA, 4-hydroxy-4-methyl-2-pentanone); the second step is the dehydration of DAA to mesityl oxide (MO, 4-methyl-3-penten-2-one); the final step is the selective hydrogenation of the carbon–carbon double bond of MO to form MIBK. The most commonly observed side reactions are over-condensations and unselective hydrogenations (also shown in Fig. 1).

Many aldol condensation reactions, including acetone condensation, are practiced industrially using homogeneous aqueous-base catalysts such as sodium and calcium hydroxide. These processes generate significant wastewater streams that must be neutralized and properly disposed, adding to the production cost. Developing an active and selective heterogeneous catalyst could simplify the production process significantly, and minimize or possibly eliminate this cost.

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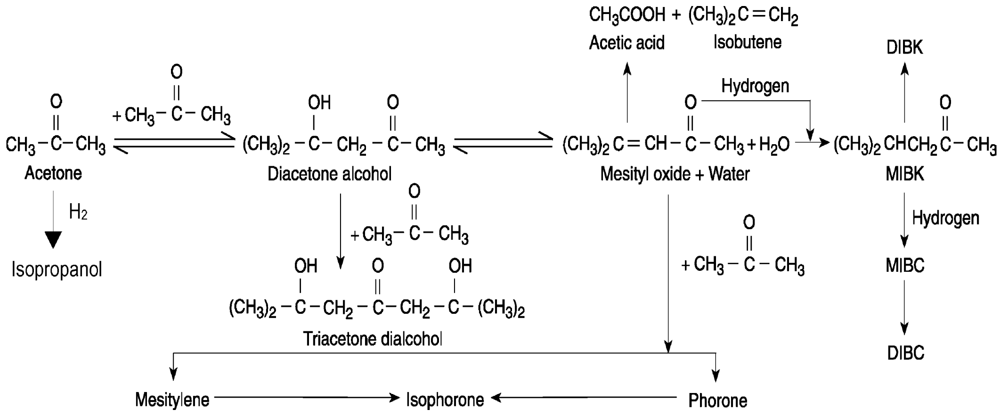

Fig. 1. Main reaction pathways in the acetone condensation process (from [1]).

Among the solid base catalysts that are active for aldol condensation are alkali (Na_2O, K_2O, Cs_2O) [1], alkaline earth (MgO, CaO, BaO) [5–9], transition metal oxides [10,11] and phosphates [12–15], ion-exchange resins [12,16], zeolites [17–20] and clay minerals and hydrotalcites [21–31]. The reactions of interest in Fig. 1 require a catalyst with acidic and/or basic sites, as well as hydrogenation activity. The condensation of acetone to DAA is catalyzed by either basic or acidic sites, the dehydration of DAA to MO is acid-catalyzed, and the selective hydrogenation of MO to MIBK requires metal sites [11,12,29].

There are also strong thermodynamic equilibrium limitations to the acetone condensation reaction. According to the data in Table 1, the condensation/dehydration of acetone to MO is limited to about 20% conversion at 140 °C [12], although there is no equilibrium limitation to the overall acetone-to-MIBK reaction. This, coupled with the possibility of numerous thermo-dynamically favorable side reactions that are also acid/base-catalyzed (Fig. 1), suggests that the acid/base and hydrogenation properties of the catalyst must be balanced [19,20].

Promising catalysts derived from hydrotalcite (Mg–Al hydroxyl-carbonate) precursors, possessing both basic and acidic properties, and dispersed noble metals (Pt or Pd) having hydrogenation activity, have been reported [24–31]. Pd and Pt catalysts have also been reported to selectively hydrogenate the C=C bond of unsaturated ketones (as opposed to the C=O bond) to produce saturated ketones [8,19,20,32], but no direct comparison of these metals on the same support has been reported.

The objective of this research is to compare the activity and selectivity of Pt and Pd for the condensation and selective hydrogenation of acetone on hydrotalcite-derived Mg–Al support. The correlation between the physical and chemical properties of these catalysts and their activity and selectivity for the condensation of ketones is of particular interest for the development of more economically attractive and environmentally benign processes.

2. Experimental methods

2.1. Catalyst synthesis and characterization

A hydrotalcite powder (Mg–Al hydroxyl-carbonate, Mg/Al = 1.8; LaRoche Industries Inc.) was impregnated without any prior treatment, using aqueous solutions of palladium chloride ($PdCl_2$) or hexachloroplatinic acid (H_2PtCl_6) to produce catalysts with nominal metal loading of 0.1, 0.7, and 1.5 wt%. The catalysts were dried at 120 °C for 2 h, calcined at 350 °C for 2 h, and then crushed and sieved to particle size of 370–840 μm. Prior to reaction, the samples were reduced ex situ at 450 °C for 8 h in flowing hydrogen [27,28].

The catalysts were characterized by various methods. Their surface area was measured by the BET method (N_2 physisorption at −196 °C) in a Quanta Chrome NOVA 1000 instrument. Their crystal structure was identified by X-ray diffraction (XRD), and their actual metal loading was obtained by inductively coupled plasma/optical emission spectroscopy (ICP/OES).

The reducibility of the dispersed Pt or Pd metal was determined by temperature-programmed reduction (TPR) using a Zeton-Altamira AMI-100 catalyst characterization system. Catalyst samples of 0.05–0.1 g were pretreated to 200 °C in flowing Ar for 30 min, then were cooled to 50 °C, and were reduced under 10% H_2/Ar while increasing the temperature by 10 °C/min up to 600 °C [27,28].

Table 1
Thermodynamic equilibrium of the acetone condensation/hydrogenation reaction

Reaction	ΔH_{400K} (kcal/mol)	ΔG_{400K} (kcal/mol)
$\underset{\text{(Acetone)}}{2CH_3COCH_3} \Leftrightarrow \underset{\text{(Mesityl oxide)}}{(CH_3)_2=CHCOCH_3} + H_2O$	−5.2	+3.3
$\underset{\text{(Mesityl oxide)}}{(CH_3)_2=CHCOCH_3} + H_2 \Leftrightarrow \underset{\text{(MIBK)}}{(CH_3)_2CHCH_2COCH_3}$	−14.5	−12.1
$\underset{\text{(Acetone)}}{2CH_3COCH_3} + H_2 \Leftrightarrow \underset{\text{(MIBK)}}{(CH_3)_2CHCH_2COCH_3} + H_2O$	−19.7	−8.8