



Conversion of ethanol over transition metal oxide catalysts: Effect of tungsta addition on catalytic behaviour of titania and zirconia



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ABSTRACT

Ethanol dehydration was investigated at atmospheric pressure with 1.43 h⁻¹ WHSV in nitrogen, in the temperature range 423–773 K over titania and zirconia, as such and modified by addition of WO₃. As for comparison, data on other WO₃-free and WO₃-containing catalysts are also discussed: a strong Lewis acid (alumina), a covalent oxide (silica) and a basic material (calcined hydrotalcite). The catalysts were characterized using FT-IR of adsorbed pyridine and of wolframate species, and by UV-vis spectroscopy. The results presented here show that WO₃/ZrO₂ and WO₃/TiO₂ are excellent catalysts for ethanol dehydration. Their performances may compete with those of zeolites and alumina for conversion to diethyl ether and to ethylene. The addition of WO₃ to both ZrO₂ and TiO₂ introduces strong Brønsted acid sites that are supposed to represent the active sites in the reaction, but also inhibits the formation of byproducts, i.e. acetaldehyde and higher hydrocarbons. This is attributed to the poisoning of basic sites and of reducible surface Ti and Zr centres, respectively.

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1. Introduction

Ethanol produced by fermentation of lignocellulosics, denoted as “second generation bioethanol”, could become a primary intermediate in the frame of a new industrial organic chemistry based on renewables [1,2].

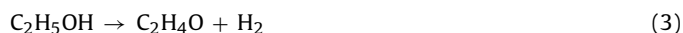
Among the secondary intermediates potentially obtainable by converting (bio)ethanol, ethylene and diethyl ether can be obtained by catalytic dehydration



Reaction (1) has already been applied at the industrial level in the 1960s using aluminas as the catalysts [3,4]. Different opinions exist on the potential practical improvement that can arise by the use of protonic zeolite catalysts instead of aluminas [5,6]. On both alumina [7] and some zeolites almost 100% yield to ethylene can be obtained at moderate temperature in lab scale experiments. Reaction (2) occurs on the same catalysts at moderate ethanol

conversion, allowing very high selectivities and significant yields (>70%).

Also acetaldehyde can be obtained by ethanol, through dehydrogenation:



This reaction has been used industrially in early times using either metal or zinc oxide catalysts [8]. Several other chemical intermediates can be obtained from ethanol, such as, e.g. acetic acid [9], ethyl acetate [10], higher olefins [11], isobutene [12], butadiene [13,14], and others.

The conversion of alcohols is also largely used as a test reaction for surface acido-basicity characterization [15–18]. Dehydration to olefins or ethers is typically observed on acid catalysts but the roles of Brønsted and Lewis acidity on these reactions are still under discussion. Alcohol dehydrogenation to carbonyl compounds is instead assumed to occur on basic catalysts. However, as said for acetaldehyde synthesis, industrial alcohols dehydrogenations are carried out either on metal catalysts or on ZnO [19], more than on typical bases.

Metal oxides are characterized by Lewis type acidity and basicity as a function of the ionicity of the metal–oxygen-bond, size and charge of the cation [20]. Brønsted acidity is observed on the oxides of high oxidation state elements. Among these elements, hexavalent tungsten is reported to give rise to stable, very acidic

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Table 1
The properties of investigated catalysts.

Notation	Commercial name and composition	Manufacturer	Preparation	Crystal phase	S _{BET}
MgO–Al ₂ O ₃	Pural MG70 (Mg:Al 70:30)	Sasol	Calcined at 773 K for 4 h	Amorphous	195 ± 10
SiO ₂	Silica Gel SG127	Grace Davison	As received	Amorphous	300
ZrO ₂	–	–	Prepared from Zr nitrate	Monoclinic	94
TiO ₂	Titania	Rhône-Poulenc	as received	Anatase	70
Al ₂ O ₃	Puralox SBA 200	Sasol	From boehmite via Al alkoxides	Gamma	190 ± 10
WO ₃ /MgO–Al ₂ O ₃	13.6% (wt/wt) WO ₃ Mg:Al 70:30	Home-made	Impregnated, dried and calcined at 673 K for 3 h	Amorphous	168 ± 10
WO ₃ /SiO ₂	13.6% (wt/wt) WO ₃	Home-made	Impregnated, dried and calcined at 673 K for 3 h	Amorphous	110 ± 10
WO ₃ /ZrO ₂	13.6% (wt/wt) WO ₃	Home-made	Impregnated, dried and calcined at 673 K for 3 h	Monoclinic	81 ± 10
WO ₃ /TiO ₂ (H)	13.6% (wt/wt) WO ₃	Home-made	Impregnated, dried and calcined at 673 K for 3 h	Anatase	60 ± 10
WO ₃ /TiO ₂ (C)	Titan A-DW-1 13.6% (wt/wt) WO ₃	Bayer	As received	Anatase	80

catalytic materials active as catalysts of several acid-catalyzed processes, including alcohol dehydration reactions [21–25]. In particular, tungsta–zirconias represent very interesting acid catalysts, already developed at the industrial level for paraffin isomerization [26], but the reasons of their high activity has not been fully clarified [27,28].

