Synthesis of Self-Bonded Pellets of ETS-4 Phase by New Methodology of Preparation

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Abstract. We hereby present the results of a research in order to prepare self-bonded pellets of ETS-4 phase by a new methodology of preparation. In particular, the pellets were prepared by kneading crystals of ETS-4 phase and a dry gel, the latter being the precursor for the synthesis of the ETS-4 phase crystals. One of the innovative aspects that is proposed and highlighted in this work is represented by the fact that the dry-gel acts as a “binder”. It is characterized by the same chemical composition of crystals, thus avoiding contamination with other elements. In addition, dry-gel allows, the promotion of nucleation phenomena and thus the formation of new crystals of ETS-4 during the pellets baking phases. The pellets were characterized by X-ray diffraction (XRD), Electron microscopy (SEM) and mechanical strength by hardness tester.

1.  Introduction
In this research the ETS (Engelhard Titanium silicate), object of study, is an important family of microporous materials. Two important molecular sieves belong to this family, ETS-4 and ETS-10, that were first synthesized from Kuznicki [1-3]. The ETS-10 phase is an extremely interesting titanosilicate microporous material, due to its high thermal stability and its wide open pores (pore apertures close to 0.8 nm). The structure of ETS-10 was proposed by Anderson et al. [4-6]. However, the ETS-4 phase is a small-pore microporous titanosilicate molecular sieve with an effective pore opening of about 3.7 Å [7-8]. During the last decades, in addition to the study of their structure, many researches, have given particular attention to the synthesis of these materials [9-15]. Other studies regard the possibility of inserting hetero-atoms different from silicon and titanium in the structure of these materials to improve or modify their characteristics [16-19]. These materials are very versatile and can be applied in a variety of applications such as water purification and heavy metal removal [20-27], gas adsorption [28-31] and also for their photocatalytic action [32-35]. Generally these materials are obtained in the form of powders after synthesis. For many years, a great deal of research has been directed towards the synthesis of microporous materials in the form of pellets in as much as this guarantees better utilization and recovery after their use. The preparation of the pellets, however, requires the use of a binder, which can obstruct the porous structure resulting in decreased pores' accessibility and hence reducing property resulting from the porous structure such as ion exchange, molecular sieving, adsorption and catalysis [36, 37]. For this reason, some research has been focused on the preparation of pellets of microporous and zeolite materials without the use of a binder [38]. Even for ETS phases, the conditions, to obtain self-bonded pellets directly for synthesis without the use of a binder, have been studied. In 2008 Vuono et al. proposed the synthesis of self-bonded pellets ETS-4 and ETS-10
Further researches include heteroatoms inside pellets with the aim of modifying their characteristics [40, 41]. Recent studies report self-bonded ETS-10 and ETS-4 pellets with carbon nanotube insertion [42]. The aim of this research was to synthesize ETS-4 phase microporous materials in the form of pellets by an innovative process. In particular, the pellets were prepared by kneading crystals of ETS-4 phase with dry-gel, the latter is a precursor for the synthesis of the same ETS-4 phase crystals. One of the many innovative aspects that is proposed and highlighted by this work is represented by the fact that acting as "binder", is dry-gel, that is characterized by the same chemical composition of crystals. In addition, dry-gel can lead to the promotion of nucleation phenomenon during the pellet baking phases and, thus, the formation of new crystals of ETS-4.

2. Materials and methods
This research was developed through different stages:
- preparation and pretreatment of the gel-dry precursor of the crystalline phase ETS-4;
- synthesis of crystals of the ETS-4 phases;
- preparation of pellets.

The characterization of the obtained materials was carried out through chemical-physical techniques. The RX diffractograms were obtained using the diffractometer model Philips PW 1730/10, equipped with a vertical goniometer PW 1830, with CuKα radiation type, scan speed of 1°/min and scanning angle 2θ between 5°-45°. The samples were observed by Scanning Electron Microscope (SEM) FEI "Quanta" 200 FEG (E = 10kV, SE Image). Vanderkamp VK200 hardening tester was used for the test of mechanical resistance.

2.1. Preparation and pretreatment of the precursor gel of the selected crystalline phase
The preparation of precursor gels for the synthesis of the ETS-4 phase was carried out according to the procedures reported by Pavel et al. [43]. In particular, gels were prepared by the following molar systems: 2Na2O-0.6KF-0.2TiO2-2.56HCl-1.49SiO2-39.5H2O. The gels were obtained preparing an acidic solution (A) by dissolving HCl (37 wt.%, Carlo Erba), TiCl4 (50 wt.%, Merck) and KF (40 wt.%, Merck) in distilled water, and a basic solution (B) by dissolving sodium silicate (8 wt.% Na2O, 27 wt.%SiO2,Merck) in NaOH (50 wt.%, Carlo Erba). Solution (A) was poured into solution (B), and the gel obtained was stirred for 5 min. under stirring for 1 min. This preparation of the gel was followed by a drying procedure at 100 °C in a stove for 24 hours. Subsequently, it was finely pulverized in a mortar obtaining the so-called dry-gel. The X-ray diffraction spectra of the gel has already been reported in a previous work [39].

