



Priority Communication

Zirconia modified by Cs cationic exchange: Physico-chemical and catalytic evidences of basicity enhancement

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ABSTRACT

Zirconia promoted with Cs was prepared by cationic exchange of zirconium hydroxide with Cs, then calcined at 550 °C, and refluxed in ethanol to remove weakly bonded Cs species. The promotion with Cs stabilized the ZrO₂ tetragonal phase and has significantly increased the amount and the strength of the basic sites titrated by microcalorimetry of CO₂ adsorption. XPS gave evidence of an electronic enrichment of Zr and O atoms and an enhanced amount of superficial carbonates over ZrOCs. In vegetable oil transesterification, TOFs higher than those of ZrO₂, MgAl-HDT, and NaOH were achieved over ZrOCs, demonstrating the potential of this novel solid base.

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1. Introduction

In many areas of chemical industry, the search for regenerable solid bases to substitute soluble analogues such as NaOH and KOH remains a challenge [1]. For instance, most of the commercial biodiesel units are still using homogeneous catalyzed processes. Soluble alkali bases are still preferred although they cause many problems such as base elimination from fatty acid esters and glycerin which leads to the production of considerable amount of waste water. However, soluble bases present undisputable advantages such as low cost and higher activity in mild temperature conditions. Hence, investment on equipment is low as regards to the transesterification process carried out under high temperature and therefore high pressure. Higher temperature and pressure are generally required when a heterogeneous catalyst is used to overcome its lower activity [2]. Substitution of soluble bases by a solid catalyst presents the advantage of being able to produce glycerol of high quality without purification steps. In this field, there is no doubt about the real interest of developing a solid catalyst which would be as active as the homogeneous alkali bases in mild conditions. Here, we show that zirconia modified by Cs exchange may have this potential. The modification of zirconia with potassium was recently reported by Georgogianni et al. [3] who reported the impregnation of zirconia by KNO₃ and its use in soybean transesterification at 60 °C, with a methanol/oil molar ratio close to 250, a catalyst amount of 10 wt% (/oil) and reaction

time of 24 h which is reduced to 5 h when ultrasonication is applied. This catalyst was reported to be less effective than MgAl-HDT which resulted in the conversion of total oil into FAMES after 24 h of reaction. In addition, the authors concluded that 2 wt% NaOH (/oil) was much more efficient than potassium containing zirconia. Another recent study by Rekha Sree et al. [4] reported the “exceptional” activity of ZrMg oxide in transesterification reaction at 65 °C. The mixed oxide ZrMgO was prepared by coprecipitation from nitrate precursors. A complete oil conversion was reached in less than 1 h using a 10 wt% catalyst (/oil) and a methanol/oil molar ratio of 50. Not surprisingly, the rate of reaction was lowered by a factor of 3 when the methanol to oil molar ratio was reduced to 25.

In contrast to the studies of Georgogianni et al. [3] and Rekha Sree et al. [4] who reported the synthesis of K and Mg-promoted zirconia using nitrates as precursors, in the present work, we describe the promotion of zirconia with an alkaline cation by cationic exchange. The solid ZrOCs was prepared by cationic exchange of zirconium hydroxide with Cs cations in a basic medium. This is achieved using cesium carbonate as a precursor. The influence of Cs exchange on the crystallization of zirconia was investigated by XRD and TGA-DTA. XPS analyses were performed to show the role of the alkaline on the electronic environment of superficial atoms. The basicity of ZrOCs catalyst was measured by calorimetry of CO₂ adsorption and compared to the un-promoted ZrO₂. Finally, the activity of ZrOCs and ZrO₂ was evaluated in the transesterification of rapeseed oil with ethanol and methanol at 79 °C and 65 °C, respectively. A comparison of NaOH-catalyzed oil transesterification and a reference solid catalyst MgAl-hydrotalcite was made and discussed based on turnover rates.

