The mechanism and kinetics of methyl isobutyl ketone synthesis from acetone over ion-exchanged hydroxyapatite

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ABSTRACT

The synthesis of methyl isobutyl ketone (MIBK) can be carried out by the condensation of acetone in the presence of hydrogen over a supported metal catalyst. Previous studies have shown that hydroxyapatite is an excellent catalyst for condensation reactions. The present investigation was undertaken in order to elucidate the reaction mechanism and site requirements for acetone coupling to MIBK over a physical mixture of hydroxyapatite and Pd/SiO_2. The reaction is found to proceed by consecutive aldol addition to form diacetone alcohol (DAA), dehydration of DAA to mesityl oxide (MO), and hydrogenation of MO to MIBK. The products formed by feeding DAA and MO reveal that aldol addition of acetone is rapid and reversible, and that the subsequent dehydration of DAA is rate-limiting. Pyridine and CO_2 titration show that aldol dehydration occurs over basic sites via an E_{1cB} mechanism. A series of cation-substituted hydroxyapatite samples were prepared by ion-exchange to further investigate the role of acid-base strength on catalyst performance. Characterization of these samples by PXRD, BET, ICP-OES, XPS, CO_2-TPD, and Raman spectroscopy demonstrated that the exchange procedure used does not affect the bulk properties of hydroxyapatite. DFT calculations reveal that in addition to affecting the Lewis acidity/basicity of the support, the size of the cation plays a significant role in the chemistry: cations that are too large (Ba^{2+}) or too small (Mg^{2+}) adversely affect reaction rates due to excessive stabilization of intermediate species. Strontium-exchanged hydroxyapatite was found to be the most active catalyst because it promoted α-hydrogen abstraction and C—O bond cleavage of DAA efficiently.

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1. Introduction

Acetone is produced industrially as a byproduct in the production of cumene. While acetone can be used as a solvent, its value can be increased by upgrading it to form methyl isobutyl ketone (MIBK) [1,2]. MIBK is used for manufacturing paints, rubbers, and pharmaceuticals [3]. It is also used for liquid-liquid extraction of precious metals, due to its low miscibility with water [1]. Traditionally, MIBK is produced in a batch reactor in three steps: acetone coupling to form diacetone alcohol catalyzed by sodium hydroxide, diacetone alcohol dehydration to mesityl oxide catalyzed by sulfuric acid, and mesityl oxide hydrogenation to MIBK over a metal catalyst (Scheme 1) [1]. More recently, it has been demonstrated that MIBK can be produced more efficiently via a single step using a metal-supported catalyst [4–11]. The support catalyzes acetone condensation to mesityl oxide and the metal promotes the subsequent hydrogenation of this intermediate to

MIBK. The acidity/basicity of the support dictates whether acetone condensation follows an enol or enolate mechanism, and the strength of the acid/base sites affects the rate of reaction [4]. While many different supports (ionic resins [5,6], metal oxides [7–9], mixed metal oxides [10,11]) are known to be active for MIBK formation, the relationship between support acid/base strength and catalytic performance remains unclear because it is difficult to modify the chemical properties of the support without changing its structure. For example, several groups have studied aldol condensation over MgO/Al_2O_3 with varying Mg/Al ratios [12,13]. Areal reaction rates are highest over pure MgO, which has been attributed to the high density of strongly basic O^{2-} sites that enhance α-hydrogen abstraction [12]. However, changing the Mg/Al ratio also affects the bulk structure and crystallite size of the supported MgO, making it difficult to determine whether differences in rates are attributed solely to differences in acid/base properties.

Hydroxyapatite (HAP; $Ca_5(PO_4)_3OH$) is an attractive candidate support because it can accommodate a host of cationic ($Ca^{2+} \rightarrow Mg^{2+}$, Sr^{2+}, Ba^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Cd^{2+}) [14–17] and anionic ($PO_4^{3-} \rightarrow VO_4^{3-}$, AsO_4^{3-}, CO_3^{2-}, SO_3^{2-}; $OH^- \rightarrow F^-$, Cl^-)
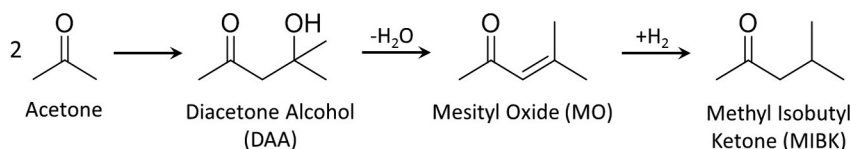
Scheme 1. Acetone condensation to methyl isobutyl ketone (MIBK).

[18–20] substitutions that can affect its catalytic performance. The unsubstituted form of HAP has been shown to be effective for a number of C—C bond forming processes, including Guerbet coupling of ethanol and dimerization of 2-hexanone [21,22]. However, there have been relatively few studies showing the effects of ion substitution on catalyst activity and selectivity. Ogo et al. have shown that HAP substituted with VO_4^{3-} anions increases its selectivity for acetaldehyde dimerization to crotonaldehyde [23]. Silvester et al. have prepared CO_3^{2-} and Sr^{2+} substituted samples of HAP and found that a balance of acid and base sites is needed to maximize selectivity for the Guerbet coupling of ethanol [24,25]. It should be noted, though, that each of these catalysts was prepared by incorporating the new cations or anions during synthesis via co-precipitation. While this approach does not affect the crystal structure of HAP, it can induce changes in particle morphology and acid/base site densities, as shown by electron microscopy and TPD desorption experiments, respectively [18,26].

