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Mechanism study of stabilization of double-base propellants by using zeolite stabilizers (nano- and micro-clinoptilolite)



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Abstract The mechanism of stabilization of double-base rocket propellants (DBPs) using inorganic stabilizer (nano- and micro-clinoptilolite) was investigated. The surface structures of the stabilizers, the double-base propellants containing the new stabilizers and the effect of the stabilizers on the surface behavior of propellants and vice versa were checked using XRD and Electron Microscope (AFM and TEM techniques). The results obtained from XRD suggested that the crystalline structure of the new inorganic stabilizers was completely changed when it was introduced into the propellants which may be attributed to the pressing processes of DBPs with stabilizers under very high pressure during their mixture preparation. The results obtained from Atomic Force Electron Microscope (AFM) and TEM indicated that nano-clinoptilolite particles become more regularly arranged on the propellant surface than micro-clinoptilolite which gives the stabilizer a higher ability to absorb more nitrogen oxide. The work aimed chiefly to use zeolite stabilizers for DBPs instead of classically used organic compounds; in order to avoid the harmful and carcinogenic organic products coming from the reaction of NO_x gases with these organic stabilizers. This is achieved by studying the thermal behavior of these zeolites via investigation of their surface interaction with NO_x gases obtained during stabilization process and suggesting possible interaction mechanism. © 2013 Production and hosting by Elsevier B.V. on behalf of King Saud University. This is an open access

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1. Introduction

The nitric esters of double base propellants decomposed at rates dependent on time and temperature. This decomposition corresponds to the rupture of the $O-NO_2$ bonds, and releases nitrogen oxides. Without a stabilizer, the products resulting from the decomposition have a catalytic effect on the decomposition reaction rate. The reaction is controlled when stabilizers are included. In a research work extending over a long

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period (Macleod and Johnson, 2006; Fryš et al., 2011) researchers investigated the stabilizing effect of various organic substances particularly naphthalene, mononitronaphthalene, N,N-diphenylbenzamide, carbazol, diphenylamine and diphenylnitrosoamine. The role of stabilization of organic stabilizers for double base propellants (DBPs) depends on chemical reactions between the stabilizer and the nitrogen oxide gas evolved through thermal decomposition of the propellants (Macleod and Johnson, 2006; Fryš et al., 2011). These reactions mostly lead to the formation of poisoning compounds which can be avoided by the use of inorganic stabilizers.

Generally the use of inorganic stabilizers for DBPs in the literature is scanty (Wayne et al., 2005), an aluminum silicate molecular sieve was added to propellants that give off gases such as N_2 , CO_2 , CO_2 , F_2 and NO_x during the aging process. The aluminum silicate molecular sieve was selected to have a pore size of less than about 10 Å. This brought about absorption of these undesirable gases during the aging process and thereby prevented degradation of the propellant (Robert, 1976). Zeolites are a large group of natural and synthetic hydrated aluminum silicates. They are characterized by complex three-dimensional structures with large, cage like cavities that can accommodate sodium, calcium or other cations (positively charged atoms or atomic clusters); water molecules; and even small organic molecules. Ions and molecules in the cages can be removed or exchanged without destroying the aluminosilicate framework. Zeolites find wide use as ion-exchange agents, catalysts, and molecular filters in several industrial processes (Tearpock and Bischke, 2002; Perraki and Orfanoudaki, 2004; Penn et al., 2010).

Clinoptilolite is used in many applications such as a chemical sieve, gas absorber, feed additive, food additive, odor control agent and as a water filter for municipal and residential drinking water and aquariums. Its applications are related to a large amount of pore space, high resistance to extreme temperatures and chemically neutral basic structure (Hassan, 2011; Hossein et al., 2008).

