Applied Catalysis A, General 542 (2017) 271–281

Contents lists available at ScienceDirect

Applied Catalysis A, General

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

Research Paper

Role of the surface intermediates in the stability of basic mixed oxides as catalyst for ethanol condensation

Jorge Quesada, Laura Faba, Eva Díaz, Salvador Ordóñez*

Department of Chemical and Environmental Engineering, University of Oviedo (Faculty of Chemistry), Julián Clavería s/n, 33006 Oviedo, Spain

ARTICLE INFO

Keywords:
Guerbet reaction
DRIFT spectroscopy
Butanol
Aldol condensation
Deactivation

ABSTRACT

The ethanol condensation catalyzed by mixed oxides is studied in this work, considering not only the activity but also the stability of these materials. Concerning to the activity, different weight hourly space velocities (WHSV) were tested, obtaining the highest conversion and 1-butanol selectivity with Mg-Al, mainly at 673 K and a WSHV of 7.9 h^{-1}. On the other hand, dehydration products, observed with Mg-Zr in relevant amounts, limit the results obtained with this material. Deactivation studies were carried out by combining the measurement of reactant and products in the gas phase and in the catalytic surface using spectroscopic techniques (DRIFT). Good stability was observed with both materials at low temperatures (lower than 673 K), whereas at the highest one, Mg-Zr suffers relevant deactivation justified by the permanent adsorption of aldehydes and oxygenated oligomers on the active sites. It has been demonstrated that Mg-Al mixed oxides are promising catalyst for 1-butanol production from ethanol not only in terms of activity, but also in terms of catalyst stability.

1. Introduction

Bioethanol (obtained by fermentation from different biomass feedstocks [1]) is nowadays produced in large amounts, highlighting the United States production (58 millions of cubic meters per year), being around the 60% of the world global production [2]. The large availability, as well as its potential as reactant for different catalytic conversions, justify the high interest for its upgrading as an alternative sustainable raw material, not only for obtaining biofuels [3–5], but also as a platform for the manufacture of other petrochemicals, such as butadiene, butanol or acetone [6]. Among the different technological alternatives [7], the chemo-catalytic route is considered as the most promising one, even above the biological ones [8]. 1-Butanol is the most interesting condensation adduct that can be obtained from bioethanol when its condensation is combined with a partial hydrogenation (Guerbet reaction). It has been proposed as renewable fuel, with better properties than the starting bioethanol (higher energetic density and less hydrophilic behavior) [7]. Besides, 1-butanol can be used as a direct solvent or as starting material for other chemicals production, like acrylic acid, acrylic esters, butyl glycol ether, butyl acetate, dibutylether, etc. [9–12].

