



Ethanol and diethyl ether catalytic conversion over commercial alumina and lanthanum-doped alumina: Reaction paths, catalyst structure and coking

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ABSTRACT

Commercial high-pore-volume alumina and La-doped aluminas have been characterized and tested as catalysts for ethanol conversion to ethylene and diethyl ether and for diethyl ether cracking. In order to go deeper on reaction paths and mechanisms, steady state, TPSR and static experiments in an IR cell were performed. It is established that ethylene forms from ethanol by two parallel ways: i) cracking of ethoxy groups that occurs already at low temperature, and ii) the parallel synthesis and cracking of DEE at intermediate temperatures. Coordination of diethyl ether on Lewis sites represents the first step in its decomposition path. Lewis bonded DEE first cracks to ethoxy species and ethylene gas, while ethoxy species in part crack to a second step to another ethylene gas molecule and in part (only at low temperature) can desorb as gaseous ethanol. Commercial low loading lanthanum-doped alumina contain dispersed $\text{La}^{3+}\text{-O}^{2-}$ species mainly interacting with the most reactive defect, edge and corner sites of alumina nanocrystals. At higher loading (4 wt% La_2O_3) very small La_xO_y clusters also appear. Lanthanum doping slightly reduces the number of active sites for ethanol dehydration as well as for DEE cracking, thus reducing catalytic activity, but does not modify significantly selectivities and ethylene yields at high temperature. However, it also considerably reduces the amount of carbonaceous residues formed upon both reactions over the catalyst. Thus, La-doping is proposed as a way to improve the alumina catalyst stability in the process. Catalytic cracking of DEE at 673 K does not represent a good way to remove odorous and dense DEE vapours from air, due to the coproduction of small amounts of acetaldehyde together with ethylene.

1. Introduction

The conversion of bioethanol to (bio)ethylene has been industrially performed for several years. According to Morschbacker [1], the first commercial plant to produce ethylene from ethanol was built and operated, using an alumina catalyst, at Elektrochemische Werke GmbH at Bitterfeld in Germany in 1913. Several processes have been commercially developed and operated [2]. Even after steam cracking was established as the main technology to produce light olefins from oil cuts, and ethanol was mostly produced by ethylene hydration, still industrial plants producing ethylene from ethanol were active in some countries such as China [3]. The interest in bioethanol dehydration technology reappeared recently [4,5] to produce renewable ethylene (bioethylene), with the development of new processes such as IFPEN-Axens (AtoI) [6],

BP-Technip (Hummingbird) [7], Braskem [8], G.I. Dynamics [9] and Biochemtex [10]. In these processes, acid catalysts are generally used: alumina, silica-alumina, zeolites, heteropolyacids and phosphoric acid are mostly considered [1,2,4,5]. Ethylene yields in industrial conditions are very high (> 95%), with almost total ethanol conversion. Previous studies showed that the performances of $\gamma\text{-Al}_2\text{O}_3$ [2,5,11], although very good, are limited at low temperature by uncomplete conversion and diethyl ether synthesis, while at high temperatures by the co-production of small amounts of higher hydrocarbons [12–14]. An additional main point is represented by the growth of carbonaceous materials that may progressively deactivate the catalyst [14]. Thus, catalyst regeneration is needed every couple of months [5] and is pursued mainly by steaming at relatively high temperature. Both phenomena might be supposed to be due, at least in part, to acid-catalyzed

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overconversion of ethylene.

Over all acid catalysts, diethyl ether is the main product at low temperature and conversion. In fact, diethyl ether (DEE) can be manufactured industrially from ethanol dehydration over acid catalysts. Alumina is again the most cited catalyst in the literature and is applied in industrial processes [15,16]. In this case, ethanol conversion is limited to around 60–80% per pass, unconverted ethanol being separated and recycled. DEE process yield is near 90% with coproduction of small amounts of ethylene.

A debate still exists on the details of ethanol dehydration mechanism, DEE being a possible intermediate in the reaction [17,18]. Additionally, DEE and ethylene may also appear as byproducts in processes for the conversion of bioethanol to other chemicals, such as hydrogen by steam reforming, butenes, butadiene, acetone, etc., in particular when using alumina-supported or bifunctional catalysts [19,20]. DEE is also an odorous Volatile Organic Compound largely used as a solvent. Thus, the investigation of DEE cracking reaction is relevant not only in relation to the mechanism of ethanol conversion [18] but also as a possible way to abate DEE from air and reducing its smelling [21].

The improvement of alumina as a catalyst for DEE and/or bioethylene production may be attempted by doping, in particular to limit ethylene overconversion to higher hydrocarbons and coke, thus improving ethylene selectivity and catalyst stability. In a previous paper [22] we reported on the impregnation of a commercial “small pore-volume” γ -Al₂O₃ sample with lanthanum nitrate, producing 5 wt% La₂O₃-Al₂O₃ catalyst (calculated as wt_{La2O3}/wt_{Al2O3}). This material, although significantly less active than the corresponding pure alumina (γ -Al₂O₃) in converting ethanol, was an even slightly more selective catalyst towards ethylene at full ethanol conversion. On the other hand, lanthanum is reported to be a relevant additive to alumina in catalysts formulation: it improves alumina properties by increasing its mechanical strength [23], it stabilizes spinel-type alumina with respect to sintering and loss of surface area [24] and it activates alumina-supported metallic catalysts [25]. In particular, we found an interesting activation effects of lanthanum doping for alumina supported Ni catalysts applied to reactions useful in the environmental catalysis field, such as ethanol steam reforming and biomass tar steam reforming [26] as well as CO₂ methanation [27]. Thus, much interest is focused today on the preparation and characterization of La-containing aluminas [28–30]. Recently, Sasol commercialized La-containing aluminas powders [31]. In spite of this great interest, deep spectroscopic characterization studies of La₂O₃-Al₂O₃ systems are still very limited.