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2. Catalysts preparation and catalytic tests

ZrOCs catalysts were prepared by cationic exchange of zirconium hydroxide with cesium carbonate, in a basic medium. First, zirconium hydroxide was precipitated at pH 10 starting from $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ as described previously [5]. The maximum amount of exchangeable hydroxyls was deduced from thermogravimetric analysis of the zirconium hydroxide. The exchange was carried out as follows: 0.003 mol of Cs_2CO_3 was dissolved in 16 ml of water (pH 11), then 1 g of zirconium hydroxide was added, and mixed for 15 min. The exchanged solid was removed by filtration, dried at 110 °C, and calcined at 550 °C. In order to remove the weakly bonded Cs species which might be leached during the reaction tests, the calcined solid was first refluxed for 5 h in ethanol at 79 °C, in the conditions of transesterification (equivalent equipment, ethanol/catalyst ratio, agitation). The leached solid was then separated by filtration and the recovered ethanol was tested by the reaction itself to check the occurrence/absence of homogeneous catalysis. This was done until the recovered ethanol was inactive. After the second treatment, the recovered ethanol gave a conversion in transesterification close to that of the blank experiment: 6 mol% against 4 mol% for the blank test realized in the absence of a solid catalyst and with pure ethanol. After ZrOCs was washed twice, the catalyst Cs content equaled 6.8 wt%. Only the solid refluxed twice in hot ethanol for 5 h was used in the liquid-phase transesterification and characterized by calorimetry of CO_2 adsorption and XPS analysis.

For XPS analysis, the binding energies' values were corrected using the C1s binding energy of adventitious carbon at 284.6 eV.

The transesterification reaction was performed in a two-necked Pyrex flask, equipped with a vigorous magnetic agitation and a water-cooled condenser kept under Ar atmosphere. Because of the heterogeneity of the reaction media, the analysis of the reaction media was performed at the end of the reaction only by adding a known amount of THF to get a homogeneous solution for GC analysis described previously [6].

3. Results and discussion

3.1. Physico-chemical features

ZrCsO obtained after calcination at 550 °C is poorly crystalline, but only the diffraction peaks of tetragonal zirconia are present. We have checked that the increase of the calcination temperature to 650 °C favors crystallization of the tetragonal phase only. The absence of monoclinic ZrO_2 phase suggests the occurrence of a homogeneous interaction between the zirconium hydroxide and Cs^+ cations which precludes the crystallization of monoclinic ZrO_2 . This phenomenon has been well described for zirconium hydroxides modified with oxoanions as sulfates or tungstates [5,7]. This interpretation was also strengthened by TGA-DTA analysis of the Cs-modified zirconia. The TGA-DTA profiles of ZrCs consist of two main phenomena: the first one is weight loss of hydration water at $T < 120$ °C, and the second one is dehydroxylation occurring between 120 and 600 °C. At 600 °C, a strong exothermic phenomenon occurs due to the crystallization of the ZrO_2 tetragonal phase. It should be recalled that the DTA curve of Cs-free zirconium hydroxide is characterized by an exothermic peak at lower temperature, 400 °C, due to the crystallization of the monoclinic ZrO_2 phase [7]. Both XRD and TGA-DTA analyses demonstrate the occurrence of a homogeneous $\text{Zr}(\text{OH})_x$ exchange with Cs^+ which leads to the ZrO_2 crystallization into the metastable tetragonal phase. These results indicate that the modification of zirconium hydroxide with anions or cations leads to the modification of the ZrO_2 crystallization in a similar manner.

The BET surface area of ZrOCs calcined at 550 °C equals $71 \text{ m}^2 \text{ g}^{-1}$ and the calcined solid is mainly mesoporous.

The basic properties of the ZrOCs samples were determined by CO_2 adsorption at 30 °C which is monitored by microcalorimetry. The catalyst was first treated at 400 °C under secondary vacuum before CO_2 adsorption. Fig. 1 presents the evolution of the differential heat of CO_2 adsorption with the CO_2 coverage. The calorimetric curve of ZrOCs presents few strong sites with differential heat of ammonia adsorption higher than 130 kJ mol^{-1} and extended plateau near 120 kJ mol^{-1} accounting for the presence of a high density of basic sites of homogeneous strength. The total amount of basic sites reached $350 \mu\text{mol g}^{-1}$. By contrast, un-doped ZrO_2 is characterized by a reduced number of basic sites of heterogeneous strength, $110 \mu\text{mol g}^{-1}$ (Fig. 1). They are less energetic, with an average heat of CO_2 adsorption of 100 kJ mol^{-1} . These data show the benefit of Cs insertion on the basicity enhancement. For comparison, the calorimetric curve obtained for the reference solid base, a hydrotalcite of Mg/Al molar ratio of 3, is also reported in Fig. 1. MgAl-HDT has a higher density of basic sites than un-promoted ZrO_2 , $160 \mu\text{mol g}^{-1}$ and the sites' strength is more homogeneous with a plateau observed at 100 kJ mol^{-1} .

