

In-situ synthesis and characterization of biodegradable estolides via epoxidation from canola biodiesel

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S1. Cermak and Isabell's contributions on formulation of estolides

Cermak et. al (2001) patented a technology to synthesize biodegradable oleic estolide ester having saturated fatty acid end group useful as lubricant basestock [1]. Cermak and Isabell (2001) prepared oleic acid based estolides via addition of various saturated fatty acids (butyric through stearic) by treating with 0.4 equivalents of perchloric acid at either 45 or 55 °C to produce complex estolides. They found that shorter-chain saturated fatty acids, i.e., butyric and hexanoic, provided material with higher degrees of oligomerization (EN = 3.31) than stearic acid (EN = 1.36). Further, as the chain length of saturate capping material increased from C₄ to C₁₀, the low temperature performance of the 2-ethylhexyl estolide esters, pour point, decreased to -39 °C. The other mid-chain, saturated 2-ethylhexyl estolide esters C₆ through C₁₄ also had superior low temperature properties compared with their competitors; i.e. soy-based, synthetic-based and petroleum-based oils. The amount of oligomerization (EN) had an important role with the viscosities, viscosity increased with higher oligomerization [2, 3]. Later on, the saturate-capped, oleic estolides were esterified with 2-ethylhexanol to obtain high yields of the corresponding ester. The new coco-oleic estolide esters displayed superior low temperature properties (-36 °C). Further, Cermak and Isabell (2003) also evaluated the oxidative stability of coconut-oleic estolide 2-ethylhexyl ester (coco) and oleic estolide 2-ethylhexyl ester (oleic) by the rotating bomb oxidative test (RBOT). These two estolide esters have displayed far superior oxidative stability, 504 (coco) and 426 (oleic) min, and their estolides were more suitable as a basestocks for biodegradable lubricants and functional fluids [4, 5].

Cermak and Isabell (2004) formulated Cuphea-oleic estolides and esters from cuphea and oleic FA with various amounts of perchloric acid (0.01 to 0.40 equiv) at 60 °C and new cuphea-oleic estolide esters displayed good low-temperature properties (pour point -42 °C and cloud point -41 °C) [6]. Further, Castor and lesquerella FA esters were combined with different types of saturated, unsaturated, and branched FAs to produce estolides. Castor and lesquerella estolide esters had the best cold temperature properties when capped with oleic (pp = -54 °C for castor and pp = -48 °C for lesquerella) or capped with a branched material, 2-ethylhexanoic acid (pp = -51 °C for castor and pp = -54 °C for lesquerella) [7]. Tallow-oleic estolide 2-ethylhexyl (2-EH) esters were synthesized in a perchloric acid catalyzed one-pot process from industrial 90% oleic and tallow fatty acids at various ratios. The 100% tallow estolide 2-EH ester had modest low-temperature properties (pour point = -15 °C and cloud point = -14 °C) [8]. Saturated mono-estolide methyl esters and enriched saturated mono-estolide 2-EH esters were synthesized, the resulting pour point values showed a linear relationship between the saturated capping chain length and pour point. As the saturated capping chain length increased the pour points also increased (higher temperatures): C₂ capped -30 °C, C₁₀ capped -12 °C, and C₁₈ capped 3 °C. The viscosities for the C₄ saturated mono-estolide methyl ester was 9.5 cSt at 40 °C and 2.6 cSt at 100 °C, while medium chain length derivations (C₁₀ saturated mono-estolide methyl ester) were 19.7 cSt at 40 °C and 4.2 cSt at 100 °C, and at the longer chain length derivations (C₁₈ mono-estolide methyl esters) were 27.6 cSt at 40 °C and 10.7 cSt at 100 °C [9]. A new series of petroselinic (*Coriandrum sativum* L.) based estolide 2-ethylhexyl (2-EH) esters were synthesized, as the capping material varied in length and in degrees of unsaturation, in a perchloric acid catalyzed. The kinematic viscosities ranged from 53 to 75 cSt at 40 °C and 9.1 to 14.6 cSt at 100 °C with a viscosity index (VI) ranging from 151 to 165. The caprylic (C₈) capped coriander estolide 2-EH ester had the lowest low-temperature properties (pour point = -33 °C and cloud point = -33 °C), while the coco-coriander estolide 2-EH

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ester produced an estolide with modest low temperature properties (pour point = -24 °C and cloud point = -25 °C) [10]. Acetic- and butyric-capped oleic estolide 2-ethylhexyl (2-EH) esters were synthesized by using perchloric acid as catalyst by Cermak et. al (2013) via one-pot process. Pour points of these estolides were found to be -45 °C and -27 °C respectively [11].