Clinoptilolite is a low field strength zeolite for which the cation specivities $Cs^+ > Rb^+ > NH_4^+ > K^+ > Na^+ > -Li^+ > H^+$, and $Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$ are predicted (Kugbe et al., 2009; Palomino et al., 2008; Xu et al., 2008; Yang et al., 2009; Shang et al., 2009). Charge-balancing of cations present on the surface of very fine-grained clinoptilolite can be replaced by high-molecular weight quaternary amines (Gu et al., 2008), such as hexadecyltrimethylammonium (HDTMA) whereas the internal zeolite cavities remained accessible for small cations. Surfactant modified zeolites (SMZ) absorb CrO_4^{2-} , benzene and perchloroethylene (PCE) suggesting that a stable HDTMA bi-layer formed on the external surface of the zeolite. Non-polar organic solutes were absorbed by the organic phase whereas anions (CrO_4^{2-}) were retained on the outward pointing positively charged head groups of the surfactant bi-layer (Gu et al., 2008). Various types of surfactants on clinoptilolite were applied to extract benzene, toluene and xylenes from petrochemical spills (El-Naggar et al., 2008). The modified clinoptilolite exhibited enhanced sorption of cations (Jha and Hayash, 2009; Novosad et al., 2005).

The use of conventional organic stabilizers forms nitrosamines that have toxic and carcinogenic effects. As a result, these conventional stabilizers should be replaced (Bergens and Danielsson, 1995). The use of inorganic stabilizers for double-base propellants can solve this problem (Robert, 1976; Asthana et al., 1992; Dominic and Wilmington, 1975; Sakizci et al., 2011; Zayed et al., 2012). Therefore, in this work clinoptilolite and centralite stabilizers are used in the mechanism of stabilization study.

2. Experimental

2.1. Preparation of clinoptilolite in nano-scale

Clinoptilolite stabilizer was prepared in its nano-form by grinding its micro-form (50–75 μ m) (which was purchased from Ostim, Ankara, Turkey) for 8 h with a rate of 400 RPM (Round Per Minute) using a grinder of type (Retsch GMBh & Co.KG, Model 2005, Rheinische Straße 36, 42781 Haan, Germany), in the Science and Technology Center of Excellence (Ministry of military production, Egypt).

2.2. Preparation of DBP samples

Samples of double-base smokeless powders were manufactured by solvent less process using (3% w/w) centralite I as a reference stabilizer in sample C₁, 2.0–4.0% (w/w) nano-clinoptilolite stabilizer in samples S₁–S₅ and 3% micro-clinoptilolite stabilizer in sample S₆.

2.3. Different thermal tests used to check the stability of DBP samples

The classical thermal stability tests (Bergmann – Junk and calorimetric tests) (Johns et al., 2008; Soliman, 2004) were used to evaluate the stability of the prepared DBP samples S_1 – S_6 and C_1 .

2.3.1. Bergmann – Junk test at 120 °C (B–J)

The B–J test was done on sample pieces with a length of approximately 3–4 mm and a diameter of 2 mm and dried at 45 °C for 16 h. The prepared powder (5 g) was introduced into the test tube and treated as explained by Bergmann – Junk (Johns et al., 2008; Soliman, 2004).

2.3.2. Calorimetric test

Calorimetric test was carried out in calorimetric bomb with a capacity of 450 cc as explained by Hassan (Hassan, 2011; Zayed et al., 2012) to estimate the calorific values of the investigated samples (S_1 – S_6 and C_1).

2.4. Different tests used to check the surface structure of stabilizers and DBP samples containing the stabilizers

X-ray Diffraction and electron microscope (both AFM and TEM techniques) analyses were used to check the surface structure of nano-clinoptilolite, micro-clinoptilolite and centralite I stabilizers and DBPs samples containing the stabilizers, and to study the effect of stabilizers on the surface structure of double-base propellants and vice versa (Hassan, 2011).

