Characterization and catalytic behavior of potassium-modified ZrO$_2$ base catalysts

Zhi-Jian Li$^a$, Hillary A. Prescott$^a$, Jens Deutsch$^b$, Annette Trunschke$^b$, Heiner Lieske$^b$, and Erhard Kemnitz$^{a,*}$

$^a$Humboldt-Universität zu Berlin, Institut für Chemie, Brook-Taylor-Strasse 2, D-12489 Berlin, Germany
$^b$Institut für Angewandte Chemie Berlin-Adlershof, Richard-Willstätter-Strasse 12, D-12489 Berlin, Germany

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Potassium-modified ZrO$_2$ base catalysts were prepared by wet impregnation of hydrous zirconia and anhydrous zirconia with potassium compounds and calcined at 600 °C in air. The properties of the catalysts were characterized and compared. Catalytic activities were examined for the vapor-phase double-bond isomerization of 1-butene at 150 °C and the liquid-phase Michael addition of 2-methylcyclohexane-1,3-dione to methyl vinyl ketone at room temperature. The properties of the modified ZrO$_2$ i.e., basic site strength, were greatly affected by the ZrO$_2$ precursors and the potassium modifiers. High yields of 2-butene with relatively high cis/trans ratios were found. Leaching of the potassium-modified ZrO$_2$ makes the system less suitable for use in liquid-phase reactions.

KEY WORDS: potassium-modified ZrO$_2$; base catalysts; isomerization of 1-butene; Michael addition.

1. Introduction

ZrO$_2$ has attracted more and more attention as a promising catalyst and catalyst support because of its high thermal stability, amphoteric nature, and redox properties [1]. Until now, ZrO$_2$ has been transformed into strong, solid acid catalysts by modification with sulfate [2–7], WO$_3$ [8], MoO$_3$ [9], or B$_2$O$_3$ [10,11]. These ZrO$_2$-based solid acid catalysts show high activity and selectivity in many reactions [2–11]. However, few efforts have been made to turn ZrO$_2$ into a base catalyst by taking advantage of its natural basicity, although several studies have been done on a highly effective alkali-modified ZrO$_2$ catalyst for the oxidative coupling of methane [12,13]. In general, it is common to prepare base catalysts by modifying or supporting alkali metal oxides on various supports [14]. Various alkali metal oxides have been loaded on different supports, such as magnesium oxide [15], zeolites [16–19], alumina [19–21], and silica [22], by the decomposition of alkali compounds. These catalysts have proved to be excellent solid-base catalysts for numerous vapor-phase probe reactions, such as isopropanol dehydrogenation [16,19,22], the isomerization of 1-butene [17,23,24] and cis-but-2-ene [25], the methylation of phenol [22], toluene [26], and catechol [27] with methanol. However, alkali metal oxides–supported catalysts used in liquid-phase, base-catalyzed reactions have been investigated less. It is not clear whether this kind of catalyst is a real heterogeneous catalyst in liquid-phase reactions. Recently, Wang et al. [25] used a dry impregnation process to prepare KNO$_3$/ZrO$_2$ superbases, which possessed a base strength of H$_\text{ac}$ = 27.0 and were very active for cis-but-2-ene isomerization under mild conditions. Here, we report on the properties of potassium-modified ZrO$_2$ prepared by the calcination of hydrous zirconia and anhydrous zirconia after impregnation with potassium compounds. The catalytic activity of this system was studied in the vapor-phase isomerization of 1-butene and in the liquid-phase Michael addition of 2-methylcyclohexane-1,3-dione to methyl vinyl ketone.

2. Experimental

2.1. Catalyst preparation

Hydrous zirconia, ZrO(OH)$_2$ $\cdot$ aq, was prepared from ZrOCl$_2$ $\cdot$ 8H$_2$O (Fluka, 99%) according to Parida et al. [28]. Pure anhydrous ZrO$_2$ was obtained by calcination of hydrous zirconia at 600 °C in air for 4 h. The supported catalysts were prepared by wet impregnation of ZrO(OH)$_2$ (ZRH samples) and ZrO$_2$ (ZRO samples) powders with aqueous solutions of KHCO$_3$, K$_2$CO$_3$, KOAc, and KNO$_3$ (in most cases, about 1.0 mL solution for 1.0 g powder). The theoretical K/Zr ratios were 0.2. After impregnation, the excess solution was evaporated at room temperature. The samples were then dried at 110 °C (for the samples modified with KHCO$_3$, 80 °C was used instead), calcined at 600 °C in flowing air for 4 h, and stored in closed containers until used.

