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MIBK from acetone on Pd/H-[Ga]ZSM5 catalysts: Effect of metal loading

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ABSTRACT

This work presents the preparation and characterization of three bifunctional catalysts consisting of palladium supported on H-[Ga]ZSM5 zeolite, with a Si/Ga atomic ratio of 16 and Pd contents of 0.09, 0.50 and 1.02 wt%. The lowest and highest Pd content solids, which were assessed by transmission electron microscopy (TEM), show dispersion of the supported phase of 90% and 73%, respectively. The XPS characterization studies of the catalysts allowed to detect the presence of framework, tetrahedral Ga species, Pd(0) aggregates and Pd(0) atomically dispersed. These solids were tested in the synthesis of methyl isobutyl ketone (MIBK) from acetone. The results confirm that the catalyst with 1.02 wt% Pd, shows an initial global activity about twice as higher as that of 0.09 wt%Pd/H-[Ga]ZSM5, and additionally the selectivity to MIBK of the former is four times higher. These results show that the catalyst with lower Pd content do not have a high number of active metallic sites to catalyze the hydrogenation of Mesityl oxide to MIBK, even though it showed an excellent dispersion, while the catalyst with 1.02 wt% Pd seems to be a catalyst with a proper balance of the acidic-hydrogenating functions.

1. Introduction

Methyl isobutyl ketone (MIBK) is an industrial chemical derived from acetone, which is widely used as a solvent for paints and other protective coatings, as an extracting solvent, and as an intermediate for the production of various plastics and resins [1,2]. Industrially, MIBK has been produced by liquid-phase processes involving three separate steps: First a base catalyzed condensation to "aldol"-type intermediate, followed by the acid catalyzed dehydration of this intermediate, and finally selective hydrogenation of the olefinic bond of the resulting, -unsaturated ketone [1,3]. This type of process generates huge amounts of wastes that can be avoided by a purely heterogeneous "one-pot" process. This allows to reduce the complexity and cost of the separation processes, with, consequently, a reduction of the by-product disposal. Thus, one-step liquid-phase processes using heterogeneous bifunctional catalysts with combined acid, basic and hydrogenating properties have been developed [4–6], most of them using palladium impregnated on cation exchange resins as catalysts working at relatively low temperatures (between 120 and 200 °C) but having the disadvantage of operation under high pressures (10 to 100 bar) [6]. Other catalysts that have been tested in liquid-phase consist also of palladium on supports such as $CaO–MgO–SrO–Al_2O_3$ [7], $ZrO(OH)_2$–carbon [8], Nb_2O_5/SiO_2 [9], a Zn–Cr mixed oxide [10], and SAPO-11 [11]. The reaction scheme of the one-step MIBK synthesis is shown in Scheme 1 (Eq. b), where the main competitive route leads to propane (Eq. a).

At variance with the liquid-phase processes, one-step gas-phase MIBK synthesis studies have been carried out mostly under atmospheric pressure conditions, in a range of temperatures similar to the liquid-phase reactions. Palladium-based catalysts (among other metals such as Ni, Cu or Pt) have been used for gas-phase reactions. In particular, Yang and Wu [11] employed AlPO-11 and SAPO-11 as supports for Pd, demonstrating that selectivity to MIBK was improved by loading the metal by ion-exchange instead of impregnation. This was assigned to a closer proximity between metallic sites and acidic (and/or basic) sites in the ion-exchanged catalysts. Pd supported on a $Zn^{II}–Cr^{III}$ (1:10) mixed oxide was shown to be a very efficient bifunctional catalyst for the synthesis of MIBK from acetone in both liquid-phase and gas-phase processes [10]. Ziyad and co-workers [12] reported production of MIBK from acetone in the gas-phase over hydroxiapatite supported Pd catalysts. The study was carried out between 100 and 200 °C under atmospheric pressure and varying Pd loadings, reaction temperature being the most important experimental variable, with maximum conversion at 150 °C. Finally, Yang and coworkers [13] studied the synthesis of MIBK in the gas-phase at temperatures between 120 and 220 °C, under high pressure (40 atm), using Pd catalysts supported on MCM-56. The maximum catalytic performance was obtained at 180 °C, H_2/acetone molar ratio of 0.2 and 0.5 wt% Pd loading.

In previous works, some of us reported the use of Pt/H-[Al]ZSM5 bifunctional catalysts for the gas-phase synthesis of

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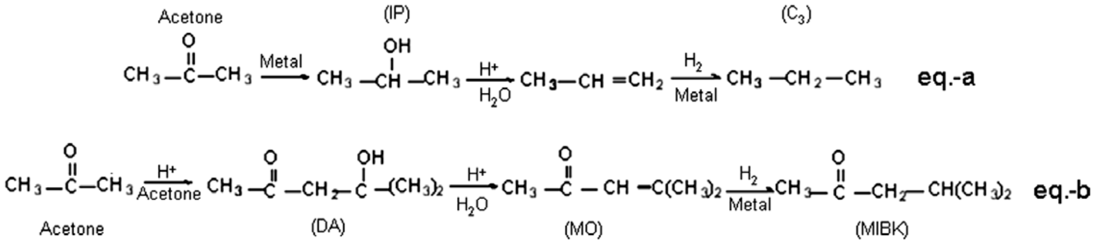

Scheme 1. Reaction scheme of MIBK synthesis from acetone.