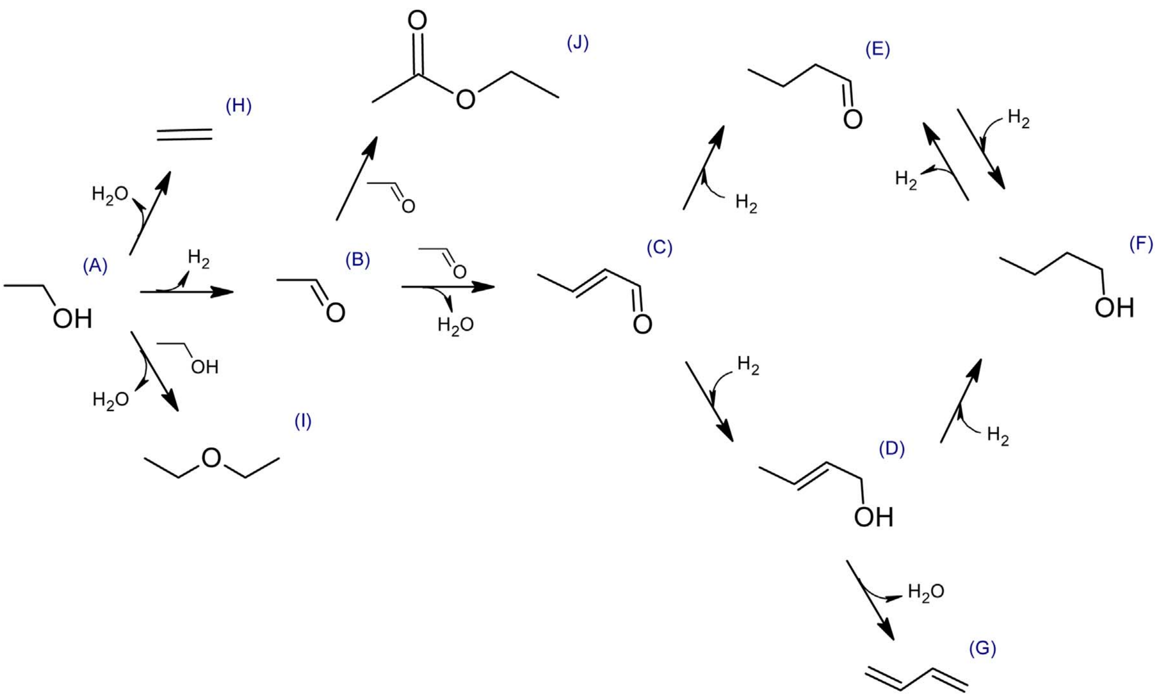
First approaches for transforming bioethanol into higher alcohols (butanol, hexanol, etc.) were carried out in liquid phase, using alkali, alkaline-earth hydroxides, transition metal oxides and alkali metal salts as homogeneous catalysts [13,14]. However, alternative heterogeneous processes are currently being studied due to several advantages (e.g., easier separation and recovery of the used catalyst and its possible recycling, lowering corrosion phenomena, reduced environmental constraints) [15,16]. Some authors have proposed three different reaction pathways for this reaction over heterogeneous catalysts: the direct condensation of two alcohol molecules [9,17–19]; the aldehyde (produced by the dehydrogenation of the starting alcohol) and alcohol condensation followed by a hydrogenation step [18,20]; and a four-step reaction process comprising alcohol dehydrogenation to produce aldehyde, subsequent aldol condensation of two aldehyde molecules followed by two hydrogenations [9,21–25]. Analyzing the evolution of the different compounds obtained in previous studies as well as their kinetic ratios, it was concluded that the four-step pathway prevails over the other mechanisms [21–26], and the ethanol condensation is kinetically limited by a previous dehydrogenation step, yielding acetaldehyde [3]. Working in gas phase allows reaching the temperatures needed to overcome this resistance at atmospheric pressure, being the most typical conditions considered in the last studies [25–27].

The considered mechanism for the gas-phase ethanol upgrading, showed in Scheme 1 [5,9,28–30], is a complex process involving different individual steps (dehydrogenations, dehydrations, aldol condensation, hydrogenations, coupling reactions) catalyzed by different active sites. The appropriate tuning of the catalytic properties, would allow shifting the reaction to one or other reaction products. Thus, different catalysts have been used in the ethanol upgrading in order to

---

* Corresponding author.
E-mail address: sordonez@uniovi.es (S. Ordóñez).

http://dx.doi.org/10.1016/j.apcata.2017.06.001
Received 14 April 2017; Received in revised form 30 May 2017; Accepted 1 June 2017



Scheme 1. Proposed reaction mechanism for the ethanol gas-phase condensation [5,9,28–30]. Symbols: (A) ethanol; (B) acetaldehyde; (C) crotonaldehyde; (D) crotyl alcohol; (E) butanal; (F) 1-butanol; (G) 1,3-butadiene; (H) ethylene; (I) diethyl ether; (J) ethyl acetate.

Table 1
Best results reported in the literature for the ethanol gas-phase condensation.

