

MgO supported on activated carbon for conversion of bio-ethanol into butanol: effect of the MgO load and of the presence of water on the catalytic performance.

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Introduction

Bio-ethanol is currently used as a fuel additive. It can be mixed with gasoline in a limited amount [1] due to its water solubility, corrosivity and low calorific value. Due to these limitations substitution of ethanol for butanol has been recently proposed.

Bio-butanol can be produced by ABE fermentation of suitable biomasses. The process provides, in addition to butanol, acetone and ethanol. The fraction of ethanol can be upgraded to butanol via catalytic routes [2] through a process increasing the carbon number of alcohols, known as Guerbet reaction [3]. Previous results of catalytic tests carried out on MgO powder [4] and MgO dispersed on γ -Al₂O₃ [5] highlighted the key role of basic sites, provided by MgO, in the butanol formation.

In this work magnesium oxide was dispersed on activated carbon with high surface area in order to investigate the effect of MgO dispersion on the catalytic performance in the Guerbet reaction by comparing results with unsupported MgO. Furthermore, the effect of the presence of water in the feed, unavoidable when using the ethanol/water azeotropic feed mixture, was also studied.

Experimental

Preparation of reference MgO and MgO/AC.

Reference MgO powder was obtained from Mg(NO₃)₂ solution by addition of ammonia solution with 5:1 NH₃/Mg ratio. The precipitate was stirred at 60°C for 6h in a closed bottle and, after filtration, dried at 120°C overnight and calcined at 450°C for 2h.

An aqueous solution of Mg(NO₃)₂ was also used for incipient wetness impregnation of Darco activated carbon (AC) 20x40 mesh granules supplied by Norit to obtain 10, 20 and 30 wt% MgO load respectively. After drying at 120°C catalysts were calcined 2 h at 600°C under N₂.

A mechanical mixture consisting of 20% MgO and 80% AC was also prepared as reference sample to verify both the effect of MgO dispersion and of MgO-AC interaction.

Characterization of catalysts

XRD analysis was performed with a Bruker D2 Phaser diffractometer. Specific surface area was evaluated using a Quantachrome Autosorb 1-C by N₂ adsorption at 77 K after degassing samples for 2h at 150°C. SEM analysis of cross sectioned AC granules was carried out with a FEI Inspect instrument equipped with an energy dispersive X-ray (EDX) probe.

Catalytic tests

Catalytic tests were carried out at 350-400°C by feeding a 3% vol. ethanol/N₂ mixture to a lab-scale fixed bed reactor of 1 g catalyst, as described in [4]. An N₂ flow passes through a bubbler containing liquid ethanol at room temperature. The ethanol concentration was determined according to the Antoine equation. A second N₂ line was added downstream the bubbler to avoid possible condensation of ethanol and other products into the pipe-lines. In some tests the second nitrogen line flowed through a bubbler containing distilled water at room temperature, thus adding about 2% H₂O to the feed. Reactants and products were analysed by an online GC (Hewlett Packard 1540A) equipped with FI detector and a ZB-WAXplus column.

Ethanol conversion was reported as ethanol reacted/ethanol fed x 100 (vol./vol.). Butanol yield was expressed as butanol produced/ethanol fed x 100 (vol./vol.).

Results and discussion

In Table 1 a list of catalyst with corresponding BET areas is reported. A significant decrease of the original surface area of AC particles was observed upon dispersion of 10% MgO. Further addition of MgO up to 20 % does not modify the surface area, however, dispersion of 30% MgO leads to a drop of BET area of about 37% with respect to that of the parent carbon.

Table 1. BET surface area of AC support and catalysts.

Catalyst	BET area (m ² /g)
MgO powder	26
AC	641
10%MgO/AC	576
20%MgO/AC	578
30%MgO/AC	403

XRD patterns of both AC and 10%MgO/AC are shown in Figure 1. Reflections of well crystallized MgO periclase (JCPDS 45-946) were found in the pattern of unsupported MgO powder (not shown). The same signals, although very weak, are detectable in AC supported MgO sample, in addition to the broad signals of carbon.

