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Kinetics of depolymerization of paraformaldehyde obtained by thermogravimetric analysis

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ABSTRACT

Solid paraformaldehyde is a source of formaldehyde that is preferred when anhydrous conditions in chemical processes are required. In this contribution, several depolymerization models were proposed for paraformaldehyde in powder (PFP) and prills (PFS), and they were validated with experimental thermogravimetric analysis (TGA). For description of PFP depolymerization, a model of a single step was adequate, and for PFS the best model included two simultaneous mechanisms. Kinetic models were determined using Master Plot method; for PFS, small intervals of conversion were used in order to obtain the best model at each finite point of the progress of reaction. Apparent activation energies (E_a) were obtained by isoconversional methods. For PFP, E_a was 31.7 kJ mol^{-1} and the model corresponded to Avrami-Erofeyev 2 (A2). For PFS decomposition, the activation energy of the two mechanisms was $E_a = 105.4$ kJ mol^{-1} for a contracting volume (R3) model and $E_a = 48.4$ kJ mol^{-1} for the Avrami-Erofeyev model.

1. Introduction

Formaldehyde, HCHO, is one of the simplest products of the methanol partial oxidation and one of the most reactive organic substances; hence, it is important in many reactions, for example as a raw material in polymerization processes [1]. In 2012 formaldehyde global production stood at 46.4 million tons [2]. HCHO is usually commercialized in aqueous solution, stabilized with methanol to avoid its polymerization, and in solid form as polymers: paraformaldehyde (PF) with 8–100 oxymethylene units or polyoxymethylene homopolymer (POM-H) with higher molecular weight, containing up to 500 or even more monomeric units [3]. PF is typically used as HCHO source when anhydrous reaction conditions are mandatory; for instance, for obtaining homoallylic alcohols from the Prins condensation of alkenes and HCHO [4]. This reaction has been widely studied to obtain nopol from β-pinene and PF over tin catalyst supported on mesoporous materials [5]. According to Table 1, nopol yield could be strongly affected by the specific properties of PF, in contrast to PF commercialized in powder, the nopol yield using PF commercialized in prills was lower and significantly affected by particle size. Furthermore, the activity of the catalytic system depends on the availability of *in situ* HCHO generation, which could be assessed by the kinetics of HCHO production from its polymers, information that is not deeply analyzed for PF in the open literature. An aim of this contribution is to understand the differences between PF commercialized in powder and in prills that could be related with nopol production.

Decomposition patterns are characteristic to each kind of polymer, and in some cases they can be used for identification purposes [8]. There are some reports about depolymerization analysis of POM-H [9–16], most of them using TGA but without detailed kinetic analysis; for PF the information is scarce [16,17]. As polyoxymethylenes (POM) is one the most important engineering polymers for automotive, mechanical, medical and consumer goods applications, its thermal decomposition has been readily studied; this process involves the stabilization by acetylating "—OH" chain ends, introducing comonomer in small proportions or using nanocomposite materials. The degradation of POM is carried out by stepwise thermal depolymerization from the chain ends, oxidative attack to produce hydroperoxides leading to chain scission and depolymerization, acidolytic cleavage in the presence of formic acid as a byproduct of HCHO oxidation, or thermal chain scission at elevated temperatures [18 and references therein].

Grassie and Roche [11], reported the former studies on depolymerization kinetics of POM-H by a technique known as thermal volatilization analysis (TVA), where pressure evolution is measured; the authors found that the degradation rate was proportional to the average molecular weight of the polymer raised

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to the 0.8 power. In an earlier work, Kern and Cherdron [16] found a pseudo-first order kinetics if PF (molecular weight of 1200 Da) was depolymerized by heating. More recently, Fray et al. [14] carried out TVA isothermal experiments to measure the pressure evolution until equilibria, obtaining that the initial rate of thermal depolymerization of POM-H was proportional to POM-H mass, and that the Arrhenius parameters depended on the POM-H sources, effect that was attributed to the differences of the chain length or impurities. In this contribution, detailed kinetics of depolymerization of PF, commercialized in powder and prills, was obtained by TGA, using a modification of the Master Plot method [19].

2. Experimental

2.1. Materials

Two sources of PF with 95% of purity, bought to Sigma–Aldrich, were used as received. PF in powder as fine particles, PFP (product number: 158127-500G, batch number: 11529JA), and PF in prills as spherical particles, PFS (product number: 441244-1KG, batch number: 7223CC).

2.2. Characterization of materials

PFP and PFS were characterized by X-ray diffraction (XRD), infrared spectroscopy, differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA). XRD was carried out in a Bruker diffractometer D8 ADVANCE with CuKα radiation. For Fourier transform infrared spectroscopy (FTIR), pellets, prepared with controlled amounts of PF and KBr, were measured at room temperature in a SpectrumOne PerkinElmer instrument with a deuterated tri-glycine sulfate pyroelectric (DTGS) detector, at frequencies from 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1}. DSC were obtained in a TA instrument model Q100 under nitrogen atmosphere; samples at room temperature were cooled to −80 °C at 20 °C min^{-1}, and the analyses were carried from −80 °C to 300 °C using a heating rate of 5 °C min^{-1}. The TGA experiments were carried out by non-isothermal method using a Q-500 TA instruments; the samples, with mass between 10 and 15 mg, were heated at three different heating rates β = 5, 7.5 and 10 °C min^{-1}, with a continuous nitrogen flow of 40 mL min^{-1} from 20 to 300 °C.