The oleic estolide was esterified with a series of 16 different alcohols that were either branched or linear-chained. The linear-chain esters had higher low temperature properties (PP = -9 to -33 °C) but still compete well with other commercial bio-based materials. The branched alcohol produced the best PP (-24 to -39 °C) and CP (-30 to <-50 °C) with the best PP performers being a 2-hexyldecanol, a 16 carbon-chained branched material, and 2-octyldodecanol, a 20 carbon branched material, with a PP at -39 °C. The viscosities (55–209 cSt at 40 °C) and viscosity indexes (VIs) (169–192) performed well [12]. Coco-oleic dimer estolide and trimer estolides were esterified with a series of different branched alcohols; the coco-oleic dimer estolide esters had the lowest PP = -45 °C when esterified with 2-hexyldecanol and PP = -39 °C with 2-octyldodecanol. The coco-oleic dimer estolide esters ranged 27.5–51.7 cSt at 40 °C and 3.0–9.5 cSt at 100 °C, whereas the coco-oleic trimer estolide esters ranged 120.8–227.7 cSt at 40 °C and 17.9–29.4 cSt at 100 °C for the same series as the dimer esters [13].

Erhan et al. (1993) reported the conditions for production of estolides from mixed meadowfoam fatty acids, commercial oleic acid, high-oleic sunflower oil fatty acids, 5,13-docosadienoic acid, petroselinic acid and linoleic acid. Oleic acid, when treated with 1.0 equivalent of perchloric acid at 50 °C produced a 76% yield of polyestolide [14]. Over a range of temperatures from room temperature to 100 °C reaction rates increased at higher temperatures. Other acids catalyze the condensation of oleic acid to form estolide with the following relative rates: $\text{HClO}_4 > \text{H}_2\text{SO}_4 > \text{Para-toluene sulfonic} > \text{BF}_3 \cdot \text{Et}_2\text{O} > \text{montmorillonite K-10} > \text{HCl} > \text{H}_3\text{PO}_4, \text{HNO}_3$ [15]. Erhan et al. (1995) manipulated the reaction equilibrium to enhance the estolide yields. Reactions were conducted at 180 °C, where water was vented out of the reactor at specific times, not only gave dimer-free estolides but also yields up to 30%. Steam has also been used instead of water with similar results. Estolides were quite stable at temperatures up to 250 °C, even when they were exposed to air [16]. Meadowfoam fatty acids (83% monoenoic fatty acid), reacted with 0.01-0.1 mole equivalents of perchloric acid, gave 33-71% yield of estolide, resulting from self-condensation [17]. The production of estolide from oleic acid with sulfuric acid as a catalyst was optimized for minimal acid concentration and temperature. Commercial oleic acid forms estolide optimally when reacted at 55 °C with 5% vol/vol concentrated sulfuric acid for 24 h under vacuum. Temperature plays a critical role in the rate of estolide formation as well as in the overall yield, with higher temperatures providing faster rates but lower yields. The ratio of sulfuric acid to oleic acid equivalents also plays a role, where higher acid concentrations gave faster rates and higher yields of estolide [18].

In order to develop better quality vegetable based lubricants, pour point, melting point and viscosity (40 and 100°C) were determined for a series of esters (methyl, butyl, decyl, oleyl, 2-propyl, 2-ethylhexyl, C18-Guerbet and C24-Guerbet) of meadowfoam, crambe and oleic fatty acids and estolides. Oleic estolide esters had the lowest melting points of all derivatives studied. Of the oleic estolide series the 2-ethylhexyl and C18-Guerbet esters had the lowest melting points, -34 and -43 °C, respectively. In a similar fashion, viscosity increased with higher oligomerization and free acid estolides were generally several hundred centistokes (cSt) more viscous

