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The role of oxide location in HMF etherification with ethanol over sulfated ZrO_2 supported on SBA-15

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ABSTRACT

The etherification of 5-hydroxymethyl-2-furfural (HMF) over ZrO_2 and sulfated ZrO_2-SBA-15 was chosen as a case study to analyze (i) the quantitative relationship between the concentration of Lewis and Brønsted acid sites and the catalytic behavior in the above reaction, which is also of industrial relevance for the production of biodiesel additives, and (ii) how the location of zirconia nanoparticles inside or outside the mesoporous channels of SBA-15 could significantly influence the specific reactivity in this reaction, both before and after sulfation. Depending on the loading of zirconia (about 10 or 35 wt%), the characterization data by different techniques (TEM, XRD, BET, Dr-UV–vis, and XPS) agree in indicating that zirconia is located predominantly outside the mesoporous channels as small zirconia nanoparticles for the lower loading, and predominantly inside the mesoporous channels for the higher loading. The concentration of medium–strong Lewis and Brønsted acid sites were determined by pyridine chemisorption monitored by IR spectroscopy. While the concentration of Brønsted acid sites (formed after sulfation) is linearly dependent on the amount of zirconia in SBA-15, a marked deviation is observed for Lewis acid sites. The same conclusion was derived from analysis of the dependence of the catalytic activity in Lewis- or Brønsted-acid-site-promoted reactions. The analysis of these results indicated that the characteristics of the zirconia nanoparticles deposited outside or inside the mesoporous silica channels differ in terms of acid features and in turn of catalytic reactivity.

1. Introduction

There is increasing interest in the use of oxides supported on mesoporous silica materials as catalysts, particularly SBA-15, which has ordered channels with larger size than those in MCM-41. In the field of biomass conversion, SBA-15 may provide a way to increase the active surface area of the supported oxide, while limiting the number of micropores, which can be detrimental to selectivity in the transformation of bulky molecules. For this reason, various authors have recently studied oxides supported on SBA-15 in this type of reactions. Zirconia was often utilized as an oxide for its acid–base properties [1–4] (tunable by sulfation [5–7]) and for the presence of both Lewis and Brønsted acid sites. There is general interest in the development of solid acid catalysts containing both Brønsted and Lewis acid sites for the conversion in the aqueous phase of molecules of interest for biomass conversion [8–10].

Recent studies have evidenced that in the etherification of 5-hydroxymethylfurfural (HMF) with alcohol over ZrO_2 supported on mesoporous silica, the type and strength of acidity considerably influence the path of transformation and selectivity [11,12].

Several authors have also investigated the esterification of aldehydes, phenols, and acids in bio-oils [13–15]. Kuwahara et al. [16] have investigated the esterification of levulinic acid with ethanol over sulfated Zr-SBA-15 catalysts, observing a correlation between the catalytic activity and the density of acid sites. They also remarked that the dispersion of the acid sites and the associated accessibility of the reactants play an important role in determining the overall activity. Sulfated zirconia on SBA-15 was also investigated for cellobiose hydrolysis [17], and a correlation with Brønsted acidity was indicated, but not quantified. Therefore, there is general interest in studying these catalysts in various types of reactions of interest for biomass conversion, particularly etherification or esterification reactions, where a relation between the acidity and the catalytic activity was observed, but never quantified. A promotional role of SBA-15 as a support (over the unsupported oxide) was observed, but the reasons were not analyzed in detail.

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We may remark that oxides in mesoporous silica may be present in various forms, although their specific catalytic role was not clearly identified. The oxide may be present as nanocrystallites deposited on the external surfaces of crystallites, inside the channels, or forming monolayer-type species (mono- or polynuclear species formed by reaction with surface silanol groups), which may lead to the reconstruction of the inner walls of the mesoporous channels (the so-called corona area [18,19]). Katryniok et al. [20] observed that by grafting zirconia onto SBA-15, a very high dispersion of zirconia within the mesoporous silica (indicated as a nanocomposite) could be obtained, with a linear relationship between the amount of introduced zirconia and the number of acid sites. On the other hand, Schlögl and co-workers [21] observed that upon introduction of molybdenum oxide species into the channels of SBA-15, the limited availability of anchor silanol groups at high loadings forced the MoO_4 groups to form strained configurations, giving enhanced reactivity and reasonably different acid-based properties. A similar mechanism probably occurs for zirconia, suggesting that a nonlinear correlation between the concentration of zirconia species and acidity/reactivity is expected.

Ballem et al. [22] noted that zirconia nanoparticles inside SBA-15 have small dimensions (~4 nm) and are faceted with 110 surfaces termination, suggesting enhanced reactivity and acidity with respect to nanoparticles deposited on the external surface. Wang et al. [23] observed that the acid strength of sulfated ZrO_2/MCM-41 (with monolayer coverage) is lower than that of bulk sulfated zirconia, in contrast with the other indications discussed above and for example with what was found by Gao et al. [24] in the esterification of oleic acid.