An alternative approach for introducing new cations and anions is post-synthetic ion-exchange, a method that enables modification of the surface composition without alteration of the bulk properties [16]. Several authors have reported the successful substitution of Ca^{2+} by other divalent cations using this approach [27,28]. However, the exchange process can lead to partial dissolution and surface restructuring of HAP under certain conditions, which should be avoided in order to make a fair comparison between catalysts [29]. Prior studies have shown that the dissolution process can be minimized by performing the exchange in neutral to basic solutions to limit HAP solubility [30].

The goal of this study was to investigate the mechanism and kinetics of MIBK synthesis over HAP and to identify the role of cations other than Ca^{2+} at the catalyst surface on the catalyst activity. To this end, we describe a method for preparing a set of cation-exchanged HAP samples (Mg, Ca, Sr, Ba, Cd, Pb) and show through various characterization techniques that the bulk structure is unaffected. The acid/base properties are modulated through the identity of the cation, which in turn affects the catalyst performance. The mechanism is found to initiate with the condensation of acetone to diacetone alcohol, which then undergoes dehydration to form mesityl oxide. This rate-limiting step is catalyzed by basic sites on the surface of HAP. Since the reaction of acetone to mesityl oxide is endoergic, mesityl oxide needs to be hydrogenated to MIBK using silica-supported Pd in order to achieve high conversions of acetone. The rate of acetone condensation to mesityl oxide is strongly dependent on the basicity of O on the catalyst surface, which is influenced by the nature of the divalent cation connected to the O atom. Highest activity is observed when Ca^{2+} is replaced by Sr^{2+}. Density functional theory (DFT) calculations were performed to map out the free energy landscape for the condensation of acetone to mesityl oxide and to identify how the properties of the divalent cation connected to lattice O atoms affect their activity for the dehydration of diacetone alcohol.

2. Experimental methods

2.1. Catalyst synthesis

Hydroxyapatite (HAP) was synthesized using a modification of the procedure reported by Tsuchida et al. [31] and Hanspal et al.

[32] Aqueous solutions of 0.25 M $Ca(NO_3)_2 \cdot 4H_2O$ and 0.55 M $(NH_4)_2HPO_4$ were prepared and brought to a pH of 11 by addition of ammonium hydroxide. The calcium solution was added dropwise to the phosphorus solution at room temperature and stirred for 0.5 h before heating to 353 K for an additional 3 h. The resulting slurry was filtered and washed with DI water.

The calcium in HAP was exchanged with other cations by ion-exchange. Mg-, Sr-, Ba-, Cd- and Pb-HAP were prepared by adding 0.2 g of HAP into a 30 mL aqueous solution of the respective nitrate precursor ($Mg(NO_3)_2 \cdot 6H_2O$, $Sr(NO_3)_2$, $Ba(NO_3)_2$ = 2.5 mmol; $Cd(NO_3)_2 \cdot 4H_2O$, $Pb(NO_3)_2$ = 0.25 mmol). Smaller quantities of Cd and Pb nitrates were used to offset the greater ease of substitution of these cations compared to Mg, Sr, and Ba [33,34]. The pH of the HAP solution was adjusted to 7 by addition of HNO_3 or NH_4OH. For Pb substitution, a solution pH of 6 was used to avoid precipitation of lead hydroxides. The solution was stirred for 5 h at 298 K, filtered, washed with DI water, and dried at 393 K overnight in air.

3 wt%Pd/SiO_2 was prepared by incipient wetness impregnation using an aqueous solution of $Pd(NO_3)_2 \cdot 2H_2O$ on a silica support (SiliaFlash150A). The catalyst was dried at 298 K overnight and calcined in 100 mL/min of air at 823 K for 2 h before use.

2.2. Characterization techniques

Powder X-ray diffraction (PXRD) patterns were taken with a Bruker D8 GADDS diffractometer equipped with a Cu-Kα source (40 kV, 40 mA). BET surface areas were calculated from nitrogen adsorption isotherms obtained using a Micromeritics Gemini VII 2390 surface area analyzer after degassing the catalyst overnight at 393 K. Basic site density was measured by temperature-programmed desorption (TPD) of CO_2 using a Micromeritics Auto-Chem II 2920 instrument equipped with a thermal conductivity detector. Samples were pretreated under He flow at 823 K for 1 h before cooling to 313 K. CO_2 (30 mL min^{-1}) was introduced for 0.5 h at 313 K, after which the samples were purged with He for 0.5 h at 313 K to remove any physisorbed species from the surface. Desorption of adsorbed CO_2 was performed in flowing He (50 mL min^{-1}) using a temperature ramp rate of 5 K min^{-1}.

Bulk compositions were determined by ICP-OES using an Optima 7000 DV instrument with yttrium as an internal standard. Surface compositions were determined using a Kratos Axis Ultra DLD X-ray photoelectron spectrometer (XPS). Measurements were performed with an Al-Kα source (15 kV, 10 mA) at a pressure of ~9 nTorr. Kinetic energies were defined by shifting the spectra so that the C 1s binding energy of adventitious carbon was 284.8 eV. Initial elemental compositions were obtained by normalizing the intensity of the characteristic peaks with an internally calibrated relative sensitivity factor. However, this normalization relies on the assumption that the sample is homogeneous across the probing depth of photoelectrons (~1 nm), which was found to be invalid when compared to elemental analysis data. Instead, the degree of ion-exchange on the surface was calculated by using the general XPS equation:

$$I_{element} = F_x S\sigma \int_0^{0.3nm} c_{element} e^{-z/\lambda_{Ek}cos\theta} dz \qquad (1)$$

$I_{element}$ = intensity of XPS peak
F_x = x-ray flux