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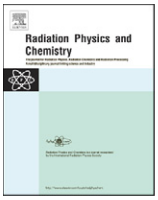

Catalytic activity of poly[(methacrylato)aluminum(III)] obtained at different gamma-radiation doses

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ABSTRACT

A novel coordination polymer was obtained throughout the polymerization of aluminum(III) methacrylate at different doses (10, 20, 30, 40, 50 and 80 kGy) using gamma-radiation as initiator. The materials were characterized by electronic paramagnetic resonance (EPR), thermogravimetric analyses (TGA) and scanning electron microscopy/electron dispersive X-ray analyses (SEM/EDAX) techniques; particle size distribution and surface areas were also determined. The samples of poly[(methacrylato)aluminum(III)] obtained at different γ-doses were found to catalyze 2-propanol dehydrogenation and dehydration to acetone and propene. A noticeable activity was observed with Poly[(methacrylato)aluminum(III)] obtained at 50 kGy, which has higher conversion of 2-propanol and the highest selectivity to acetone (~90%). Results suggest that the decomposition of 2-propanol is correlated with the effect of gamma-radiation on the structure and surface area of the catalysts.

1. Introduction

Metal-containing polymers (MCP) acquire specific physical–mechanical features (Pittman et al., 1990), they turned out to be efficient and selective catalysts for various reactions (Guyot, 1988) or they can have biocide activity, among other useful properties (Pomogailo, 1990). Development of MCP as support or catalyst is motivated by two major advantages, first MCPs allow uncomplicated physical separation of the catalyst from the reagents and the products; it is possible to use a large excess of one of the reagent in consequential reactions, without the loss of costly catalysts. The second expected advantage is the "polymer effect", which may enhance activity of the catalysts by site isolation or, on the contrary, by cooperative effects of the neighboring groups. However, industrial applications are not frequent except for the Merrfield synthesis and the acid catalysts (Leadbeater and Marco, 2002; Bergbreiter, 2002).

A general approach for the synthesis of MCP consists of synthesizing a metal-containing monomer and then usually polymerizing that monomer in solution with peroxides or azo-compounds as initiators (Odian, 1991). Gamma-radiation can also be applied over a metal-containing monomer in solid phase to initiate the polymerization reaction. The efficiency of gamma-radiation relies on its capability of penetration, control of the polymerization ratio as a function of the applied dose, high conversions in short reaction times and, in addition, further purification processes are not required because there is no contamination by a catalyst or sub-products (Filardo et al., 2002).

The importance of alumina as support has been widely recognized in many catalytic processes of industrial importance such as isomerization, alkylation, catalytic cracking or polymerization. Furthermore, the acid–base properties of alumina play a major role in interfacial reactions and, due to its inherent acidic properties, have been useful in the preparation of a variety of catalysts (Sárbu and Beckman, 1999).

Dehydration of 2-propanol to propene is an important catalytic test to identify acidic and basic sites in heterogeneous catalyst (Linnekoski et al., 1998; Mourgues et al., 1967). Acidity and basicity are paired concepts usually invoked to explain the catalytic properties of metal oxides (Tananbe et al., 1989). The complete description of surface properties requires the determination of amount, nature (Brønsted or Lewis type) and strength of the acidic and the basic sites. Alcohol decomposition has been carried out in a large number of catalysts showing strong or medium acidity, like silicoaluminates or alumina (Knözinger et al., 1972; Knözinger and Schengllia, 1974) in which, the isopropylether selectivity is minor to 10% in these catalysts, and propene is the major product. Since selectivity in alcohol decomposition depends on the strength and distribution of the acid sites, efforts have been recently made in order to design catalysts with controlled acidity (Ai, 1975; Pérez-Hernández et al., 2005; Hathaway and Davis, 1976). Although several new systems were

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proposed for different reactions with Al_2O_3-base catalysts, no decisive novelty appeared in the last years. In this context, new highly active and selective catalysts are necessary in order to advance new process in the industry.

In this paper, we report a solid-state synthesis of the microcrystalline, and submicrometric, novel poly[(methacrylato)aluminum(III)] (PMAAl), which was obtained by gamma-radiation at different doses. The catalytic activity of this coordination polymer over the decomposition of 2-propanol was also studied.

2. Experimental

2.1. Synthesis of aluminum methacrylate (MAAl)

The monomer of aluminum methacrylate was obtained by reacting methacrylic acid (MAc), $NaHCO_3$ and $AlCl_3 \cdot 6H_20$ in deionized water. The method was described previously by Galvan et al. (1999). Formation of the MAAl was confirmed by gravimetric and spectrophotometric analyses (Vilchis-Nestor et al., 2006).

2.2. Polymerization of MAAl

Samples of 1 g of monomer were placed in a glass tube, degassed and then vacuum-sealed. Polymerization of MAAl was carried out by irradiation of the samples at room temperature in a gamma-cell unit (Transelektro-LGI-01), provided with a ^{60}Co γ-ray source. Doses of 10, 20, 30, 40, 50 and 80 kGy were applied to the monomer at dose rate of 3.5 kGy/h. PMAAl showed insolubility to most common solvents.

