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A comparative study of methanol carbonation on unsupported SnO_2 and ZrO_2

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ABSTRACT

The aim of this work was to explore the catalytic properties of SnO_2 in the coupling of methanol with carbon dioxide to afford dimethyl carbonate. SnO_2 nanopowders were produced by hydrolysis of tin tetra-*tert*-butoxide dissolved in *n*-butanol. The samples were much more active than a commercial one due to their higher surface areas. In addition, they exhibited excellent recyclability. However, comparison with ZrO_2, prepared and tested under the same experimental conditions, showed that zirconia-based catalysts were more selective and are, among the heterogeneous catalysts already reported, still the more selective. SnO_2 also catalyzed the formation of dimethyl ether likely due to lower rates in the formation of the key intermediate $CH_3OC(O)O$–Sn and its subsequent alkylation by activated methanol. This lack of selectivity contrasts with that of soluble organotin(IV) which are totally selective to DMC formation. Structural characterization of SnO_2 was performed by X-ray powder diffraction, laser Raman spectroscopy, transmission electron microscopy, and nitrogen isotherm. As found from X-ray diffraction line broadening, the crystallite size of all powders was in the nanometric range (cassiterite structure) which was confirmed by transmission electron microscopy. Moreover, the low-frequency Raman scattering allowed to determine an average particle size diameter of 4 nm.

1. Introduction

In recent years methanol is receiving much attention for developing alternative technologies in the energy sector [1]. But still its current major application is in the chemical sector. Considering the stimulative context of non-fossil carbon resources for making organics, coupling methanol with CO_2 presents the unique advantage of utilizing only CO_2 as carbon feedstock, provided methanol is thereof obtained by hydrogenation [2–4]. One of the challenging targets is dimethyl carbonate (DMC) [5,6]. DMC finds applications ranging from organic synthesis [7] and phosgene-free synthesis of polymers [8] to gasoline blending [9]. Interestingly enough, DMC has low toxicity, rapid biodegradability [8] and low impact on air quality [10]. However, its scale-up production based on the on-stream technologies is limited due to intrinsic constraints of the processes [11,12]. Therefore, its synthesis from CO_2 and methanol according to reaction (1) is highly attractive.

$$2CH_3OH + CO_2 \rightleftharpoons DMC + H_2O \qquad (1)$$

The current main issue is to enhance the rate and conversion of methanol. One option has been demonstrated in adding water traps to the catalytic systems for preventing catalyst deactivation by water as well as to shifting the equilibrium [13,14]. Nevertheless, there is a need for exploring new catalysts and understanding the reaction mechanism for rate enhancement in the absence of water trap additives. In recent years, a variety of heterogeneous catalysts have been screened under different *P*–*T* reaction conditions. The reaction is commonly run under high pressure, 100–300 bar, at 130–180 °C over ZrO_2 [15–17], H_3PO_4/ZrO_2 [18], CeO_2 [19], mixed ZrO_2–CeO_2 [20], polyoxometalates [21], supported copper (Ni, V, O) [22], copper–nickel/graphite [23], and V-doped Cu–Ni/AC catalysts [24]. Among the catalysts studied, zirconia-based are still those exhibiting the highest selectivity to DMC (~100%). A thorough understanding of the reaction mechanism shows that surface Zr–OH groups and $Zr^{4+}O^{2-}$ sites act as Lewis acid–base pairs for the bifunctional activation of methanol. The insertion of CO_2 into the CH_3O–Zr bond to form hemicarbonate $CH_3OC(O)O$–Zr species is the key elementary step

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[17,18]. Subsequent fast methyl transfer to $CH_3OC(O)O–Zr$ from CH_3OH activation on acid sites likely occurs for getting the high selectivity to DMC. During the processes of methanol activation, the concomitant formation of water may induce $CH_3O–Zr$ hydrolysis, therefore leading to a decrease in catalyst activity.

Interestingly enough, organometallic complexes such as diorganotin(IV) compounds are also active precursors and, importantly, totally selective [14,25–27]. The reversible insertion of CO_2 into the $CH_3O–Sn$ bond of dialkyldimethoxystannanes has been evidenced which accounts for the need of high CO_2 pressure under catalytic conditions. Nonetheless, the corresponding complexes bearing the hemicarbonate $CH_3OC(O)O–Sn$ moiety have been isolated and structurally characterized [26,28]. This result stresses on the similarity of reaction events on both types of catalysts for this particular reaction. Concerning the tin species involved in the catalytic cycle, we could very recently isolate during the course of the reaction multinuclear dibutyloxocarbonato tin(IV) intermediates, that play a key role in the process. Their structure elucidation by single-crystal X-ray diffraction allows to view these species as organo-oxides [29,30]. It was therefore tempting to look at the catalytic behavior of SnO_2 to screen for the impact of ligand-free catalytic sites on their activity and selectivity for DMC synthesis. To the best of our knowledge, there is only one report in a patent on the relevant catalytic behavior of SnO_2, but the reaction selectivity was not reported [13].