In this paper results are reported on the catalytic activity of some metal oxides in ethanol conversion. In particular, the focus is on the addition of tungsten oxide to transition metal oxide catalysis, i.e. zirconia and titania. As for comparison, data on other WO₃-free and WO₃-containing catalysts will also be discussed, such as a strong Lewis acid (alumina), a covalent oxide (silica) and a basic material (calcined hydrotalcite). The aim of this work is to test several potentially interesting catalysts and look at products selectivities, in order to have more information on the catalytic activity/surface structure/bulk structure relationships for metal oxide systems.

2. Experimental

2.1. Catalysts

The catalyst properties are summarized in Table 1. ZrO₂ was prepared from Zr(NO₃)₄ (MEL Chemicals, solution 40%) as in a previous study [29]. The preparation of tungsten-supported catalysts was accomplished by impregnating the supports with an aqueous solution of 5(NH₄)₂O·12WO₃·5H₂O from Carlo Erba, followed by drying and calcining for 3 h at 673 K. The virtual composition of the catalysts is 13.6% (wt/wt) WO₃/support, as in the commercial WO₃/TiO₂ sample, also considered in the paper.

2.2. Catalytic experiments

Catalytic experiments were performed at atmospheric pressure in a tubular flow reactor (i.d. 6 mm) using 0.5 g catalyst (60–70 mesh sieved, thus with a ratio between the particle diameter and the internal reactor diameter near 25) and feeding 7.9% (v/v) ethanol in nitrogen with 1.43 h⁻¹ WHSV (total flow rate of 80 cm³/min). The carrier gas (nitrogen) was passed through a bubbler containing ethanol (96%) maintained at constant temperature (298 K) in order to obtain the desired partial pressures. The temperature in the experiment was varied stepwise from 423 K to 773 K.

Ethanol conversion is defined as usual:

$$X_{\text{EtOH}} = \frac{n_{\text{EtOH(in)}} - n_{\text{EtOH(out)}}}{n_{\text{EtOH(in)}}$$

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

$$S_i = \frac{n_i}{v_i(n_{\text{EtOH(in)}} - n_{\text{EtOH(out)}})}$$

where *n_i* is the moles number of compound *i*, and *v_i* is the ratio of stoichiometric reaction coefficients.

The outlet gases were analyzed by a gas chromatograph (GC) Agilent 4890 equipped with a Varian capillary column “Molsieve

5A/Porabond A Tandem” and TCD and FID detectors in series. In order to identify the compounds of the outlet gases, a gas chromatography coupled with mass spectroscopy (GC–MS) Thermo Scientific with TG–SQC column (15 m × 0.25 mm × 0.25 μm) was used.

2.3. Catalyst characterization

UV–vis analysis has been performed using a Jasco V570 instrument, equipped with a DR integration sphere for the analysis of fresh and spent catalysts powder. All the spectra have been recorded in air at room temperature.

Acidity measurements were done using the pure powders pressed into thin wafers and activated in the IR cell connected with a conventional outgassing/gas-manipulation apparatus at 773 K. The activated samples were contacted with pyridine vapour (*p*_{py} ~ 1 Torr) at room temperature for 15 min; after which the IR spectra of the surface species were collected under continuous outgassing at increasing temperature.

3. Results

3.1. UV–vis study

The diffuse reflectance UV–vis spectra, recorded in air, of the fresh catalysts are presented in the Fig. 1. In case of ZrO₂ the inflection point of the absorption edge is near 240 nm due to O²⁻ → Zr⁴⁺ charge transfer transitions, corresponding to the excitation of electrons from the valence band (having O 2p character) to the conduction band (having Zr 4d character) [30–32]. For titania the absorption edge is stronger, near 380 nm, due to charge transfer transition from valence band (having O 2p character) to the conduction band (having Ti 3d character) [33,34].

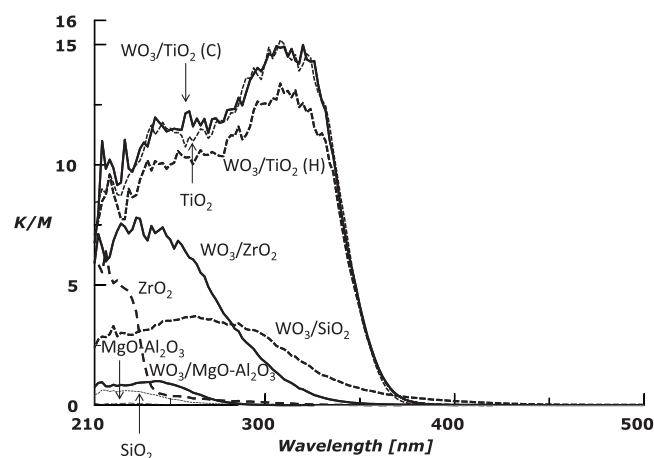


Fig. 1. UV–vis spectra of fresh catalysts.

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