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1 Article

2 Zeolite nanocrystals protect the performance of 3 organic additives and adsorb acid compounds during 4 lubricants oxidation

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12 **Abstract:** Zeolite nanocrystals were used as proactive agents to extend the lifetime of commercial
13 lubricants by protecting the performance additives from depletion and adsorbing the acid formed
14 during oxidation. The nanosized zeolites were introduced into four lubricants and subjected to
15 oxidation (90 °C and 150 °C). A strong affinity towards protection of zinc dialkyldithiophosphate
16 (ZDDP) additive was demonstrated by ³¹P NMR and FTIR spectroscopy even after heating at 150
17 °C for 24h. FTIR profiles of lubricants aged in the presence of LTL showed lower oxidation degree
18 while the formed oxidation products (aldehydes, ketones, and acids) were adsorbed on the zeolite
19 crystals acting as scavengers.

20 **Keywords:** Zeolite; lubricants; additive protection; anti-oxidant; FTIR; NMR.

21

22 1. Introduction

23 Lubricants are indispensable to maintain the good functioning of vehicle engines. In addition to
24 reducing friction and wear within the metallic parts, lubricants carry out a range of other
25 complimentary tasks including: corrosion prevention, providing a liquid seal at moving contacts,
26 and removal of wear and soot particles[1]. On the other hand, the environmental impact resulting
27 from their production, use, recycling, and disposal is high.

28 Their replacement by the more environmentally friendly vegetable oils could have been
29 considered as an option despite of their low thermal stability and easy oxidation at elevated
30 temperatures[1],[2]. Another alternative solution is the use of synthetic lubricants that ensure a
31 higher thermal stability, longer lifetime, and modifiable chemical and physical properties to meet
32 the requirements. Commercial lubricants are available with special formulations; the base oil which
33 constitutes more than 90% of the mixture is mainly responsible for lubricating the metallic parts. Its
34 preservation, maintaining its function, and introducing other complimentary tasks is governed by
35 the performance additives[1],[3]. These are phenols, aromatic amines, alky or aromatic sulfides as
36 antioxidants to delay the auto oxidation of the base oil[1],[4], zinc dialkyldithiophosphate (ZDDP)
37 as antiwear[1],[5], poly(acrylates), olefin copolymers or styrene–butadiene copolymers as viscosity
38 index improvers[1],[6], amphiphilic molecules as detergents and dispersants to adsorb wear and
39 soot particles and keep them in colloidal suspension in the base fluid[1],[4]. While the performance
40 additives especially the antioxidants are in function, the lubricant is said to be in the “pro-active”
41 domain. The critical depletion of these products renders the base oil unprotected in presence of air
42 and heat, this is the so called “responsive domain” when it is highly advised to replace the
43 lubricant.

44 In order to reduce the high environmental impact resulting from lubricant disposal, several
45 re-refining techniques were developed including acid/clay treatment, solvent extraction,
46 distillation/clay treatment and distillation/hydrotreatment, all of which generate chemical wastes
47 that needs additional treatment[1]. Recycling of used lubricant can be also considered an option
48 where unoxidized base oil is separated and recovered from the oxidized oil fraction and the
49 depleted additives[1],[7].

50 Despite of these end-of-use treatments, different solutions were proposed to extend the
51 lubricant lifetime. Additives such as TiO₂[8],[9] and Cu[10] nanoparticles, fullerenes[11],
52 nano-diamond[12] and MoS₂[13] demonstrated excellent antiwear properties. Additionally,
53 chemical filters based on mesoporous materials[14],[15] or strong bases (metal oxides)[16],[17],[18]
54 were developed to adsorb and neutralize acids generated from the lubricants circulating in the
55 engine, respectively. While the incorporation of these new additives counts for extending the
56 proactive domain, their complicated synthetic protocols and expensive starting materials create a
57 potential limitation[3]. On the other hand, the main action of the modified chemical filters starts
58 when the oil is already oxidizing.

