



# Influence of base strength on the catalytic performance of nano-sized alkaline earth metal oxides supported on carbon nanofibers



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## ABSTRACT

Nano-sized (3 nm) alkaline earth metal oxides supported on carbon nanofibers were prepared by a facile impregnation and heat treatment method of the corresponding nitrates. These supported catalysts showed a significant improved activity for the aldol reaction and transesterification compared to the respective bulk materials which did not show any appreciable activity. A linear correlation was found between the initial reaction rate and the strength of the basic sites as determined by CO<sub>2</sub> calorimetry indicating the importance of the base in the rate determining step of the reactions.

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## 1. Introduction

Base catalysts draw increasing interest mainly due to the growing biomass field and related conversions such as transesterification and aldol condensations [1–3]. Solid base catalysts offer several advantages with respect to their homogeneous counterparts such as easy regeneration, easy separation as well as being less corrosive [4–6]. The drawback of bulk solid bases is the low number of sites per unit mass. Supporting a solid base as nano-sized particles will, however, overcome this drawback [7,8]. The activity of solid bases is determined by the number and the base strength of the sites. Here, we will report on the preparation, characterization, and catalytic actions of monodispersed supported alkaline earth metal oxides (MO). This allows us to investigate the role solely of base strength on base-catalyzed reactions.

Bulk MgO, CaO, SrO, and BaO have been investigated as base catalysts for conversion such as isomerization reactions [9,10], Claisen–Schmidt condensations [11,12], Knoevenagel condensation [13], Michael additions [14], Tishchenko reactions [15], aldol condensations [16], and transesterification reactions [17] (for more details we refer to a landmark review of Corma and Iborra [1]).

Though a number of groundbreaking papers appeared on supported solid base catalysts [18,19], a comprehensive study on the independent influence of the number and strength of basic sites is, to the best of our knowledge, lacking.

Haneda et al. studied alkaline earth metal oxides supported on Co<sub>3</sub>O<sub>4</sub> for direct NO decomposition [20]. It was found that the alkaline earth metal oxide interacted closely with the support, forming mixed oxides being the catalytic active species, e.g., SrCoO<sub>2.5+δ</sub>. Catalytic conversion depended on the number of base sites and their strength, though the latter was not quantified.

Vasefir and Parvari used  $\gamma$ -alumina-supported alkaline earth metal oxides and  $\gamma$ -alumina-supported cobalt for mercaptan oxidation [21]. The number of base sites for the MO varied with that of MgO being significantly higher than for the other supported oxides. Both the number of active sites and the base strength was considered to be important for the catalytic performance. It was assumed that the base strength increased down the group though it was not quantified.

TPD and calorimetry of CO<sub>2</sub> are powerful tools to analyze number and strength of base sites [22,23,18]. TPD reveals the amount of adsorbed CO<sub>2</sub> by evaluating the peak area in the TPD trace. The position of the TPD peaks is indicative for the strength with which CO<sub>2</sub> was bonded to the surface, i.e., indicative for the base strength. Chen et al. used this tool to study the influence of the calcination procedure on the amount and strength of basic sites in MO on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> [24]. Irrespective of the calcination temperature, the peak

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position in the TPD was located at increasing temperatures when going down the group of alkaline earth metal oxides showing that the base strength increased down the group.

Calorimetry of CO<sub>2</sub> adsorption is able to reveal the strength of base sites. For example, Horiuchi et al. used this technique to investigate the basicity of ceramics based on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and MO [25]. The heat of CO<sub>2</sub> adsorption was found to increase with decreasing electronegativity of the investigated metals in the materials, showing that the base strength increased down a group.

In this study, we have investigated the influence of base strength on catalytic activity for supported alkaline earth metal oxide containing the same number of active sites per unit mass. MO were supported on carbon nanofibers (CNF) starting from the cheap and widely available nitrate precursors. Carbon nanofibers have been used as support to suppress support/metal oxide interactions as often seen for traditional oxide support as discussed above [20]. Bulk MOs prepared from the same precursors were included for comparison. After preparation, the materials were characterized by CO<sub>2</sub>-chemisorption, CO<sub>2</sub>-calorimetry, XRD, and TEM. Biomass-related processes as the transesterification and the self-condensation reaction of acetone to diacetone alcohol (DAA) as example of an aldol reaction were chosen as test reaction (Scheme 1).

## 2. Materials and methods

### 2.1. Preparation of the catalysts

#### 2.1.1. Bulk metal oxides

The bulk metal oxides were prepared from the nitrate-precursors, magnesium nitrate hexahydrate (Acros, 99+%), calcium nitrate tetrahydrate (Sigma–Aldrich, 99%), strontium nitrate (Sigma–Aldrich, p.a.), and barium nitrate (Fluka, p.a.) by heat treatment at 700 °C for 2 h (10 °C min<sup>-1</sup>) in stagnant air.

A high surface area MgO (230 m<sup>2</sup> g<sup>-1</sup>) from Stream Chemicals was stored under N<sub>2</sub> and used without any activation procedure.

