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Effect of the preparation technique of Cu-ZSM-5 catalysts on the isothermal oscillatory behavior of nitrous oxide decomposition

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Abstract:

A set of Cu-ZSM-5 samples (Si/Al = 25) was synthesized by wetness impregnation, aqueous phase ion exchange and solid-state ion exchange, SSIE. Copper(II) acetate was used as precursor during both wetness impregnation and aqueous phase ion exchange to prepare excessively-exchanged samples (*i.e.* Cu/Al > 1), whereas SSIE was carried out by sublimating copper(I) chloride. Additionally, a Cu-ZSM-5 sample with extremely low Al content (Si/Al = 500) was prepared by impregnation.

The samples were tested in the catalytic decomposition of N₂O, with the aim of studying possible effects of the preparation technique on the isothermal oscillatory behavior of the reaction rate in a series of tests carried out by varying both the temperature and the residence time. The SSIE sample led to a non-oscillating system, whereas the highest Cu content samples prepared by the two aqueous procedures exhibited clear oscillations of the reaction rate. The Cu-ZSM-5 with Si/Al = 500 was quite inactive, but, surprisingly, gave rise to oscillations of both unconverted N₂O and produced O₂ concentrations at the reactor outlet.

A combined IR spectroscopy and H₂-TPR study showed the role of oligomeric Cu_xO_y species with extra-lattice oxygen close to the Al atoms on the observed oscillations. Such species are much more abundant in the samples prepared by either impregnation or ion-exchange, when Cu/Al > 1. In contrast, the sample prepared by SSIE resulted to be rich in Cu⁺ isolated species, active for the reaction, but not inducing oscillation.

31 **Keywords:** Cu- ZSM-5, nitrous oxide, decomposition, oscillation, impregnation, ion exchange, solid state
32 ion exchange.

33 1. Introduction

34 Interest in Cu-substituted zeolites (ZSM-5, Beta, SSZ-13, etc.) is related to their promising properties in
35 DeNO_x lean-burn applications [1,2]. Among them, copper-exchanged ZSM-5 exhibits since the early '90s
36 very interesting and incomparable properties, especially in the reaction of direct decomposition of nitric
37 oxide, of which Cu-ZSM-5 is probably the unique existing effective catalyst [3]. However, as is well
38 documented by decades of continuous papers such a catalyst is unable to sustain the practical operating
39 conditions, most of all due to its poor hydrothermal resistance.

40 Actually, Cu-ZSM-5 shows unique properties in the decomposition of NO, but also very interesting activity
41 in the classical reduction with ammonia (catalyzed at very low temperatures) and in the fascinating
42 alternative of reduction of NO_x with unburned hydrocarbons and/or CO. Such a catalyst is also very active
43 in the decomposition of N₂O which is a harmful compound by itself and also the key intermediate of NO
44 decomposition over such a catalyst.

45 In fact, Nitrous oxide (N₂O) is considered a greenhouse gas, since it lasts approximately 150 years in the
46 atmosphere, it has 310 and 21 times greater warming potential than CO₂ and CH₄, respectively, and it
47 contributes to the destruction of the stratospheric ozone layer. The main anthropogenic sources of N₂O
48 are, *inter alia*, fertilizers, nitric acid, adipic acid, caprolactam and glyoxal production, fossil fuels and
49 biomass combustion, and sewage treatments. As a whole, nitric and adipic acid production plants are
50 considered the largest industrial sources of N₂O emissions, with higher N₂O concentration in tail gas
51 emissions from adipic acid plants (usually 20 – 40 v/v %) than from nitric acid production (around 300–
52 3500 ppm). Indeed, it has been reported that around 10 % of N₂O yearly released into the atmosphere
53 originates from adipic acid production, and therefore much efforts have been made to abate the N₂O
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62 3500 ppm). Indeed, it has been reported that around 10 % of N₂O yearly released into the atmosphere
63 originates from adipic acid production, and therefore much efforts have been made to abate the N₂O
64 deriving from such source. The catalytic N₂O decomposition to N₂ and O₂ is among the most attractive

65 processes for its abatement, as it does not necessitate any reductant species and renders N₂O abatement
66 possible (at the emission source) at lower temperatures (300-500 °C) than the conventional thermal
67 technology. Not only Cu-ZSM-5 but also several other catalysts demonstrated promising performance in
68 the reaction, including hydrotalcites [4,5], mixed-oxides [6,7], perovskites [8] and other metal-exchanged
69 zeolites [9–12]. When catalyzed by a reducible oxide, the reaction proceeds differently from when
70 catalyzed by a reducible cation- exchanged zeolite: to this respect, Cu-ZSM-5 is one of the most
71 promising candidates for the catalytic N₂O abatement, since it shows relatively higher activity at low
72 temperatures in comparison to other metal-exchanged zeolites, as firstly demonstrated by Li and Armor
73 [13].

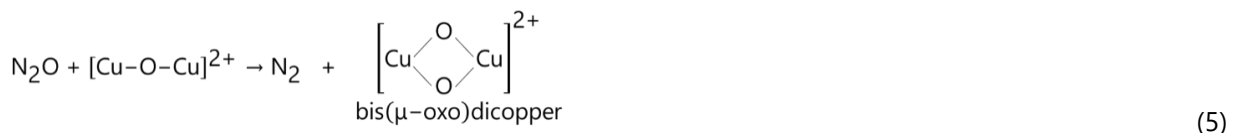
74 However, the most interesting features of Cu-ZSM-5 in this reaction is its ability to induce an oscillatory
75 behavior of the reaction rate under certain reaction conditions. The earliest investigation on the
76 isothermal oscillation of N₂O decomposition over a Cu-ZSM-5 catalyst dates back to 1994, when Lintz and
77 Turek discovered an irregular oscillation of N₂O, NO and O₂ concentrations during an isothermal reaction
78 at 450 °C [14]. A following study by Ciambelli *et al.* demonstrated the effect of both catalyst pre-treatment
79 and reaction temperature on the oscillation pattern and the resulting N₂O conversion [15]. They found
80 that the reducing pre-treatment, during which most of the copper species were reduced to Cu⁺, resulted
81 in a shorter transient period and a slightly higher N₂O conversion than the oxidizing pre-treatment. It was
82 also discovered that the oscillation frequency increased with temperature, though too high temperatures
83 (*i.e.* above 400 °C) could quench, or even eliminate, the oscillation. In a separate study, the effect of
84 residence time on the oscillatory behavior and N₂O conversion was also discussed [9]. Specifically, it was
85 reported that a lower residence time helped improving the regularity of the oscillation, finally leading to a
86 higher N₂O conversion.

87 The oscillatory behavior of N₂O decomposition over Cu-ZSM-5 catalyst was initially associated to periodic
88 changes of copper oxidation states, which exploit the duality of N₂O as both oxidant and reductant
89 species [15]. Based on the premise that both Cu⁺ and Cu²⁺ species may coexist in the catalyst, the reaction
90 mechanism proposed by Ciambelli *et al.* is expressed by the following steps (eq. 1-4) [9]:

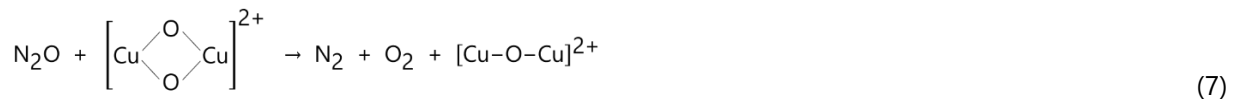


95 Step 1 concerns the adsorption of N₂O on two vicinal Cu⁺ sites, which further leads to the formation of
 96 mono(μ-oxo)dicopper species, [Cu – O – Cu]²⁺, and, simultaneously, to the reduction to N₂. Step 2
 97 describes the reduction of [Cu – O – Cu]²⁺ species by N₂O back to Cu⁺ as well as the decomposition of
 98 N₂O to N₂ and O₂. Step 3 and 4 concern the possibility of spontaneous desorption of extra-lattice oxygen
 99 (ELO) from [Cu – O – Cu]²⁺ species as dioxygen molecule.

100 Different rates of those elementary steps were supposed to cause the oscillation: step 1 is the fastest one,
 101 due to the presence of active Cu⁺ sites, whereas both step 3 and 4 are rate-limiting. Through an operando
 102 UV-vis spectroscopy study, Groothaert *et al.* proposed a similar reaction mechanism, where, instead, the
 103 step 2 was split into two elementary steps (eq. 5 and 6), involving bis(μ-oxo)dicopper species (eq. 5) as
 104 another reaction intermediate [16]:



107 Being the step 6 rate-limiting, the release of O₂ was supposed to be governed by the reduction of bis(μ-
 108 oxo)dicopper species by N₂O back to [Cu – O – Cu]²⁺(eq. 7) and not necessarily to proceed through Cu⁺...
 109 Cu⁺ pairs, as in step 6.



111 With the proposed mechanisms, the authors claimed that the reaction and its oscillatory behavior do
 112 depend on the oxidation state of copper, which in turn depends of the catalyst preparation technique.

113 The synthesis of Cu-ZSM-5 by ion-exchange, especially with copper cations in excess with the respect to
 114 zeolite sites (namely an "over-exchanged" metal-zeolite), has been adopted in many studies, as it is
 115 believed to promote the formation of [Cu – O – Cu]²⁺ species, which actively take part in the reaction
 116 [9,17,18]. Less attention, instead, has been paid to other synthesis techniques, such as impregnation and
 117 sublimation, which may give rise to different oxidation and dispersion states of copper. An XPS/XAES
 118 study by Shpiro *et al.* demonstrated that in over-exchanged Cu-ZSM-5, copper occurred in small clusters
 119 or as isolated Cu⁺/Cu²⁺ ions (depending on the reaction atmosphere), whilst in impregnated Cu-ZSM-5
 120 copper occurred in large aggregates at the zeolite external surface [19]. Spoto *et al.* proposed a solid-
 121 state ion-exchange (SSIE, or sublimation route) synthesis of Cu-ZSM-5 by exchanging the zeolite Brønsted

122 acid sites with sublimated Cu^+ ions [20,21]: SSIE resulted in isolated Cu^+ sites, easily accessible to probes
123 like carbon monoxide and nitric oxide. Actually, the nature of Cu species in the Cu-ZSM-5 has been widely
124 characterized, but no sure conclusion can be drawn yet, and also in relation to the occurrence of
125 oscillation in the decomposition of N_2O , no sure attribution of responsible Cu species still exists.

126 In the present work, we explored three different syntheses of Cu-ZSM-5 catalysts, namely wet
127 impregnation, ion-exchange, and SSIE, using the same H-ZSM-5 parent zeolite ($\text{Si}/\text{Al} = 25$), trying to
128 obtain catalyst with variable copper loading and observe their effect on the conversion and the isothermal
129 oscillatory behavior of N_2O decomposition. Moreover, a further Cu-ZSM-5 sample was also prepared over
130 a very low Al-containing zeolite ($\text{Si}/\text{Al} = 500$) with the purpose to enlighten the effects of not-exchanged
131 copper species. In order to support the results of catalytic activity tests, the catalysts were characterized
132 by means of CO adsorption at room temperature, as followed by IR spectroscopy, and H_2 -TPR
133 (Temperature Programmed Reduction).