59 Zeolites, a special class of aluminosilicate inorganic materials are known for their excellent
60 sorption properties owing to their porous structure, high surface area, and large internal voids. The
61 selective behavior towards gases and liquids can be tuned following a systematic modification of
62 their composition and structure. The acidic properties of these materials are highly influenced by
63 their form[19]. For instance, while the proton (H) form demonstrate strong Lewis and Brønsted
64 character, the cationic zeolites present a basic character suitable to neutralize weak acids [20],[21].
65 LTL and FAU nanosized zeolites have already demonstrated high capabilities as antioxidants for
66 the preservation of palm oil during the early stages of oxidation[22],[23],[24]. The primary oxidation
67 products “peroxides” are stabilized by the zeolite charge compensating cations with a strong
68 influence driven by the type of cation used. On the other hand, the secondary oxidation products
69 “aldehydes, ketones, and carboxylic acids” are adsorbed and immobilized on the external surface
70 and in the internal voids of the zeolite. LTL nanocrystals were also reported for the purification of
71 lubricants at the late stages of oxidation; the secondary oxidation products are adsorbed by the
72 zeolite and stabilized by the strong interactions of their carbonyl groups with the potassium
73 cations[25], consequently, they are filtered out from the non-oxidized fraction allowing its proper
74 reuse[26]. LTL nanocrystals were further tested as anti-oxidant for synthetic lubricants in the
75 presence or in the absence of performance additives[2]. The study revealed a strong capacity of
76 these nanocrystals in adsorbing the oxidation products and thus delaying the formation of
77 undesired polymers. The experiments were made on lubricants with special formulations adapted
78 to the study, thus does not predict the exact behavior of zeolite in a commercial lubricant where
79 numerous additives are available.

80 Herein we report the synthesis of LTL zeolite nanocrystals (15-20 nm) prepared from inorganic
81 starting materials in absence of organic structural directing agents as proactive agents to extend the
82 lifetime of commercial lubricants used for car engines. LTL nanocrystals demonstrate a dual role by
83 (i) delaying the depletion of additives and hence extending the proactive domain, and (ii) absorbing
84 the generated secondary oxidation products formed, and hence delays the lubricant degradation.

85 2. Materials and Methods

86 Materials

87 Two grades of commercial lubricants (C2 and C3) from two different suppliers (SA and SB)
88 were provided from Sogefi group, Al(OH)₃ was purchased from Acros Organics, Ludox SM-30 and
89 KOH were purchased from Sigma Aldrich, dd H₂O: double distilled water.

90 Preparation of LTL nanocrystals

91 Nanosized LTL zeolite was prepared starting from the following molecular composition of the
92 precursor suspension: 5 K₂O, 10 SiO₂, 0.6 Al₂O₃, 200 H₂O.

93 In a polypropylene bottle, KOH (7.77 g) was dissolved in dd H₂O (15 g) followed by the slow
94 addition of Al(OH)₃ (1.3g). The resulting suspension was stirred overnight to afford a light white

95 suspension which was then added in a dropwise manner over a solution of Ludox SM-30 (27.7 g) in
96 dd H₂O (13.7g) under stirring. The resulting suspension was kept on a shaker for 48 h then placed
97 in an autoclave at 170 °C for 8 h.

98 The crystalline material was separated from the liquid phase by centrifugation (20000 rpm, 40
99 min) then purified by five cycles and redispersed in water followed by centrifugation. The LTL
100 nanocrystals were freeze dried, then activated at 150 °C for 24 h prior to use.

101 **Oxidation process**

102 Commercial Lubricants (100 g) were mixed with 1 wt% of LTL zeolite nanocrystals (1 g) and
103 allowed to oxidize under stirring at 90 °C for 35 days or at 150 °C for 24 h. 5 g of each sample were
104 withdrawn periodically; the zeolite nanocrystals were separated from the lubricants by
105 centrifugation (20000 rpm, 1h). For comparison, similar amount of lubricants (100 g) was oxidized
106 in absence of zeolite nanocrystals.

107 **Characterization**

108 **Characterization of zeolite nanocrystals**

109 *X-ray diffraction (XRD) characterization:* the purity and crystallinity of the zeolite powder before
110 and after lubricant oxidation were studied by XRD analyses carried out with PANalytical X'Pert
111 Pro diffractometer with CuK α monochromatized radiation ($\lambda = 1.5418 \text{ \AA}$).

112 *High-Resolution Transmission Electron Microscopy (HRTEM):* the crystal size, morphology, and
113 crystallinity were characterized using a FEI Tecnai G2 30 microscope (Vacc=300 kV, LaB6).

114 *Dynamic light scattering (DLS):* the size of the zeolite nanoparticles was measured by a
115 Malvern Zetasizer Nano instrument using a backscattering geometry (scattering angle of 173°,
116 He-Ne laser with a 3 mW output power at a wavelength of 632.8 nm). Analyses were performed on
117 water suspensions with a solid concentration of 2 wt%.