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than the corresponding esters [19]. Lesquerella and castor hydroxy triglycerides were converted to their corresponding estolides by reacting the oils with saturated fatty acids (C_2 – C_{18}) in the presence of a tin 2-ethylhexanoate catalyst (0.1 wt.%) and utilizing the condensation of hydroxy with corresponding anhydride or heating under vacuum at 200 °C. Physical properties (pour point, cloud point, viscosity, and oxidative stability) were compared for this estolide series. The longer chain saturate capped estolides (C_{14} – C_{18}) had the highest pour points for both mono-capped (9 °C, $C_{18:0}$) and full-capped (24 °C, $C_{18:0}$) lesquerella estolides. Castor mono-capped (9 °C) and full-capped (18 °C) triglyceride estolides gave identical properties. However, pour points improved linearly when the shorter saturated fatty acid capping chain lengths were esterified with the hydroxy triglycerides. Lesquerella capped with a $C_{6:0}$ fatty acid had pour points of -33 °C for the mono-capped and -36 °C for the full-capped and castor had -36 and -45 °C, respectively. Viscosity index ranged from 130 to 202 for all estolides with the shorter chain length capped estolides gave the lower viscosity index values. Viscosity at 100 °C ranged from 13.9 to 26.6 cSt and the 40 °C viscosity ranged from 74.7 to 260.4 cSt where the longer chain length capped estolides gave the highest viscosities [20].

Several diesters were prepared from commercially available oleic acid and common organic acids. The key step in the three step synthesis of oleochemical diesters entails a ring opening esterification of alkyl 9,10-epoxyoctadecanoates (alkyl: propyl, isopropyl, octyl, 2-ethylhexyl) using propionic and octanoic acids. It was discovered that increasing chain length of the mid-chain ester and branching in the end-chain ester had a positive influence on the low temperature properties of diesters. The mid-chain ester plays a larger role in oxidation stability than the end-chain ester [21]. The ricinoleic acid reacted with saturated fatty acid from C_8 – C_{18} . These reactions were conducted under vacuum at 60 °C for 24 h without solvent. The reaction used acid catalyst, sulphuric acid. The new saturate ricinoleic estolide esters show superior low-temperature properties (-52 °C) and high flash point (>300 °C). The yield of the neat estolide esters ranged from 52 % to 96 %. The viscosity range was 51 to 86 cp. These new saturated estolide esters were also compared with saturated branched estolide esters [22]. Castor and lesquerella estolides are derived from either their triglycerides or their free fatty acids utilizing their hydroxyl moiety to establish the estolide bond. The saturated capped estolides of oleic that have both good low temperature properties (pour point -5 to -39 °C) and good oxidative stability. Estolides from meadowfoam fatty acids do not have good low temperature properties but have been extensively used in cosmetics where they provide good moisturizing properties [23].

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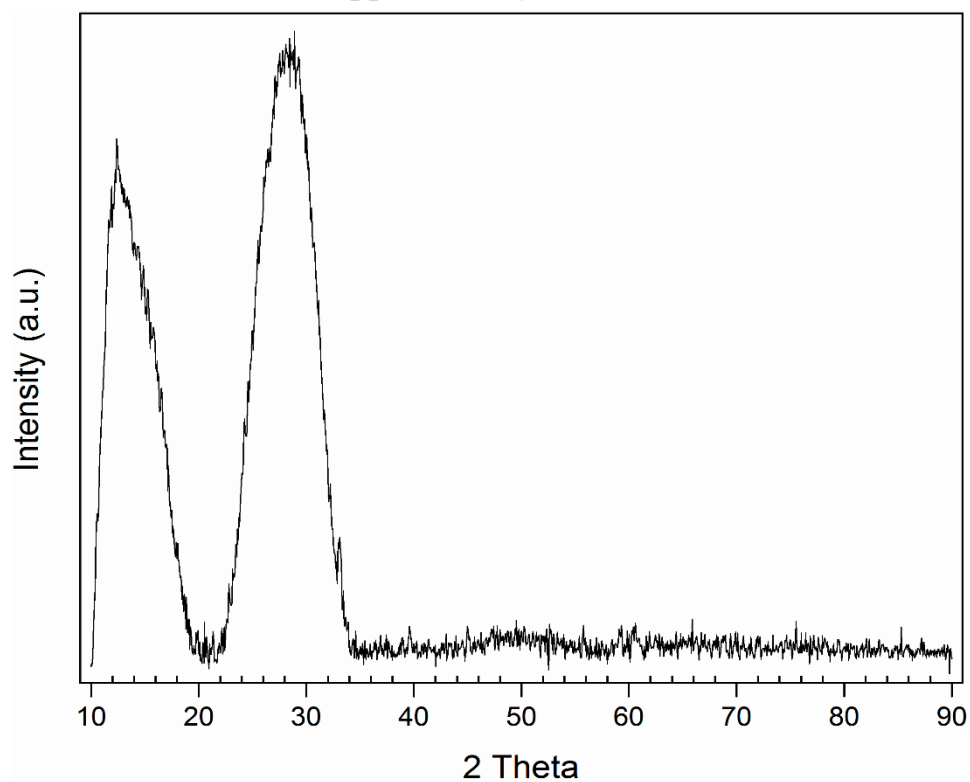


