Catalysis Today 173 (2011) 21–27

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Effect of MgO activation conditions on its catalytic properties for base-catalyzed reactions

V.K. Díez, C.A. Ferretti, P.A. Torresi, C.R. Apesteguía*,[1], J.I. Di Cosimo

Catalysis Science and Engineering Research Group (GICIC), INCAPE, UNL-CONICET, Santiago del Estero 2654, 3000 Santa Fe, Argentina

ARTICLE INFO

Article history:
Received 7 December 2010
Received in revised form 20 February 2011
Accepted 28 February 2011
Available online 9 April 2011

Keywords:
MgO activation
Base-catalyzed reactions
Monoglycerides
Hydrogen transfer
Aldol condensation

ABSTRACT

The effect of the MgO calcination temperature on its basicity and catalytic properties was studied. Three MgO samples calcined at 673, 773 and 873 K (samples MgO-673, MgO-773 and MgO-873) were characterized by different physical and spectroscopic techniques. The surface base properties were probed by temperature-programmed desorption of CO_2 and infrared spectroscopy after CO_2 adsorption at 298 K and sequential evacuation at increasing temperatures. The dimensions of face-centered cubic unit cell for MgO samples decreased while crystallinity and mean crystallite size increased with calcination temperature. MgO samples contained surface sites of strong (low coordination O^{2-} anions), medium (oxygen in Mg^{2+}–O^{2-} pairs) and weak (OH^- groups) basicity. The density of strong basic sites was predominant on MgO-673, but decreased with the calcination temperature together with the density of OH^- groups; on the contrary, the density of Mg^{2+}–O^{2-} pair sites increased with calcination temperature. The catalytic properties of MgO samples were explored for the cross-aldol condensation of citral with acetone to obtain pseudoionones (PS), the transesterification of methyl oleate with glycerol to yield monoglycerides (MG), and the gas-phase hydrogen transfer reaction of mesityl oxide with 2-propanol to form 4-methyl-3-penten-2ol (UOL). The initial PS and MG formation rates decreased with calcination temperature following a trend similar to the density of strong basic sites which suggested that the rate limiting steps for both reactions involve coordinatively unsaturated O^{2-} active sites. In contrast, the initial UOL formation rate in mesityl oxide/2-propanol reaction increased with MgO calcination temperature following the same trend as medium-strength basic sites, thereby indicating that Mg^{2+}–O^{2-} pairs promote the formation of the six-atom cyclic intermediate needed in the Meerwein–Ponndorf–Verley mechanism.

1. Introduction

Lately, increasing research efforts have been devoted to the use of solid bases for obtaining fine chemicals, pharmaceuticals and valuable compounds from renewable raw materials. In particular, pure and promoted MgO has been studied for catalyzing Cannizzaro and Tischenko reactions [1], Michael, Wittig and Knoevenagel condensations [2], double-bond isomerizations [3], aldol-condensations [4], and alcohol coupling [5]. However, the MgO basicity needed for efficiently promoting these reactions depend on the rate-limiting step requirements. For example, MgO is often doped with alkali metal cations, in particular Li^+, when stronger basic active sites are needed [6]. The density, nature and strength of surface base sites on MgO depend on the preparation method. MgO is usually produced by decomposition of $Mg(OH)_2$ which in turn is obtained by different preparation methods such as sol–gel, MgO hydration, chemical vapor deposition (CVD), and precipitation. Bailly et al. [7] have reported that after $Mg(OH)_2$ decomposition at high temperature (1023 K), the relative distribution of surface low-coordination O^{2-} anions is shifted toward the less coordinated ions along the series MgO-CVD < MgO-hydration ≈ MgO-precipitation < MgO-sol–gel. The same order was observed for MgO activity to convert 2-methylbut-3-yn-2-ol into acetone and acetylene, a base-catalyzed reaction [7].