118 *Nitrogen adsorption analysis:* the porosity was measured using a Micrometrics ASAP 2020
119 volumetric adsorption analyzer. Samples were degassed at 250 °C under vacuum overnight prior to
120 the measurement. The external surface area and micropore volume were estimated by alpha-plot
121 method using Silica-1000 (22.1 m²·g⁻¹ assumed) as a reference. The micropore and mesopore size
122 distributions of samples were estimated by the Nonlocal Density Functional Theory (NLDFT) and
123 Barret-Joyner-Halenda (BJH), respectively using the desorption branch of the isotherm.

124 *FTIR:* The zeolite nanocrystals separated from lubricants were thoroughly washed by diethyl
125 ether to eliminate traces of physically adsorbed products and dried overnight under vacuum. The
126 zeolite powder was diluted in KBr (1%), pressed (~10⁷ Pa) in disks (2 cm² area, 100 mg·cm⁻²), and
127 placed in an IR cell equipped with KBr windows. IR spectra were recorded using a Nicolet 6700 IR
128 spectrometer equipped with a mercury cadmium telluride (MCT) detector and an extended KBr
129 beam splitter. Spectra were recorded in the 400–5500 cm⁻¹ range at 4 cm⁻¹ with 128 scans.

130 **Characterization of lubricants**

131 ¹H NMR analyses were carried out using a Bruker AVIII spectrometer 600 MHz. Lubricant
132 samples (400 mg) dissolved in deuterated chloroform (CDCl₃) (0.5 ml) were used, and 1000 scans
133 were applied. The chemical shifts are calibrated to residual proton resonance of Si(CH₃)₄ ($\delta\text{H} = 0$
134 ppm).

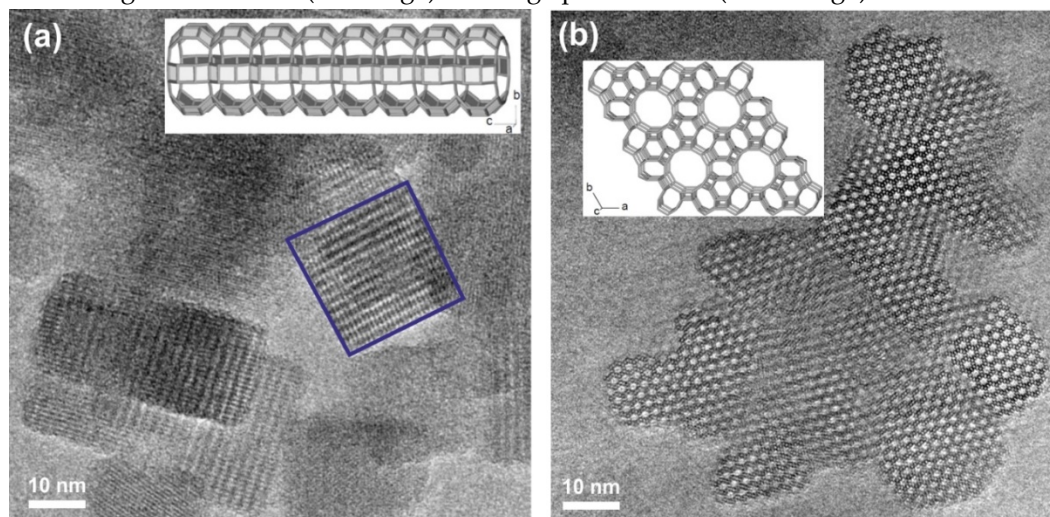
135 ³¹P NMR analyses were carried out using a Bruker AVIII spectrometer 600 MHz. Lubricant
136 samples (400 mg) dissolved in CDCl₃ (0.5 ml) were used and 6000 scans were applied. The chemical
137 shifts are calibrated to the resonance of H₃PO₄ ($\delta\text{P} = 0$ ppm).

138 *Rheology:* the evolution of lubricant viscosity throughout the oxidation process was monitored
139 by a Malvern Kinexus Rheometer. The analyses were performed by applying a shear stress of 1 Pa
140 at 25 °C. Three independent measurements were performed for each sample and the average value
141 was used.

142 *FTIR:* The stability of the lubricants and the formation of oxidation products were monitored
143 by FTIR spectroscopy in liquid phase using Perkin Elmer System 2000 spectrometer. Lubricants (0.5
144 ml) were introduced in a ZnSe liquid cell (1 mm spacer) and analyzed in the 400–5500 cm⁻¹ range
145 with 128 scans.