$^*$To whom correspondence should be addressed.
E-mail: erhard.kemnitz@chemie.hu-berlin.de
2.2. Characterization

2.2.1. XRD and textural properties

Identification of the samples was performed using X-ray powder diffraction with Cu Kα radiation (XRD 7, Rich. Seifert & Co., Freiberg). The nitrogen adsorption and desorption isotherms at 77 K were measured using a Micromeritics ASAP 2010 system after the calcined samples were degassed at 200°C overnight. Surface areas were calculated using the BET method. Pore volumes and pore distributions were calculated using the BJH method. The contents of carbon, hydrogen, and nitrogen were determined by elemental analysis. Potassium and zirconium contents were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES).

2.2.2. TG-DTG-DTA

Thermogravimetry (TG), differential thermogravimetry (DTG), and differential thermal analysis measurements (DTA) were performed using a NETZSCH STA409C system equipped with a skimmer-coupled mass spectrometer in airflow, with a heating rate of 10°C/min up to 700°C, and Al2O3 as a reference.

2.2.3. CO2-TPD

CO2-TPD was used to measure the strength of basic sites. The pelleted sample (approximately 300 mg, 0.3–0.5-mm diameter fraction) was pretreated in a nickel reactor under Ar (70 mL/min) at 600°C for 1 h. The sample was then cooled to 50°C and exposed to a stream of Ar and CO2. The sample was flushed for over 1 h at 50°C to remove physisorbed CO2, after which the TPD program (10°C/min, up to 600°C, held for 30 min) was started. The desorption of gas-phase CO2 was detected by monitoring the band at 2349 cm−1 with FTIR spectroscopy (FTIR system 2000, Perkin–Elmer).

2.3. Catalytic screening procedure

2.3.1. Vapor-phase reaction: double-bond isomerization of 1-butene

The isomerization of 1-butene was performed in a down-flow, fixed-bed glass reactor. Equal volumes of the pelleted, calcined catalyst (about 300–450 mg, 0.3–0.5 mm diameter fraction) were exposed to the feed stream mixture of nitrogen (10 mL/min) and 1-butene (0.6 mL/min) at 150°C. Prior to the reaction, the catalyst was pretreated in N2 at 600°C for 2 h. On-line gas chromatography (Shimadzu GC-17A, FID, quartz capillary: PONA (methylsiloxane), 50 m, 0.2 mm × 0.5 μm) was used to determine the composition of the reaction mixture of 1-butene and cis/trans-2-butene after a time onstream (TOS) of 10, 30, 60, and 90 min. Owing to 100% product selectivity, the reaction conversion is given by the yield of 2-butene product. Product yields were normalized by the mass of the catalyst used at 30 min in order to compare the catalysts’ results with each other.

2.3.2. Liquid-phase Michael addition

The Michael addition is given in scheme 1. The reaction was carried out in a 50-mL round-bottomed flask at room temperature. Methyl vinyl ketone (22.5 mmol, Aldrich, 99%), 2-methylcyclohexane-1,3-dione (15.0 mmol, Acros, 98%), dimethyl phthalate (3.75 mmol, Acros, 99%, internal standard for monitoring the product formation), and the solvent methanol (10 mL, Aldrich, 99%) were stirred for 30 min to saturate the mixture with 2-methylcyclohexane-1,3-dione (which is only slightly soluble in methanol), before the powdered solid catalyst (0.225 g) was added. Samples of the reaction slurry (about 0.3 mL) were collected after a specific amount of time, centrifuged, and concentrated on a rotary evaporator to remove the solvent and unreacted methyl vinyl ketone. The yield of the target product was analyzed by 1H NMR spectroscopy (solvent: DMSO-d6) using the integrals of the CH2-signal of 2-(γ-oxobutyl)-2-methylcyclohexane-1,3-dione (1.11 and 2.04 ppm) and dimethyl phthalate (3.83 ppm).

3. Results and discussion

Table 1 gives the notations and characteristics of the samples. Figure 1 shows the XRD patterns of some samples after calcination. Amorphous, hydrous zirconia formed monoclinic ZrO2 after calcination at 600°C (figure 1(a)). However, after the modification of hydrous zirconia using C-containing potassium compounds mentioned above and calcination, the main phase of KC-ZRH, KHC-ZRH, and KAC-ZRH (figure 1(b)) was metastable, tetragonal ZrO2. Both the tetragonal and monoclinic phase were found in KN-ZRH (figure 1(c)). It has been postulated that the K⁺ ions are incorporated in the vacant sites on the surface of hydrous zirconia and stabilize the tetragonal ZrO2 phase [25,29]. All of the ZRH samples, except for KN-ZRH, also have sharper and more intense XRD peaks than those of the pure ZrO2 and the ZRO samples; this indicates higher sample crystallinity of the ZRH samples. Almost no phase or intensity change was found in the XRD patterns of the impregnated,