2.4.1. X-ray diffraction analysis

The composition of the investigated DBP samples and stabilizers used (Clinoptilolite and Centralite I) was determined by the X-ray diffraction technique (XRD) using PHILIPS PW 3710/ 31 diffractometer, scintillation counter, Cu-target tube and Ni filter at 40 kV and 30 mA. This instrument is connected to a computer system using APD program and PDF-2 database for mineral identification. The scan covered a 2-theta range of $5-80^{\circ}$ with a step size of 0.02° and a 0.5-s count time per step. The slits used consisted of 1-degree fixed divergence and anti-scatter slits and a 0.2-mm receiving slit.

2.4.2. Electron microscope analysis

Two different techniques of electron microscope (Transmission Electron Microscope, TEM JOEL JSM-1230 and Atomic Force Microscope, AFM, JEOL JXA-840A) were used to determine the grain size of clinoptilolite and showing its surface structure. On the other hand only AFM technique was used to show the surface structure of nano-clinoptilolite and DBP samples containing (weight/weight, w/w%) 3% nano-clinoptilolite, 3% micro-clinoptilolite and 3% centralite I, and to know the effect of each stabilizer on the surface structure of the propellant samples and vice versa.

3. Results and discussion

The evaluation and determination of the mechanism of stabilization of clinoptilolite for DBPs depend on a comparative study of thermal and surface behavior of these inorganic stabi-

Table 1 Composition of the investigated double-base propellant samples.									
Sample no.	NC %	NG %	DBP %	DNT %	Lead stearate %	Carbon black %	Stabilizer type	Stabilizer %	Grain-size of stabilizer
S ₁	59	31	5	2.7	2	0.3	Clinoptilolite	4.0	30 nano
S_2	59	31	5	2.7	2	0.3	Clinoptilolite	3.5	30 nano
S_3	59	31	5	2.7	2	0.3	Clinoptilolite	3.0	30 nano
S_4	59	31	5	2.7	2	0.3	Clinoptilolite	3.0	30 nano
S ₅	59	31	5	2.7	2	0.3	Clinoptilolite	2.5	30 nano
S ₆	59	31	5	2.7	2	0.3	Clinoptilolite	2.0	2 μm
C1	59	31	5	2.7	2	0.3	Centralite I	3.0	2 µm
$NC = N(t_{1}, t_{2}, t_{3})$									

(NC = Nitrocellulose, NG = Nitroglycerine, DBP = Dibutylphthalate, DNT = Dinitrotoluene).

 Table 2
 Bergmann – Junk test and Calorimetric test results for the double-base propellant samples containing different stabilizers percents.

Sample no.	Stabilizer type	Stabilizer %	Bergmann at 120 °C (mL	of 0.05 N NaOH)	Calorific value (Cal g^{-1})	Grain size of stabilizer
S ₁	Nano-clinoptilolite	4.0	6.6		875	30 nm
S_2	Nano-clinoptilolite	3.5	7.0		853	30 nm
S ₃	Nano-clinoptilolite	3.0	7.0		863	30 nm
S_4	Nano-clinoptilolite	2.5	8.5		615	30 nm
S ₅	Nano-clinoptilolite	2.0	9.0		844	30 nm
S_6	Micro- clinoptilolite	3.0	7.2		845	2 μm
C ₁	Micro- centralite I	3.0	7.2		735	2 μm

N.B. mL NaOH = $[NO_x \text{ gases}]$.



Figure 1 XRD for clinoptilolite stabilizer.

lizers with the results of the classical stabilizer (N,N-diethyldiphenyl urea) ($C_1 = 3\%$ w/w). The compositions of the tested DBPs samples are given in Table 1.