2.2. Synthesis and characterization of ETS-4 phase crystals
The ETS-4 phase crystals were obtained using gels prepared as described in the previous section but without performing the drying step. Once prepared, the gel was placed in Morey autoclaves (constituted externally by a steel jacket and internally by a teflon container) and subjected to hydrothermal synthesis in a stove at 190 °C for five days. After the baking time, the autoclaves were cooled down and then opened. The synthesis product was filtered and washed subsequently characterized by X-ray diffraction in order to verify its quality and to confirm the obtained phase. The RX diffraction spectra of the ETS-4 crystalline phase have already been reported in a previous work [39].

2.3. Preparation of pellets
Once the ETS-4 dry-gel and crystals were obtained, the pellets were prepared by a mixing phase crystals ETS-4 and dry-gel (precursor of the same crystalline phase) to different ratios crystals / dry-gel (%wt/wt) = 1, 3, 9 and by adding some mL of distilled water in order to make the system functional. This mixture was then preformed into pellets using a hydraulic press capable of applying 400 bars. The pellets obtained had a diameter of 1.3 cm and a thickness of 0.7 cm. For each system studied, three pellets were prepared. Subsequently the pellets, once prepared, underwent three different
treatments: (a) ageing at 25 °C for 3 days; (b) drying at 100 °C in a thermo-ventilated stove for 3 days; (c) hydrothermal synthesis. In particular, in the latter, the pellets were placed in Morey type autoclaves where a support made of teflon was placed with the purpose of maintaining the pellet raised from 5 mm of distilled water in order to create a hydrothermal system. The autoclaves were then hermetically closed with screws and put in the oven at 190 °C for three days. The pellets extracted from the autoclave were filtered, washed with distilled water and dried in oven at 100 °C for 24 hours.

3. Results and discussion

As shown below, the results and discussion of:  -preparation of phase pellets ETS-4 with new procedure, -activating of the ETS-4 phase pellets with addition of indicators, are reported.

3.1. Phase Pellets ETS-4 as made

The following Figure 1 shows the X-ray diffraction spectra of the pellets obtained by varying the crystals/dry-gel ratio and the treatment modes. Figure 1 shows that the pellets are well formed, retain their shape even after hydrothermal synthesis at 190 °C and are white in color for all systems.

![Fig. 1](https://example.com/fig1.png)

**Figure 1.** Imagines (a) and X-ray diffraction spectra (b) of the pellets obtained varying the crystals/dry-gel ratio and the treatment modes.

X-ray diffraction spectra relating to ETS-4 phase pellets (Fig. 1b) show a marked increase in crystallinity, depending on the crystals/gel-dry ratio and the treatment mode. The increase in crystallinity by the augmentation in the crystals/dry-gel ratio is obviously due to higher amounts of crystals in the initial pellet preparation system. This occurs when the temperature of the treatment is increased due to crystallization of the dry gel. The characteristic peaks of the structure of the ETS-4 are easily observable in all the samples examined and, moreover, we must point out that the characteristic peak attributable to the dry-gel (32°/theta) tends to decrease both with the increase in the crystals/dry-gel ratio, and by increasing the temperature of post-pelletization treatment, confirming dry-gel crystallization phenomenon. On the whole this is more apparent for the system with crystals/dry-gel ratio equal to 50, in fact the characteristic peak of the gel is evident at 25 °C but disappears at 190 °C.

3.2. Mechanical strength of pellets

Figure 2 (see below) shows the mechanical resistance of the ETS-4 pellets as a function of the crystals/dry-gel ratio and the treatment temperature.
We may observe in Figure 2 the mechanical resistance of ETS-4 pellets. All the pellets gave satisfactory results. Only in two cases, the resistance values drop below 30 N with a minimum corresponding to 21.57 N (crystal/dry-gel= 9 and T = 190 °C) which, however, is an acceptable result. The maximum resistance value, equal to 168.67 N, is recorded for T = 100 °C and for crystal / gel-dry= 1. If we analyze the graph carefully, it is clear that the change in the resistance is relative to the used variables (Crystal/ dry-gel ratio and mode treatment).

We may note by observing the graph from left to right, that while the crystal/gel-dry ratio increases, the resistance decreases and this is, of course, due to the decrease of the amount of dry-gel (binder).

Another aspect that can be highlighted is the increase in resistance from pellets subjected to baking for 24h at 100 °C as regard to pellets left at room temperature (T= 25 °C). However, by switching from 100 °C to the hydrothermal treatment at 190°C, the resistance decreases once more whilst because the crystallinity is increased due to the favorable conditions which allow the dry-gel to crystallize, though good values of resistance are always confirmed.

3.3 Mechanical resistance of the pellets after immersion in water
An important parameter to be evaluated in the ability of pellets is withstanding in water, since they may find applications in aqueous solutions for the particular peculiarities of the ETS-4 phase, such as heavy water purification, molecular sieving, etc.