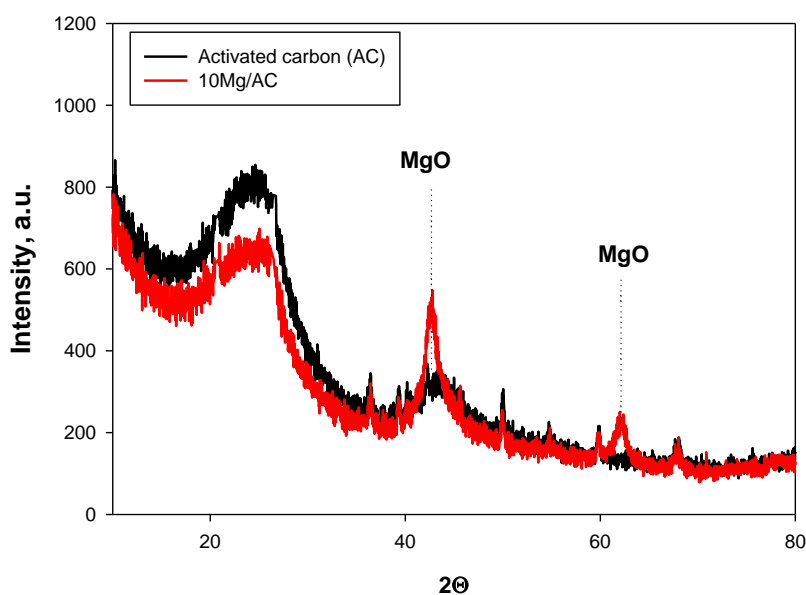


Figure 1. XRD patterns of AC and 10%MgO/AC.

In Figure 2 the Mg EDX mapping performed on the corresponding SEM image shows the quite uniform magnesium distribution.

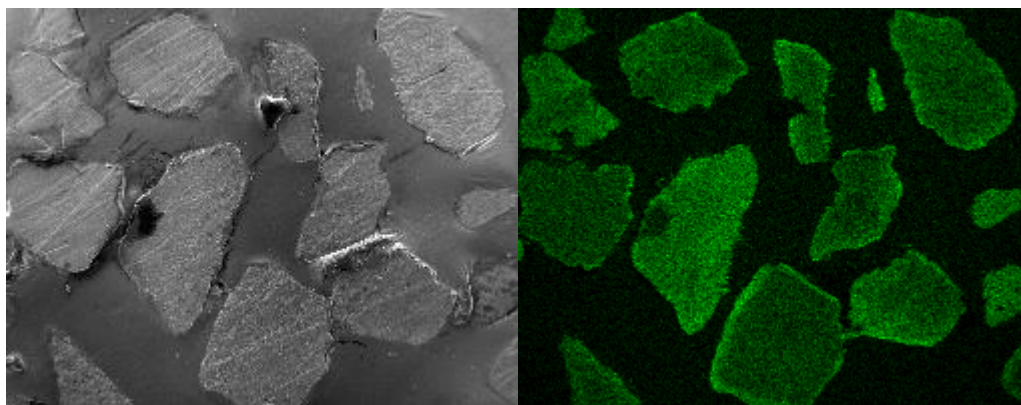


Figure 2 SEM image (left) and Mg EDX mapping (right) of 20%MgO/AC.

In Figure 3 ethanol conversion and butanol yield obtained at 400°C on 10-30% MgO/AC are compared with performance of bulk MgO under the same operating condition. The main product of the reaction, in addition to butanol, was acetaldehyde

