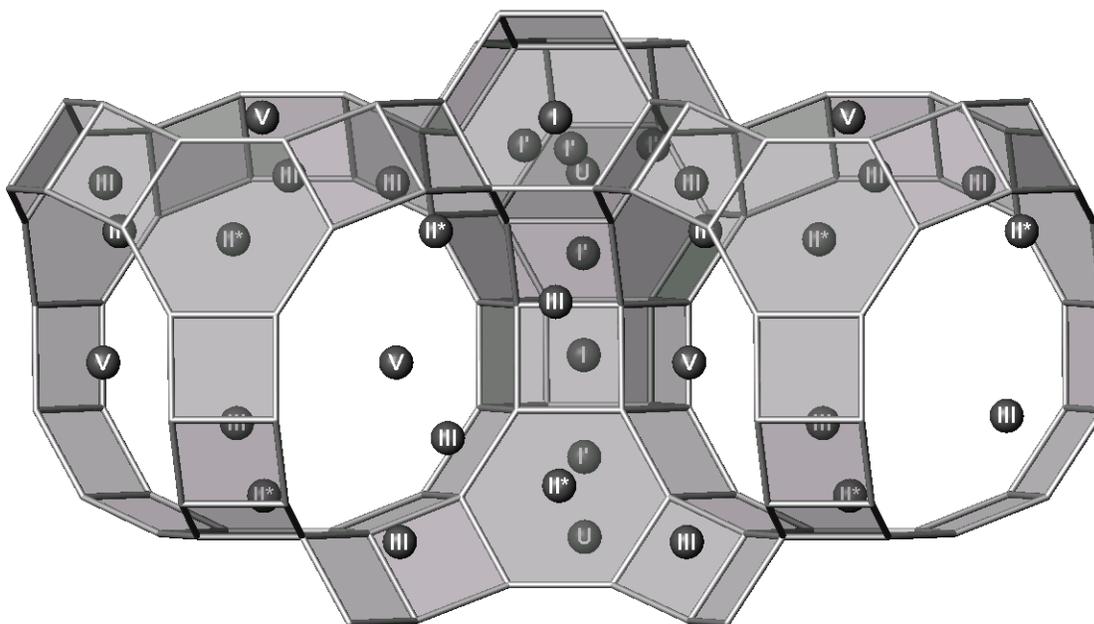


Supplementary Material

NO_x adsorption site engineering in Ru/Ba,Na-Y zeolite

Sylvia Smeekens, Steven Heylen, Nikki Janssens, Kristof Houthoofd, Johan A. Martens, Christine E. A. Kirschhock

Selected cation positions in FAU



SI : centre of double 6-ring (D6R). Occupied by Ru³⁺ during NO_x adsorption under oxidising conditions

SI': in the sodalite cage (sod) in front of a 6R belonging to D6R. Typically occupied by Ba²⁺.
U: centre of sod. Rarely found occupied in FAU. Here assigned to Ru⁰ after NO_x desorption under reducing conditions.

SII': in sod in front of a 6R belonging to the supercage (sc). Found to be occupied by Ba²⁺ at high Ba-exchange rates. (not shown in figure)

SII*: in the supercage (sc) in front of a 6-ring. Typically occupied by Ba²⁺ and, if sterically allowed, by Na⁺. Na⁺ usually is found close to the 6-ring compared to Ba²⁺.

SIII: in the sc in front of a 4R. Mostly observed occupied by Na⁺. Distance of this position to the framework was found to be highly sensitive to presence of Ru³⁺ on SI.

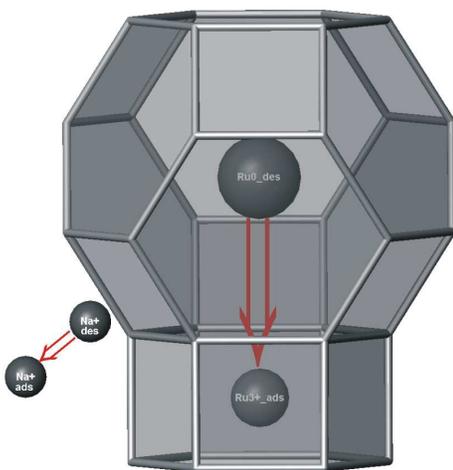
SV: centre of 12 ring (12R). Occupied by Na⁺ in presence of water.