146 **3. Results and discussion**

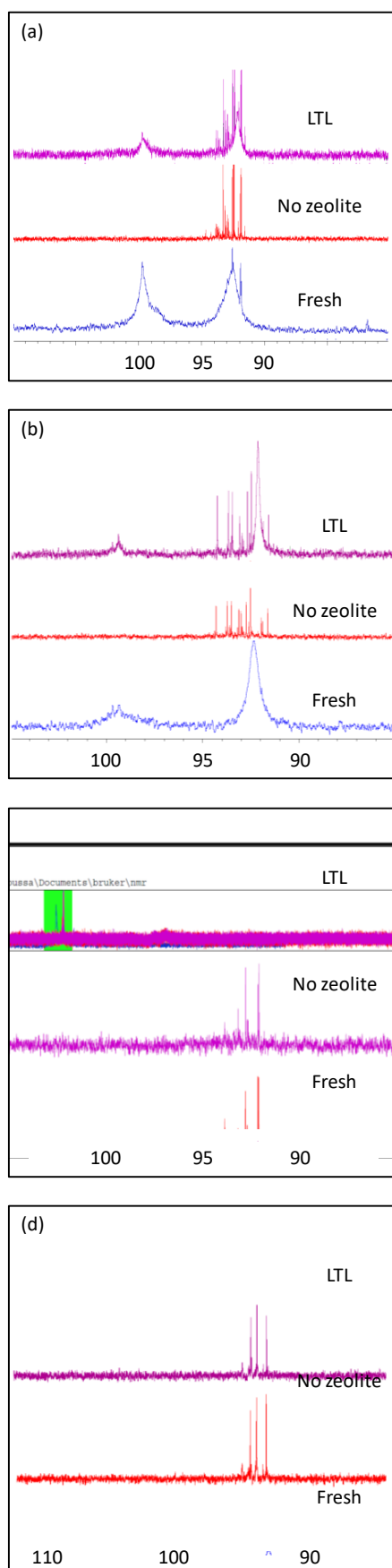
147 The LTL nanozeolite used in this study is prepared free of organic structural directing agents,
 148 thus avoiding energy expenditure and CO₂ release resulting from high temperature calcinations.
 149 This zeolite was selected due to the high efficiency towards adsorbing products of lubricant
 150 oxidation[22],[23],[24],[26], absence of Brønsted or Lewis acidity[26], hence cannot catalyze the
 151 oxidation of lubricants, in addition to the absence of toxicity on the living cells[27]. XRD pattern of
 152 the prepared zeolite reveals broad Bragg peaks typical for small nanoparticles with shifts
 153 corresponding to pure LTL structure in absence of other phases (Figure S1). The high crystallinity
 154 was further demonstrated by HRTEM that revealed particles with parallel cylindrical morphology
 155 of 15-20 nm corresponding to the 1-D structure of LTL (Figure 1). N₂ sorption analyses (Figure S3)
 156 monitored a high surface area (454 m².g⁻¹) and large pore volume (0.66 cm³.g⁻¹).



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158 **Figure 1.** HRTEM images of LTL nanocrystals projected along the directions [100] in (a) and [001] in
 159 (b) (SG P6/mmm).