XPS analysis performed on ZrO_2 and ZrOCs confirmed the influence of Cs promotion. On ZrCs, 4.7 at% of Cs was detected at a binding energy of 724.0 eV for Cs 3d5/2. The binding energies of O1s measured at 530 eV on ZrO_2 shifted to 529.1 eV after Cs promotion. This is indicative of electron enrichment on the oxygen atoms which are the basic centers. Similarly, the binding energy of Zr 3d5/2 is also influenced by the Cs cations: a value of 182.0 eV is measured on ZrO_2 and of 181.1 eV on ZrOCs showing the parallel electronic enrichment of the Zr atoms after Cs exchange. In addition, XPS revealed the presence of an increasing amount of carbonate species after the Cs exchange. Fig. 2 presents the C1s peaks for ZrO_2 and ZrOCs. In both cases, the C1s can be decomposed into three components. The two major ones, observed at 284.6 and 288.8 eV on ZrO_2 , are, respectively, ascribed to aliphatic carbonaceous deposits and carbonate species. The minor peak at 286.0 eV is ascribed to adsorbed oxygenate organic species. The atomic percentage of the carbonate species increased strongly upon Cs exchange, from 13.3% to 30.0%. This is in agreement with the improved basicity of zirconia promoted by Cs.

3.2. Catalytic properties

The catalytic performances of ZrO_2 , ZrOCs, and MgAl-HDT were evaluated in ethanolysis under the following standard conditions: $T_{\text{reaction}} = 79$ °C, reaction time 5 h, ethanol/oil molar ratio = 18, $\text{cat} = 0.45$ g. The results are summarized in Table 1. The solid catalyst, ZrOCs, gives a remarkable oil conversion of 64 mol% and a selectivity to fatty ethyl esters higher than 91%. This is indicative of the rapidity of all the intermediate steps since monoglycerides are formed with a fairly low selectivity, 8.5 mol%. By contrast,

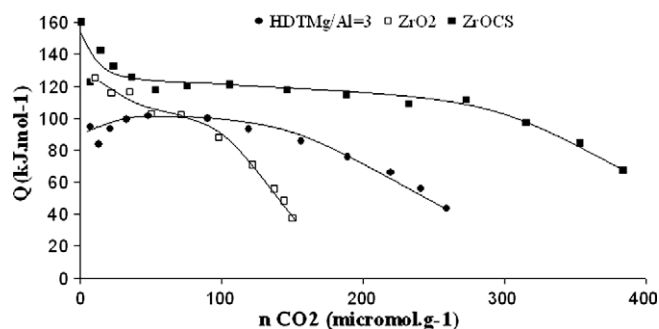


Fig. 1. Differential heat of CO_2 adsorption as a function of CO_2 coverage.