3.1. Classical thermal stability tests for double-base propellant samples

Bergmann – Junk test (B–J) and Calorimetric classical thermal test (Johns et al., 2008; Soliman, 2004) results for the double-base propellant samples containing different stabilizers percents are given in Table 2, in which mL NaOH (0.05 N) is equivalent to the amount of NO_x gases evolved during stabilization thermal test process. The quantitative stability results (B–J); indicated that nano-clinoptilolite percentages were divided into two groups according to their stabilizing effect in comparison with classical stabilizer. The first group includes $S_1 = 4\%$, $S_2 = 3.5\%$ e and $S_3 = 3\%$ nano-clinoptilolite, which have a higher stabilizing effect (6.6, 7 and 7 mL of NaOH equivalent to evolved NO_x gases respectively) than the classical one (7.2 mL of NaOH). The second group includes $S_4 = 2.5\%$ and $S_5 = 2\%$ nano-clinoptilolite which have a lower stabilizing effect (8.5 and 9 mL NaOH respectively) than the classical stabilizer. 3% Micro-clinoptilolite has the same stabilizing effect (7.2 mL NaOH) as the classical stabilizer. This means that, 4% nano-clinoptilolite sample has shown the best stabilizing effect and classical stabilizer.

The calorific values of samples S_1 , S_2 , S_3 , S_5 and S_6 (875, 853, 863, 844 and 845 Cal g⁻¹ respectively) are higher than that



Figure 2 XRD for N,N-diethyldiphenyl urea (Centralite I) stabilizer.



Figure 3 XRD for DBP sample containing 3% nano-clinoptilolite stabilizer.

of the sample containing classical stabilizer (735 Cal g^{-1}) and only sample S₄ has lower calorific value (615 Cal g^{-1}) than the classical stabilizer. Therefore, these values confirm that, sample four still has the highest stabilization effects on DBPs.

3.2. X-ray diffraction analysis (XRD)

X-ray diffraction analysis is probably the easiest and best mean to identify clinoptilolite and centralite I stabilizer textures and also identify the resulted nature of the double-base propellant samples containing these stabilizers. A representative XRD diffractogram for the stabilizers and the DBP samples containing the stabilizers are shown in Figs. 1–5. The d-spacing and relative peak intensities for clinoptilolite and centralite I stabilizers are listed in Table 3. The ASTM (American Society of Testing Materials) cards were used to identify the stabilizers and DBP samples.

The zeolite sample which is shown in Fig. 1 composed mainly of clinoptilolite of ASTM Card No. (22-1236). Clinoptilolite is iso-structure with heulandites (Hossein et al., 2008), therefore XRD analysis of the two phases is nearly identical which makes the differentiation difficult. These two zeolite phases are distinguished by the differences in thermal stability, Si/Al ratio and cation content.



Figure 4 XRD for DBP sample containing 3% micro-clinoptilolite stabilizer.



Figure 5 XRD for DBP sample containing 3% centralite I stabilizer.

Centralite I sample is	shown	in Fig.	2; it co	mpose	ed mainly
of N,N-diethyldiphenyl	urea	ASTM	Card	No.	(3-0042)
(Zayed et al., 2012).					

Table 3 XRD Data for clinoptilolite and centralite I.						
Clinoptilolite	Zeolite	Centralite I				
d(Å)	I/I_0	d(Å)	$I/I_{ m o}$			
8.92	100	8.40	50			
7.97	4	7.69	100			
6.78	4	6.24	60			
5.15	8	5.29	40			
4.65	14	4.92	80			
4.35	2	4.66	80			
3.96	55	4.20	40			
3.90	55	4.09	70			
3.55	6	3.78	70			
3.48	4	3.65	50			
3.32	4	3.42	40			
3.17	14	3.18	60			
3.12	16	2.98	40			
3.07	8	2.58	50			
2.974	80	2.52	40			
2.793	15	2.46	10			
2.728	35	2.39	10			
2.719	16	2.33	40			
		2.09	30			
		1.83	30			

Where I an I_0 are X-ray diffraction parameters and I/I_0 is the X-ray ratio.



Figure 6 AFM of nano-clinoptilolite.



Figure 7 TEM of nano-clinoptilolite.