To go deeper on the chemistry of (bio)ethanol on oxide catalysts, as well as on the catalytic behaviour of lanthanum doped alumina, we investigated the conversion of both ethanol and diethyl ether over commercial γ -Al₂O₃ and La- γ -Al₂O₃ at 423–773 K with diluted ethanol feed at ambient pressure. In particular, we report here on the characterization of high pore-volume γ -Al₂O₃ and La- γ -Al₂O₃ (La₂O₃ ~ 1% and 4% wt), recently commercialized by Sasol, using XRD, skeletal IR, Field Emission Scanning Electron Microscopy (FE-SEM) as well as IR studies of surface hydroxy- groups, adsorbed pyridine and CO₂. Moreover, we investigated the effect of lanthanum addition on the behaviour of alumina as catalyst for ethanol dehydration to DEE and ethylene and of DEE cracking.

2. Experimental

2.1. Materials

The catalysts were commercial materials from Sasol, used without any further pretreatment. The notation used is the following: PTH for pure alumina Puralox TH 100/150, PL1 for Puralox TH 100/150/L1 and PL4 for Puralox TH 100/150/L4. The properties of these materials are summarised in Table 1.

Table 1

Samples notations and surface area.

Sample	%La ₂ O ₃ (wt _{La2O3} / wt _{CAT}) ^a	S _{BET} [m ² / g _{CAT}] ^a	Å ² CAT/ at _{La}	at _{La} /nm ² _{CAT}	Theoretical monolayer fraction ^b	%La ₂ O ₃ (wt _{La2O3} / wt _{CAT}) ^c
PTH	0	146	–	0	0	0
PL1	1.20	151	344	0.29	0.06	1.5
PL4	4.0	155	104	0.96	0.18	5.5

^a Data from the producer.

^b Assuming 5.2 La atoms per nm² of alumina as the monolayer coverage.

^c from EDX analysis.

2.2. Materials characterization

X-Ray diffraction patterns were recorded using Cu K α radiation ($\lambda = 0.15406$ nm) by means of a Philips X'Pert diffractometer, in the 2 θ angle range varying from 10° to 100° with a step of 0.02° and an acquisition time of 17 s for each step.

IR studies were performed using a Nicolet Nexus Fourier Transform instrument on compacted powder disks of 15–30 mg activated in vacuum at 773 K before adsorption experiments. CO₂ (30 Torr) was adsorbed at room temperature (r.t.) and spectra were recorded in the presence of the gas and after outgassing at room temperature and at increasing temperature. Pyridine (5 Torr) was put in contact with the catalysts for ten minutes and then outgassed at r.t. and upon increasing temperatures (373–773 K).

DR-UV-vis-NIR spectra were collected with a JASCO V570 instrument equipped with an integrating sphere.

SEM-EDX analysis were performed by a scanning electron microscope ZEISS SUPRA 40 VP, with a field emission gun as emitter. This instrument is equipped with a high sensitivity “InLens” secondary electrons detector to investigate morphology, with a solid state back-scattered detectors to enhance compositional contrast and with a Energy Dispersive X-ray Spectrometer OXFORD “INCA Energie 450 × 3” to evaluate the composition of the overall samples and of the different constituting phases (EDXS).

2.3. Catalytic experiments

2.3.1. Steady state catalytic measures (steady state flow reactor study – SSFR)

Catalytic experiments were performed at atmospheric pressure in a tubular flow reactor (i.d. 6 mm) using 0.500 g catalyst (60–70 mesh sieved, thus achieving a ratio between the particle and internal reactor diameter near to 25) and feeding ethanol (99.8% assay, from Sigma Aldrich) in nitrogen with 12 h⁻¹ WHSV (total flow rate of 80 cc/min). The carrier gas (nitrogen) was passed through a bubbler containing ethanol maintained at constant temperature (298 K) in order to obtain the desired partial pressures (7.9% ethanol/ 92.1% N₂). In the DEE experiments, the same catalysts weight have been used and a part of the carrier gas has been saturated with DEE at 293 K obtaining the following composition in the gas phase 4% DEE/96% N₂ achieving a WHSV of 12.8 h⁻¹. In both cases, the furnace temperature has been varied stepwise from 423 K to 773 K.

The outlet gases were analyzed by a gas chromatograph (GC) Agilent 4890 equipped with a Varian capillary column “Molsieve 5A/ Porabond Q Tandem” and TCD and FID detectors in series. In order to identify the compounds of the outlet gases, GC-MS Thermo Scientific with TG-SQC column (30 m × 0.25 mm × 0.25 μ m) was used.

Reactant conversion is defined as usual:

$$X_R = (n_{R(in)} - n_{R(out)})/n_{R(in)} \text{ with } R = \text{DEE or EtOH}$$

While selectivity to product *i* is defined as follows:

$$S_i = n_i / (v_i(n_{R(in)} - n_{R(out)}))$$

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