3. Results and discussion

3.1. Characterization of paraformaldehyde

3.1.1. Structure and morphology

As POM-H with low polymerization degree is called PF, POM-H will be taken as a reference for the analysis of PF. Actually, PF exhibits almost the same XRD pattern and infrared spectrum as POM-H, which suggests that the molecular and crystal structures of these two materials are very similar [20,21]. Fig. 1 shows the main peaks and diffraction to planes [22] in agreement to those reported for POM [23], and are close to the calculated positions for POM-H in the 2θ scan about d_{100} = 22.9°, d_{105} = 34.6° and d_{115} = 48.4° [18]; then, both PFP and PFS samples consist of hexagonal crystals with chains in helical conformations, which are the structural characteristics reported for POM [18]. The apparent crystallite size (ACS) [23] of the PF samples analyzed in this contribution and calculated according to the Scherrer equation, Eq. (1), is shown in Table 2. As the crystallite size of PFS was about 2% higher than PFP, it is possible to suggest that significant differences are not obtained at crystal level for both PFP and PFS samples; however, crystal sizes of PF samples analyzed in this contribution were higher that reported POM crystal size (Table 2, line 3).

Table 1
Activity on nopol synthesis with different sources of solid PF over catalytic system based on Sn-MCM-41. Adapted from Ref. [6].[a]

Time, (min)	dp, (μm)[b]	Yield PF in powder, (%)[c]	Yield PF in prills, (%)[c]
2	58	12.5	5.0
2	338	11.5	1.8
5	58	23.0	10.2
5	338	19.9	2.7

[a] Reaction conditions: 0.25 mmol β-pinene, 0.5 mmol PF, 2.2 mg sieved catalyst (Sn-MCM-41 obtained by hydrothermal method with tin loading of 43 μmol g^{-1} [7]), 0.5 mL toluene, 90 °C, stirring rate 1000 rpm.

[b] Average between sizes of standard series mesh.

[c] Further description of these samples in Section 2.1. The standard deviation of measurements was in average 1.1% units.

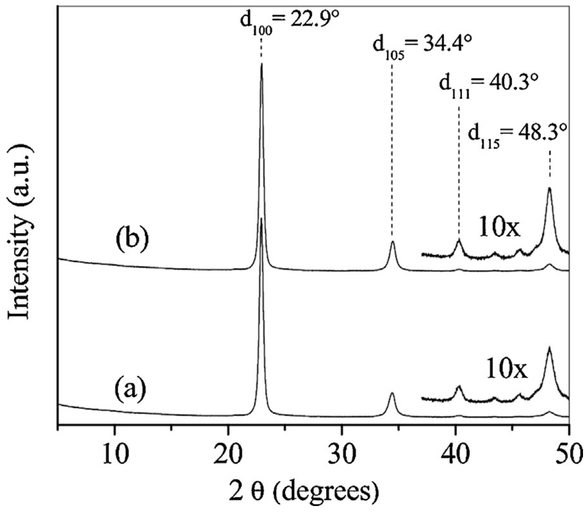

Fig. 1. XRD of paraformaldehyde samples. (a) PFP and (b) PFS.

$$\mathrm{ACS} = \frac{K\lambda}{(\Delta 2\theta)\cos(\theta)} \tag{1}$$

where K is a constant related to crystallite size taken as 1, λ is the wavelength (0.15418 nm), $\Delta 2\theta$ is the integral breadth (ratio between peak area and peak height in radians), and θ is the corresponding peak angle.

Fig. 2 shows that the majority of the bands in the FTIR spectra for both PFP and PFS samples are common; furthermore, those bands have been reported in the literature for POM [20,21,23–25]. Although there are some bands that have not been identified yet, important differences between the two PF samples are observed. It has been reported that the intensity of the 903 cm^{-1} band is proportional to the degree of polymerization [20]; however, no significant difference was found for this band in the samples analyzed. The morphological structure of crystalline POM-H, at a scale lower than micrometer level but higher than crystal lattice, may be classified as extended-chain crystals (ECCs) and folded-

Table 2
XRD parameters of peak corresponding to plane d_{100}.

Sample	d_{100} position 2θ, (°)	FWHM, (°)[b]	ACS, (nm)[c]
PFP	22.92	0.394	17.57 (20.60)
PFS	22.96	0.390	17.98 (20.78)
POM[a]	23.00	0.699	13.0 (12.9)

[a] Copolymer F30-03 as reported in Ref. [23].

[b] FWHM: full width at half maximum.

[c] In parenthesis the crystallite size obtained with Eq. (1) using FWHM instead of integral breadth and K = 0.9.