We herein report the catalytic performance of SnO_2 with emphasis on DMC yield with reaction time and recyclability of the catalyst. The synthesis of SnO_2 was achieved by a free-chloride sol–gel route from tin tetra-*tert*-butoxide. The prepared catalysts were characterized by X-ray powder diffraction (XRD), laser Raman spectroscopy, transmission electron microscopy (TEM) and nitrogen isotherm for determining the crystalline phase, grain size, and morphology. ZrO_2 was also prepared, on purpose, by the same method to get a reference under our reaction conditions as it exhibits the highest selectivity among the heterogeneous catalysts reported so far.

2. Experimental

2.1. General

All manipulations were carried out under argon by using standard Schlenk techniques. Methanol (Carlo Erba, RPE grade) was dried and distilled from $Mg(OCH_3)_2$, *tert*-butanol (Fluka, >99%) and *n*-butanol (Fluka, >98%) dried over 3 Å molecular sieves. Deionized water was refluxed for 2 h prior to use. Carbon dioxide N45 TP purchased from Air Liquide was used without further purification. Tin tetra-*tert*-butoxide was synthesized from $SnCl_4$ (Aldrich, 99%) according to a published procedure [31]. Zirconium tetra-*n*-butoxide (80 wt% *n*-BuOH solution, Aldrich) was used without further purification. A commercial nanopowder of tin(IV) oxide from Aldrich was used for comparison.

2.2. Synthesis of SnO_2 and ZrO_2

Tin and zirconium oxides were synthesized by hydrolysis of $Sn(O^tBu)_4$ and $Zr(O^nBu)_4$, respectively. The afforded white powders were obtained with yields >90%, based on the starting alkoxides. In a typical experiment, a *n*-butanol solution (100 ml) of $Sn(O^tBu)_4$ (25 g, 0.06 mol) was added dropwise over 5 h under vigorous stirring to deionized water (600 ml) maintained at 15 °C. The slurry was kept stirring for 1 h, then overnight for settling, and finally subjected to centrifugation with a Biofuge Startos Heraeus apparatus. The solid was washed with distilled water and submitted to lyophilisation overnight (FTS systems, EZDRY). Analysis for residual carbon was performed at the Institut de Chimie Moléculaire de l'Université de Bourgogne, Dijon. All samples have C content <0.2%.

2.3. Catalyst characterization

X-ray powder diffraction (XRD) patterns were collected with a Siemens D5000 diffractometer using Cu-Kβ (λ = 0.139222 nm) radiation.

Transmission electron microscopy (TEM) was performed using a JEOL JEM-2100 microscope at 200 kV accelerating voltage. Sample preparation consisted in dispersing the SnO_2 powder in ethanol under sonication, then dropping the dispersion on a copper grid coated with amorphous carbon membrane.

The Raman spectra were obtained at room temperature using a Jobin-Yvon T64000 spectrometer coupled to an Olympus microscope. Excitation was provided by an Ar laser operating at 514.5 nm. The laser power was kept as low as possible to prevent local heating. The resolution of the spectrometer was 1 cm^{-1}.

Nitrogen sorption data were obtained at −196 °C with a BELSORP-mini apparatus after outgassing the samples at 100 °C for 12 h. The specific surface area (SSA) was calculated from the BET method.

Thermogravimetric analysis (TGA) was performed with a Setaram TAG 24 system at a heating rate of 1 °C min^{-1} to 500 °C under $N_2–O_2$ atmosphere ($N_2:O_2$ = 75:25; flow rate, 0.15 mL min^{-1})

2.4. Catalytic experiments

Caution: since high pressures are involved, appropriate safety precautions must be taken.

The catalysts (0.100–0.550 g) were pretreated under vacuum at 120 °C for 2 h, then 20 ml of dried methanol was added. The suspension was transferred under argon into a 120-ml batch stainless steel autoclave, followed by the admission of either 40 or 20 g of CO_2 with an ISCO 260D pump to get a working pressure of either 200 or 120 bar. The autoclave was heated to 150 °C (controlled by an internal K-thermocouple). After a given reaction time, the autoclave was cooled down to 0 °C, pressure gently released through a valve, and the liquid phase transferred for GC analysis with a Fisons 8000 apparatus (FID detector, toluene as internal standard, column: J&W Scientific DB-WAX 30 m capillary column). Identification of the products was done by GC–MS (Fisons MD800, J&W Scientific DB-5MS 60 m capillary column). For recycling experiments, the catalyst was recovered by centrifugation, then pretreated at 120 °C for 2 h under vacuum, loaded into the autoclave following the aforementioned procedure. DMC yield was also analyzed as a function of time during the course of the reaction by sampling with a high pressure valve. At the end of such experiments, degassing the autoclave at 0 °C followed by GC analysis of the liquid phase allowed to check consistency between the two procedures; the fit was better than 3% (relative error).

3. Results and discussion

3.1. DMC synthesis from methanol and CO_2

All catalytic tests were performed at 150 °C under CO_2 pressure in a batch autoclave. The working pressure was set at either 120 or 200 bar. These values were chosen for their relevance to two different domains in the fluid phase diagrams of the $MeOH/CO_2$ binary mixtures herein used [29]. With *P–T* conditions of 120 bar–150 °C, the reacting mixture is a two-phase liquid–vapor consisting in methanol-rich liquid and CO_2-rich vapor phases. At 200 bar–150 °C, the reactants are totally miscible, thus forming a single supercritical phase. Switching from biphasic to monophasic conditions induces changes in reactant concentration, adsorp-