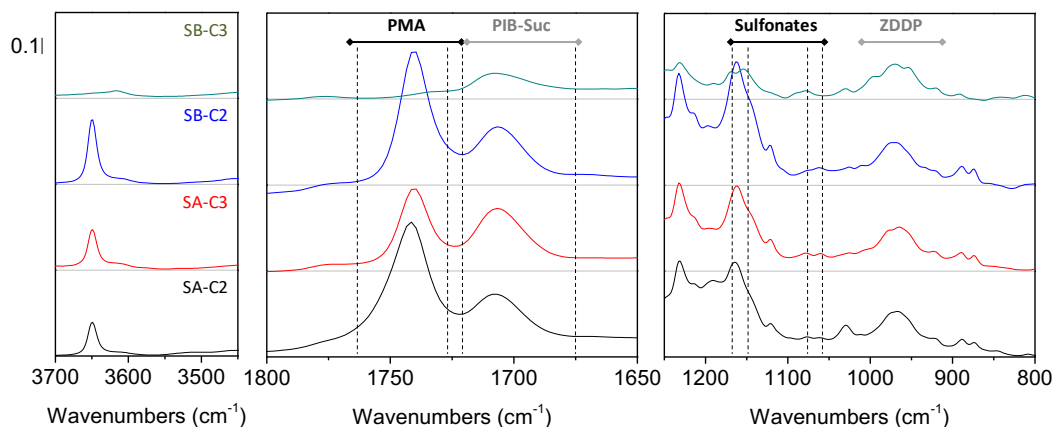
160 Four fully synthetic, commercial light lubricants ($\eta = 0.103\text{--}0.116$ Pa.s, Table S1) designed by 2
 161 different suppliers for the use in car engines were tested. ¹H NMR revealed saturated hydrocarbons
 162 constituting more than 90% of these lubricants, thus confirming their designation as fully synthetic
 163 (Figure S4). A minority of peaks was recorded in the aromatic region corresponding to alkylated
 164 phenol antioxidant in SA-C2, SA-C3, and SB-C2 in addition to an unidentified aromatic additive
 165 available in all the samples (Figure S4). The presence of phosphorous containing additives was
 166 verified by ³¹P NMR; basic and neutral ZDDP (zinc dialkyldithiophosphates) acting as antiwear and
 167 antioxidant were identified in all the samples[5] (Figure 2). The presence of numerous performance
 168 additives with different functional groups resulted in a complicated FTIR (Figure 3 and Figure S5).
 169 The following interesting features (bands) in the spectra were identified: at 975 cm⁻¹ (P-O-C
 170 vibrations from ZDDP[28]), at 1705 cm⁻¹ (C=O vibrations from polyisobutylene succinimide
 171 “PIB-suc” dispersant[29]), at 1740 cm⁻¹ (C=O from esters and polymethacrylates “PMA” viscosity
 172 modifiers) and at 3650 cm⁻¹ (phenolic OH).



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Figure 2. ^{31}P NMR spectra of (a) SA-C2, (b) SA-C3, (c) SB-C2, and (d) SB-C3 in their fresh form (blue) or following 24 h of oxidation at 150 °C in absence (red) or presence (violet) of LTL nanozeolite.



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Figure 3. FTIR main features of fresh lubricants: SA-C2 (black), SA-C3 (red), SB-C2 (blue) and SB-C3 (green).

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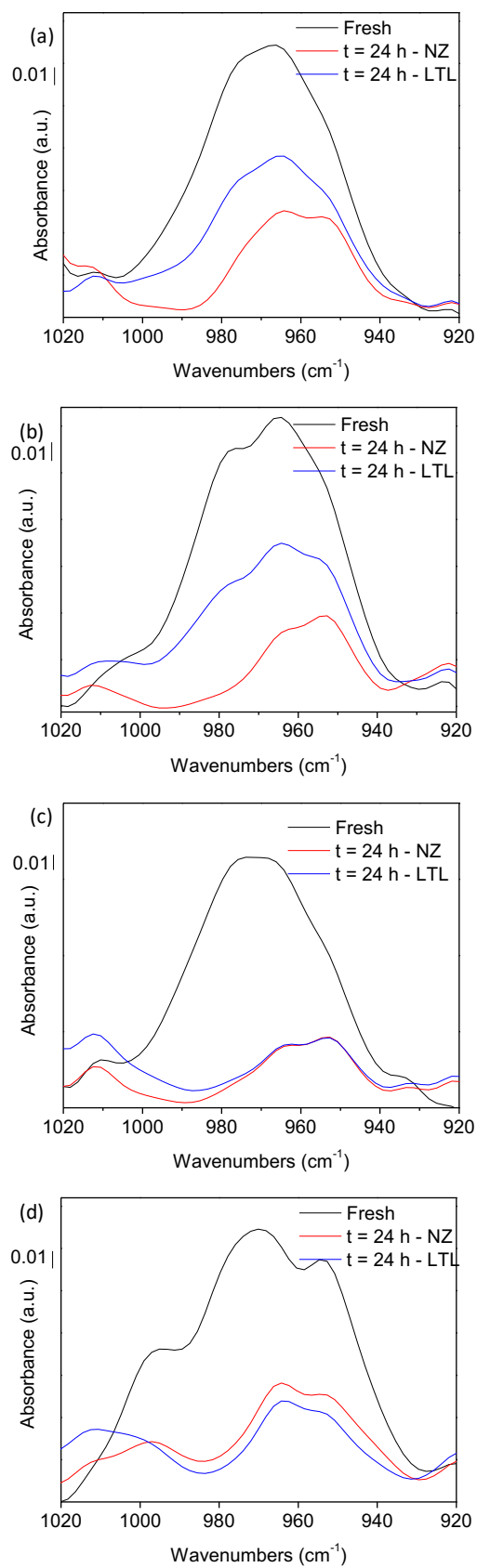
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Oxidation was first conducted at 90 °C for 35 days in the absence and in the presence of 1 wt% of zeolite. All the lubricants showed high stability under these conditions, *that is*, no remarkable changes were identified on their viscosity, NMR or FTIR spectroscopic profiles.