134

135 **2. Experimental**

136

137 *2.1. Catalyst synthesis*

138 The H-ZSM-5 support (Si/Al ratio = 25/1) was prepared by calcination of NH_4 -ZSM-5 commercial powders
139 (Alfa Aesar) at 550 °C for 5 h in air, while a second sample of H-ZSM-5 characterized by a very low Al
140 content was already available in a commercial H-form (Zeolyst, $\text{Si}/\text{Al} = 500/1$). A series of samples were
141 prepared: two Cu-ZSM-5 catalysts with different copper loading were prepared by ion exchange (referred
142 to as CZ-EX-A and CZ-EX-B) and by wet impregnation (CZ-IM-A and CZ-IM-B). A fifth sample was
143 prepared by SSIE and will be referred to as CZ-SU. These five samples were prepared over the parent H-
144 ZSM-5 zeolite characterized by the Si/Al ratio equal to 25. Finally, a further sample were prepared via
145 impregnation over the H-ZSM-5 zeolite characterized by a much higher Si/Al ratio, equal to 500 (CZ-IM-
146 500).

147 In a typical wet impregnation, 1 g H-ZSM-5 powder was added to 50 mL of 10 mM (sample CZ-IM-A) or
148 20 mM (sample CZ-IM-B and CZ-IM-500) aqueous solution of $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ and the mixture was
149 kept under vigorous stirring at 80 °C, till complete water evaporation. The impregnated zeolite was
150 directly dried overnight at 60 °C and finally treated in a two-step calcination, as detailed below.

151 In a typical ion exchanged, 50 mL of 10 mM (sample CZ-EX-A) or 20 mM (sample CZ-EX-B) aqueous
152 solution of $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ were used to exchange 1g of H-ZSM-5. The mixture was kept under
153 vigorous stirring at 50 °C for 2 h. The ion exchanged zeolite was recovered by centrifugation and
154 repeatedly washed with bidistilled water and ethanol before drying overnight at 60 °C.

155 The sample CZ-SU was prepared as follows: before sublimation, 0.033 g CuCl and 0.5 g H-ZSM-5 were
156 separately treated under vacuum (10^{-3} mbar) at 100 °C for 2 h and at 400 °C for 3 h, respectively. Then,
157 they were mixed and heated under vacuum in a double-bulb glass cell at 300 °C for 20 min. A final
158 outgassing treatment at 500 °C was carried out in order to remove excess CuCl.

159 The six catalysts were finally calcined under a reductive environment (333 ml min^{-1} of He at 550 °C for 2 h)
160 and subsequently under a mild oxidative environment (333 ml min^{-1} of 1%-vol O_2 in He gas at 550 °C for 2
161 h).

162

163 *2.2. Catalytic activity testing*

164 Before catalytic tests, the catalyst powders were pressed and sieved at the average size of 250 μm . 100 mg
165 catalyst was used in most of the tests. A typical flow-reactor setup with a fixed-bed U-tube Quartz reactor,
166 a K-type thermocouple, a PID-controlled vertical furnace was used in the catalytic activity testing. A non-
167 dispersive infrared (NDIR) analyzer was connected to the reactor exit. Prior to the test, the catalyst was
168 pre-reduced under 200 ml min^{-1} of He at 550 °C for 2 h. The tests were mostly carried out by flowing a
169 200 ml min^{-1} (W/F ratio = $0.03 \text{ cm}^3 \text{ s}$, where W = catalyst weight and F = feed gas volumetric flow rate) of
170 1000 ppm of N_2O in He through the reactor while the reactor temperature was kept isothermal at 400 °C.
171 The reaction under such conditions was kept running for about six hours to better observe the reaction
172 oscillation. A separate set of tests with the same flow conditions was performed by lowering and raising
173 the reaction temperature periodically in the 350 - 450 °C range in order to observe the effect of
174 temperature on the oscillatory behavior. Finally, a set of isothermal tests with different flow conditions was
175 performed by varying the W/F ratio between 0.015 and $0.06 \text{ g cm}^3 \text{ s}$ in order to observe the effect of
176 residence time on the reaction oscillation.

177

178 *2.3. Catalyst characterization*

179 The catalysts specific surface area (SSA) and total pore volume were measured by N_2 physisorption at -196
180 °C on powders pre-outgassed at 250 °C for 2 h (Tristar II 3020 Micromeritics). SSA was calculated
181 according to the BET (Brunauer-Emmett-Teller) method, the corresponding values being reported in Table
182 1, along with other relevant data.

183 The samples copper loading (wt%) was measured on each sample by energy dispersive X-ray (EDX)
184 analysis (AZTec, Oxford Instruments) on three different areas of about 0.1 mm^2 : the average values (wt%)
185 are reported in Table 1.

186 For IR measurements, the powders were pressed as thin self-supporting wafers (*ca.* 8 mg cm⁻²) and were
187 outgassed at 500°C for 2 h in a homemade quartz cell equipped with (IR transparent) KBr windows. The IR
188 spectra were recorded at 2 cm⁻¹ resolution on a BRUKER EQUINOX-66 spectrometer equipped with a
189 mercury cadmium telluride (MCT) cryodetector. IR spectra were recorded by dosing at room temperature
190 (r.t.) increasing amounts of CO (1-3000 Pa equilibrium pressure range) on the outgassed samples. In order
191 to better allow comparison, the IR spectra in both Figure 6 and 7 were normalized with respect to the
192 integrated absorption of framework overtone bands (2090 – 1550 cm⁻¹), though wafers with very similar
193 area and weight were used. The difference spectra in Figure 7 were obtained by subtracting the IR
194 spectrum of the naked wafer (before CO adsorption): after CO adsorption, an evacuation step at r.t. was
195 performed each time, in order to check the reversibility of the interaction.

196 The catalysts reducibility was analyzed by H₂-TPR (Temperature Programmed Reduction) on a TPD/R/O
197 instrument (TPDRO 1100, Thermo Scientific). Prior to the analysis, a reductive pre-treatment (40 ml min⁻¹
198 of He at 550 °C) was applied to about 50 mg as-calcined catalyst for 1 h. The TPR analysis was carried out
199 by feeding 20 ml min⁻¹ of 5%-v H₂ in Ar to the sample holder and under a gradual heating from r.t. to 800
200 °C at a rate of 10 °C min⁻¹.

201

202 **3. Results and discussion**

203

204 *3.1. Textural properties of the catalysts*

205 XRD patterns of the prepared Cu-ZSM-5 samples did not show appreciable differences with respect to the
206 parent zeolite, except with samples CZ-IM-B and CZ-IM-500 (Figure S1 Supporting Information), where
207 two sharp peaks were detected at 2θ = 35.5 and 38.7°, likely due to the formation of bulky CuO at the
208 external surface of the zeolite particles, as confirmed by FESEM analysis (Figure S1).

209 As far as the metal content is concerned, the Cu wt.% values measured by EDX are reported in Table 1. In
210 principle, the neutralization of two zeolite negative charges by a single divalent Cu²⁺ cation is only
211 possible if the former are sufficiently close, as it may occur in low Si/Al ratio zeolites [22]. On the other
212 hand, monovalent (Cu²⁺-OH)⁺ species were found to compensate one zeolite negative charge in ion-
213 exchanged Cu-ZSM-5 samples prepared using copper(II) precursors [23,24]. Thus, only copper loadings
214 larger than 3.7 wt% (corresponding to a Cu/Al ratio of 1 for a H-ZSM-5 with Si/Al = 25) may be actually
215 indicative of excessively-exchanged samples. In contrast, we found that with all samples the Si(OH)Al
216 Brønsted sites were not entirely exchanged (*vide infra*), even with Cu/Al > 1.

217 The impregnated samples (CZ-IM-A and CZ-IM-B) showed markedly different copper loading, close to the
218 nominal value, whereas just a smaller difference was observed with the ion-exchanged samples (CZ-EX-A

219 and CZ-EX-B). Actually, the pH of the exchange solution and the copper precursor (acetate vs nitrate, for
220 instance) are probably the most determinant factors affecting the eventual copper loading in ion-
221 exchanged samples, as reported in the literature [25]. Residual Cl (0.6 wt.%) was evidenced by EDX
222 measurements in CZ-SU, suggesting the presence of some unreacted CuCl precursor (and/or its
223 derivatives produced during calcination). The presence of Cu- and Cl-containing particles at the external
224 zeolite surface was confirmed by FESEM/EDX analysis (Figure S2). As far as the SSA of the samples is
225 concerned, the values in Table 1 show that the S_{BET} of the Cu-ZSM-5 samples is generally lower than that
226 of the parent H-ZSM-5 ($412 \text{ m}^2 \text{ g}^{-1}$). Both S_{BET} and total pore volume decrease at increasing copper
227 loading. Actually, the copper richest sample (CZ-IM-B, 6.5 wt%) exhibits the lowest values of both S_{BET} (250
228 $\text{m}^2 \text{ g}^{-1}$) and pore volume, thus suggesting the presence of CuO aggregates also within the zeolite
229 channels.

230

231 3.2. Catalytic activity testing

232 Figure 1A shows the evolution of N_2O outlet concentration during the isothermal reaction at $400 \text{ }^\circ\text{C}$, over
233 the five catalysts prepared on the ZSM-5 sample characterized by the Si/Al ratio equal to 25 (the W/F ratio
234 was maintained at $0.03 \text{ g cm}^{-3} \text{ s}$ in each test).

235 All the catalysts exhibit a certain activity in the decomposition of N_2O , though quite variable among the
236 different samples. Such a property seems to be basically correlated to the catalyst copper content, rather
237 than to the preparation procedure. For instance, the CZ-EX-A sample is able to convert only about 10% of
238 the fed N_2O , probably because it contains the lowest amount of copper (2.4 wt.%). Conversely, CZ-IM-B
239 can convert about 75% of the fed N_2O , even if the reaction occurs with an oscillation, and indeed it
240 possesses a much higher Cu loading (6.5 wt%). However, with some of the catalysts, the outlet N_2O
241 concentration does not reach a stable and constant value during the time on stream, but exhibits an
242 oscillating pattern, in agreement with previous works [9,14,15]. In particular, the impregnated samples
243 (CZ-IM-A and CZ-IM-B) demonstrate a very pronounced and regular oscillatory behavior, while only the
244 copper richest exchanged zeolite sample (CZ-EX-B) demonstrates a similar pattern. Finally, no oscillations
245 were observed over the CZ-SU sample, notwithstanding its significant N_2O decomposition activity. The
246 CZ-SU sample, indeed, seems to have different copper species, in agreement with the fact that it was
247 prepared by using a Cu^+ precursor (CuCl), whereas both the impregnated and the ion-exchanged samples
248 were prepared by using a Cu^{2+} precursor ($\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$). The oscillation induced by CZ-IM-B started
249 quite promptly after the reagent flowed through the catalytic bed, while the reaction over CZ-IM-A

250 started to oscillate after a delay (or “ignition time”) of almost one hour, as occurred in previous works
251 [9,15,18]. Such a delay is also observed with CZ-EX-B, yet it seems shorter than that of CZ-IM-A.
252 CZ-IM-B provides the highest average N₂O conversion, whereas CZ-IM-A and CZ-EX-B have comparable
253 activity (and Cu content, Table 1). In the decomposition test carried out over CZ-SU, despite the slightly
254 higher Cu content, N₂O conversion reaches about 50%, i.e. it is very similar to the average performances
255 of both CZ-IM-A and CZ-EX-B.

256 Fig.1B reports the magnification of the oscillation in the time range from 175 to 245 min for the three
257 oscillating catalysts: comparison of the behavior of CZ-IM-A and CZ-IM-B shows that the oscillation
258 frequency seems to increase with the copper content. While the former sample induces a 3.7 mHz
259 oscillation with a regular amplitude (*ca.* 180 ppm), the latter produces a more rapid oscillation with an
260 average frequency of 4.5 mHz and variable amplitudes. The oscillation induced by CZ-EX-B has a
261 remarkable regularity, in that no decay of amplitude is observed even after an overnight test. However,
262 the oscillation occurs at a lower frequency (1.4 mHz) and the maxima of the oscillation seem to last longer
263 than the minima.