The base site properties of MgO may also be regulated by controlling both the $Mg(OH)_2$ decomposition and MgO activation conditions. For example, Vidruk et al. [8] recently reported that densification of $Mg(OH)_2$ before its dehydration to obtain MgO generates a significant increase of surface basicity. In this work, we have investigated the effect of stabilization temperature of MgO obtained by $Mg(OH)_2$ decomposition on its base and catalytic properties. Specifically, $Mg(OH)_2$ was decomposed in N_2 at 623 K and the resulting MgO was treated for 18 h in N_2 either at 673 K, 773 K or 873 K generating samples MgO-673, MgO-773 and MgO-873, respectively. The density and strength of surface base sites of MgO-*x* samples (*x* being the MgO stabilization temperature) was determined by temperature-programmed desorption of CO_2 and

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* Corresponding author. Tel.: +54 342 4555279; fax: +54 342 4531068.
E-mail address: capesteg@fiq.unl.edu.ar (C.R. Apesteguía).

[1] http://www.fiq.unl.edu.ar/gicic/.

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doi:10.1016/j.cattod.2011.02.060

by infrared spectroscopy of CO_2 adsorbed at 298 K and desorbed at increasing temperatures. The activity and selectivity of MgO-*x* samples were probed for the liquid-phase cross-aldol condensation of citral with acetone to obtain pseudoionones (PS), the liquid-phase transesterification of methyl oleate (FAME) with glycerol to yield monoglycerides (MG), and the gas-phase hydrogen transfer reduction of mesityl oxide with 2-propanol toward 4-methyl-3-penten-2ol (UOL). Results show that the base properties of MgO, and as a consequence its catalytic properties, may be tuned by modifying the solid calcination temperature.

2. Experimental

2.1. Catalyst preparation

Three magnesium oxide samples were prepared by hydration of commercial MgO (Carlo Erba, 99%, 27 m^2/g). 250 ml of distilled water were slowly added to 25 g of commercial MgO and stirred at room temperature. The temperature was then raised to 353 K and stirring was maintained for 4 h. Excess of water was removed by drying the sample in an oven at 358 K overnight. The resulting $Mg(OH)_2$ was decomposed in N_2 (30 ml/min STP) to obtain MgO which was then treated for 18 h in N_2 either at 673, 773 or 873 K to give samples MgO-673, MgO-773 and MgO-873, respectively.

2.2. Catalyst characterization

The decomposition of $Mg(OH)_2$ was investigated by differential thermal analysis (DTA) using a Shimadzu DT30 analyzer, by temperature programmed decomposition (TPDe) using a flame ionization detector (FID) with a methanation catalyst (Ni/Kieselghur) operating at 673 K and by X-ray diffraction (XRD) in a Shimadzu XD-D1 diffractometer equipped with Cu-Kα radiation source ($\lambda = 0.1542$ nm) and a high temperature chamber. Samples characterized by X-ray diffraction were heated at 5 K/min until 773 K, taking diffractograms at 373, 573, 673 and 773 K.

Surface areas and pore volumes were measured by N_2 physisorption at 77 K using the BET method and Barret–Joyner–Halender (BJH) calculations, respectively, in an Autosorb Quantochrome 1-C sorptometer.

The structural properties of MgO-*x* samples were determined by X-ray diffraction (XRD) using the instrument described above. Analysis was carried out using a continuous scan mode at 2°/min over a 2θ range of 20–80°. Scherrer equation was used to calculate the mean crystallite size of the samples.

Sample base site densities were measured by temperature-programmed desorption (TPD) of CO_2 preadsorbed at room temperature. MgO-*x* samples were pretreated in situ in a N_2 flow at its corresponding stabilization temperature (673, 773 or 873 K), cooled to room temperature, and then exposed to a mixture of 3% CO_2/N_2 until surface saturation was achieved (10 min). Weakly adsorbed CO_2 was removed by flushing in N_2 during 1 h. Finally, the temperature was increased to 773 K at 10 K/min. Desorbed CO_2 was converted into CH_4 on a methanation catalyst and then analyzed using a FID.