A faster aging was provoked by increasing the temperature up to 150 °C. Consequently, the P-O-C FTIR vibrations of the ZDDP additive were strongly influenced evidenced by a sharp decrease of the band area from 54% to 44% for the initial sample SA-C2 and SAC3 after 16 h of heating in absence of zeolite (Figure 4 and Figure S6). Meanwhile, a further decrease to 27% and 16% for samples SA-C2 and SAC3, respectively after 24 h of oxidation was recorded. The fast depletion of the ZDDP additive was diminished in the presence of LTL nanocrystals, more precisely, 14% and 25% preservation of the P-O-C vibrations were recorded after 16 h and 24 h of heating for both samples. Notably, the efficiency of zeolite nanocrystals in limiting the loss of the FTIR vibrations increases with time; this is exemplified by the progressive increment of the difference in the P-O-C band area available after oxidation of lubricants in presence and absence of LTL as a function of time. On the other hand, both samples SB-SC2 and SB-C3 encountered a fast oxidation leading to a major loss of P-O-C vibrations after only 16 h with no remarkable influence identified for the zeolite.

The evolution of ZDDP was further examined by ³¹P NMR spectroscopy. The transformation of the broad features resulting from the tetrahedron structure of Zn metal center[30] into sharp narrow peaks at lower chemical shifts gives a clear indication of thermal degradation and oxidation.[31] Upon aging at 150 °C, the broad feature vanished completely in absence of zeolite nanocrystals (Figure 2), leading to say that the ZDDP is completely decomposed. The set of peaks present at 90-95 ppm corresponds to (RO)₂P(S)SR', a rearrangement product resulting from a high thermal stress of ZDDP. On the other hand, despite of the partial dissociation of ZDDP in SA-C2 and SA-C3 aged in the presence of LTL, the broadening is clearly identified in their ³¹P NMR spectra giving a definitive proof of their preservation. This result reveals the more important role for LTL than that suggested by the FTIR experiments. In the absence of zeolite, the ZDDP is decomposed and the bands recorded



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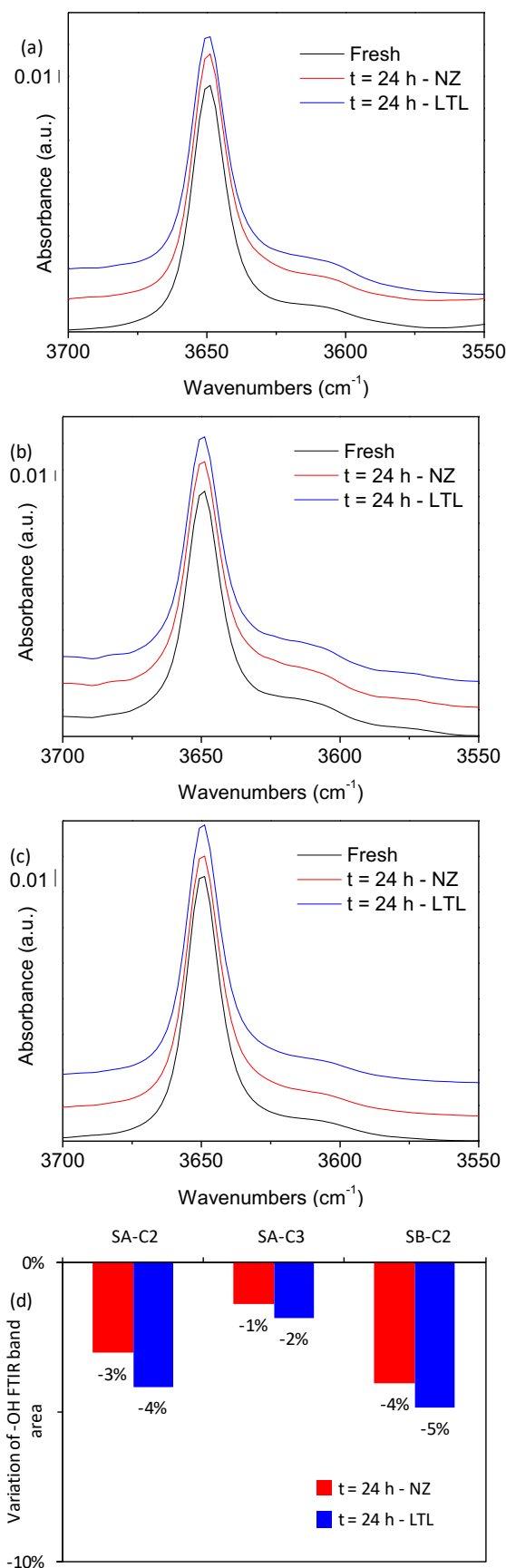
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Figure 4. P-O-C FTIR band vibrations of (a) SA-C2, (b) SA-C3, (c) SB-C2, and (d) SB-C3 in their fresh form (black) or following 24 h of oxidation at 150 °C in absence (red) or presence (blue) of LTL nanozeolite.