264

265 3.2.1. *Effect of temperature*

266 Figure 2 reports the results of isothermal tests with a step change of temperature carried out over the
267 samples that exhibited the oscillation, namely CZ-IM-A, CZ-IM-B and CZ-EX-B; the temperature step
268 progression was as follows: 350 °C – 375 °C – 400 °C – 375 °C – 400 °C – 350 °C. The lowest temperature
269 range was selected to better observe the sensitivity of the oscillation to the temperature change. It can be
270 observed that the oscillation induced by these three catalysts generally occurs at higher temperatures; the
271 higher the temperature, the higher the oscillation frequency. The topmost plot in Fig.2A shows the test
272 progression over CZ-IM-A. An oscillation with low frequency (at about 1.39 mHz) and low amplitude is
273 observed at 375 °C while at a higher temperature the oscillation becomes very regular and has a much
274 higher frequency (about 3.13 mHz). At 350 °C, the oscillation is not observed, probably due to a too short
275 isotherm duration. The N₂O conversion in this range of temperature spans from 15% to 50%, the highest
276 conversion being achieved at 400 °C.

277 The middle plot in Figure 2A summarizes the test progression over CZ-IM-B: the conversion span is clearly
278 much higher than with the other two catalysts in the series (about 50% at 375 °C and 80% at 400 °C).
279 Likewise, the oscillation pattern induced by the catalyst varies with temperature: lower-frequency
280 oscillation is observed at the lower temperature (1.85 mHz at 375 °C) and high-frequency oscillation is

281 observed at higher temperature (4.17 mHz at 400 °C). On the second repetition, the oscillation frequency
282 at 375 °C slightly decreases to about 1.67 mHz while that at 400 °C decreases to 3.70 mHz.

283 The bottommost plot in Fig.2A reports the test progression over CZ-EX-B: the sample exhibits a unique
284 behavior, in that it induces a very low frequency oscillation. At the lowest temperature, the oscillation
285 seems to be nonexistent, and the conversion is very low (almost 5%). During the second isotherm, where
286 the temperature was increased by 25 °C, the reaction hardly oscillated except right towards the end of the
287 isotherm, where a “valley” of N₂O concentration appears, presumably marking the beginning of the
288 oscillation. This temperature step was eventually repeated right after the completion of the first isotherm
289 at 400 °C and was carried out almost twice as long to allow the oscillation to occur. In this step, a regular
290 oscillation occurred very slowly at a frequency of 0.49 mHz (almost equal to 2 oscillations per hour). At
291 400 °C, the oscillation appears more frequent at an average frequency of 1.28 mHz and the temperature
292 switch does not seem to affect the oscillation at the same temperature in the second repetition. Because
293 of the long oscillation induction time, we repeated the isotherm at 350 °C in the last step for few more
294 hours. After about 3 h of a flat, non-oscillating reaction, the concentration of N₂O oscillated very slowly at
295 a frequency of about 0.18 mHz, which is almost equal to 2 oscillations in 3 h (see the inset). As previously
296 seen in Fig.1, CZ-EX-B is the only sample in the series whose oscillation takes a unique form; the duration
297 of the maxima is incomparably longer than that of the minima.

298 Similar tests were also conducted for CZ-EX-A and CZ-SU, the two samples that did not induce an
299 oscillatory behavior during the reaction at the previously investigated temperature (400 °C). The
300 conversion range was smaller for CZ-EX-A, but larger for CZ-SU (up to 80% at the highest temperature).
301 We have performed the tests with a longer duration per isothermal step, yet we have never observed any
302 oscillations during the reactions.

303

304 *3.2.2. Further insight into the oscillations' phenomenon*

305

306 Figure 3 analyses in more detail what happens during the oscillations of the rate of N₂O decomposition in
307 the entire gas phase. As it will be done in the following graphs, Figure 1 and 2 show the pattern of the
308 concentration of the unconverted N₂O at the reactor outlet as detected by a continuous gas analyzer. This
309 is done for the sake of simplicity, but the adopted system allows analyzing the outlet concentration
310 profiles of O₂, NO and NO₂ too.

311 Looking at the plots reported in Figure 3 related to a kinetic test carried out over CZ-IM-A chosen as
312 representative sample, the oscillation of the outlet concentration of N₂O are accompanied by the

313 oscillations of the produced O_2 , and by the oscillating by-production of NO and NO_2 , as well. The average
314 production of molecular oxygen is basically in agreement with the average conversion of nitrous oxide,
315 although the shape of the two signals appear not specular and in some way, different. Different
316 considerations can be made on NO_x formation ($NO+NO_2$) which are not expected from the stoichiometry
317 of pure N_2O decomposition. In fact, Turek [26] already observed the production a certain amount of NO in
318 the oscillating decomposition of N_2O , while Fanson et al. [27] provided spectroscopic evidence that
319 surface nitrate species are present under oscillatory conditions. Thus, Fanson et al. proposed a slow build-
320 up of surface nitrates during oscillating cycle, followed by the rapid nitrate decomposition responsible of
321 an increase in the rate of N_2O decomposition.

322 The present results are in agreement with those previous findings. We found the by-production of both
323 NO and NO_2 , *i.e.* two secondary products of N_2O conversion (actually, products of the oxidation of N_2O
324 and not of its decomposition). They are always present in a simultaneous way and at a fixed NO/ NO_2 ratio
325 (probably at its thermodynamically limited value), because the interconversion of NO into NO_2 is strongly
326 activated by Cu-ZSM-5 [28], and can be roughly estimated with a selectivity of around 3-4% with respect
327 to the amount of converted N_2O . Such a NO_x by-production occurs in form of spikes or peaks
328 appearances, rather than proper oscillations. Such spikes appear to be simultaneous for both NO and
329 NO_2 , but also for O_2 . Actually the oscillations of O_2 appear to much less irregular than those of the
330 unconverted nitrous oxide. Such a peak production of O_2 , NO and NO_2 always occurs at the beginning of
331 the period of maximum activity of the catalyst towards the decomposition of N_2O , since the concentration
332 of the unconverted nitrous oxide is at its minimum in the cycle and the oxygen production is reaching its
333 maximum in the oscillation' period. Moreover, the mass balance is consistent with the over-emission of
334 NO_3 -like species, whose accumulation and subsequent decomposition was proposed by Fanson et al. [27].
335 Such a behavior is a general trend for all the N_2O decomposition tests, where the oscillations have been
336 observed.

337 A further test of N_2O decomposition was carried out also over the CZ-IM-500 sample (Figure 4), with the
338 purpose of enlightening the effects of not-exchanged copper species. Surprisingly, despite the presence
339 of very few exchangeable sites due to the low Al content ($Si/Al = 500$), the catalyst does possess a very
340 weak, though measurable, activity in the decomposition of N_2O . We can evaluate around 4-5% N_2O
341 conversion, as also confirmed by the production of the corresponding and stoichiometric amount of O_2 .
342 However, even if somewhat surprising, such results indirectly confirm that the ionically exchanged Cu
343 species are responsible for the activity in the N_2O decomposition, since the level of measured activity is

344 very far from what expected on the mere copper content (6.2 %wt.). The comparison with the results
345 reported in Figure 1 is blatantly revealing the difference.

346 Even more unexpectedly, we observed a sort of dynamic and periodic behavior of both N₂O and O₂ outlet
347 concentration too, as well as of the by produced NO and NO₂. We may describe it as the appearance of
348 "oscillations", even if a careful look reveals that the phenomenon would be better described observing the
349 appearance of periodic peaks of products production and peaks of reactant consumption over stable
350 values of concentration. It is clear that the peak of O₂ production is associated to the peak of N₂O over-
351 consumption, and it is simultaneous to the peak production of NO and NO₂ (with same level of selectivity
352 observed over the CZ samples characterized by a much lower Si/Al). However, such a phenomenon shows
353 a period of the same order of magnitude of that observed for the oscillations over the Cu-ZSM-5 catalysts
354 prepared from parent zeolite with Si/Al = 25.

355

356 3.2.3. *Effect of residence time*

357 Figure 5 finally summarizes the results from the isothermal tests with various W/F ratios. Only the
358 oscillation-inducing catalysts, namely CZ-IM-A, CZ-IM-B and CZ-EX-B, were tested. Previous experiments
359 were conducted with constant W/F ratio (0.03 g cm⁻³ s), whereas in this series of experiments, the
360 temperature was kept constant at 400 °C while the W/F ratio was halved (0.015 g cm⁻³ s) and doubled
361 (0.06 g cm⁻³ s). The plots in Fig.3A show the complete transient profile of N₂O outlet concentration within
362 the first hours of the tests, during which the eventual ignition of the unsteady-state phenomenon occurs,
363 while in Fig.3B the respective magnified profiles are reported with the purpose of better analyzing the
364 oscillating phenomenon and accurately characterizing its features. Generally, it appears evident that, over
365 all the three catalysts, the oscillatory behavior is significantly affected by the contact time. Doubling the
366 W/F ratio to 0.06 g cm⁻³ s obviously leads to an increment of N₂O conversion. The effect of the W/F ratio
367 on the oscillations seems to be not negligible, as a general trend of frequency enhancement with
368 increasing W/F is observed over all the samples. However, in the case of the impregnated samples at the
369 longest residence time explored, the oscillations seem to decay. Such an effect is not observed with CZ-
370 EX-B, over which the phenomenon is still observed, even after a much longer induction time (two hours of
371 transitory period). Finally, the features of the oscillation induced by CZ-EX-B at such W/F ratio differ from
372 those at lower W/F ratio; indeed, besides showing lower amplitude, the oscillation maxima have a shorter
373 duration than the minima, as if the superimposition of two different phenomena was taking place.

374 The results of the catalytic activity tests showed a stronger correlation of the N₂O conversion to the
375 catalyst copper content rather than to the adopted preparation technique. On the other hand, the

376 oscillatory behavior seems to depend on the type of copper precursor: indeed, the use of copper (I)
377 precursor leads to a non-oscillating system. The effect of temperature on both reaction conversion and
378 oscillatory behavior is clear: the higher the temperature, the higher the conversion, and the higher the
379 oscillation frequency. The effect of residence time is clearly observed on the conversion, yet it cannot be
380 neglected on the oscillatory behavior: whilst a higher residence time always leads to higher N₂O
381 conversion, in certain cases, it leads to an oscillation decay.

382

383 3.3. Catalysts characterization

384 In order to shed light on the species responsible for the different catalysts behavior, we focused on the
385 characterization of four representative samples prepared by different procedures, *i.e.* CZ-IM-B, CZ-EX-A,
386 CZ-EX-B, and CZ-SU. The first one showed the highest N₂O conversion and an oscillatory behavior; the
387 second one showed limited conversion and no oscillatory behavior; the last two showed a comparable
388 N₂O conversion, but only CZ-EX-B showed the oscillatory behavior.