MIBK from acetone [14–16]. The pore structure of MFI-type zeolites is well suited for this reaction, as the medium size of its pores should limit the formation of high molecular weight condensation products that leads to deactivation by coking [16]. Nevertheless, strong deactivation by coke formation was observed for the Pt/MFI catalysts, which prompted us to modify the acidity of the support by substituting Ga for Al in the MFI support [17–19], as this isomorphous substitution should render a solid with the same topology but decreased strength of the acid sites. However, a strong interaction between Pt and Ga was observed, which inhibited the metallic function of platinum [17,18]. Further improvements could be obtained by employing a different metal, and as shown in the works cited above, palladium would be a suitable candidate.

In this paper, it is reported the use of H-[Ga]ZSM5 as support of palladium for the synthesis of MIBK from acetone. We present the preparation and characterization of H-[Ga]ZSM5 and *x*Pd/H-[Ga]ZSM5 ($x = 0.09–1.02$ wt%), as well as their catalytic properties for MIBK synthesis at 160 °C, under atmospheric pressure.

2. Experimental

A gallosilicate of the MFI-type (bulk Si/Ga = 16) was synthesized according to the literature [18,20]. The MFI structure of this gallosilicate was confirmed by powder XRD analysis, using a Siemens D-5005 diffractometer and Cu Kα radiation. The specific surface area (SSA) was assessed by N_2 physisorption at −196 °C, employing a Quantasorb QS-17 instrument. The values of Si/Ga atomic ratios reported throughout this paper were obtained by means of inductive coupled plasma-atomic emission spectroscopy (ICP-AES), using a Perkin Elmer EAA-LL CGB instrument.

The synthesized gallosilicate was used as support in the preparation of three bifunctional catalysts: 0.09 wt%Pd/H[Ga]ZSM5; 0.50 wt%Pd/H[Ga]ZSM5 and 1.02 wt%Pd/H[Ga]ZSM5. The bifunctional catalysts were prepared by the ion-exchange-impregnation method, employing an aqueous solution of $Pd(NH_3)_4Cl_2$, which was kept in contact with the gallosilicates for 24 h at pH 10 (exchange). Afterwards, this suspension was submitted to a slow evaporation process at 60 °C (impregnation). Finally, the catalysts were dried, calcined under dry air at 500 °C for 6 h and reduced "in situ" in hydrogen atmosphere at 500 °C for 6 h.

The catalysts were evaluated by ICP-AES and transmission electron microscopy (TEM), using a Hitachi CM-10 equipment operated at 120 kV; these techniques were used to verify the actual content of supported Pd and its dispersion over the surface of the gallosilicate support. The SSA and XRD powder patterns were obtained as indicated above. The catalysts were further analyzed by X-ray Photoelectron Spectroscopy (XPS), with a VG Scientific ESCALAB 220i-XL spectrometer, equipped with a hemispherical electron analyzer and a double anode Mg–Al non-monochromatic X-ray source [18]. The pressure in the analysis chamber was kept below 10^{-9} Torr. The samples were reduced by heating at 500 °C for 2 h under hydrogen flow. The reduced simples were protected from exposure to the atmosphere by immersion into hydrocarbon solvent (purified hexane) while transferring from the reactor to the spectrometer.

The MIBK synthesis was carried out in a fixed-bed dynamic flow reactor at 160 °C, 1 atm pressure, acetone/hydrogen molar ratio = 3 and variable WHSV. The reactor effluents were analyzed with a HP-6890 gas chromatograph, equipped with a FID detector, a CP-SIL 5 CB column (30 m length, 0.25 mm diameter and a composition of 5% phenyl methyl siloxane).

3. Results and discussion

3.1. Physicochemical characterization of catalysts

The XRD patterns of the H-[Ga]ZSM5 support and of 0.09 wt%Pd/H[Ga]ZSM5; and 1.02 wt%Pd/H[Ga]ZSM5, are shown in Fig. 1a, b and c, respectively. The observed signals, especially those appearing at peaks at $2\theta = 7.8–8.7°$ and 22–25° confirm that all the as-synthesized samples give MFI-type XRD patterns. No peaks other than those corresponding to the MFI structure were observed, indicating the high purity of products [21], particularly, signals of Ga_2O_3 or of any other Ga compound were absent. The addition of Pd and the successive calcination and reduction treatments at 500 °C do not modify the structure of the support.

The values of SSA for the bifunctional catalysts range within 378 and 382 m^2/g, implying that the palladium loading does not significantly alter the surface area of the H-[Ga]ZSM5 (390 m^2/g), neither it blocks the microporosity of the catalyst, which guarantees the proximity of both types of active sites (acidic and metallic), a requirement for a proper and balanced bifunctional catalyst.

3.2. Transmission microscopy electron analysis (TEM)

Metallic nanoparticles dispersed on inorganic oxides are widely used in a variety of catalytic reactions, and the effective preparation methods of supported nano-sized metal particles have been extensively explored as a key issue to develop new efficient catalytic systems [22–24]. Transmission electron microscopy was used to determine the metallic particle dispersion, *D*, for each one of the bifunctional catalysts. The average particle diameter, $\bar{d}_s$, was calculated assuming spherical shape, by the expression [18]:

$$\bar{d}_s = \sum_i n_i d_i^3 / n_i d_i^2$$

where n_i is the number of particles in the sample with diameter d_i. From the obtained average diameter of the particles (expressed in nanometers) the dispersion, *D*, can be calculated by means of [25]:

$$D(\%) \cong 100/\bar{d}_s$$

This procedure was applied to a large number of particles, typically more than 500 for each catalyst.

Figs. 2 and 3 show typical TEM micrographs of the palladium metallic particles for the 0.09 wt%Pd/H-[Ga]ZSM5 and 1.02 wt%