#### 2.1.2. Alkaline earth metal oxide supported on carbon nanofibers

Oxidized carbon nanofibers (CNF) (pore volume 0.7 ml g<sup>-1</sup>) were prepared from syngas at 550 °C and 3 bars overpressure using a 5 wt% Ni/SiO<sub>2</sub> catalyst as described in detail elsewhere [7]. 2.5 g CNF was dried overnight at 120 °C, followed by evacuation for half an hour. The desired metal was introduced to the support by incipient wetness impregnation using an aqueous solution of the metal nitrate salt. The loadings were 3.4 wt% MgO, 4.8 wt% CaO, 8.8 wt% SrO, and 13 wt% BaO on CNF. These loadings result in equimolar amounts of metal oxide in the catalysts. In case of BaO, three impregnations with barium nitrate were needed to obtain the high

loading. After impregnation, the samples were equilibrated for 12 h followed by drying in stagnant air for 12 h at 120 °C. The samples (25–150  $\mu$ m fraction) were heat treated in 30 ml min<sup>-1</sup> N<sub>2</sub> at 600 °C for 3 h (5 °C min<sup>-1</sup>) immediately prior to the catalytic test.

### 2.2. Catalyst testing

#### 2.2.1. Self-condensation of acetone to diacetone alcohol

The self-condensation of acetone was carried out at 0 °C in a 200-ml double-walled thermostatted batch glass reactor using 100 g of acetone as reactant, 6 g of iso-octane as an internal standard, and 1 g of catalyst. Prior to the experiment, the reactor was flushed with nitrogen and during the entire experiment a nitrogen atmosphere was kept over the reaction to avoid exposure to air. The reaction mixture was mechanically stirred with 1700 rpm. Aliquots of 1 ml solution were taken at specific times during a total of 24 h. The samples were filtrated through hyflo (Sigma Aldrich) in order to remove traces of catalyst before GC analysis.

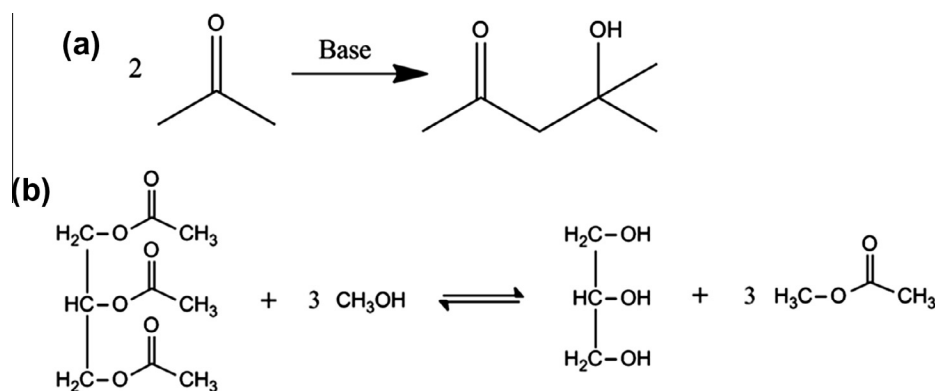
#### 2.2.2. Regeneration test

The first catalyst test was performed as described above. After 24 h of test, the catalyst was isolated by centrifugation and decantation and washed with 3  $\times$  30 ml acetone and 2  $\times$  30 ml heptane followed by drying at 120 °C for 18 h in stagnant air. After this procedure, the catalyst was heat treated in 30 ml min<sup>-1</sup> N<sub>2</sub> at 600 °C for 3 h (5 °C min<sup>-1</sup>) immediately prior to the second catalyst test. The same procedure was carried out before the third activity experiment.

The concentration of diacetone alcohol in the aliquots was measured using a Chrompack CP 9001 gas chromatograph equipped with a CP-SIL-5 column and an FID detector in all types of catalytic experiments. Traces of by-products were identified with a Shimadzu GCMS-QP2010. Since only traces of by-products were observed, the initial catalytic activity was expressed as  $\text{mmol}_{\text{acetone converted}} \text{mmol}_{\text{MO}}^{-1} \text{h}^{-1}$  over the first 15 min of the reaction where  $\text{mmol}_{\text{acetone converted}}$  was defined as  $2 \times \text{mmol}_{\text{DAA formed}}$ .

#### 2.2.3. Transesterification

The transesterification reaction was carried out in N<sub>2</sub> atmosphere at 60 °C in a 100-ml round-bottom flask using 10 g triacetin, 11.7 ml methanol, 0.3 ml toluene as internal standard, and 100 mg of catalyst while stirring at 500 rpm. Aliquots of 0.2 ml solution were taken at specific times during a total of 3 h and diluted with 1 ml dichloromethane. The samples were filtrated through a micropore filter in order to remove traces of catalyst before GC analysis. The triacetin concentration was measured on a Shimadzu GC 2010 with a CP8822 column equipped with an FID detector, and the activity was expressed as  $\text{mmol}_{\text{triacetin converted}} \text{mmol}_{\text{MO}}^{-1} \text{h}^{-1}$ .



**Scheme 1.** (a) Self-condensation of acetone to diacetone alcohol and (b) transesterification of triacetin with methanol.

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