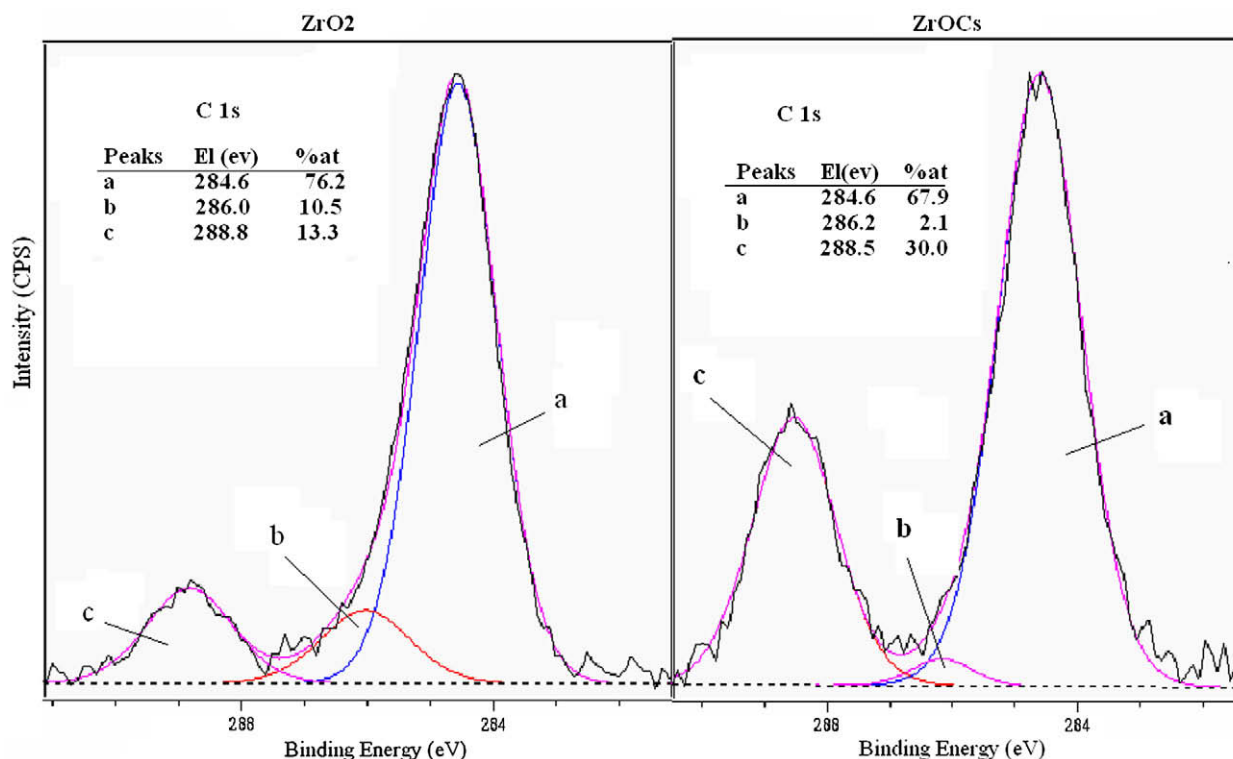


Fig. 2. XPS C 1s peaks for ZrO₂ and ZrOCs.

Table 1

Solid bases and NaOH-catalyzed transesterification of rapeseed oil with ethanol or methanol.

Catalyst or wt% NaOH/oil	mmol basic sites in the reaction media ^c	Conversion ^a (mol%)	Selectivities ^b (mol%)			TOF ^d (h ⁻¹)
			Esters	Mono-glyceride	Di-glyceride	
<i>Ethanolysis</i>						
ZrOCs	0.14	64	91	8.5	0.5	46
ZrO ₂	0.064	<4	–	–	–	–
HDT-MgAl	0.072	6	40	0	60	2
NaOH 0.5%	1.25	100	99.8	0.2	0	–
NaOH 0.07%	0.17	11	72	2.5	25.5	1.5
<i>Methanolysis</i>						
ZrOCs	0.14	100	99.5	0.5	0	–

Reaction conditions: $T_R = 79^\circ\text{C}$ (ethanolysis), $T_R = 60^\circ\text{C}$ (methanolysis), rapeseed oil = 10 g, alcohol/oil molar ratio = 18, m cata = 0.4 g, duration = 5 h, catalyst pre-treatment: 1 h under vacuum at 400°C .

^a Oil conversion = sum of the molar yields in fatty acid esters, monoglycerides and diglycerides corrected by the amount of fatty chains.

^b The molar selectivities are corrected by the amount of fatty chains.

^c For the solid bases: amount of sites with $Q_{\text{diff}} \text{CO}_2 > 80 \text{ kJ mol}^{-1}$.

^d Deduced from initial rate, oil conversion < 16%.

ZrO₂ does not catalyze the transesterification reaction and MgAl-HDT is poorly active, the oil conversion reaching only 6% in the latter case. This is only slightly higher than the conversion level obtained in blank experiments, which give conversions of 4%. Over MgAl-HDT, the product selectivities are quite different; a selectivity of 60 mol% in the main diglyceride intermediate is obtained. Thus, the two previous solids, ZrO₂ and MgAl-HDT, lead to significantly lower conversions than ZrOCs in our standard conditions. These catalytic performances and the ranking of the solid basicity established by microcalorimetry of CO₂ adsorption suggest that the high density of basic sites of strong/medium strength present on ZrOCs solid is much more efficient than the pool of sites of weaker strength and lower density present on MgAl-HDT or ZrO₂. It should be noted that the solids were pretreated at 400°C under vacuum, for the calorimetry measurements as well as for the catalytic tests, in order to remove the hydration water, a

