

Effect of the MgO Activation Conditions on its Basicity and Catalytic Properties

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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 promoting Cannizzaro and Tischenko reactions, Michael, Wittig and Knoevenagel condensations, olefin isomerizations and the synthesis of organic chemicals by either self- or cross-condensation reactions. However, the MgO basicity needed for efficiently catalyzing these reactions depend on the rate-limiting step requirements. For example, MgO is often doped with Li^+ cations when stronger basic sites are needed. In this work, we have investigated the effect of calcination temperature on the MgO basicity, i.e. nature and strength of surface basic sites, and on the catalytic properties. The activity and selectivity of MgO calcined at increasing temperatures were probed for the cross-aldol condensation of citral with acetone to obtain pseudoionones (PS), the transesterification of methyl oleate (FAME) 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 2-ol (UOL) (Figure 1).

Materials and Methods

Commercial MgO was hydrated with distilled water and the resulting $\text{Mg}(\text{OH})_2$ was calcined in N_2 at 673, 773 or 873 K for 18 h, thereby obtaining three magnesium oxide samples (MgO_x samples, where x is the calcination temperature). The textural and structural properties of MgO_x samples were determined by N_2 physisorption at 77 K and X-ray diffraction. Surface base properties were probed by TPD of CO_2 , and IR spectroscopy after CO_2 adsorption at 298 K and sequential evacuation at increasing temperatures.

Results and Discussion

XRD diffractograms showed that the dimensions of fcc unit cell for MgO_x samples decreased while crystallinity and mean crystallite size increased with calcination temperature. Three different CO_2 adsorption species were identified on Mg_x samples by FTIR: unidentate carbonate, formed on isolated O^{2-} ions, bidentate carbonate, formed on $\text{Mg}^{2+}\text{-O}^{2-}$ pair sites, and bicarbonate species, involving hydroxyl groups. The strength order for surface basic sites was: low-coordination O^{2-} anions > oxygen in $\text{Mg}^{2+}\text{-O}^{2-}$ pairs > OH groups. The base site density of MgO_x samples was obtained by TPD of CO_2 preadsorbed at 298 K. From the CO_2 TPD profiles we determined the density of weak (n_{OH}), medium ($n_{\text{Mg-O}}$), and strong (n_{O}) base sites. Results are presented in Figure 2 and show that n_{O} and n_{OH} decreased while $n_{\text{Mg-O}}$ augmented with the MgO calcination temperature.

The initial PS formation rate from the aldol condensation of citral with acetone decreased with calcination temperature (Figure 3), following a similar trend than n_{O} values in Figure 2. The

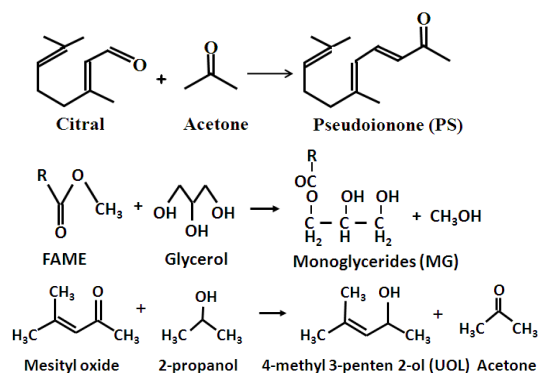


Figure 1: MgO-catalyzed reactions

the formation of the six-atom cyclic intermediate needed in Meerwein-Ponndorf-Verley mechanism for preferentially transferring hydrogen from the 2-propanol donor molecule to the CO bond of mesityl oxide, in agreement with previous reports [3].

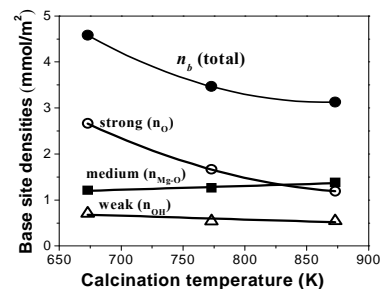


Figure 2: Effect of MgO calcination temperature on base site densities

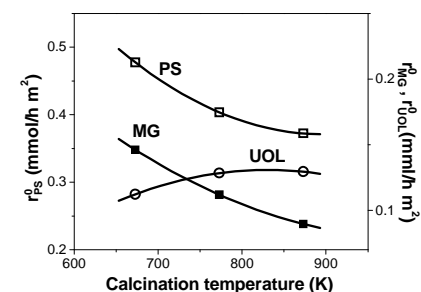


Figure 3: Initial formation rates of PS, MG and UOL

Significance

The density and strength of MgO base sites, and consequently its activity and selectivity for base-catalyzed reactions, can be regulated by changing the calcination temperature.

References

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initial MG formation rate from the glycerolysis of FAME also decreased with calcination temperature (Figure 3). These results are consistent with previous work showing that the rate limiting steps for both reactions involve strong O^{2-} basic sites [1,2]. In contrast, the initial UOL formation rate in mesityl oxide/2-propanol reaction slightly increased with calcination temperature following the same trend than $n_{\text{Mg-O}}$ values in Figure 2. This suggests that $\text{Mg}^{2+}\text{-O}^{2-}$ pairs promote