For this reason, pellets obtained, according to the procedures reported in paragraph 2.3, were subsequently treated by immersion into distilled water for 10 minutes at a temperature of 25 °C. After the established time, they were dried and placed in a silica gel dryer for 24 hours. Subsequently, the mechanical compressive strengths were measured on pellets. Figure 3a shows the images of pellets obtained after immersion in water.

In particular, it is evident that despite the immersion into water, all samples retained their form with the exception of very few cases where slight splits around the border appeared. Overall, all the pellets retained their compactness and integrity as before being submerged in the water immersion cycle.

Figure 3 (b) reports data of the mechanical resistances of the ETS-4 phase pellets after immersion in water. Mechanical resistance data showed, in all cases, a lowering of compression resistances, although in many cases the resistance continues to be significant. In particular, it can be noted that the resistance value is reduced to a minimum of 7.85 N (for a crystal/dry-gel ratio equal to 9 and at T=...
190 °C (hydrothermal synthesis) which, however, remains an good result. The maximum resistance value of 133.37 N is, however, recorded for a T= 100 °C and a crystal / dry-gel ratio equal to 1. It is furthermore apparent that there is a variation in the resistance relative to the variables used (crystal / gel-dry ratio and treatment mode).

Figure 3. Image of ETS-4 pellets (a) and mechanical resistance (b) as a function of crystal/dry-gel ratio and treatment at temperature after immersion in water for 10 minutes at a temperature of 25°C followed by drying.

Figure 4. SEM images of the surface (s) and internal (i) of the pellets obtained with the variation of the ratio crystal/gel-dry (R) and the temperature at two different magnifications.
We may notice a decrease in resistance if we observe the graph from left to right, as the crystal/gel-dry ratio increases and the dry-gel (binder) decreases. Conversely, an increase in resistance can be observed for pellets subjected to baking for 24 hours at 100 °C respect to pellets left at room temperature (T = 25 °C). However, from treatment at 100 °C to treatment at T = 190 °C, the resistance decreases once more, due to the fact that when dry-gel is subjected to hydrothermal synthesis its crystallization is favored towards the ETS-4 phase decreasing its binding action.

3.4. Characterization by Scanning Electronic Microscope (SEM)
The interior and surface of the prepared pellets were observed by scanning electron microscopy at different magnification. The following Figure 4 shows the images of the pellets prepared in different temperature conditions and with different crystal/gel ratios. The SEM images show that, in all cases, the pellets have the same morphological appearance both inside and on the surface. As the treatment temperature increases, the hydrothermal treatment at 190 °C leads to the nucleation of the dry gel, in fact, an intercrescence of new crystals is visible on the surface of the crystals initially added. It is confirmed that the hydrothermal treatment leads to the crystallization of the dry gel in which it loses the binder function under these conditions. During treatment at 25 °C and 100 °C this phenomenon is practically absent and the amorphous phase of the gel is visible. The surface of the crystals is clean without the intercrescence of new crystallization nuclei.

4. Conclusions
The aim of this work was the preparation of self-bonded ETS-4 pellets by a new procedure. The results obtained allow us to draw the following conclusions:

The procedure of using crystals of ETS-4 mixed with a dry gel, precursor of the same crystalline phase, was found to be effective for the preparation of self-bonded pellets. The two variable parameters were particularly influential, i.e. the crystal/dry-gel ratio and the treatment modes after the pelletization phase.

- The obtained pellets were expected to be more crystalline by increasing the crystal/dry-gel ratio but at the expense of resistance, owing to a lower percentual of dry-gel acting as a binder.
- The pretreatment mode after the pelletization phase induces the system to behave differently: at 25 °C gel-dry does not crystallize, in fact, X-ray diffraction spectra present the most intense peak of the dry gel (32 2theta), which is more apparent for low crystal/dry-gel ratios. Through this latter treatment, the dry gel performs to the binder function, in fact, significant compression resistances are obtained.
- Treatment at 100 °C is more advantageous than in the previous one because the pellets, obtained with the same variability, have greater resistance since the dry-gel cannot crystallize, even in this case, pellets undergo a degree of consolidation.
- Treatment of pellets subjected to hydrothermal synthesis at 190 °C indicates that under these conditions the dry gel crystallizes. This results in an increase in the crystallinity of the pellets but as a result of a lowering in the resistance.
- Water immersion resistance tests have shown that all ETS-4 pellets have the ability to resist immersion in water for ten minutes. The pellets were subjected once more to compression strength testing after water immersion, and after drying. Once again, resistance values were decreased, though equally elevated.

In summary, we may state that treatment at 100 °C has proven to be the best of those used as compared to the resistance of the pellets obtained.

In particular, the best ETS-4 pellets, which represent the best compromise between the characteristics considered are those obtained from crystal/dry-gel ratio =1 at 100 °C. Indeed, in these experimental conditions the pellets recorded the highest compression resistance value at around 168.67 N and good crystallinity (around 270 cps). Resistance dropped by only 20% after a 10 minute water immersion, and high values continued –i.e 133.37N.
5. References

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