Figure S1. XRD spectra of the mesoporous aluminosilicates catalyst.

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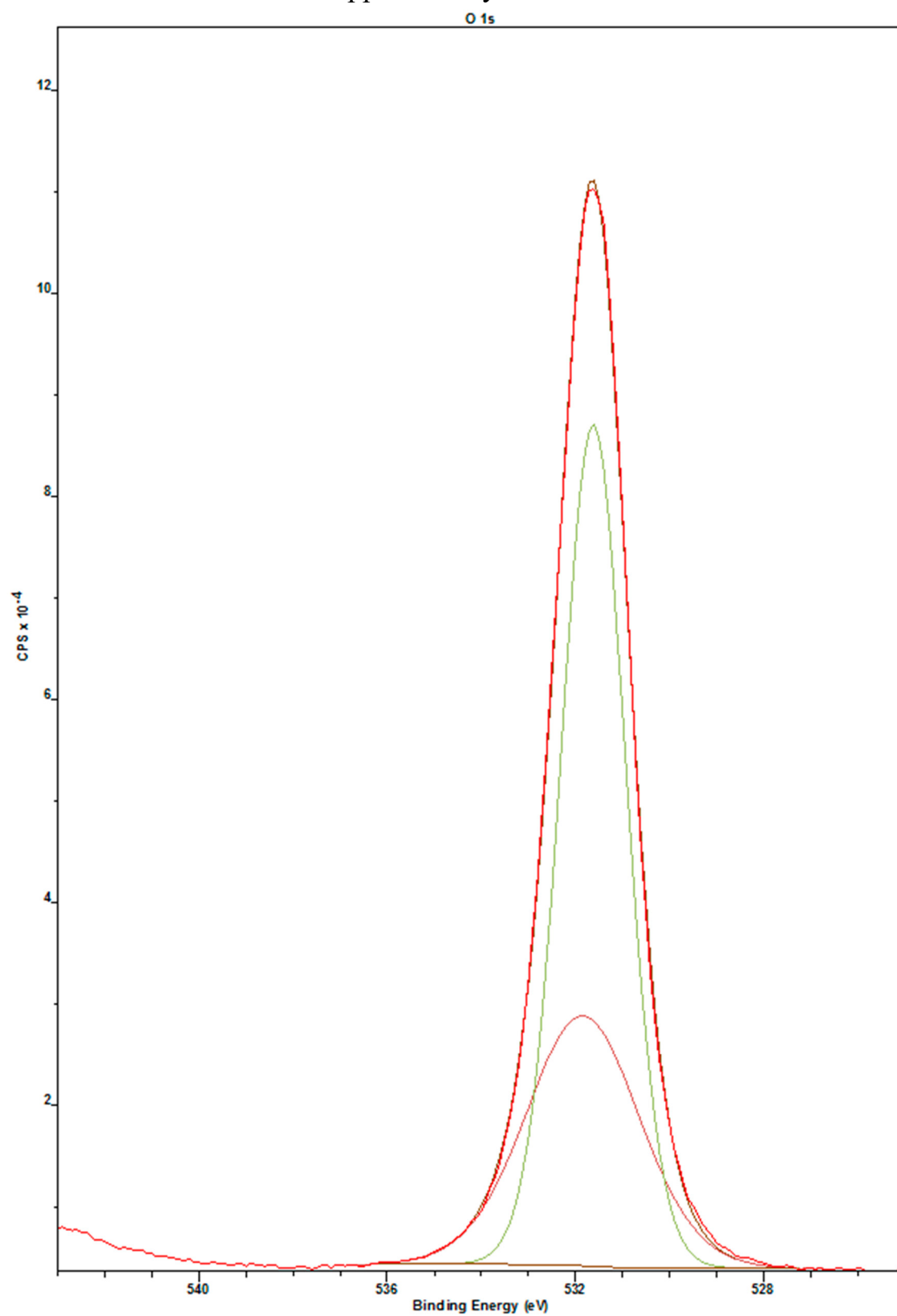


Figure S2. XPS spectra of O (1s) for SiO₂ in mesoporous aluminosilicates.