There are thus contradictory results on the influence of the location of oxide species in SBA-15 on their properties and reactivity. Intuitively, small oxide nanoparticles deposited on the external surface of a porous support could be preferable, because (i) the interaction with silanol groups is reduced (most are present inside the channels [25,26]) and (ii) the accessibility of bulky molecules is higher. Although in theory the channel diameter in SBA-15 (around 6–9 nm, depending on the preparation) avoids the presence of diffusional problems, the length of channels (typically in the range 300–600 nm) may create issues of full access to active sites in the inner part of the channels [27,28]. Similarly, the deposition of the oxide may not occur in the whole channels, but only at or close to the entrances of the mesopores [29]. Landau et al. [30] remarked how TiO_2 and ZrO_2 can be inserted inside the pores of SBA-15 in different locations depending on the preparation. Janssen et al. [31] observed that small zirconia particles (2–3 nm) inside the mesopores of SBA-15 are not distributed uniformly in all the channels.

The objective of this paper is thus to understand better how the location of zirconia in ZrO_2/SBA-15 catalysts influences the acidity and catalytic activity in reactions of biomass conversion sensitive to acidity characteristics and how the sulfation of these samples would influence these properties. As a reaction highly sensitive to the acid characteristics of the catalysts (type and strength of the acid sites) in terms of different transformation pathways, we have selected 5-hydroxymethyl-2-furfural (HMF) etherification with ethanol. A reason for interest in this reaction, in addition to its being a model reaction to analyze the acid characteristics of the catalyst as discussed below, is that the products obtained are of commercial interest as high-cetane-number biodiesel additives [32,33]. Three main types of products could be detected [12]: 5-(ethoxymethyl)furan-2-carbaldehyde (EMF), 1,1-diethoxyethane (DE), and ethyl 4-oxopentanoate (EOP) (Scheme 1).

The selectivity to EMF and EOP was related to the presence of Lewis and/or Brønsted acidity on the catalyst, while the formation of DE depended on defect sites, which, being less reactive, catalyzed the side reaction of co-reactant ethanol to DE only when strong Lewis and/or Brønsted acid sites were absent.

Luo et al. [11] showed recently that under pressure (70 bar) in HMF etherification with 2-propanol, catalysts with Lewis acidity or weak Brønsted acidity are active in the transfer of hydrogen from the alcohol to HMF to produce 2,5-bis(hydroxymethyl)furan (in their case), with subsequent reactions to form mono- or diethers. However, at lower pressure and using a primary alcohol, this reaction was negligible, thus reducing in part the complexity of the reaction network.

Therefore, HMF etherification with ethanol is a useful model system (besides its applicative interest) to analyze the role of the location of the oxide in ZrO_2/SBA-15-based catalysts on the acid properties and in turn the catalytic reactivity. However, understanding the role of location also requires having good model catalysts with different locations of the oxide, for which analysis may thus provide insight into the above aspects. In preparing ZrO_2/SBA-15 catalysts, we observed (as detailed later) that a different location of ZrO_2 is observed depending on the initial loading, with preferential external or internal deposition of small nanoparticles at 10 and 35 wt%, respectively. The reasons for this effect are still under investigation (probably related to the gradients of concentration realized during the preparation), but these two catalysts, before and after sulfation of zirconia, and in comparison with pure SBA-15 and ZrO_2 (before and after sulfation) samples, were good model systems to understand the effect of oxide location in oxide/mesoporous systems in the acid characteristics and in turn the catalytic behavior.

2. Experimental

2.1. Catalyst preparation

Mesoporous SBA-15 was prepared as a support according to the synthesis procedure in the literature and the detailed procedure described elsewhere [34]. Different ZrO_2 loadings (theoretical 10 and 35 wt%) were dispersed on the SBA-15 support by a urea hydrolysis method using zirconium(IV) oxychloride ($ZrOCl_2{\cdot}8H_2O$) as a zirconia source [35]. The mixture was refluxed at 90 °C for 5 h (pH about 8), and the resulting gel was filtered and washed with distilled water until removal of chloride. After centrifugation, the ZrO_2-SBA-15 gel was dried and calcined at 550 °C for 6 h. The samples are indicated hereafter as $Z_{x\%}$-SBA.

Pure ZrO_2 was prepared by the sol–gel method. A portion of 20 ml of zirconium *n*-propoxide was mixed with 26.6 ml of *n*-propanol and stirred with a magnetic stir bar. Then 2.8 ml of water was added dropwise to carry out the hydrolysis and gelation of zirconium *n*-propoxide. The gel was aged for 1 h at room temperature and then placed in an oil bath at 75 °C to remove alcohol. The solid was then dried at 120 °C for 12 h and calcined at 550 °C for 12 h [36]. This reference material is indicated hereafter as Z.

All samples were further sulfated using H_2SO_4 1 N (15 ml/g) at room temperature, dried and calcined at 550 °C for 3 h. These catalysts are indicated hereafter as $SZ_{x\%}$-SBA and SZ.

2.2. Catalyst characterization

Small angle X-ray diffraction was performed using a Philips PW1729 diffractometer with Bragg–Brentano geometry θ–2θ and Cu $K\alpha$ radiation and a zero background quartz holder. The spectra were collected in the range of 2θ from 0.5 to 5° with step interval of 0.02°. The d_{100} value was calculated from Bragg's law, while a_0 for the hexagonal unit cell was calculated using the equation $a_0 = (2d_{100})/\sqrt{3}$.

X-ray photoelectron spectra (XPS) were measured at 45° takeoff angle relative to the surface plane with a PHI 5600 Multi Technique System that offers good control of the photoelectron takeoff angle (base pressure of the main chamber 2×10^{-10} Torr) [37,38].