Exclusion of SI' and SII* and SIII



Occupation of SI' by Ba²⁺ makes occupation of 3 SII sites in the vicinity by Na⁺ highly unlikely. As each sodalite cage was found to be occupied with 1 Ba²⁺ on SI' and 1 Ba²⁺ on SII* all 4 available SII* positions per sod were blocked to Na⁺. The same argument applies to the occupation of 3 of the 6 available SIII sites.*

Synergy between SI and SIII



Presence of Ru³⁺ on SI was found to affect the position of SIII cations. Under oxidising conditions Ru³⁺ was found in the centre of D6R with SIII (occupied by Na⁺) moved far into the sc. Reduction of Ru³⁺ caused its migration into sod. In this case SIII was found significantly closer to the framework.

Strategy of Rietveld refinement

Refinement of the structures occurred as follows: At first the structure cycled in absence of NO_x was investigated. The positions of the framework atoms were obtained from the IZA website. Right from the start dummy ions were included on typical positions SII and SI' and SII'. SI was not occupied, as it is known from literature this site is unfavourable for Na^+ and not accessible for Ba^{2+} . Initially, the framework positions were kept fixed, while background, profileshape, unit cell scaling and cation position and occupation were refined. Absorption was not refined but calculated based on known chemical composition, capillary thickness and packing density. In a second step observed and difference electron density Fourier maps were inspected. Cation sites occupied by Ba^{2+} were readily identified due to the high electron density with highly symmetric shape. In all samples Ba^{2+} was consistently found on SI' and SII* with reasonable distances between framework oxygen and Ba^{2+} (2.7-3.1 Å). Except for the twice exchanged sample which also contained Ba^{2+} on SII', sod never was occupied with more than one Ba^{2+} . Ba was inserted on the identified sites and its occupation and positions were refined. Already at this state the occupation numbers came close to the determined chemical composition. Fourier charts of singly exchanged Faujasite showed clear electron density on SV and SIII. In accordance to previous findings these were assigned to Na^+ . Inspection of the environment of SV indicated octahedral coordination of these sites by water. Initially the coordination geometry was inserted as rigid body and its orientation was freely refined while fixing the occupation numbers of cation and ligand. The final orientation of these complexes always pointed towards SIII sites. In a next step occupation numbers on SIII and SV were refined. In the case of $\text{Ba}_{17.3}\text{Na}_{17.3}\text{Al}_{52}\text{Si}_{140}\text{O}_{384}$ the refined occupation numbers appeared closely related and were therefore constrained. Refinement came very close to the elemental composition. Residual electron density in a distance to around 2.3 Å SIII was assigned to water and completed the octahedron around this site. The orientation of the SV-rigid body was then inspected for symmetry and replaced by water and sodium atoms on the respective positions. The octahedral environments of the sodium ions on SV and SIII was essentially retained during refinement. In a final step framework and thermal parameters were left to refine.

In the case of $\text{Ru}_{0.7}\text{Ba}_{17}\text{Na}_{15.8}\text{Al}_{52}\text{Si}_{140}\text{O}_{384}$ refinement of occupation of SV and SIII did not account for the number of Na^+ based on chemical composition. Inspection of the Fourier charts showed the site SII* assigned to Ba^{2+} was quite unsymmetric and was apparently composed of a split position. After inserting Na^+ on SII*, closer to the 6R than Ba^{2+} and with typical distances to the framework oxygen, refinement of the occupation numbers adequately described the chemical composition. Between SII* and SIII residual electron density was observed. This electron density was too close to Ba^{2+} to be assumed to coordinate this cation (2.4 Å). So this electron density was assigned to water interacting with Na^+ on SII* and SIII in accordance with previous observations. Free refinement of position and occupation resulted in a close match of occupation numbers of this water and Na^+ on these positions. Based on these observations occupation numbers of water and Na^+ cation were constrained before framework and temperature factors were refined. At the same time an indication of residual electron density on SU was assigned as Ru in accordance with previous results. Occupation numbers of Ba^{2+} on SI' clearly indicated that not all sod were occupied by Ba^{2+} . It appears likely Ru^0 occupies these, otherwise empty, empty sod. As final step constraints of occupation numbers were lifted and the rigid body around SV was replaced by free atom positions. Neither geometry nor occupation numbers strongly migrated from the previously obtained values. Especially this observation

strongly indicated the clustering of Na^+ ions. If those ions would be more dispersed in the zeolite, higher water contents must be expected as fewer molecules could be shared between neighboring cations.

