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One pot synthesis of WO_x/mesoporous-ZrO_2 catalysts for the production of levulinic-acid esters

Wirawan Ciptonugroho, Mohammad G. Al-Shaal, Joel B. Mensah, Regina Palkovits *

Institut für Technische und Makromolekulare Chemie, RWTH Aachen University, Worringerweg 2, 52074 Aachen, Germany

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ABSTRACT

WO_x/mesoporous-ZrO_2 (WmZr) has been successfully prepared by one-pot evaporation induced self-assembly. The resulting textural properties are highly affected by the additions of WO_3 and calcination temperatures. XRD and Raman spectroscopy were used to investigate the crystalline structures and surface states of the materials. Surface acidity was studied employing NH_3-TPD and DRIFT spectroscopy with pyridine adsorption. Catalysts loaded with 20–25 wt.% WO_3 and calcined at 800 °C exhibited the highest surface acidity with the greatest amount of Brønsted acid sites. The catalysts were tested in the esterification of levulinic acid (LA) with 1-butanol (1-BuOH). *Pseudo*- (*p*-BL) and *normal*-butyl levulinate (*n*-BL) were observed as the only products. The highest conversion of LA (64–67%) as well as a selectivity of *n*-BL of up to 97% could be achieved applying a catalyst with 20 wt.% WO_3 loading calcined at 800 °C. A clear correlation between catalyst activity and the relative ratio of Brønsted and Lewis acid sites could be confirmed.

1. Introduction

Levulinic acid esters (LAEs) can be derived from renewable cellulosic materials. They recently attracted a lot of attention due to their potential applications as fuel additives, green solvents, fragrances, lubricants and for polymer production [1,2]. LAEs can be synthesised by esterification of levulinic acid (LA) with alcohols in the presence of acid catalysts. Homogeneous catalysts such as HCl, H_2SO_4, and *p*-TSA are highly active and widely used to promote esterification. However, their major drawbacks comprehend challenges of product separation and potential corrosion. Solid acids present a promising alternative facilitating separation and avoiding challenges of corrosion, respectively. Various solid acids were utilised in the esterification of LA including zeolites [3], sulphonated SBA-15 [4], SO_4^{2-}/SnO_2 [5], Amberlyst-15 [5], sulphated zircono-silica [6] and heteropoly acids either ion exchanged or supported on clay [7]. However, for most of these catalysts challenges of stability occur at elevated temperatures and in the presence of water. WO_x/ZrO_2 (WZr) presents a potentially stable catalyst candidate to be applied in esterification. WZr was firstly developed by Hino and Arata to overcome the detachment of active SO_4^{2-} ions from SO_4^{2-}/ZrO_2 catalysts [8]. The stability of WZr is attributed to the strong interaction between the WO_x overlayer species and the ZrO_2 support [8]. Strong anchoring of WO_x on ZrO_2 through W—O—Zr bonds prevents any detachment of active WO_x from ZrO_2. In addition, WZr exhibits high mechanical and thermal stability further enhancing its potential for technical applications. Many reports revealed that WZr efficiently catalyses alkanes isomerisation [9–12]. Further studies found promising catalytic activity of WZr in liquid phase Beckmann rearrangement [13], dehydration [14], hydrolysis [15], hydrogenolysis [16,17], hydration of cyclohexene [18], selective catalytic reduction of NO_x [19] and esterification [20,21].