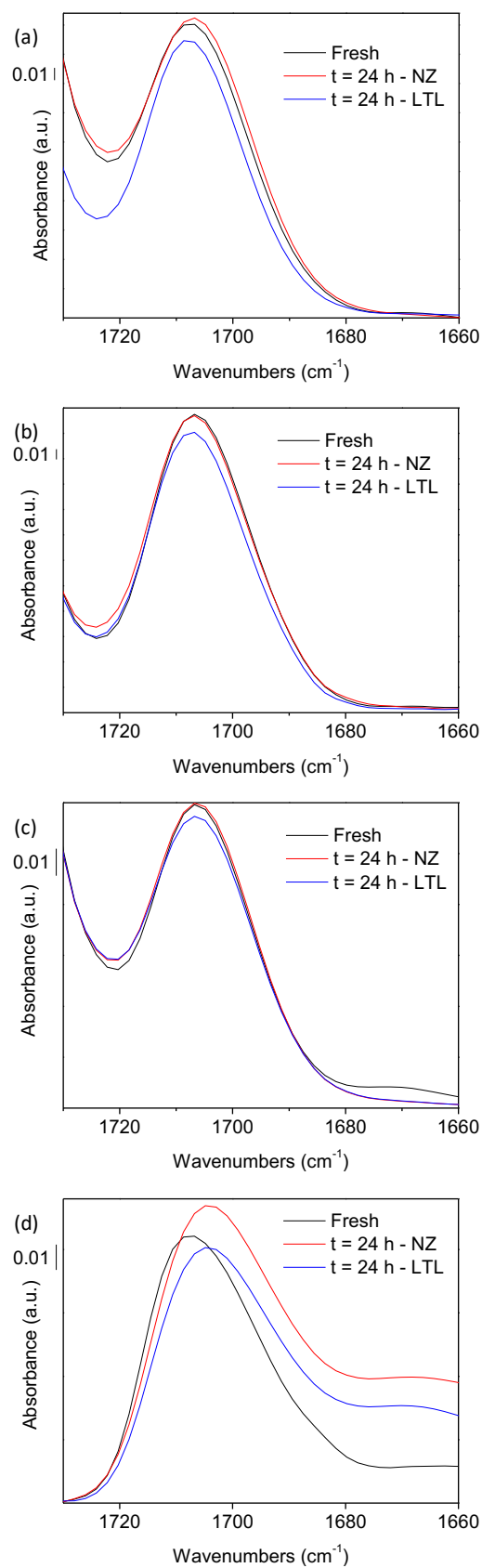
210 by FTIR correspond to the decomposition products possessing P-O-C bonds, while in the
211 presence of LTL nanocrystals, the ZDDP structure is preserved with limited dissociation being
212 detected. Besides, the ZDDP additive present in lubricants SB-C2 and SB-C3 was completely
213 decomposed with no influence of zeolite being detected, which is in agreement with the results
214 obtained by FTIR. A different behavior was recorded for the phenol antioxidant that displayed a
215 high thermal stability both in the presence and in the absence of zeolite. A minor loss, below 5%,
216 was recorded for the -OH FTIR band for samples SA-C2, SA-C3, and SB-C2 (Figure 5), meanwhile,
217 no modification in the ^1H NMR profiles was identified (Figure S7).