389

390 3.3.1. IR spectroscopy study of CO adsorption at *r.t.*

391

392 3.3.1.1. Consumption of Brønsted acidic sites after exchange procedures

393 The O–H stretching region of the IR spectra of the parent H-ZSM-5 zeolite and the selected Cu-ZSM-5
394 samples pre-treated under vacuum at 500°C is reported in Figure 6. The parent H-ZSM-5 (curve 1) shows
395 a sharp peak at 3745 cm⁻¹, a broad and weak absorption centered at 3660 cm⁻¹ and an intense band at
396 3610 cm⁻¹. The three bands are respectively assigned to the O–H stretching vibrations of (i) defective Si-
397 OH groups (silanols, mostly located at the zeolite external surface), (ii) extra-framework Al-OH groups,
398 stemming from dealumination, and (iii) bridged Si-(OH)-Al groups (Brønsted acidic sites) [21,29].

399 With the Cu-ZSM-5 samples (curves 2-5), the band of Brønsted sites is only partially consumed,
400 independently of the synthesis procedure. The ratio between the integrated absorbance of the 3610 cm⁻¹
401 band of the parent H-ZSM-5 and of the same band in the exchanged samples was used to calculate the
402 exchange percentages (%_{EX}) reported in Table 1. It has to be noticed that with respect to the
403 nomenclature introduced by Iwamoto *et al.* [30] (*i.e.* Cu/Al = 0.5 for 100% exchange), the values in the
404 Table 1 simply refer to the percentage of exchanged Brønsted sites (independently of the copper
405 oxidation state). Ion-exchanged samples showed the lowest %_{EX}, *i.e.* 47 (CZ-EX-A) and 50 %_{EX} (CZ-EX-B).
406 Notably, the double concentration of the exchange solution used for CZ-IE-B yielded an increase in the
407 copper content (2.4 vs 3.8 wt%), but only a slightly higher %_{EX}. In principle, if zeolite negative charges

408 were balanced by monovalent $(\text{Cu}^{2+}\text{-OH})^+$ species, a copper content not exceeding 1.79 and 1.90 wt%
409 should be found for 47 and 50 %_{EX} (for Si/Al = 25). Based on this analysis, the percentages of copper ions
410 in exchange position (% Cu_Z in Table 1) is ca. 75 (for CZ-EX-A) and 49 % total copper (for CZ-EX-B). The
411 obtained % Cu_Z must be taken as maximum limit values, since they were calculated by assuming that each
412 copper ion exchanges one Brønsted site (lower values would be obtained by assuming that a single Cu^{2+}
413 ion can exchange two Brønsted sites). The Cu species not directly exchanging zeolite acidic protons are
414 clearly more abundant for sample CZ-EX-B. These may include: *i*) CuO particles formed by decomposition
415 (during calcination) of precipitated $\text{Cu}(\text{OH})_2$ phase; *ii*) Cu species exchanging external Si-OH groups; *iii*)
416 oligomeric Cu_xO_y structures with extra-lattice oxygen (ELO) formed within zeolite channels. The mild pH
417 (5.6 - 5.8) and concentration (20 and 40 mM) of the exchange solutions should in principle limit the
418 precipitation of $\text{Cu}(\text{OH})_2$. Actually, both IR spectroscopy of adsorbed CO and H_2 -TPR (*vide infra*) of CZ-EX-
419 B showed the possible presence of limited amount of CuO particles, which were not detected by XRD and
420 FESEM. In contrast, with CZ-EX-B only, the integrated absorbance of the Si-OH band at 3745 cm^{-1} was
421 almost halved, suggesting that also some of the external Si-OH groups were exchanged, as previously
422 observed with copper/silica systems [31]. Finally, the formation of structures with ELO resulting from the
423 hydrolysis of hexaaquacopper(II) complex $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ and its polycondensation reactions is likely to
424 occur at the adopted exchange temperature and concentration [2][32][33], and is supported by the pore
425 volume values. Notably, divalent structures with ELO like those represented in eq. (3) and (5) (*i.e.* oxo- and
426 bis(μ -oxo)-dicopper species) cannot contribute to the copper excess if bridged on two zeolitic sites.
427 Rather, polyoxocations with a number of Cu ions ≥ 2 and with one (or two) positive charges should
428 exchange one (or two) Brønsted sites. The fate of such species upon calcination and reducing treatment is
429 uncertain. One possibility is the formation of easily reducible Cu_Z^{2+} ions bridged with Cu_xO_y oligomers via
430 oxo- (or bis(μ -oxo)) bridges. On the other hand, Ismagilov et al. [34][35] observed the formation of 1D
431 chain-like structures (*e.g.* $\text{--- O}^{2-}\text{---Cu}^{2+}\text{---O}^{2-}\text{--- Cu}^{2+}\text{--- O}^{2-}\text{---}$) stabilized inside the channels of
432 dehydrated Cu-ZSM-5 samples prepared by ion-exchange with aqueous copper acetate solutions at 60
433 and 80°C. The chain structures were found to be easily reduced and re-oxidized, being even capable of
434 self-reduction, and stabilizing states of copper ions with mixed valence $\text{Cu}^{2+}/\text{Cu}^+$, *i.e.* showing those
435 features that are believed to be indispensable for the oscillating behavior.

436 With respect to ion-exchanged samples, higher %_{EX} are obtained with CZ-SU (71 %) and CZ-IM-B (68%),
437 corresponding to a % Cu_Z of 60 and 39 %, respectively. With CZ-SU, the Cu species not in exchange
438 position mostly consist of unreacted CuCl precursor and its derivatives produced during calcination,
439 whereas the Si-OH groups were not exchanged. As expected, sample CZ-IM-B showed the largest copper

440 loading but the lower % Cu_z . Indeed, the impregnation method, besides yielding exchanged ionic species,
441 results in the formation of significant amount of *i*) CuO particles (both intra- and extra-porous) formed by
442 Cu acetate decomposition during calcination, and *ii*) Cu_xO_y structures with ELO formed within zeolite
443 channels. Finally, also with CZ-IM-B, the Si-OH groups were not exchanged, although the copper
444 precursor solution was the same as for CZ-EX-B: this could be due to the solvent evaporation during
445 impregnation, implying a pH increase that likely disfavors Si-OH deprotonation/exchange [31].

446

447 3.3.1.2. CO adsorption at r.t.

448 CO adsorption at r.t. as followed by IR spectroscopy is widely used in the characterization of Cu-ZSM-5
449 [21,25,29,36–39]: Figure 7 reports difference spectra obtained after dosing CO (1 – 5000 Pa) on the
450 selected Cu-ZSM-5 samples. The main features are the IR bands due to the formation of mono- (2157 cm^{-1})
451 and di-carbonyl (2177 and 2150 cm^{-1}) complexes on exchanged Cu^+ ions (Cu_z^+) [21,29]. Besides those, a
452 shoulder at *ca.* 2135 cm^{-1} is observed with CZ-SU, CZ-IM-B and, to a lesser extent, with CZ-EX-B.
453 Moreover, mono-carbonyl complexes forming on Cu_z^+ are not reversible upon outgassing at r.t.

454 At low coverage, a strong absorption ascribed to $Cu_z^+(CO)$ complexes is observed at 2157 cm^{-1} : such
455 species are progressively consumed with increasing CO equilibrium pressure, and simultaneously two
456 bands, due to symmetric (2177 cm^{-1}) and asymmetric (2150 cm^{-1}) stretching modes of $Cu_z^+(CO)_2$
457 complexes, grow in intensity. The isosbestic point at *ca.* 2153 cm^{-1} clearly indicates that the di-carbonyl
458 species form at the expense of the former. Interestingly, the isosbestic point is well defined with CZ-SU
459 and CZ-EX-A (which does not shows an oscillating behavior), but not with CZ-EX-B and CZ-IM-B. Such a
460 difference suggests the possible heterogeneity of Cu_z^+ sites in the latter samples. Actually, several works
461 reported the existence of at least two kinds of Cu^+ sites in Cu-ZSM-5 [29,36–38]. In particular, it was
462 shown that CO molecules are strongly adsorbed on Cu^+ sites coordinated by two lattice oxygen atoms
463 (the corresponding IR band absorbing at 2159 cm^{-1}), whereas are weakly adsorbed on Cu^+ sites
464 coordinated by three lattice oxygen atoms (the corresponding IR band absorbing at 2151 cm^{-1}) [36,37].
465 The presence of Cu_xO_y structures with ELO close to a Cu^+ site in exchange position may actually be the
466 reason of the observed heterogeneity. Such hypothesis seems to be confirmed by comparing the
467 integrated absorbance of the symmetric and asymmetric IR stretching modes of the di-carbonyl
468 complexes on the four samples. Normalized difference IR spectra obtained at the same CO equilibrium
469 pressure (*i.e.* 1,2 kPa) were curve-fitted by using five components with Voigt profiles, the results of which
470 are shown in Figure S3 (Supporting Information). Notably, the ratio between the integrated absorbance of
471 the bands at 2177 cm^{-1} and 2150 cm^{-1} is much smaller for CZ-IM-B and CZ-EX-B (0.25 and 0.22,

472 respectively) with respect to CZ-SU and CZ-EX-A (0.40 and 0.35, respectively). Such observation suggests
473 that there may be an additional IR component that contributes to the intensity of the band 2150 cm^{-1} in
474 CZ-IM-B and CZ-EX-B, in agreement with the broader FWHM of such band ($9.4, 8.1, 7.5$ and 6.1 cm^{-1} for
475 CZ-IM-B, CZ-EX-B, CZ-SU and CZ-EX-A respectively). According to ref [36] and [37], mono-carbonyl
476 complexes on weaker Cu^+ sites may form at a higher CO equilibrium pressure (*i.e.* where stronger sites
477 already form di-carbonyl complexes), thus giving rise to an IR band overlapping to that of di-carbonyl
478 complexes at 2150 cm^{-1} . This interpretation would be in agreement with the different sharpness of the
479 isosbestic point at 2153 cm^{-1} . The different ability to coordinate one or two CO molecules may depend on
480 the different coordination sphere of Cu_z^+ , which could be affected by the vicinity of Cu_xO_y structures with
481 ELO. Interestingly, the two samples characterized by such type of heterogeneity are those showing the
482 oscillating behavior in the catalytic tests.

483 Besides IR bands due to carbonyl species forming on Cu^+ sites in exchange position (Cu_z^+), the
484 assignment of the shoulder at 2135 cm^{-1} that starts to grow at a low coverage in IR spectra concerning
485 with CZ-SU is not straightforward. Spoto *et al.* observed a similar shoulder (though located at 2142 cm^{-1})
486 on a sample prepared by SSIE and assigned it to mono-carbonyl complexes formed on CuCl aggregates
487 that were either trapped in the zeolite channels or located at the external surface of the zeolite particles.
488 Notably, $\text{Cu}^+\text{-CO}$ complexes absorbing at $2132\text{-}2137\text{ cm}^{-1}$ have also been observed to form on both
489 supported Cu_2O and CuO [25,39,40]. Indeed, heat treatment under vacuum is known to yield reduction of
490 some Cu^{2+} to Cu^+ at the CuO particles surface [41,42]. Actually, the presence of both CuO and CuCl in CZ-
491 SU were evidenced by $\text{H}_2\text{-TPR}$ (*vide infra*) and EDX measurements (Table 1), thus supporting both the
492 assignments. On the other hand, $\text{H}_2\text{-TPR}$ measurements evidenced the presence of CuO on CZ-IM-B and,
493 to a lesser extent, on CZ-EX-B. Thus, the shoulder observed at 2135 cm^{-1} in the IR spectra of CZ-IM-B may
494 is assigned to $\text{Cu}^+\text{-CO}$ complexes forming onto the partially reduced surface of some CuO particles. This
495 assignment is supported by CO adsorption onto CZ-IM-500 sample (Figure S4), for which both XRD and
496 TPR showed the presence of CuO particles. Indeed, the IR spectra taken at increasing CO coverage onto
497 CZ-IM-500 showed, as a main feature, a band at 2132 cm^{-1} (shifting to 2127 cm^{-1} with coverage) assigned
498 to $\text{Cu}^+\text{-CO}$ complexes forming onto the partially reduced surface of CuO . Weak bands due to mono- and
499 di-carbonyls forming on exchanged Cu^+ sites are also observed, but their intensity is definitely lower than
500 that observed with CZ-IM-B, according to the lower Al content.