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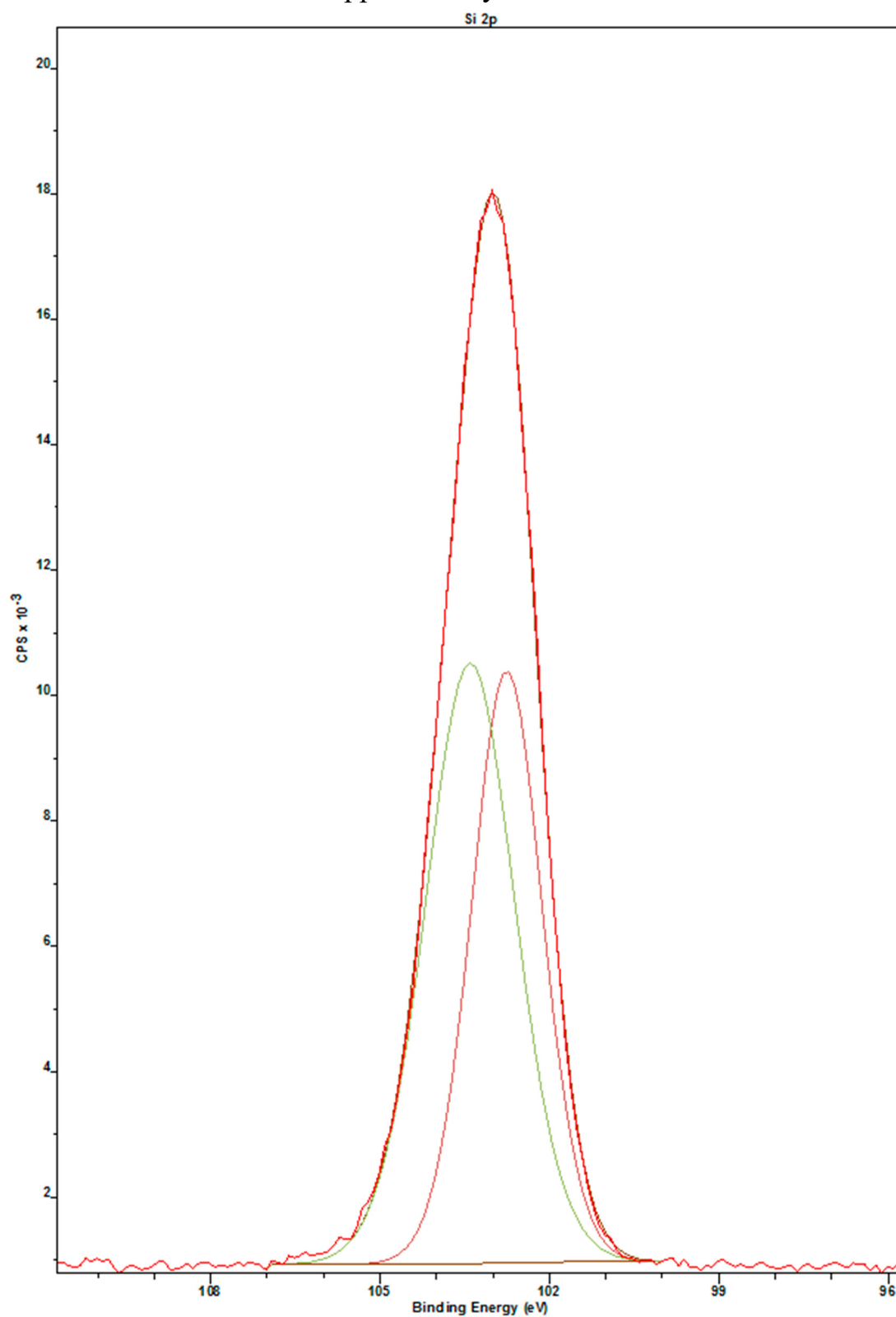


Figure S3. XPS spectra of Si (2p_{3/2}) for SiO₂ in mesoporous aluminosilicates.

