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Direct synthesis of MIBK from acetone over Pd/NaX catalysts

Alexandre Carlos Camacho Rodrigues *, José Luiz Fontes Monteiro

NUCAT-COPPE-UFRJ, Universidade Federal do Rio de Janeiro, Ilha do Fundão, C.P. 68502, CEP 21945-970, Rio de Janeiro, Brazil

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ABSTRACT

The one-step synthesis of MIBK from acetone in gas phase was studied over palladium catalysts on NaX zeolite (1 and 3 wt% of Pd). A greater selectivity to MIBK was observed for a H_2/acetone ratio of 6.2. Although increasing the reaction temperature caused an increase of the selectivity to condensation products, the temperature for which the selectivity to MIBK was maximum was the lower one (523 K). Decreasing the reduction temperature from 633 to 573 K for PdNaX enhanced the hydrogenation activity and decreased MIBK selectivity. Selectivities to MIBK as high as 80% were obtained.

1. Introduction

Methyl isobutyl ketone (MIBK) is the most important product obtained from acetone (Ac). It is used mainly as a solvent for paints, inks, lacquers and protective coating systems [1,2], but it is also used in the extraction and purification of inorganic ions [3–6], in the dewaxing mineral oils [7], in the purification of conventional wet process phosphoric acid (from Mg^{+2}, Al^{+3}, Fe^{+3}) [8], in the initiation of polymerization (initiator) and in the recovery of lactic acid from aqueous solutions [9]. It is produced commercially by a three-step process in liquid phase: (i) aldol condensation of acetone to diacetone alcohol (DAA) over basic ($Ba(OH)_2$, NaOH, KOH, $Ca(OH)_2$) or acidic catalysts; (ii) acid (H_3PO_4, H_2SO_4)-catalyzed DAA dehydration to mesityl oxide (MO); (iii) selective hydrogenation of MO olefinic double bond (C=C) to MIBK over nickel or copper chromite or over noble metal catalysts [1,3,10–12]. The first two steps are conventional homogeneous processes and are usually equilibrium limited and the third one may yield a relatively large amount of less useful methyl isobutyl carbinol (MIBC) and 2-methyl pentane (2MP). A one-step process using a catalyst that may perform condensation, dehydration and reduction simultaneously would reduce/eliminate the many separation and neutralization steps, the corrosion problems, the significant risk to the environment (eco-friendly process) and the high operational costs associated to the conventional process. Hydrogenating MO to MIBK simultaneously with the other two previous steps would favorably shift their equilibrium and prevent the formation of high-boiling products from additional condensation [13].

Pd catalysts supported on various acidic and basic supports, such as KOH–Al_2O_3 [14], MgO–SiO_2 [15], CaO–MgO–SrO–Al_2O_3 [16], Nb_2O_5 [17,18], $Zr_3(PO_4)_2$ [1,10], $ZrO(OH)_2$–C [19], Ce, Hf and/or Ta oxides-C [20], resin [21], C(+resins) [22], $Nb_2O_5 + SiO_2$ [23] and calcined hydrotalcites [24–27] have been used in liquid phase for the one-step synthesis of MIBK.

Batch process often shows rapid decrease in its reactional rate, due to water build-up in the system [18,23], which can be overcome by the use of a continuous system. Continuous processes often have temperatures in the range 393–433 K, pressures between 20–50 bar and hydrogen/acetone molar ratios of 0.15–0.4, and very stable operation can be achieved [1,18,23]. Although very high selectivities to MIBK ($>$90%) at acetone conversions of about 30–40% have been reported, the high operating pressures are a limitation of the liquid phase single-step process [28].

Alternatively, gas phase single-step processes operating at atmospheric pressure have been investigated. These processes use Pd, Pt, Ni and Cu supported on various oxides and zeotypes such as: SAPO-34 [29], SAPO-11 [11], $AlPO_4$-11 [11], calcined hydrotalcites [25,30–33], ZSM-5 [34–37], Na–MgO [7], MCM 56 [38], MCM 22 [39] and MCM 49 [40], with Pd; ZSM-5 [12,36,41–43] with Pt; MgO [28], ALPON [44], Al_2O_3 [45,46], calcined hydrotalcites [29,33,47] and ZSM-5 [48] with Ni and MgO [3,49] and calcined hydrotalcite [32] with Cu. The results show that selectivities to MIBK in gas phase are usually below 80%, especially due to the parallel hydrogenation of acetone leading ultimately to propene. Catalyst stability, whenever reported is always very poor over acidic

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* Corresponding author at: ANP, Agência Nacional do Petróleo, Gás Natural e Biocombustíveis, Av. Rio Branco, 65, 20090-004, Rio de Janeiro, RJ, Brazil. Tel.: +55 21 25628307; fax: +55 21 25628300.
E-mail address: acamacho@anp.gov.br (A.C.C. Rodrigues).

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supports, since on these supports coke formation leads to fast deactivation of the catalyst [12,36,37,41,42,45]. On mildly acidic or basic supports, reported catalyst stabilities [7,11,30,32] were somewhat better, but still limited. The only exception seems to be the work of Chikán et al. [3], who reported a reasonable constant MIBK yield along 24 h TOS (conversion decrease was counter-balanced by increasing MIBK selectivity along the run) at 553 K on Cu/MgO catalyst. The temperature of reaction is usually kept below 473 K so as to minimize further condensation reactions leading to the formation of high-boiling point products and catalyst deactivation. Increasing the hydrogen/acetone molar ratio reduces the deactivation on the one hand but increases the hydrogenation of acetone to isopropyl alcohol, so reducing the yield of methyl isobutyl ketone, on the other, while a too low hydrogen/acetone ratio not only contributes to catalyst deactivation but also limits acetone conversion. The production of MIBK requires 1 mol of hydrogen for every 2 mol of acetone (not taking into account the direct hydrogenation of acetone) so that hydrogen is the limiting reactant for hydrogen/acetone ratios below 0.5.