The chemical nature of adsorbed surface CO_2 species was determined by infrared (IR) spectroscopy after CO_2 adsorption at 298 K and sequential evacuation at increasing temperatures. Experiments were carried out using an inverted T-shaped cell containing the sample pellet and fitted with CaF_2 windows. Data were collected in a Shimadzu FTIR Prestige-21 spectrometer. The absorbance scales were normalized to 20-mg pellets. Each sample was pretreated in vacuum at its corresponding stabilization temperature and cooled to room temperature, after which the spectrum of the pretreated catalyst was obtained. After admission of 5 kPa of CO_2 to the cell at room temperature, the samples were evacuated consecutively at 298, 373, 473, and 573 K, and the resulting spectrum was recorded at room temperature. Spectra of the adsorbed species were obtained by subtracting the catalyst spectrum.

2.3. Catalytic testing

2.3.1. Cross-aldol condensation of citral with acetone

The cross-aldol condensation of citral (Millennium Chemicals, 95% geranial + neral) with acetone (Merck, p.a.) was carried out at 353 K under autogenous pressure (≈250 kPa) in a batch Parr reactor, using acetone/citral = 49 (molar ratio) and catalyst/(citral + acetone) = 1 wt.% ratio. The reactor was assumed to be perfectly mixed and interparticle and intraparticle diffusional limitations were verified to be negligible. Reaction products were analyzed by gas chromatography in a Varian Star 3400 CX chromatograph equipped with a FID and a Carbowax Amine 30 M capillary column. Thirteen samples of the reaction mixture were extracted and analyzed during the 6-h reaction. The main product of the citral/acetone reaction was PS (cis- and trans-isomers). Moreover, diacetone alcohol and mesityl oxide were simultaneously produced from self-condensation of acetone. Trace amounts of unidentified heavy compounds were detected in the reaction mixture, probably coming from self-condensation of citral. Selectivities (S_j, mol of product *j*/mol of citral reacted) were calculated as $S_j\ (\%) = C_j \times 100/\sum C_j$, where C_j is the concentration of product *j*. Yields (η_j, mol of product *j*/mol of citral fed) were calculated as $\eta_j = S_j\, X_{\rm Cit}$, where $X_{\rm Cit}$ is the citral conversion.

2.3.2. Glycerolysis of methyl oleate

The transesterification of methyl oleate, FAME (Fluka, >60.0%, with 86% total C18 + C16 esters as determined by gas chromatography) with glycerol (Aldrich, 99.0%,) was carried out at 493 K in a seven-necked cylindrical glass reactor with mechanical stirring equipped with a condenser to remove the methanol generated during reaction.

Glycerol/FAME molar ratio of 4.5 and a catalyst/FAME ratio ($W_{\rm cat}/n^0_{\rm FAME}$) of 30 g/mol were used. The reactor was operated in a semi-batch regime at atmospheric pressure under N_2 (35 cm^3/min). Liquid reactants were introduced into the reactor and flushed with nitrogen; then the reactor was heated to reaction temperature under stirring (700 rpm). Reaction products were α- and β-glyceryl monooloeates (MG), 1,2- and 1,3-glyceryl dioleates (diglycerides) and glyceryl trioleate (triglyceride). Reactant and products were analyzed by gas chromatography in a SRI 8610C gas chromatograph equipped with a flame ionization detector, on-column injector port and a HP-1 Agilent Technologies 15 m × 0.32 mm × 0.1 μm capillary column after silylation to improve compound detectability, as detailed elsewhere [9,10]. Twelve samples of the reaction mixture were extracted and analyzed during the 8-h catalytic run.

2.3.3. Hydrogen transfer reduction of mesityl oxide with 2-propanol

The gas-phase mesityl oxide/2-propanol reaction was conducted at 573 K and atmospheric pressure in a fixed bed reactor. MgO-*x* samples sieved at 0.35–0.42 mm were pretreated in N_2 at the corresponding calcinations temperature for 1 h before reaction in order to remove adsorbed H_2O and CO_2. The reactants, mesityl oxide (MO, Acros 99%, isomer mixture of mesityl oxide/isomesityl oxide = 91/9) and 2-propanol (IPA, Merck, ACS, 99.5%), were introduced together with the proper molar composition via a syringe pump and vaporized into flowing N_2 to give a N_2/IPA/MO = 93.4/6.6/1.3, kPa ratio. Reaction products were analyzed by on-line gas chromatography in a Varian Star 3400 CX chromatograph equipped with a flame ionization detector and a