2.3. Characterization methods

2.3.1. Electron paramagnetic resonance (EPR) analyses

To confirm that the polymerization was via free radicals, EPR analysis was carried out at room temperature immediately after irradiations using a Varian E-15 electron paramagnetic spectrometer operating at a frequency of 9.5 GHz. The instrument settings were as follows: magnetic field 330 mT, scan range 40 mT, scan time 8 min, magnetic field modulation amplitude 0.1 mT, modulation frequency 100 kHz and microwave power 2 mW.

2.3.2. Thermogravimetric analyses

Thermal degradation of monomer and polymer samples was performed using a TA Instruments TGA-51 apparatus, calibrated with a standard of calcium oxide. Experiments were conducted at 20–800 °C, with a heating rate of 10 °C/min, under nitrogen atmosphere; sample weight was around 10 mg.

2.3.3. Scanning electron microscopy and electron dispersive X-ray analysis

Polymer (PMAAl-50) morphologies, before and after catalytic activity, were analyzed and imaged with a PHILIPS XL-30 scanning electron microscope (SEM) at 25 kV coupled to a detector for energy dispersive X-ray analysis (EDAX). Samples were fixed on a copper film support and coated with gold by sputtering.

2.3.4. Particle size distribution

The particle size distribution of the polymers and the monomer was measured using a light disperser Coulter 230. Ten mg of sample dispersed in 10 ml of water was used for each analysis. Frequency of the number of particles as a function of its grain size was obtained by the software LS32 version 3.01.

2.3.5. Surface area determination

Total surface areas were obtained by the Brunauer, Emmett and Teller (BET) method. A RIG-100 multitask unit ISRI was employed for measuring the total surface area of the catalysts, using N_2 adsorption–desorption (30% N_2/He gas mixture, 30 cc/min) by the single point method. Samples (0.1 g) were first degassed and pre-activated by flowing carrier gas (30% N_2 in He) through the cell at 200 °C with a flux of 30 cc/min for one hour.

2.4. Catalytic activity

The catalytic activity of the samples was determined by testing the catalyst in the dehydration of 2-propanol. Isopropanol (Aldrich 99.9%) decomposition was determined in a continuous flow reactor. 0.1 g of each sample was re-activated in a stream of He (60 cc/min) from room temperature to 300 °C with a heating rate of 10 °C/min and held at this temperature for 1 h, after that each sample was brought up to the reaction temperature (275 °C) in He (60 cc/min). For isopropanol decomposition He was bubbled through a tank containing 2-propanol; the partial pressure of the isopropanol was 100 torr. The effluent gas of the reactor was analyzed by gas chromatography using a thermal conductivity detector (TCD). A 2 m packed Porapack Q was used at 115 °C to separate the reaction products from the isopropanol decomposition.

The activity of the catalyst is defined as C(%), the percent conversion of isopropanol to all products:

$$C\,(\%) = ([2-P]_{\text{in}} - [2-P]_{\text{out}})/[2-P]_{\text{in}} \times 100$$

The subscriptions *in* and *out* indicate the inlet and the outlet concentrations of 2-propanol, respectively. Selectivity towards acetone or propene (%) is given by

$$\%\,\text{Selectivity} = [\text{Product}(X)]/\sum[\text{All products}] \times 100$$

where [Product (X)]=concentration of the product (acetone or propene), and $\sum$[All products]$=\sum$ of the acetone+propene.

A total of three reaction cycles were tested in order to check the functional life time of the sample with the highest conversion (PMAAl-50). During each cycle, 0.1 g of sample was re-activated at 300 °C for the period of 1 h, after that, the sample was exposed to the same reaction conditions (275 °C in He with flux of 60 cc/min).

3. Results

3.1. Synthesis of monomer (MAAl)

Aluminum(III) methacrylate (MAAl) was synthesized with a yield of 89.1% . Scheme 1 shows that the reaction proceeds in two steps; first, sodium methacrylate is formed, followed by the exchange of Na^+ by Al^{3+} to form aluminum(III) methacrylate.

The reaction of aluminum(III) with the carboxylic group of the sodium methacrylate results in the formation of $[Al(OH)x(OH_2)y(O_2C(CH_3)C{=}CH_2)z]$. This product was determined by X-ray photoelectron (XPs), infrared (FTIR) and Raman analyses and it was reported elsewhere (Vilchis-Nestor et al., 2006). This structure is closely related to the carboxylate-alumoxanes $[Al(O)_x(OH)_y(O_2CR)_z]_n$ where $2x+y+z=3$, which have been synthesized and studied previously by Landry et al. (1995).

3.2. Polymerization of the monomer (PMAAl)

Formation of polymers was carried out by the gamma irradiation of the monomer at different doses: 10, 20, 30, 40, 50 and 80 kGy. In Scheme 2, the formation of poly[aluminum(III) methacrylato] via free radicals is shown.