501 Finally, the weak band at 2108 cm^{-1} (observed with all the Cu-ZSM-5 samples and stable after evacuation
502 at r.t.) could be due to either CO molecules adsorbed through the O end [43] or the adsorption of CO
503 molecules on reduced copper species (*i.e.* $\text{Cu}^0\text{-CO}$) present, however, in a minor amount [44].

504

505 3.3.2. H_2 -TPR analysis

506 Figure 8 shows the H_2 -TPR spectra of the pre-reduced catalysts. Usually, the reduction of copper species
507 in zeolites occurs in two ranges of temperatures: namely, below 300 °C, where reduction of Cu^{2+} to Cu^+
508 and/or to Cu^0 occurs, and above 300 °C, where reduction of Cu^+ to Cu^0 occurs [44–46].

509 In most of the samples, the reduction ends at relatively low temperatures, *i.e.* below 400-450°C, as
510 expected for samples loaded with excess copper. Only with CZ-EX-A, the second reduction peak is
511 observed at 510°C. Actually, Bulánek *et al.* showed that the last peak position in Cu-ZSM-5 H_2 -TPR spectra
512 is shifted to a higher temperature at decreasing copper contents [45].

513 The H_2 -to-Cu molar ratios (H/Cu) of the investigated samples (*i.e.* the ratio between the total consumption
514 of H_2 and the total amount of Cu measured by EDX) are between 0.5 (corresponding to 100% Cu(I)) and
515 1.0 (corresponding to 100% Cu(II)), as reported in Table 1. CZ-IM-500 sample shows an H/Cu ratio close to
516 unity, in agreement with the presence of mainly CuO particles, the surface of which displays only some
517 Cu^{2+} ions able to undergo self-reduction (not quantifiable by TPR but evidenced by FTIR). In contrast, a
518 lower ratio is observed with CZ-IM-B (*i.e.* 0.90, corresponding to 80% Cu(II)), indicating the presence of a
519 fraction of Cu (II) species able to undergo self-reduction. These latter likely include both exchanged Cu_Z^{2+}
520 species and the above mentioned structures with ELO. On the other hand, the samples prepared by ion-
521 exchange with Cu acetate showed higher H/Cu ratio, *i.e.* 0.85 (corresponding to 72% Cu(II) in CZ-EX-A)
522 and 0.81 (corresponding to 62% Cu(II) in CZ-EX-B). Between these two samples, CZ-EX-B has a larger
523 amount of Cu (II) species able to undergo self-reduction, although showing similar %_{EX}. This observations
524 seems to confirm that the use of more concentrated exchange solution favors the formation oligomeric
525 Cu_xO_y structure with ELO rather increasing the amount of isolated Cu_Z^{2+} ion in exchange position. Finally,
526 the lowest H/Cu ratio was obtained with sample CZ-SU, *i.e.* 0.65, corresponding to 30% Cu(II). Given the
527 mild calcination conditions, the most obvious reason for this value would be the oxidation state of the
528 copper precursor.

529 A quantitative analysis of the TPR spectra aimed at determining the H_2 consumption due to the different
530 copper species is not straightforward. Indeed, the overlapping of the temperature ranges at which the
531 different species are reduced hinders a precise quantitative correlation between the area of the reduction
532 peaks and the abundance of the different copper species. Indeed, at least four different copper species
533 may occur in the samples: (1) exchanged copper(II) ions (Cu_Z^{2+}); (2) exchanged copper(I) ions (Cu_Z^+); (3)
534 segregated CuO particles and (4) Cu_xO_y structures with ELO. Moreover, the segregated CuO species may
535 differ in size and location (inside or outside the pores). Supported CuO is generally reduced to Cu^0 in a

536 single autocatalytic step, the greater its dispersion, the lower its reduction temperature [47,48]. This
537 reduction behavior is observed with sample CZ-IM-500, showing a single asymmetric reduction peak with
538 maximum at 280°C and shoulder at 247°C. According to IR and XRD results, the very low Al content of the
539 impregnated sample results in the formation of mainly supported CuO particles and negligible amounts
540 of Cu_z species, the latter being responsible of the very weak H_2 consumption at ca. 380°C. The asymmetry
541 of the main peak may be due to CuO particles of different size (e.g. large particles on the outer surface
542 and clusters within channels).

543 According to the literature [45,49,50], the Cu_z^{2+} species are expected to be reduced in two steps: $Cu^{2+} + \frac{1}{2}$
544 $H_2 \rightarrow Cu^+$ (that generally occurs at $T < 250^\circ C$), and $Cu^+ + \frac{1}{2} H_2 \rightarrow Cu^0$ (that generally occurs at $T >$
545 $300^\circ C$). Therefore, if all Cu_z were present as copper(II) (i.e. in the absence of self-reduction phenomena),
546 two equivalent peaks would be expected at low and high temperature, respectively, while the occurrence
547 of self-reduction during He pre-treatment would result in a decrease of the first H_2 consumption. This is
548 what we observed with CZ-EX-A, i.e. the sample with the lowest copper content (2.4 wt.%), but the highest
549 % Cu_z (75% total copper). Two distinct reduction peaks at 240 (ca. $154 \mu mol g_{cat}^{-1}$) and 507°C (ca. $166 \mu mol$
550 g_{cat}^{-1}) are observed. The lower H_2 consumption of the first peak is consistent with the occurrence of self-
551 reduction during the He pre-treatment. The first peak is markedly asymmetric towards high temperatures
552 and, besides the reduction of Cu_z^{2+} to Cu_z^+ , it may include the reduction of the Cu^{2+} of structures with ELO.
553 On the other hand, the H_2 consumption of the second peak fairly matches the value calculated from %
554 Cu_z (ca. $140 \mu mol g_{cat}^{-1}$).

555 With respect to CZ-EX-A, the spectrum of CZ-EX-B shows three main different features: (1) the high
556 temperature peak is more intense and shifted towards lower temperatures (i.e. 335 °C), strongly
557 overlapping those at low-temperature; (2) a weak sharp central peak appears at 275°C; (3) the low
558 temperature peak (244 °C) shows higher H_2 consumption.

559 The increase in H_2 consumption occurring during the high temperature reduction step cannot be justified
560 only by the slight increase in the %_{EX} (47 and 50%, with CZ-EX-A and CZ-EX-B, respectively). Indeed, the
561 reduction of the Cu^{2+} species exchanging external Si-OH groups, the presence of which was evidenced by
562 the consumption of the band at $3745 cm^{-1}$ (*vide supra*), could also occur in this temperature range. The
563 high peak temperature indicates a strong metal-support interaction, rendering the species less reducible.
564 Bond *et al.* reported that (less reducible) dispersed Cu^{2+} species in a CuO/SiO₂ system were reduced in the
565 temperature range of 300 – 350 °C [51]. Chang *et al.* has also confirmed the presence of such Cu^{2+} species
566 (chemically interacting with a silica support) and their reducibility in a similar temperature range [52].

567 As far as the central peak (at 275 °C) is concerned, the sharp shape and the temperature range correspond
568 to an autocatalytic reduction process involving limited amounts of CuO cluster within zeolite channels, not
569 detected by XRD and FESEM, but evidenced by IR spectroscopy (weak shoulder at 2135 cm⁻¹). Finally, the
570 increase in H₂ consumption during the low temperature peak is mainly due to the larger amount of Cu_xO_y
571 structures with ELO. We cannot exclude that part of such structures is reduced in a two-step process [34],
572 thus also contributing to the high temperature H₂ consumption .

573 The spectrum of CZ-IM-B is characterized by an intense and asymmetric peak, with a maximum at 258°C
574 and two shoulders at ca. 230 and 280°C, and a broad peak at 330°C. H₂ consumption at T < 300°C is due
575 to superimposition of (at least) three peaks. Actually, in this temperature range, the reduction of Cu_Z²⁺,
576 Cu_xO_y species with ELO within zeolite channels, and CuO particles occur. According to the assignments
577 done for CZ-IM-500 and CZ-EX-B, and to the trend observed in pore volumes, the components at 258 and
578 282 °C are assigned to extra-porous and intra-porous CuO particles, whereas the low temperature
579 shoulder (not present with CZ-EX-500) corresponds to the reduction of Cu_Z²⁺ and Cu_xO_y species with ELO.

580 Notwithstanding the relatively high %_{EX} measured with this sample (*i.e.* 68%), the peak due to the
581 reduction of Cu_Z⁺ (330 °C) appears less intense than that of the other samples. This feature is consistent
582 with the presence of CuO clusters in the close proximity of some Cu_Z²⁺ ions, which could be therefore
583 reduced directly to Cu(0) in a single reduction step.

584 Finally, the TPR spectrum of CZ-SU shows a profile and total H₂ consumption similar to those of CZ-EX-B,
585 but lower H/Cu ratio. Furthermore, the sharp central peak is significantly shifted toward higher
586 temperatures (316°C), being unlikely due to CuO. We assigned this peak to residual CuCl aggregates
587 probably trapped in the zeolite channels: actually, reduction of CuCl takes place at higher temperatures
588 with respect to CuO [53,54]. Furthermore, the measured H/Cu ratio indicates the presence of only 30%
589 Cu(II). Given that a copper(I) precursor and mild calcination conditions were adopted, the majority of
590 exchanged copper after He pre-treatment is likely present as Cu_Z⁺. It follows that most of Cu²⁺ is located
591 in segregated Cu-containing species, which could also imply the occurrence of some oxidation products
592 of unreacted CuCl, *e.g.* CuO and Cu₂(OH)₃Cl, the latter species being likely responsible for the reduction
593 peaks at ca. 240°C

594

595 **4. Conclusions**

596 The study of the possible effects of the preparation procedure of Cu-ZSM-5 samples on the spontaneous
597 oscillations occurring during the catalytic decomposition of N₂O provided relevant evidence of the
598 presence of various type of copper species in the Cu containing ZSM-5 catalysts. The unsteady-state

599 oscillatory phenomenon did not occur with all the prepared catalysts; in fact, we demonstrated that a
600 series of peculiar features should be exhibited by the samples for the oscillations to occur. First, a
601 minimum amount of copper is required to obtain a certain activity in the reaction as well as to observe the
602 establishment of a periodic oscillating pattern of the unconverted N₂O concentration at the reactor outlet
603 or (which, by the way, is the same) of the N₂O conversion and of the decomposition rate.

604 Interestingly, a complete exchange level (*i.e.* complete consumption of Brønsted acid sites) was not
605 observed even with the samples with high copper content (Cu/Al > 1). However, in addition to the amount
606 of exchanged sites, also the nature of copper “excess” have a crucial role in both activity and oscillating
607 behavior. The comparison between CZ-EX-A (scarce activity, and no oscillations) and CZ-EX-B (good
608 activity, and oscillations) is emblematic, as both sample showed similar exchange level. The same
609 conclusions are obtained by comparing the samples with higher Cu₂ content, *i.e.* CZ-SU (good activity, but
610 no oscillations) and CZ-IM-B (superior activity, and pronounced oscillations).