218 In contrast to the highly stable fully synthetic base oils studied, the more fragile performance
219 additive can undergo oxidation leading to the formation of aldehydes, ketones and carboxylic acids.
220 They are favoring the progressive oxidation of the performance additives, and lead to formation of
221 heavy polymers (soot) which provokes several problems such as increase of lubricant viscosity and
222 blocking of oil filters. The FTIR band at 1705 cm^{-1} corresponds to the C=O vibrations of the
223 oxidation products (aldehydes, ketones, and carboxylic acid) is found to slightly broaden for the
224 lubricants aged in the absence of zeolite nanocrystals (Figure 6). A deconvolution of this region
225 showed an increase by 6-8% (Figure S8 and Figure S9) which is corresponding to the secondary
226 oxidation products. In the presence of zeolite nanocrystals, lower values were recorded due to the
227 slower formation of oxidation products and to their subsequent adsorption on the zeolite
228 scavengers. The negative values recorded for samples SA-C2 and SA-C3 can be attributed to the
229 partial adsorption of PIB-succinimide that presents C=O vibrations in the same region. Indeed, the
230 FTIR spectra of the LTL zeolite samples separated from the lubricants revealed the presence of
231 PIB-succinimide vibrations[23],[32] (Figure 7 and Figure S10). The ratio ($1705/1770$)
232 between the two bands at 1705 cm^{-1} and 1770 cm^{-1} corresponding to this additive is found to be
233 higher in the zeolite powder samples extracted from oxidized lubricants than in the fresh
234 lubricants, suggesting the absorption of additional "C=O" containing species from oxidation
235 products on the zeolite. Note worthy, the zeolite FTIR structural bands located between 400 and
236 1000 cm^{-1} were all intact after their use in the oxidation experiments, which reflects the high stability
237 of the zeolite structure under the conditions used (Figure S10). This was further highlighted by the
238 XRD patterns showing identical features for zeolite samples recorded before and after being
239 involved in the oil oxidation process (Figure S1).



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Figure 5. FTIR band vibrations of (a) SA-C2, (b) SA-C3, (c) SB-C2, in their fresh form (black) or following 24h of oxidation at 150 °C in absence (red) or presence (blue) of LTL nanozeolite. (d) Evolution of -OH FTIR band area following oxidation.



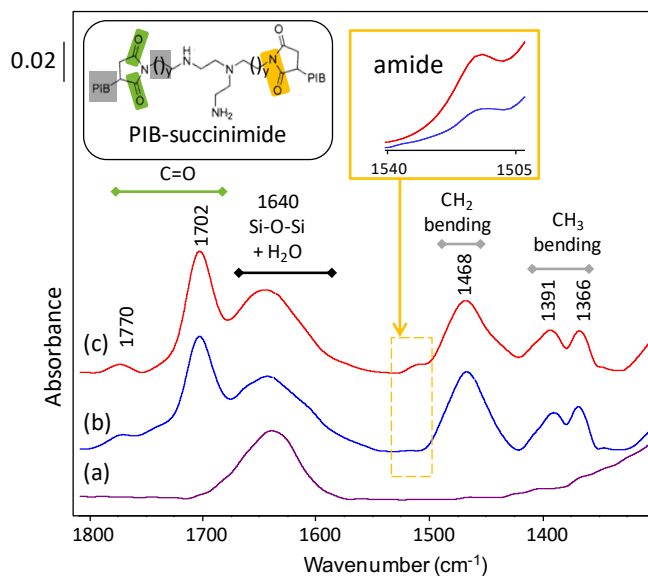
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Figure 6. C=O FTIR band vibrations at 1705 cm⁻¹ of (a) SA-C2, (b) SA-C3, (c) SB-C2, and (d) SB-C3 in their fresh form (black) or following 24h of oxidation at 150 °C in absence (red) or presence (blue) of LTL nanozeolite.



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249 **Figure 7.** FTIR spectra of (a) fresh LTL and LTL extracted after 24 h of heating at 150 °C from (b)
 250 SA-C3, and (c) SA-C2 lubricant samples. *Inset*, one possible structure of PIB-succinimide.

251 4. Conclusions

252 LTL nanozeolite prepared from organic free precursor suspensions with no post-synthetic
 253 treatment is used as a proactive agent to extend lubricant lifetime and thus reduce the
 254 environmental and economic impact from their disposal and recycling. The zeolite demonstrated a
 255 dual action: (1) it showed a high capability in preventing the depletion of ZDDP (zinc
 256 dialkyldithiophosphate) additive at elevated temperatures as proven by ³¹P NMR and FTIR
 257 spectroscopy, and (2) it acted as a scavenger that collects the oxidation products from the lubricants
 258 to prevent the further depletion of additives and oxidation of base oil leading to the formation of
 259 heavy molecules (soot particles).

260 **Supplementary Materials:** available online at www.mdpi.com/xxx/s1

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262 **Conflicts of Interest:** The authors declare no conflict of interest.

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