Refinement of $\text{Ru}_{0.76}\text{Ba}_{22.8}\text{Na}_{4.0}\text{Al}_{52}\text{Si}_{140}\text{O}_{384}$ was highly challenging as the small number of light Na^+ cations next to a high concentration of Ba^{2+} made identification of residual electron density after Ba^{2+} refinement difficult. However, based on the results of the sample with higher Na content, SV, SIII, and SII* were inserted as Na^+ positions and the occupation factors and positions left to refine. Indeed, consistent occupation factors were found. The same strategy as before, using a rigid body for the SV environment was applied and water was also assumed between SII* and SIII. These parameters described the experimental pattern quite satisfactorily. To ensure the structure model in this case was reliable a higher resolved measurement was analysed.

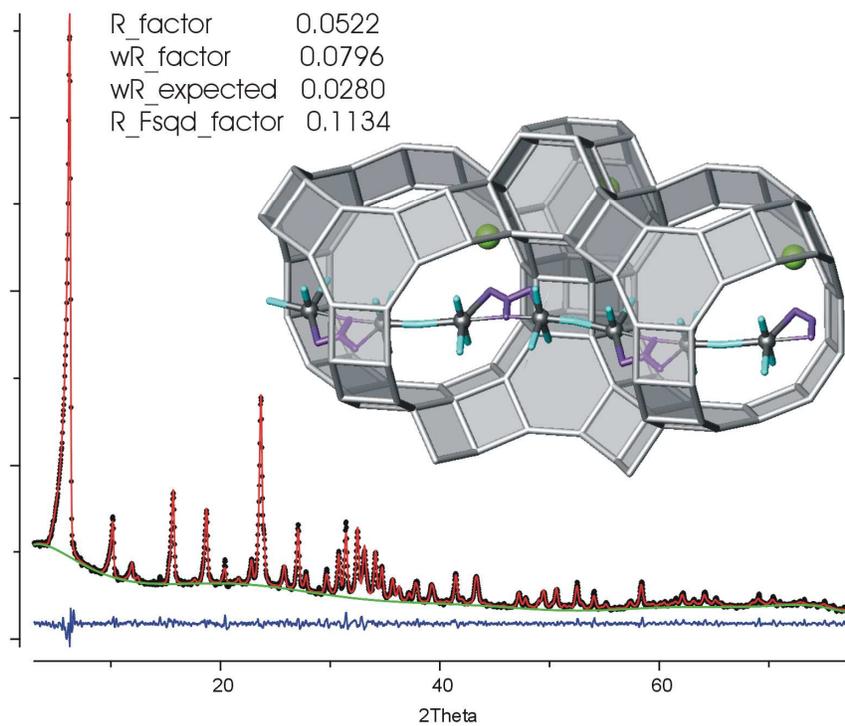
To determine the structures after NO_x adsorption the corresponding structures in its absence served as starting models. In no case a significant change of occupation numbers of cations was observed. Especially Ba^{2+} kept position and occupation number after switching to oxidising conditions and adsorption of NO_x .

Analysis of $\text{Ba}_{17.3}\text{Na}_{17.3}\text{Al}_{52}\text{Si}_{140}\text{O}_{384}$ showed no significant change of Na^+ positions and occupations neither. However vicinity of the cations was affected by adsorption of NO_2 which, according to the adsorption studies and results on pure BaY, was present as nitrate in high concentrations. Inspection of the Fourier charts eventually revealed electron density in a trigonal shape very well in accordance with the geometry of the NO_3^- moiety. This molecule was inserted as rigid body in the found location and left to re-orient freely. Further analysis revealed part of the water molecules was replaced by this entity but the octahedral surrounding of the Na^+ ions on SV and SIII was essentially retained. An interesting observation was the orientation of the nitrate species in the same molar concentration as SV and SIII. One of the oxygen atoms of the NO_3^- species pointed towards oxygen atoms of the frame (O4) with a distance of 2 Å. This can be interpreted as a hydrogen bond between framework and nitrate, which therefore best is described as adsorbed nitric acid.