We have previously reported on the one-step synthesis of MIBK from acetone over Pt/X and Pt/CsX at temperatures from 413 to 613 K and hydrogen/acetone = 0.5 and 6.2 (molar) [50], with good yields and better stability than the vast majority of the catalysts described in the literature. The goal of this work was to study the effect of hydrogen/acetone ratio, reaction temperature, metal dispersion, space velocity and metal content on this reaction over palladium (~1 and 3 wt%) on a mildly basic support such as NaX.

2. Experimental

2.1. Catalyst preparation

The parent sample was a NaX zeolite (Si/Al = 1.2) obtained from IPT (Instituto de Pesquisas Tecnológicas, São Paulo, Brazil). It was ion-exchanged with a solution of $Pd(NH_3)_4(NO_3)_2$ to give samples PdNaX and PdNaX(3), with 1% and 3% (wt.) metal content, respectively. The solutions were added dropwise under stirring for 6 h to an aqueous suspension with 4 wt% of solids at 353 K and kept at room temperature for 20 h. After filtration and washing in order to remove nitrate anions, the samples were dried overnight at 393 K. Next, they were calcined under pure O_2 (1.0 L/g/min) at 1 K/min up to 633 K and kept at the final temperature for 2 h. Then, the calcined samples were reduced under H_2 at 5 K/min up to 633 or 773 K. Three samples were obtained: (i) Pd6/X6 (PdNaX calcined and reduced at 633 K); (ii) Pd5/X6 (PdNaX calcined at 633 K and reduced at 573 K) and (iii) Pd6/X6(3) (PdNaX(3) calcined and reduced at 633 K).

2.2. Catalyst characterization

A detailed description of the characterization of the present catalysts is beyond the scope of this work. The information given here is necessary for the proper interpretation of the catalytic results.

The chemical composition was determined by atomic absorption (Na, Pd, Si and Al) spectrometry on a PerkinElmer AAS 1100B spectrophotometer and X-ray fluorescence spectrometry on a Rigaku spectrometer.

BET specific surface areas, micro- (t-plot) and mesopore (BJH) volumes were determined by N_2 adsorption at 77 K on a Micromeritics ASAP 2000.

The crystallinity of the samples was determined by XRD using a Rigaku Dmax Ultima + diffractometer with CuKα radiation, 40 kV and 40 mA.

H_2 chemisorption (Micromeritics ASAP 2900 C) was used to determine metal particle size and dispersion.

Dispersions and particle sizes were related by [51]

$$d = \frac{1}{D} \tag{1}$$

IR spectra were recorded with a PerkinElmer FTIR 2000 spectrophotometer at room temperature. Self-supported wafers were used to investigate surface hydroxyls after drying at 633 K for 2 h under He and evacuation at 10^{-4} Torr for 1 h at this same temperature without further exposure to air. All spectra were taken at room temperature.

2.3. Reaction conditions

The gas phase reaction was carried out in a fixed-bed reactor at atmospheric pressure for 6 h. Various independent runs at different temperatures, space velocities and H_2/Ac molar ratios were performed. The reactants were fed to the reactor by bubbling hydrogen through a saturator held at the desired temperature. The exit stream was analyzed by on-line gas chromatography with a CP-Sil 5 CB column and a flame ionization detector. CG-MS analyses were also used for proper product identification, in addition to the comparison of retention time of standard samples.

The conversion of acetone (X_A) and the selectivity (S) to the various products were defined on the basis of converted acetone [10,13] and was calculated from peak areas taking into account the different response factors in the flame ionization detector.

$$X_A = \frac{y_M + 2y_D + 3y_T + 4y_{Te}}{y_A + y_M + 2y_D + 3y_T + 4y_{Te}} \tag{2}$$

$$S = \frac{y_M,\ 2y_D,\ 3y_T \text{ or } 4y_{Te}}{y_M + 2y_D + 3y_T + 4y_{Te}} \tag{3}$$

where y_A, y_M, y_D, y_T and y_{Te} are, respectively, the mole fractions of acetone, monomers (IPA, C3), dimers (DAA, iMO, MO, 2MP, MIBK, MIBC), trimers (DIBK, iDIBK, DMHA, TMB, IPH), and tetramer (C12) in the product stream.

Accordingly, the activities were also defined on the basis of converted acetone (mol A_c h^{-1} $g_{cat}{}^{-1}$), as follows:

$$A_o = \frac{X_A \times \text{WHSV}}{58} \tag{3}$$

$$A_h = A_o \times S_M \tag{4}$$

$$A_c = A_o(S_D + S_T + S_{Te}) \tag{5}$$

where A_o, A_h and A_c are, respectively, the overall activity, the activity for acetone hydrogenation, and the activity for acetone condensation while S_M, S_D, S_T, and S_{Te} are the selectivities to monomers, dimers, trimers, and tetramer, respectively.

Residual activity (A_r) was defined as the rate between the activity at a fixed TOS, for our purposes, 6 h and the initial activity, which is indeed, the fraction of the initial activity remaining in the catalyst after a time of 6 h of use under operation conditions.

The MIBK yield was defined as:

$$\text{Yield}_{\text{MIBK}} = \frac{y_{\text{MIBK}} \times A_o}{(y_M + 2y_D + 3y_T + 4y_{Te})2}$$

Conversion, selectivity and activity values reported for each run refer to those taken at steady conditions, typically at 180 min TOS.