611 The oscillatory phenomenon could be associated with the occurrence of oligomeric Cu_xO_y species with
612 extra-lattice oxygen (*e.g.* chains or clusters) able to undergo reduction/oxidation cycles. Such species may
613 form by ion-exchange with polyoxocations resulting from the hydrolysis of hexaaquacopper(II) complex
614 [Cu(H₂O)₆]²⁺ and its polycondensation reactions, and are more abundant in excessively-exchanged
615 (*i.e.* Cu/Al > 1) samples prepared by either impregnation or ion-exchange. In contrast, they lack in CZ-SU,
616 *i.e.* the sample prepared by sublimation of copper(I) chloride, which, correspondingly, did not give rise to
617 oscillations. In CZ-SU, the exchanged copper species seem to be almost exclusively isolated Cu⁺ ions that,
618 even after a mild calcination, cannot be oxidized to Cu²⁺ ions, and most of all are not present in
619 aggregated forms. In this way, the kind of Cu species present in the CZ-SU sample, even if quite active in
620 the decomposition of N₂O, prevents the reaction to occur over both active sites, and hence in an unstable
621 equilibrium between the two oxidation states.

622

623

624

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770 **Table 1.** Summary of physicochemical properties of the prepared catalysts

Sample ^a	Cu loading (wt%) ^b	Cu/Al ^b	S _{BET} (m ² g ⁻¹) ^c	V _p (cm ³ g ⁻¹) ^d	%EX ^e	% Cu _Z ^g	H ₂ -to-Cu ratio ^h	% Cu(II) (atomic %) ⁱ
CZ-IM-A	3.6	1.19	360	0.21	-	-	-	-
CZ-IM-B	6.5	1.9	250	0.16	68	32	0.90	80
CZ-EX-A	2.4	0.82	388	0.24	47	75	0.85	72
CZ-EX-B	3.8	1.12	370	0.22	50	49	0.81	62
CZ-SU	4.5	1.39	355	0.21	71	60	0.65	30

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772 ^a IM = impregnation; EX = ion exchange; SU = sublimation773 ^b Cu weight percentage and Cu/Al atomic as measured by EDX774 ^c total specific surface area as measured by N₂ physisorption775 ^d total pore volume as measured by N₂ physisorption776 ^e percentage of exchange obtained from the intensity ratio between the integrated IR absorbance of the
777 3610 cm⁻¹ band in the parent H-ZSM-5 and of the same band in exchanged samples778 ^g (Cu_Z/Cu_{TOT})*100 = relative abundance of exchanged Cu species on total copper content, as calculated
779 combining %EX and Cu loading780 ^h hydrogen consumption to loaded copper quantity ratio extracted from H₂-TPR and EDX781 ⁱ relative abundance of copper (II) species calculated from H₂-to-Cu ratio, assuming that the moles of
782 consumed H₂ equal the sum of the Cu²⁺ moles of and half of the Cu⁺ moles

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793 **Caption to Figures**

794 **Figure 1.** Outlet concentration of N₂O as a function of time during the catalytic activity testing under
795 isothermal condition (A) and magnification of the oscillatory behavior of CZ-IM-A, CZ-EX-B and CZ-IM-B
796 (B). Test condition: N₂O feed concentration = 1000 ppm, T = 400°C, W/F = 0.03 g cm⁻³ s. Color legend:
797 magenta (CZ-IM-A), blue (CZ-IM-B), yellow (CZ-EX-A), green (CZ-EX-B), violet (CZ-SU).

798

799 **Figure 2.** Outlet concentration of N₂O (straight line) and reactor temperature (dashed line) as a function
800 of time (A) during the catalytic activity testing with oscillation-inducing catalysts under various isothermal
801 conditions and magnification of the oscillatory behavior of the three catalysts (B). Test condition: N₂O feed
802 concentration = 1000 ppm, W/F = 0.03 g cm⁻³ s. Color legend: magenta (CZ-IM-A), blue (CZ-IM-B) and
803 green (CZ-EX-B).

804

805 **Figure 3.** Composition of the gas at the reactor outlet during the catalytic activity testing under
806 isothermal condition of the sample CZ-IM-B: outlet concentration of N₂O and O₂ (A) and of NO and NO₂
807 (B) as a function of time. Test condition: N₂O feed concentration = 1000 ppm, T = 400°C, W/F = 0.03 g
808 cm⁻³ s. Color legend: magenta (N₂O), blue (O₂), green (NO), black (NO₂).

809

810 **Figure 4.** Composition of the gas at the reactor outlet during the catalytic activity testing under
811 isothermal condition of the sample CZ-IM-500: outlet concentration of N₂O and O₂ (A) and of NO and
812 NO₂ (B) as a function of time. Test condition: N₂O feed concentration = 1000 ppm, T = 400°C, W/F = 0.03
813 g cm⁻³ s. Color legend: magenta (N₂O), blue (O₂), green (NO), black (NO₂).

814

815 **Figure 5.** Effect of residence time on the behavior of the reaction mediated by oscillation-inducing
816 catalysts under isothermal condition. (A) Outlet N₂O concentration as a function of time and (B)
817 magnification of the oscillatory behavior. Test condition: N₂O feed concentration = 1000 ppm, T = 400 °C.
818 Color legend: magenta (CZ-IM-A), blue (CZ-IM-B) and green (CZ-EX-B).

819

820 **Figure 6.** IR spectra of the OH stretching region of the parent H-ZSM-5 zeolite (curve 1), CZ-IM-A (curve
821 2), CZ-IM-B (curve 3), CZ-EX-B (curve 4) and CZ-SU (curve 5) pre-treated under vacuum at 500°C.

822

823 **Figure 7.** IR spectra of CO adsorbed at increasing equilibrium pressure (10 – 3000 Pa) on CZ-EX-B (section
824 a), CZ-IM-B (section b), CZ-EX-A (section c) and CZ-SU (section d) at room temperature. Insets show
825 magnification of the isosbestic point.

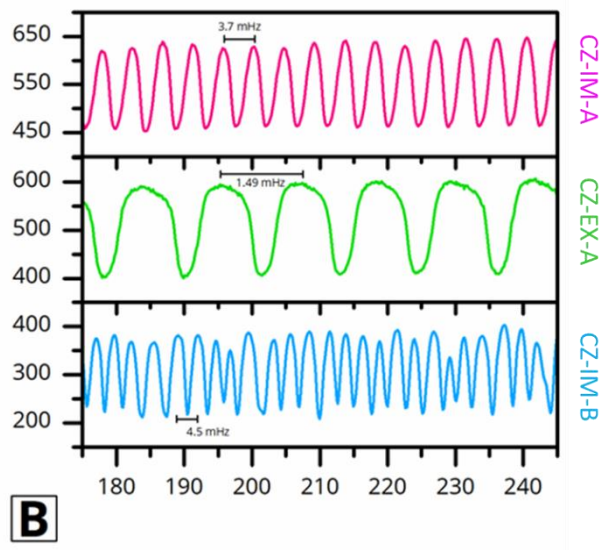
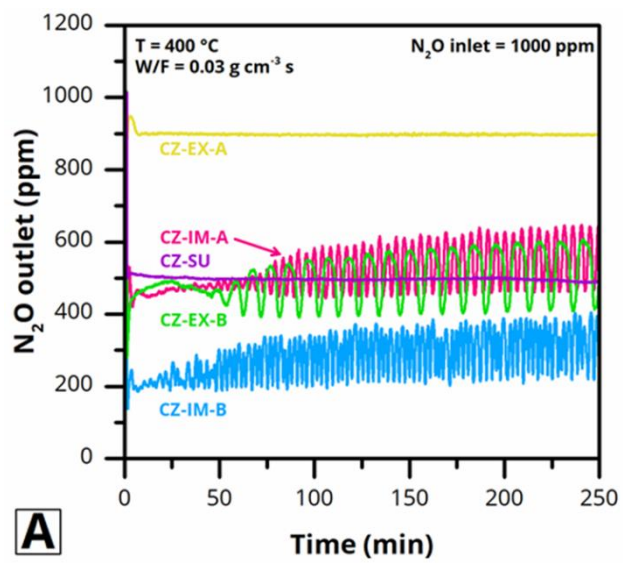
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827 **Figure 8.** H₂-TPR spectra of CZ-IM-500, CZ-IM-B, CZ-SU, CZ-EX-B and CZ-EX-A samples pre-treated in He
828 at 550°C.

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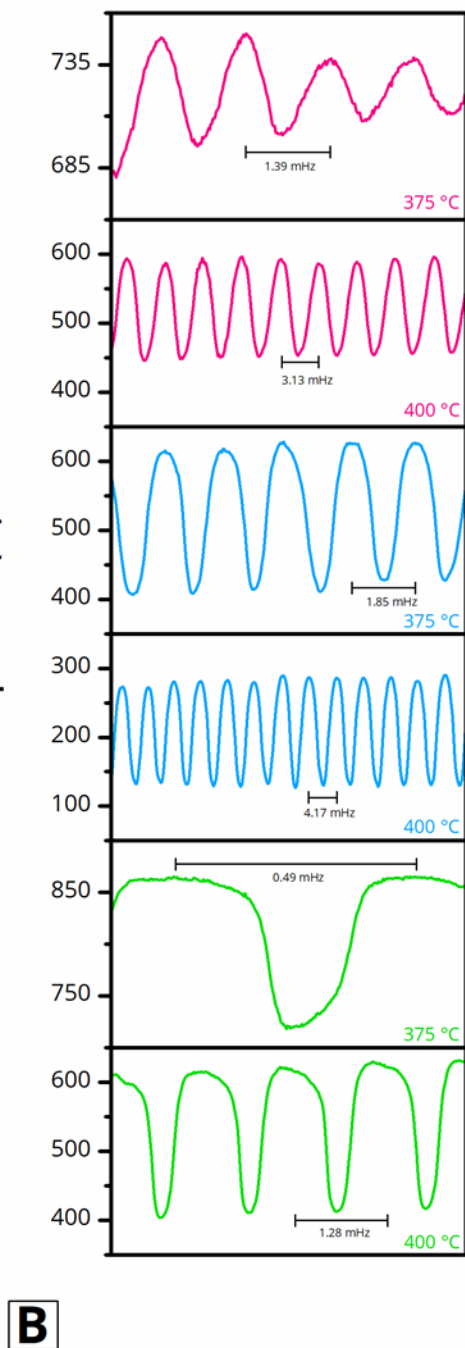
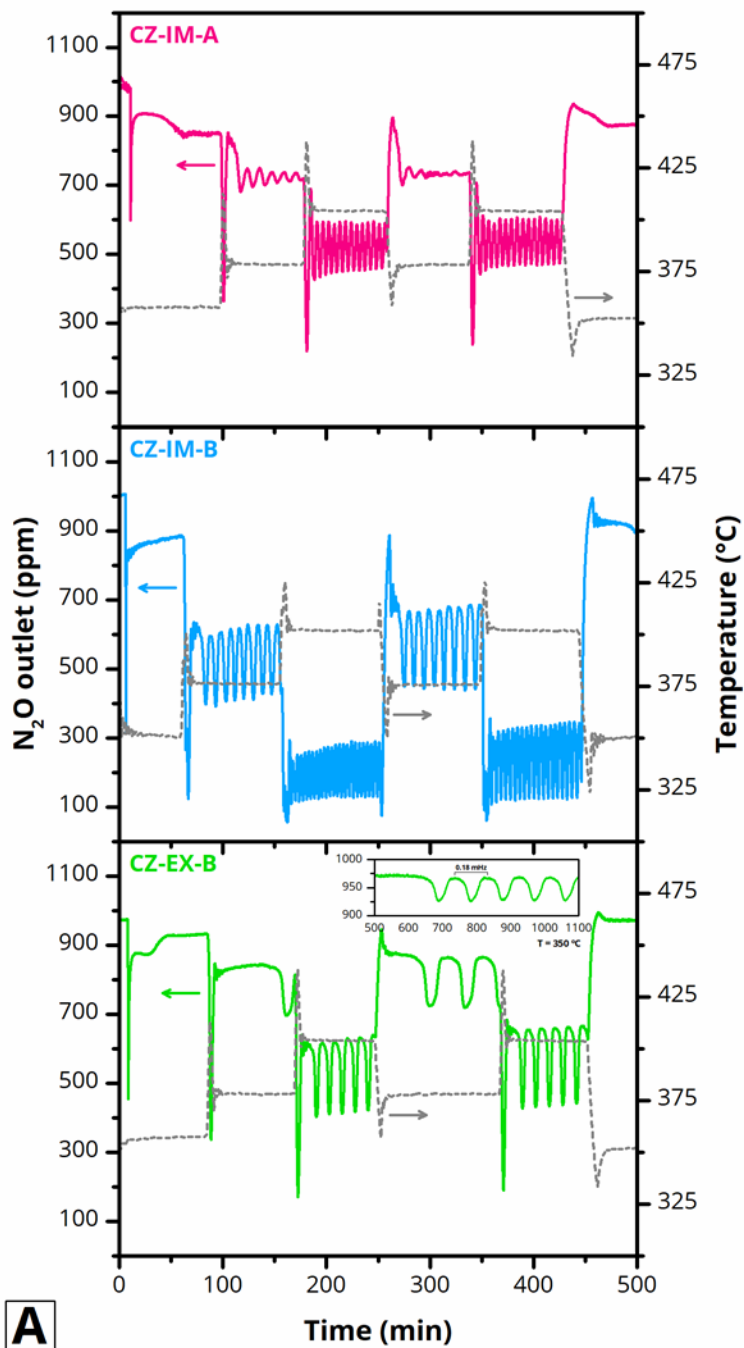
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833 **Figure 1**