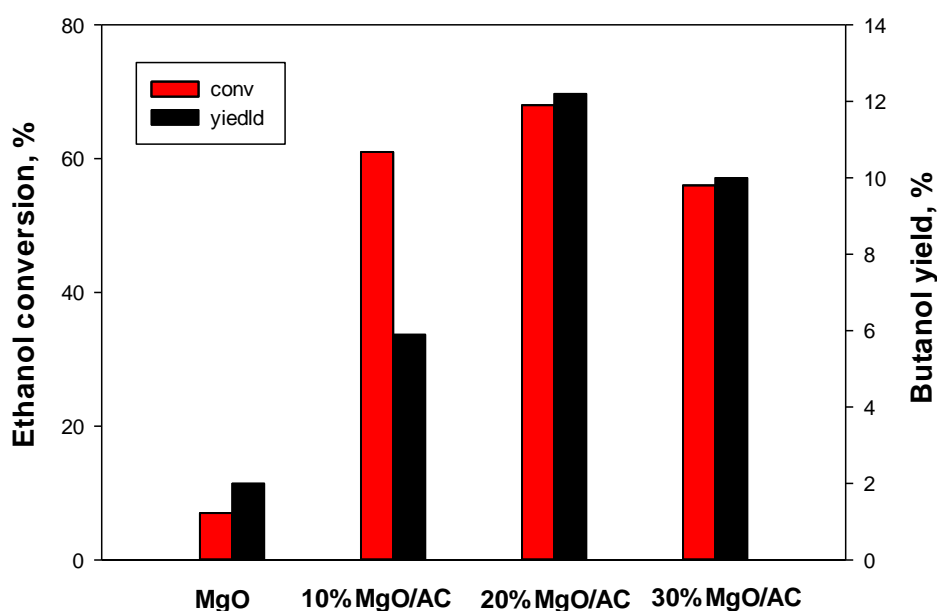


Figure 3. Ethanol conversion and butanol yield obtained in catalytic tests on pure MgO and AC supported MgO catalysts at 400°C.

Results highlight the key role of MgO dispersion. Indeed, the low performance of bulk MgO is greatly enhanced when this oxide is dispersed on the high surface area microporous carbon although the fraction of MgO in the catalytic bed is only 10-30%. Maximum performance was obtained in correspondence of 20% MgO load, at higher loads both conversion and yield start to decrease most likely related to the partial MgO aggregation evidenced by the reduction of surface area for 30% MgO load (Table 1). Moreover, the catalytic tests carried out over the mechanical mixture consisting in 20% MgO and 80% AC provided an undetectable butanol yield further confirming the superior performance of highly dispersed MgO and excluding, at the same time, that the active carbon has catalytic activity towards Guerbet reaction.

All tests described up to now were carried out under dry condition. Nevertheless, in order to investigate the effect of the presence of water, generally present in the ethanol feed or produced as by-product by the main reactions taking place during the process, some test adding H₂O to the feed were performed on the most performing catalyst (20%MgO/AC).

After a standard test under dry condition, 2% water was added to the feed keeping unchanged both the ethanol inlet concentration and the total flow rate. Then, without carrying out any regeneration water was removed from the feed and the test under dry condition repeated.

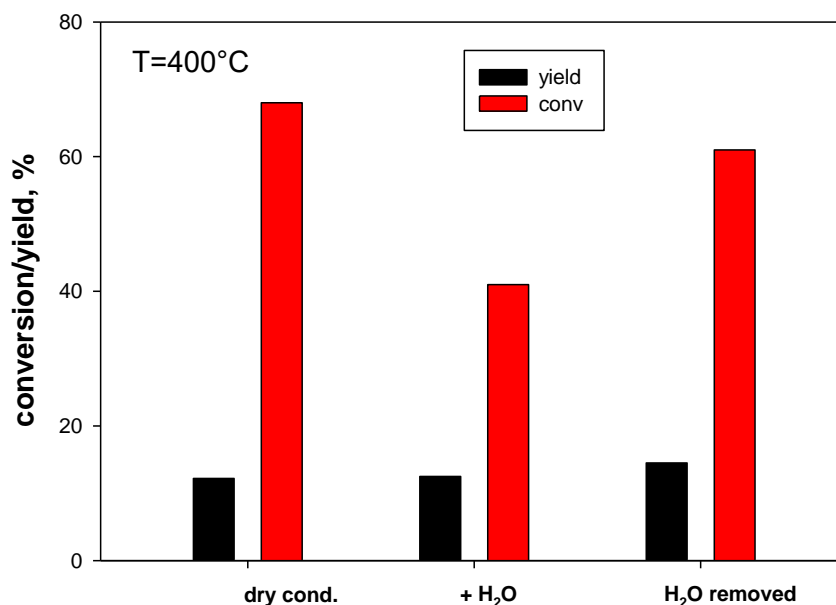


Figure 4. Ethanol conversion and butanol yield obtained on fresh 20%MgO/AC at 400°C under dry condition followed by 2% H₂O addition and H₂O removal

Comparison of results show that, although under wet condition ethanol conversion is lower than under dry condition, butanol yield is the same. This is basically due to the suppression of side reactions producing some unidentified products in the presence of water. This catalyst was monitored under wet condition for about 9h measuring a stable butanol production. Removing water from the feed a slightly improved butanol yield (14.5%) with respect the same test over the fresh catalyst was observed, likely due to an increase of surface area that can occur when water weakly gasifies the activated carbon. Indeed, the surface area of the catalyst after the exposure to water during the catalytic test increases up to 750 m²/g.

Conclusions

Active carbon supported MgO is an active and water tolerant catalyst for conversion of ethanol into butanol. The low cost and the easy preparation of this material makes it a good candidate for the upgrading of bio-ethanol to butanol as fuel additive.

References

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