Repetitive XRD data of DBP Samples containing different clinoptilolite ratios are shown in Figs. 3–5 and the d-spacing values for pure clinoptilolite and centralite samples are given in Table 3. They appear to be of amorphous shapes; so they do not give any pattern, and this indicated that the crystalline structures (crystallinity Fig. 1) of the new stabilizers (nanoclinoptilolite and micro-clinoptilolite) and of classical one (Fig. 2) were not observed in the samples (S_1 – S_6) diffractograms (Figs. 3–5). This may be attributed to the pressing processes of DBPs with stabilizers under very high pressure during their mixture preparation (Hassan, 2011; Zayed et al., 2012) and the adsorption of nitric oxides by the new stabilizers which cause changes in the crystal structure of nano- or micro-clinoptilolite stabilizers (Figs. 1 and 2 and Table 3).

3.3. Electron microscope analysis

The clinoptilolite samples in nano and micro sizes were prepared by the milling technique (Hassan, 2011; Zayed et al., 2012) and checked by two electron microscope tools (AFM and TEM). The data obtained are shown in Figs. 6–11 and Table 4; which will show the role of electron microscope analysis in clarifying the surface behavior of these inorganic stabilizers and their role in stabilizing the process of DBPs.



Figure 8 TEM of micro-clinoptilolite.



Figure 9 AFM structure of DBP sample stabilized by 3% nanoclinoptilolite.



Figure 10 AFM structure of DBP sample stabilized by 3% micro-clinoptilolite.



Figure 11 AFM structure of DBP sample stabilized by 3% Centralite I.

From the data in Table 4, the results of Atomic Force Electron Microscope (AFM) (Fig. 7) and Transmission Electron Microscope (TEM) (Fig. 8) of the clinoptilolite samples obtained by milling technique; it is observed that the average grain size (main radius of particles) of this sample is equal to 30 nm, which was calculated from the radius values of nanoclinoptilolite particles that ranged between 7 and 153 nm (Table 4). These data mean that the grain sizes of clinoptilolite samples are in a nano-scale; which is practically used for stabilizing DBP samples (S_1-S_5) (Table 1). On the other hand the TEM technique is also used to check the grain size of another sample of clinoptilolite (Fig. 9), which is also used as stabilizer for DBP sample S_6 in comparison with the nano-scale samples (S_1-S_5) . From Fig. 9, it is clear that this sample has particles of micro-scale sizes. From the AFM (Fig. 7) for nano-clinoptilolite, and scanning electron microscope (Fig. 9) for micro-clinoptilolite, we found a great difference in surface structure between them due to the difference in grain size and also the difference in some physical properties such as the surface area (as the grain size decreases the surface area increases). This means that, the difference in grain size between nano- and micro-clinoptilolite samples leads to a big difference in their stabilizing ability for DBPs.

AFM Figs. 9-11 show the surface structure of DBP sample stabilized by 3% nano-clinoptilolite, by 3% micro-clinoptilolite and that stabilized by 3% classical stabilizer (Centralite I) respectively. From these figures it is observed that, in general; clinoptilolite makes the surface of double-base propellant more ordered and homogenized as indicated by the regular map of sample surface (Fig. 10); which is greatly different from non-ordered nano-clinoptilolite sample itself (Fig. 7). This ordering and homogeneity of the stabilized DBP sample by 3% nano-clinoptilolite may be attributed to the ordering of nano-clinoptilolite particles on the surface of DBP during the process of preparation. This ordering and homogeneity lead to the high surface area of the sample that adsorbs a higher amount of nitrogen oxides evolved on its surface in an ordered and homogenized shape. But in case of double-base propellant samples stabilized by 3% micro-clinoptilolite; the ordering and homogeneity of the surface structure decrease due to the high grain size of stabilizers. The surface structure of double-base propellant sample stabilized by the (3% w/w)