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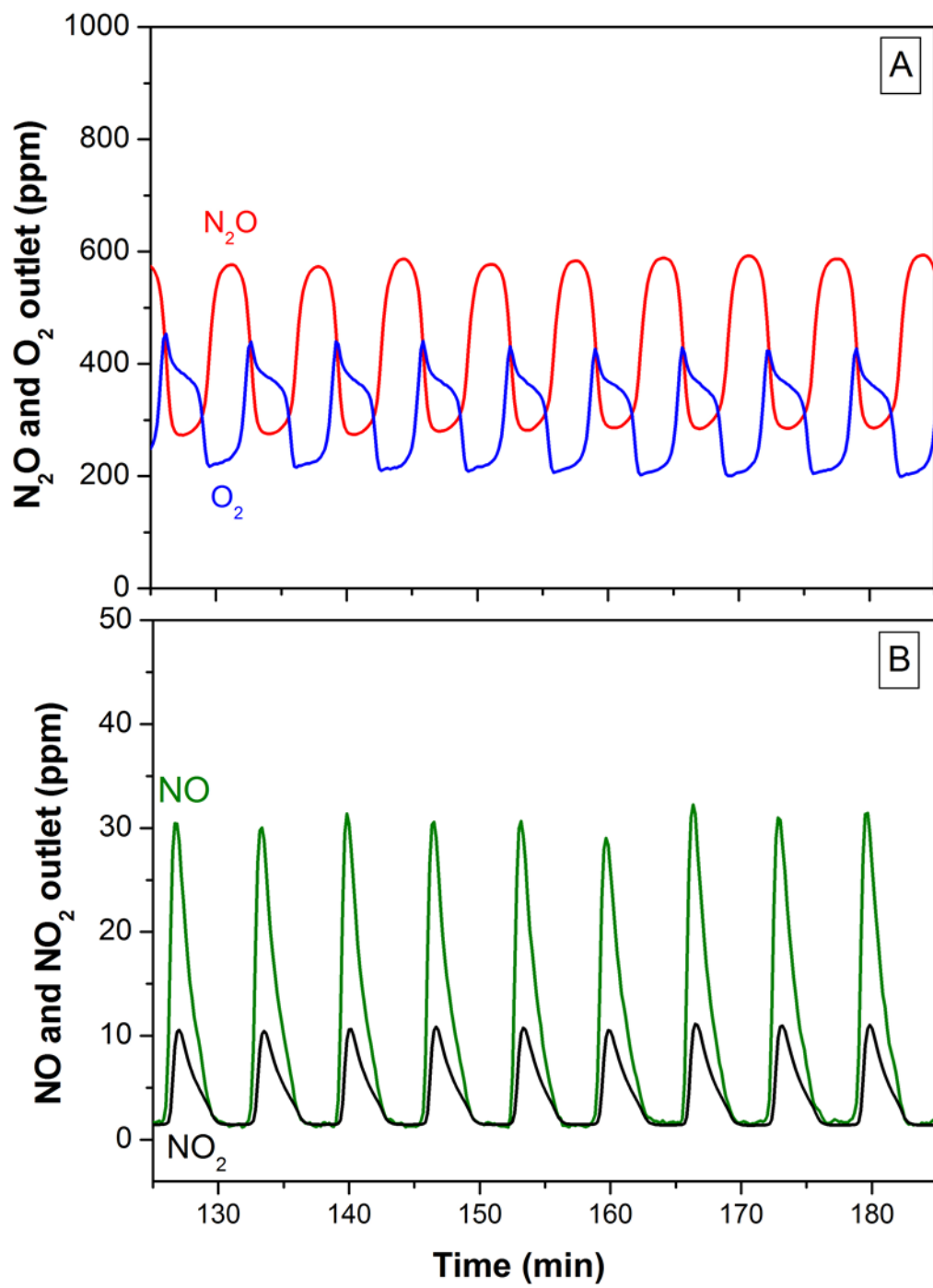


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837 **Figure 2**

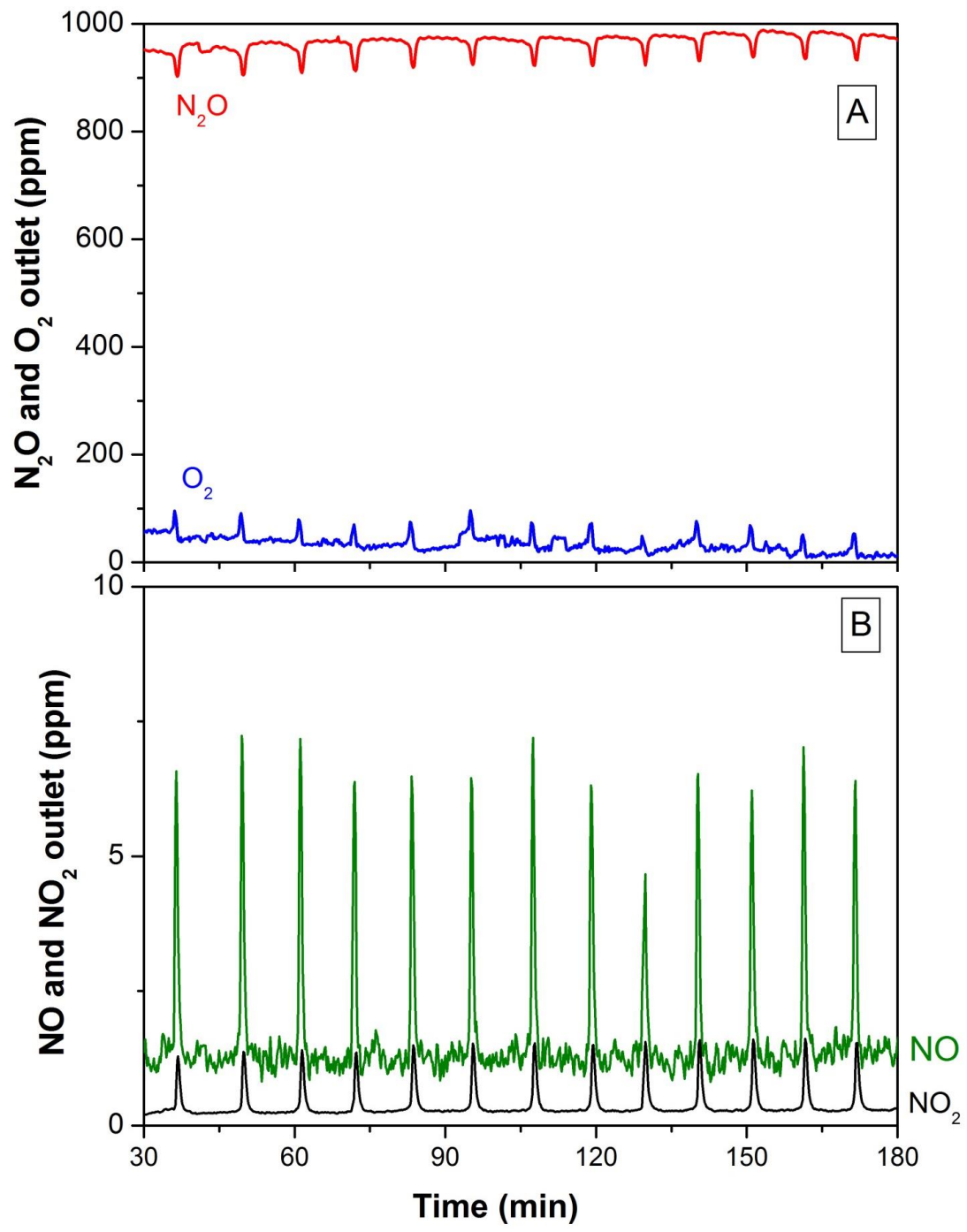
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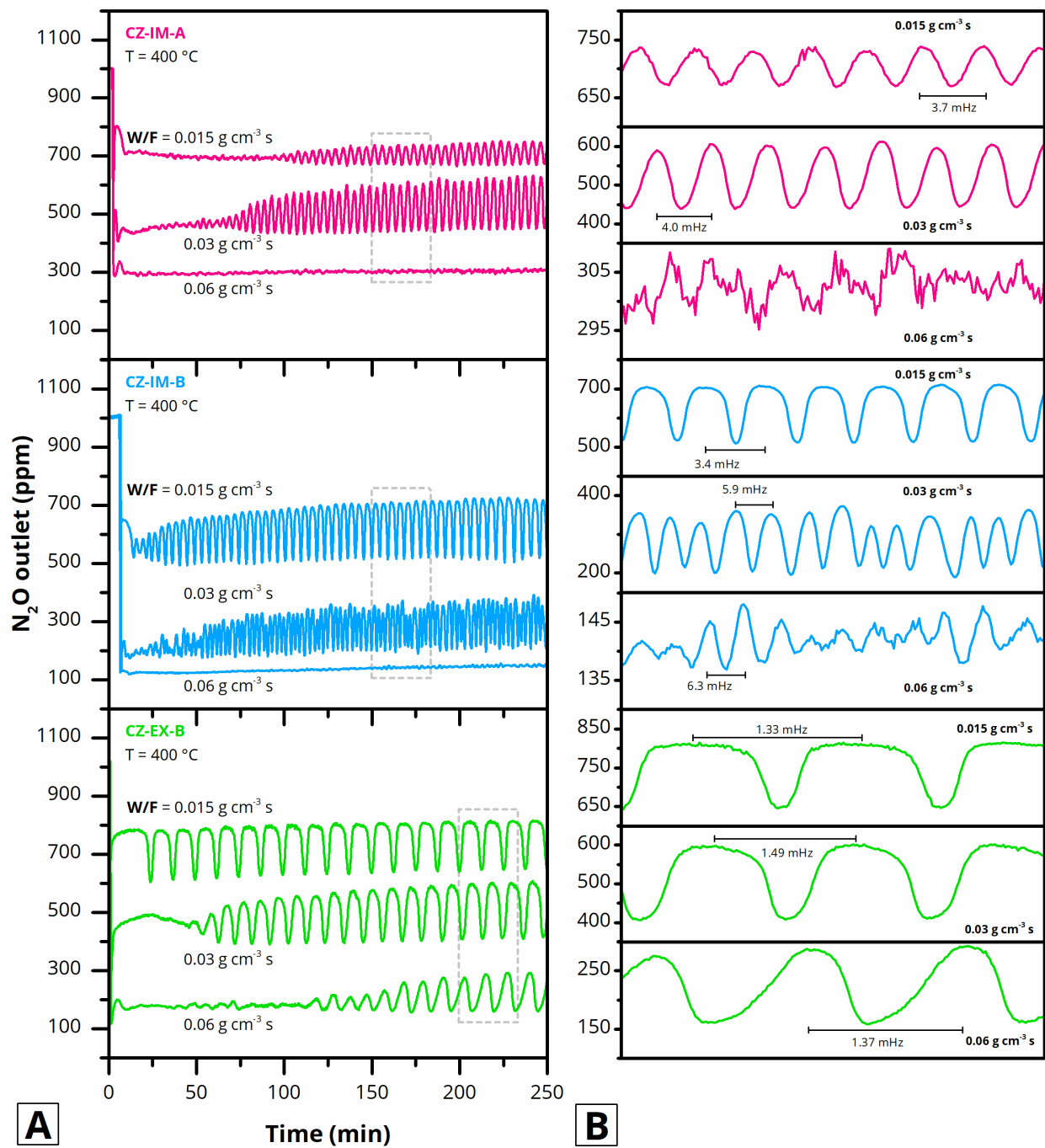
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843 **Figure 4**