parameter known to modify the basic strength. However, it is clear that this treatment is not efficient in removing the most stable carbonate species. The most stable species, resistant to treatment at 400°C , would moderate the intrinsic basicity of the solid bases. Finally, to rank the efficiency of the ZrOCs solid base in an indisputable way, rapeseed oil ethanolysis was performed with NaOH. That is why it was essential to evaluate anhydrous solid bases in order to compare their performances with NaOH-catalyzed reactions which are currently carried out in the absence of moisture when solid NaOH is used. To perform the transesterification with NaOH, usual conditions reported in the literature, i.e. 0.5 wt% of NaOH /oil, were used first. Thereafter, we have used a NaOH quantity close to the amount of basic sites present in 0.45 g of ZrOCs, a value deduced from CO₂ calorimetric titration. The amount of NaOH was then reduced by seven times, the weight percentage of NaOH/oil was lowered down to 0.07 wt%. This is equivalent to

172×10^{-3} mmol of OH^- species introduced in the reaction medium, an amount of basic sites close to that present in 0.45 g of as-synthesized ZrOCs; i.e. 158×10^{-3} meq. The results reported in Table 1 show that using 0.5 wt% NaOH/oil, a complete oil conversion was achieved with selectivity in fatty acid ethyl esters of 100%. Using 0.07 wt% NaOH/oil, the oil conversion is only 11%, with a significant proportion of diglycerides, which are the primary products. Thus, it is seen that the turnover rate measured over ZrOCs is one order of magnitude higher than that measured over NaOH, while the turnover rate measured over MgAl-HDT is close to that measured over NaOH. This emphasizes that ZrOCs significantly accelerates the transesterification reaction compared to soluble NaOH.

Methanolysis of rapeseed oil was also carried out over ZrOCs. The reaction was performed at 65 °C, which is the reflux temperature of methanol. In this case, the oil conversion and ester selectivities reached 100% using ZrOCs catalyst. The higher activity of ZrOCs for methanolysis with respect to ethanolysis is explained by the relatively higher acidity of methanol with regard to ethanol. Accordingly methanol activation via a proton abstraction by the solid base occurs readily compared to ethanol activation. The contrary is expected for acid-catalyzed transesterification as shown in the pioneering work of Freedman [8] which was confirmed more recently in the presence of strong solid catalysts like heteropolyacids [9].

In conclusion, we report the synthesis of a novel solid base, ZrOCs obtained via cationic exchange between zirconium hydroxide with Cs^+ in basic conditions followed by calcination at high temperature. This preparation is different from that reported by Georgogianni et al. [3] who prepared ZrK by impregnation, or by Rekha Sree et al. [4] who reported the synthesis of ZrMg by precipitation. The weakly bonded Cs species were removed via two hot ethanol-leaching processes to ensure the exclusive contribution of heterogeneous basic catalysis. It is shown that the promotion of zirconia with Cs^+ favors the formation of the tetragonal ZrO_2 after calcination accounting from a homogeneous distribution of

Cs^+ cations within the material. The hot ethanol-refluxed solid, which contains 6.8 wt% of Cs, presents a higher amount of basic sites than Cs-free ZrO_2 , $350 \mu\text{mol g}^{-1}$, titrated by calorimetry of CO_2 adsorption. The calorimetric curve shows a remarkable homogeneous distribution of strong/medium basic sites characterized by the presence of a plateau with a heat of CO_2 adsorption of 120 kJ mol^{-1} . XPS has shown an electronic enrichment of both Zr and O atoms due to the presence of Cs as well as numerous carbonate species. ZrOCs oxide has an excellent activity for vegetable oil transesterification with ethanol and methanol in mild conditions, while Cs-free ZrO_2 is not active in our standard conditions. In addition, this is attested by comparison with a reference solid base MgAl-HDT evaluated in equivalent mild conditions. Moreover, it is demonstrated that ZrOCs gives higher turnover rate than soluble NaOH. ZrOCs is believed to present a strong potential as a solid base catalyst due its basic features and thermal stability since this catalyst is formed via calcination at high temperature, 550 °C. The latter feature is determinant when used catalyst regeneration is required.

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