WZr catalysts are conventionally prepared by impregnating a Zr $(OH)_4$ support with a W-precursor. The material is subsequently subjected to high calcination temperatures especially above 600 °C. Variation of WO_3 content and calcination temperature enables controlling the population of WO_x species on the support, which is frequently expressed by the theoretical W surface density (W-SD). The W-SD has a significant impact on the catalytic performance of WZr and the value of W-SD producing the optimal activity has been discussed controversially. Optimum catalytic activities were proposed for W-SD forming a 2D-monolayer coverage of polymeric tungstate species. Above monolayer coverage, WO_3 nanoparticles (WO_3-NPs) start to develop on the surface of ZrO_2 causing a decline in activity. Shiju et al. showed that the highest ε-caprolactam selectivity in Beckmann rearrangement could be achieved with a W-SD of 7.3 W/nm^2 [13]. The maximum *iso*-butane yield in isomerisation of *n*-butane occurred for 5.9 W/nm^2

* Corresponding author.
E-mail address: Palkovits@itmc.rwth-aachen.de (R. Palkovits).

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W-SD [9]. Kourieh et al. reported that monolayer coverage with W-SDs of 4.7–5.3 W/nm^2 was responsible for superior activity of WZr in cellobiose hydrolysis [15]. In further studies monolayer WO_x species of a Pt–WO_x/ZrO_2 catalyst were suggested to be responsible for high conversion and selectivity to 1,3-propanediol in the hydrogenolysis of glycerol [17]. Moreover, the group of Wachs has carried out extensive studies on the WO_x surface states over metal oxide supports, particularly ZrO_2. A combination of UV–VIS DRS, XPS, and Raman spectra confirmed that Zr-stabilised WO_3 nanoparticles (Zr-WO_3-NPs) were the most active state catalysing methanol dehydration [22]. The highest concentration of Zr-WO_3-NPs was apparently found as the concentration of WO_3 slightly exceeds monolayer coverage (corresponding to W-SD = 6 W/nm^2). Wachs and co-workers also performed further studies using STEM with a high-angle annular dark-field (HAADF) facilitating a high contrast between W and Zr atoms [23]. For the most active WZr catalyst, WO_x species of higher contrast as expected for mono- and polytungstate species were observed. The authors suggested that Zr-WO_x clusters with 0.8–1 nm in size consisting of circa 10–15 WO_x units were responsible for the high activity in methanol dehydration. Li et al. found evidence for the presence of sub-nanometre Zr-WO_x clusters responsible for high catalytic activity in the Friedel–Crafts alkylation [24]. Moreover, other reports showed that the formation of crystalline WO_3-NPs on a level slightly above monolayer coverage can still give a positive effect in catalysis. dos Santos et al. verified that the presence of WO_3-NPs at 9 W/nm^2 (15 wt.% WO_3/ZrO_2 calcined at 800 °C) led to the highest conversion in the esterification of palmitic acid [21]. A similar behaviour was observed for the acetic acid esterification where at the onset of WO_3-NP formation at 6.6 W/nm^2 the highest activity occurs [20]. WO_3-NPs were also confirmed to be present when high activity in the isomerisation of *n*-hexane to *iso*-hexane could be achieved [12]. Interestingly, those investigations affirmed by Raman and XRD revealed that the highest activity correlated with the onset of WO_3-NPs formation. Relating to Wachs' investigations, it seems that the formation of active Zr-WO_x clusters is accompanied by the evolution of crystallite WO_3-NPs immediately. As a result, these WO_3-NPs and Zr-WO_x clusters coexist for most active catalysts. Nevertheless, it is noteworthy that exceeding WO_x loadings causes the formation of highly crystalline WO_3-NPs associated with a decay of catalytic activity. This explanation may pave a way to answer phenomena discovered by many investigators demonstrating that the optimal activity of WZr frequently occurs above monolayer WO_x coverage.