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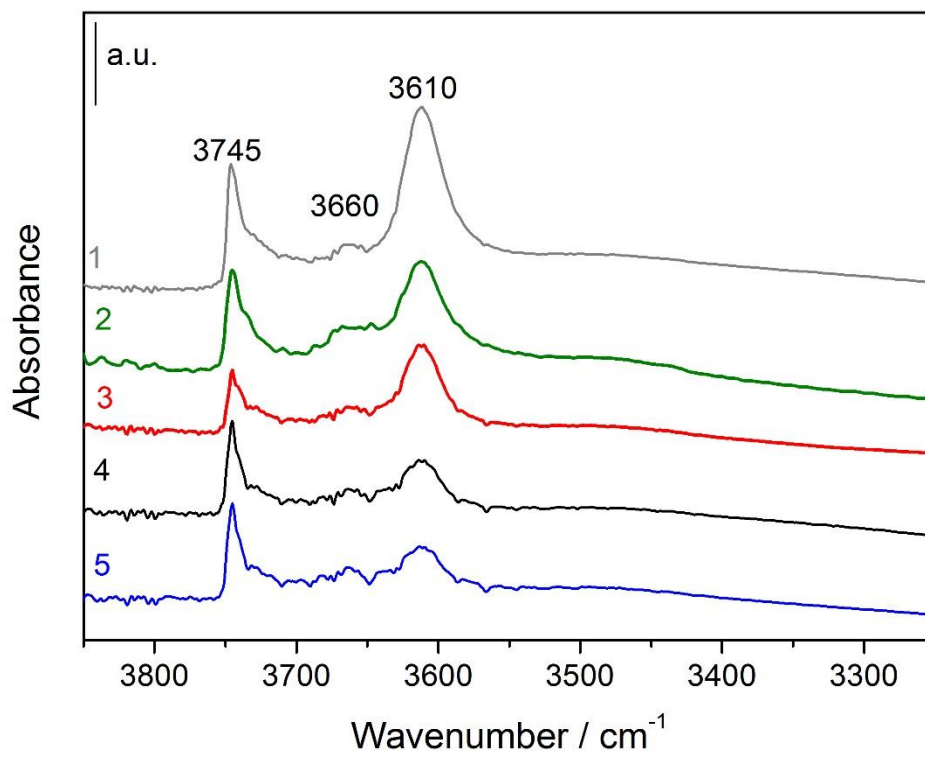


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847 **Figure 5**

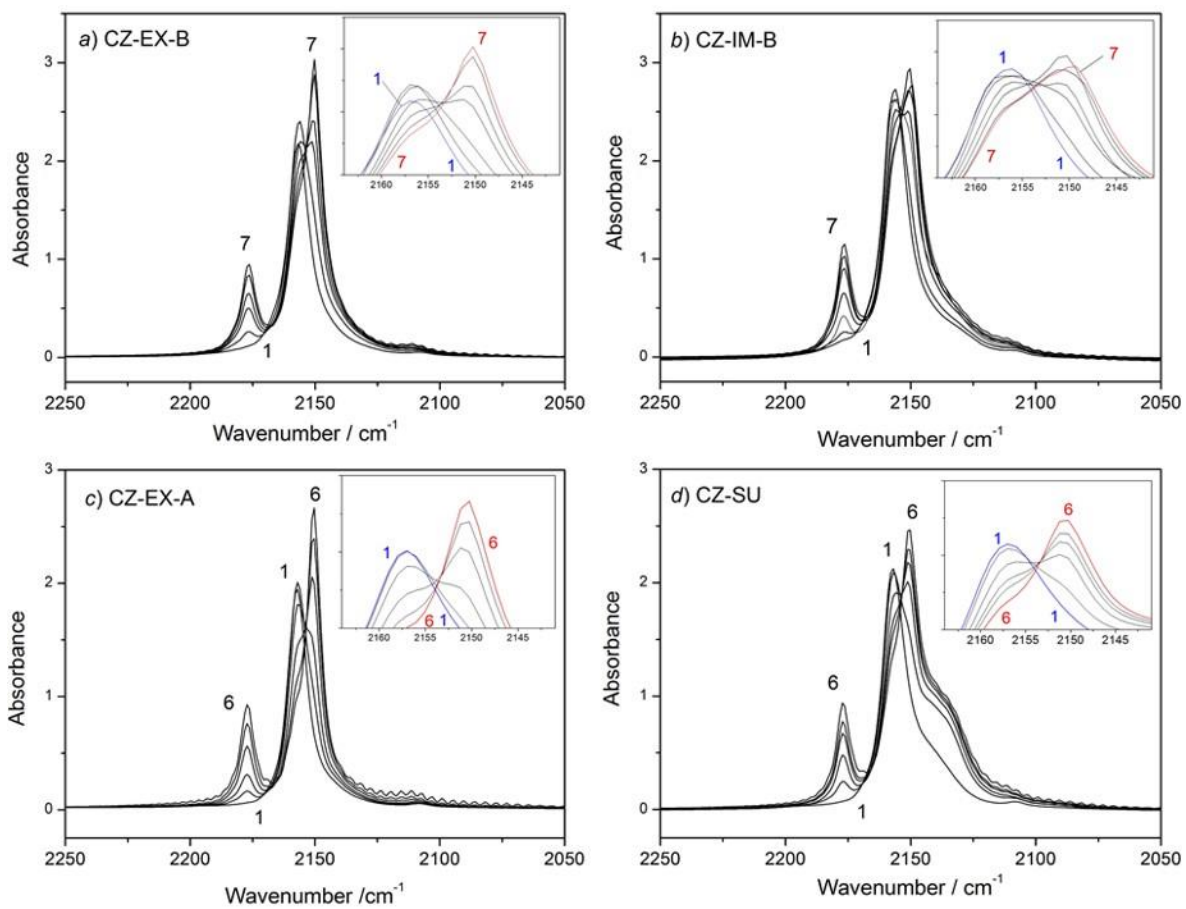
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850 **Figure 6**

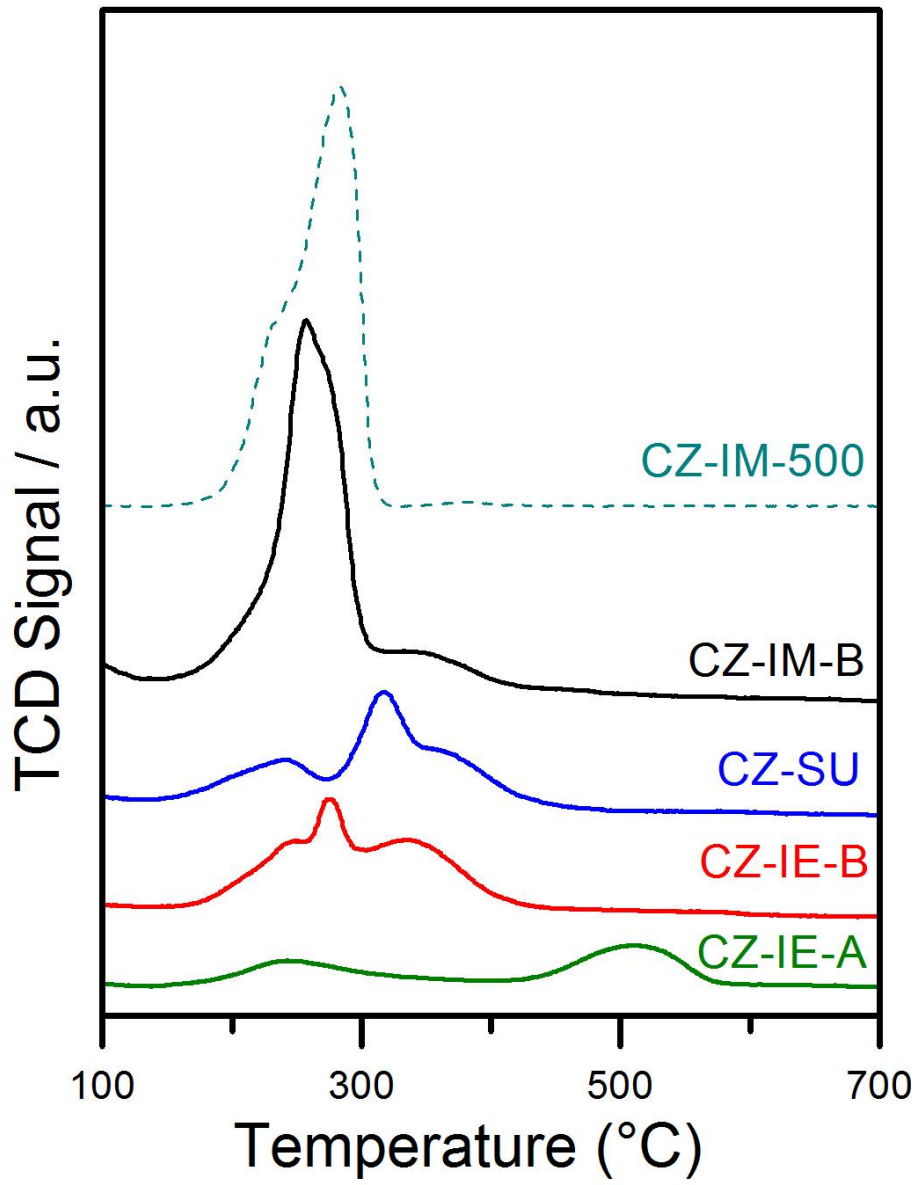
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853 **Figure 7**

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856 **Figure 8**