Catalyst	mass or volume	% vol. EtOH	WHSV	T (K)	x (%)	$\phi_{1\text{-butanol}}$ (%)	Reference
MgO	0.3 g	2	*unknown*	673	28	24	[24]
MgO	0.2 g	6.2	1.5 h^{-1}	653	7.9	40	[22]
MgO	0.2 g	8.2	2.5 h^{-1}	673	13	20	[23]
HPA	0.6 mL	20	10,000 L/h	673	22.7	62.4	[27]
HPA	0.06 g	6.2	5 h^{-1}	613	6.6	75	[22]
HPA	0.2 g	20	2 h^{-1}	623	14	71	[5]
HPA	0.3 g	5.6	0.7 h^{-1}	603	17.1	63.2	[18]
Mg_yAlO_x	0.2 g	9	1 h^{-1}	573	9.7	42.6	[30]
Mg_yAlO_x	*unknown*	9	0.4 h^{-1}	573	19	53	[9]

obtain a specific product, such as zeolites [17,31], metal oxides [20,26,32], metal mixed oxides [9,28], transition metal in the presence of basic compounds [10,33,34], and hydroxyapatites (HAP) [5,19,23]. Although results obtained with these materials cannot be directly compared (different conditions were tested in each work), best results previously reported in the literature are summarized in Table 1. As it can be observed, the HPAs highlight because of their high 1-butanol selectivity, although conversions lower than 25% were obtained in any case. On the other hand, best results obtained with Mg-Al mixed oxides are not so different, with a slight decrease in the 1-butanol selectivity but similar conversions in spite of working at softer reaction conditions and with a higher ethanol concentration in the feed stream. Despite the promising results of some of these materials (mainly mixed oxides and HAPs), there are not systematic studies about the stability of heterogeneous materials in this reaction. The only study that is reported in the literature that considers the evolution of the activity with the time on stream does not provide mechanistic justifications enough to extrapolate these results to a general behavior of these catalysts [5].

Considering the relevance of the catalyst stability, a deep deactivation study is needed for evaluating the feasibility of these technologies. In order to analyze the dynamics of the catalytic surface (changes in the morphology and physico-chemical properties), the information provided by different techniques must be gathered (physisorption, temperature-programmed oxidation, X-ray diffraction, etc.). Besides, diffuse reflectance infrared fourier transform (DRIFT) spectroscopy provides relevant information about the interaction of reactants, products and intermediates with the catalyst surface [35–38]. This technique allows analyzing the evolution chemical moieties adsorbed on the catalytic surface, being possible to identify the intermediates or final products present in these interactions.

The main aim of this work is to analyze the catalytic stability in the gas-phase ethanol condensation. Mixed oxides proposed as catalysts for this study were chosen considering the previous knowledge about these materials in our research group [28], and the possibility to modify the ratio between both cations to enhance the catalytic results. In addition, Mg-Al was previously proposed as catalyst for this reaction [9,24], but its deactivation has been scarcely studied. In addition, although the higher acidity of Mg-Zr (compared to Mg-Al with similar proportions) suggests a worse performance [39], the stability of this material has been previously studied in other gas-phase condensations with promising results [38]. Results obtained are related to the different surface properties of these materials, identifying the active sites controlling the reaction. The stability and deactivation causes were then analyzed considering the optimum conditions previously determined for both materials. Using different characterization techniques as well as the DRIFT spectroscopy, and comparing the data with the reaction results, the evolution of different compounds in the surface is analyzed and correlated to the activity loses, comparing the behavior of two materials with different surface chemistry.

2. Materials and methods

2.1. Catalysts preparation

Mg-Al mixed oxide (Mg/Al = 3) were obtained by the calcination of the corresponding hydrotalcites. The hydrotalcites were synthesized by co-precipitation of the Mg and Al nitrates at low supersaturation under sonication, following the procedure previously optimized by León et al. [28]. The gel was precipitated by increasing the pH to 10 and it was aged at 353 K for 24 h. The solid phase was then isolated by centrifugation, washed with deionized water to pH 7 and dried at 383 K for