Particle no.	Main radius µm	Particle no.	Main radius µm	Particle no.	Main radius µm
1	0.007	32	0.116	63	0.025
2	0.01	33	0.061	64	0.02
3	0.039	34	0.007	65	0.042
4	0.019	35	0.018	66	0.007
5	0.031	36	0.041	67	0.007
6	0.043	37	0.097	68	0.026
7	0.037	38	0.02	69	0.153
8	0.031	39	0.016	70	0.034
9	0.054	40	0.046	71	0.039
10	0.016	41	0.024	72	0.047
11	0.021	42	0.025	73	0.057
12	0.019	43	0.069	74	0.055
13	0.007	44	0.074	75	0.012
14	0.056	45	0.046	76	0.041
15	0.022	46	0.012	77	0.016
16	0.038	47	0.016	78	0.007
17	0.057	48	0.041	79	0.007
18	0.01	49	0.007	80	0.007
19	0.037	50	0.024	81	0.007
20	0.026	51	0.007	82	0.017
21	0.021	52	0.072	83	0.016
22	0.007	53	0.05	84	0.016
23	0.028065	54	0.018	85	0.036
24	0.028102	55	0.047	86	0.041
25	0.028139	56	0.025	87	0.057
26	0.028177	57	0.007	88	0.025
27	0.028214	58	0.013	89	0.007
28	0.028251	59	0.022	90	0.021
29	0.028289	60	0.02	91	0.047
30	0.028326	61	0.007	92	0.022
31	0.028363	62	0.023	93	0.071

classical stabilizer (Centralite I) showed the lowest ordering and homogeneity, and this may be due to the less stabilizing effect and large grain size of centralite I stabilizer. Finally it is concluded that the nano-size of stabilizer be more effective than the micro-size in DBPs stabilization process.

3.4. Mechanism of stabilization

From the data obtained (Tables 1-4) and Figs. 1-11 of XRD and electron microscope for the stabilizers (nano-clinoptilolite, micro-clinoptilolite and centralite I) and the double-base propellant samples containing these stabilizers, the mechanism of stabilization of the inorganic stabilizer (Clinoptilolite) for DBPs can be deduced. This mechanism can be explained by the first step which included the adsorption (physico- or chemi-sorption) of the evolved NO_x via interaction with cationic surface groups to form a stable bi-layer on the external surface of the zeolite. The second one included the partitioning of the evolved NO_x gases into the internal cavities of clinoptilolite together. The third one may involve specific binding of absorbed NO_x gas radicals with cationic form of zeolite at its internal base structure (Fig. 12). On the other hand centralite (Fig. 11) stabilizing mechanism is only explained by chemical absorption interaction with NO_x gases. Therefore, mechanism process depends on the adsorption of nitrogen oxides in the pore openings of clinoptilolite, and/or physical or chemi-ionic surface interaction leading (Fig. 12) to the high stability results



Figure 12 Sketching drawing of (NO_x) forming a bi-layer (tail to tail) on the surface of clinoptilolite, NO_x partitioning into the bulk and specific base binding of gas radicals.

at very high temperatures (Hassan, 2011; Dominic and Wilmington, 1975; Sakizci et al., 2011; Zayed et al., 2012). The grain size of inorganic stabilizer played an important role in the stabilization process.

4. Conclusion

Nano-clinoptilolite can be considered as a good stabilizer for DBPs. The percentage 4% w/w of nano-clinoptilolite is considered as the best between the different percentages of nano-clinoptilolite; because it shows a pronounced stabilizing effect on the propellant sample. The thermal stability tests together with XRD, AFM and AEM give good explanation of surface

behavior of these stabilizers on stabilization processes of DBPs.

The mechanism of stabilization of DBPs by using clinoptilolite can be explained by the first step which included the adsorption (physico- or chemi-sorption) of the evolved NO_x via interaction with cationic surface groups to form a stable bi-layer on the external surface of the zeolite. The second one included the partitioning of the evolved NO_x into the internal cavities of clinoptilolite. The third one involved specific binding of absorbed NO_x gas radicals with cationic form of zeolite at its internal base structure (Fig. 12).

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.arabjc. 2013.08.021.

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