Porous supports have long been applied in heterogeneous catalysis as they are able to provide higher specific surface areas for a good dispersion of the active phase. Substrate molecules have to reach the active centres within the pores to allow efficient transformations. Particularly for bulky compounds, applying microporous supports will lead to a low diffusional rate. Therefore, supports with medium pore size such as mesoporous metal oxides (D_{pore} = 2–50 nm) avoid diffusion limitations. LA esterification exemplifies that the presence of mesopores highly affects catalytic activity. Patil et al. confirmed that for a mesoporous H-BEA zeolite prepared by NaOH treatment the conversion of LA to ethyl levulinate (EL) significantly improved compared to microporous ones [25]. Fernandes et al. described superior activity of the least acidic USY-zeolite in the production of EL compared to zeolites with smaller pore diameter [5]. Apparently, its larger pore size and 3-D pore connectivity were beneficial. WO_x/mesoporous-ZrO_2 (WmZr) presents an interesting alternative acid catalyst. Larger pore openings combined with high stability characterise the promising material. Nonetheless, WZr has not been investigated as catalyst for esterification of LA yet. This study addresses the esterification of LA over WmZr catalysts. In order to direct the formation of mesostructured materials, a one pot synthesis of WmZr *via* evaporation induced self-assembly was applied. This facile route has already been demonstrated for various materials such as TiO_2 [26,27], Nb_2O_5 [28], Al_2O_3 [29] and ZrO_2 [24,30,31] allowing tailoring of structural parameters.

2. Experimental and characterisation

2.1. Catalyst preparation

In a typical synthesis, 2.43 g template (F127) and 1.53 g citric acid were dissolved into 73 ml of ethanol in a polypropylene bottle under vigorous stirring until a clear mixture was obtained. Next, 3.65 g of HCl (37%) was added into the mixture. Into this acidified solution, a corresponding amount of WCl_6, which has been previously weighed under argon atmosphere, was added and stirred until a homogeneous mixture was reached. To the homogeneous mixture, 5.84 g zirconium(IV) butoxide was added dropwise under vigorous stirring (500 rpm) and then the stirring was held for 3 h until a milky homogeneous sol was obtained. The obtained sol was then poured into a Petri dish to allow evaporation for 48 h at room temperature. Afterwards, the sample was stored overnight in the oven at 100 °C for complete drying and solidification. The dried sample was further peeled off from the Petri-dish and calcined at different calcination temperatures for 5 h with a slow ramping rate of 1 °C/min. The final catalysts are denoted as *x*WmZr-*T* where *x* and *T* stand for WO_3 loadings and calcination temperatures, respectively. For instance 20WmZr-800 means that the catalyst contains 20 wt.% WO_3 and was calcined at 800 °C. As a note, the loading of tungsten is defined as the mass of nominal WO_3 per gram of ZrO_2 support.

2.2. Catalyst characterisation

2.2.1. N_2-physisorption

N_2 physisorption was performed using Quadrasorb SI automated surface area and pore size analyser. Prior to measurements, the sample was degassed at 120 °C overnight. Subsequently, N_2 adsorption was performed at −196 °C. The surface area of the catalysts was calculated using multi point BET in the relative pressure range of 0.05–0.3. Meanwhile, the pore size distribution (PSD) was determined *via* a non-linear DFT (NLDFT) fitting based on the desorption branch.

2.2.2. X-ray diffraction

Powder X-ray diffraction measurements (XRD) were performed by Siemens D-5000 equipped with Cu Kα as a light source.

2.2.3. FT-Raman spectra

FT-Raman spectra were recorded by a Bruker RFS 100/S-instrument with 4 cm^{-1} spectra resolution. Laser source was generated using Nd:YAG (1064 nm of wavelength). The catalyst powder was pressed into an aluminium pin before measurement. The detector was cooled using liquid N_2 during the measurement.

2.2.4. NH_3-TPD

NH_3-TPD was carried out on a ChemBET Pulsar TPR/TPD automated chemisorption analyser. The sample was firstly flushed with 20 ml/min pure He flow at 400 °C for 30 min to liberate the active sites from any contaminant. Subsequently, NH_3 was dosed onto the samples by passing a mixture of 50% Ar–50% NH_3 at 95 °C and held for 15–20 min. After dosing was completed, the flow was switched back to He and held for at least 30 min. Finally, the spectra were recorded by progressively heating the samples with a ramping rate of 20 °C/min.