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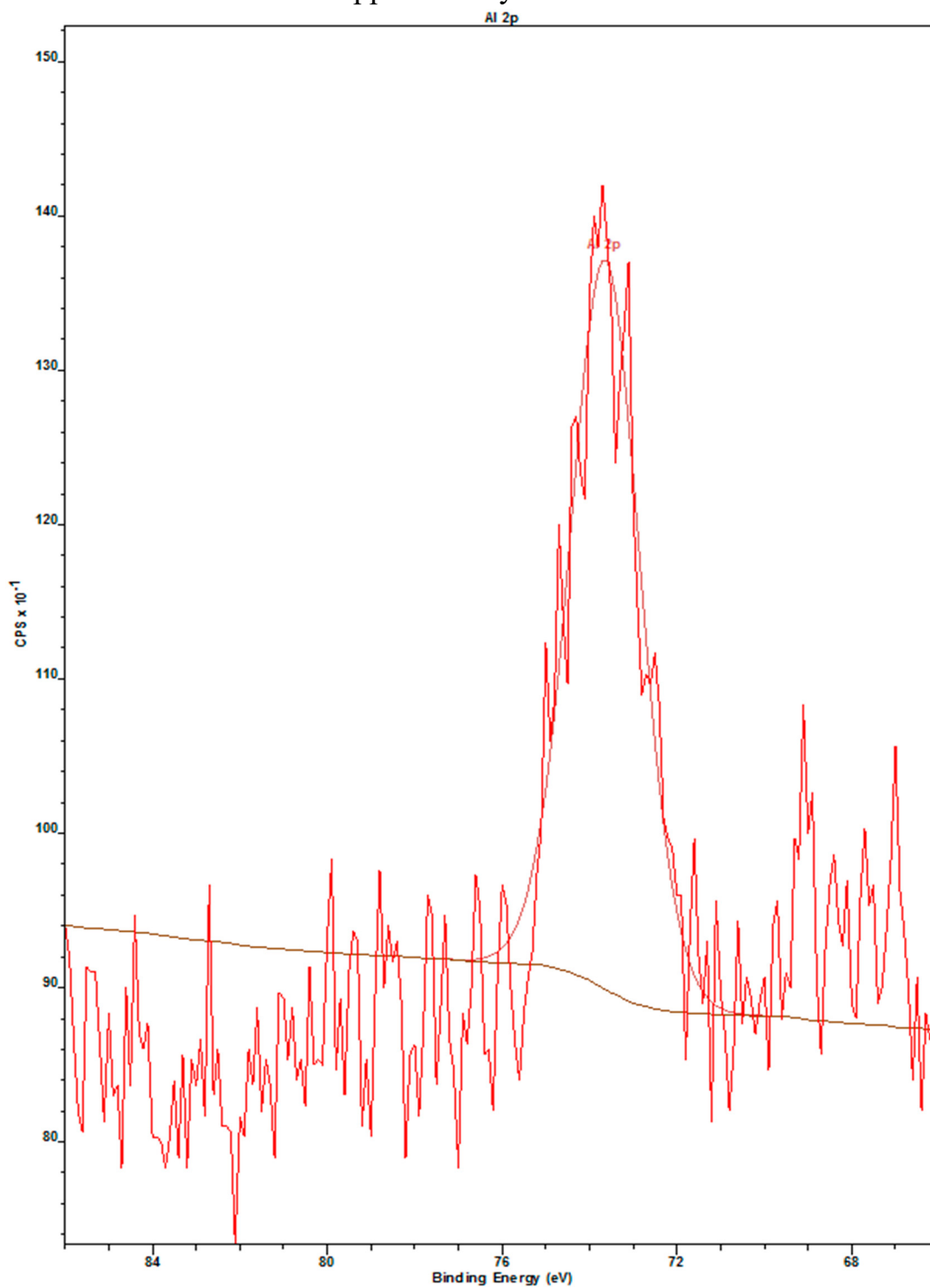


Figure S4. XPS spectra of Al ($2p_{3/2}$) for Al_2O_3 in mesoporous aluminosilicates.

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