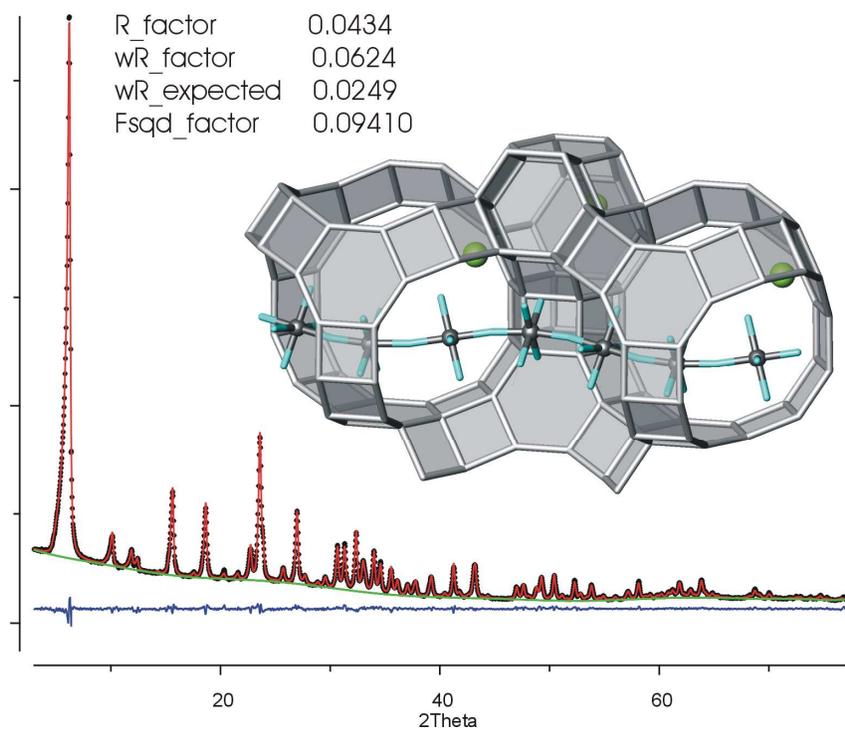
Testing the structure model of $\text{Ru}_{0.7}\text{Ba}_{17}\text{Na}_{15.8}\text{Al}_{52}\text{Si}_{140}\text{O}_{384}$ as starting parameters after adsorption of NO_x quickly showed the only significant changes were the positions of SIII sodium ions and the appearance of electron density in D6R in favour of SU. Inspection of the electron density around the new SIII site led to identification of an octahedral environment assigned to water. Of the six ligands four were shared with neighboring SV and SII* cations. Similar as before the close match of occupation of water and cations clearly indicated at local clustering of Na^+ -water networks. Though only small amounts of NO_x was adsorbed a N_2O_3 molecule was inserted at a position with residual electron density and left to re-orient. Eventually its orientation closely resembled the arrangements found in materials in absence of Ru and Ba^{2+} . A slight improvement of the goodness of fit and the R-values indicated this position to be feasible if not proven.

In a similar way the structure of $\text{Ru}_{0.76}\text{Ba}_{22.8}\text{Na}_{4.0}\text{Al}_{52}\text{Si}_{140}\text{O}_{384}$ was investigated. As site for the N_2O_3 molecule the previously found position was used but not refined.

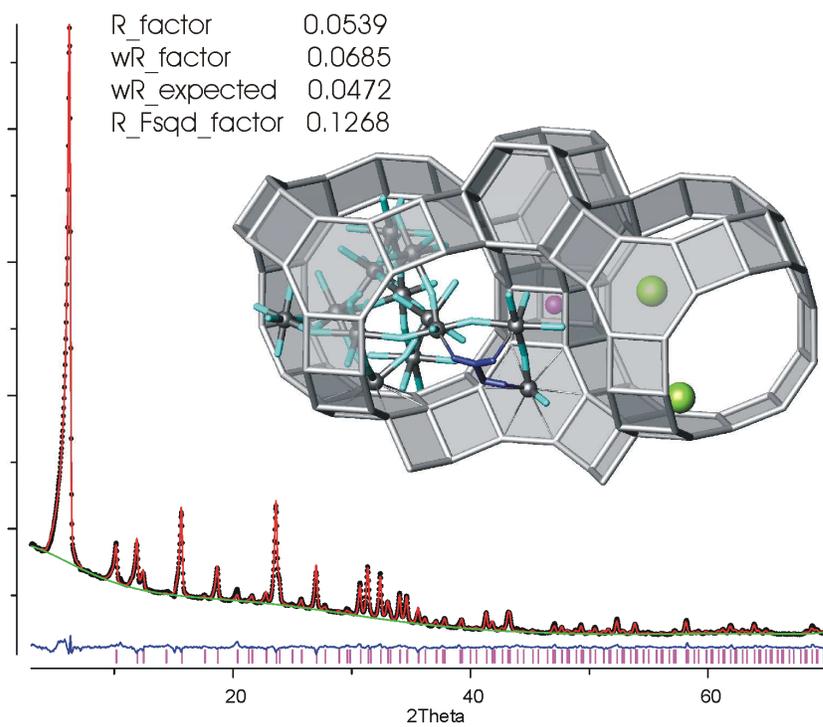
BaNaY ads



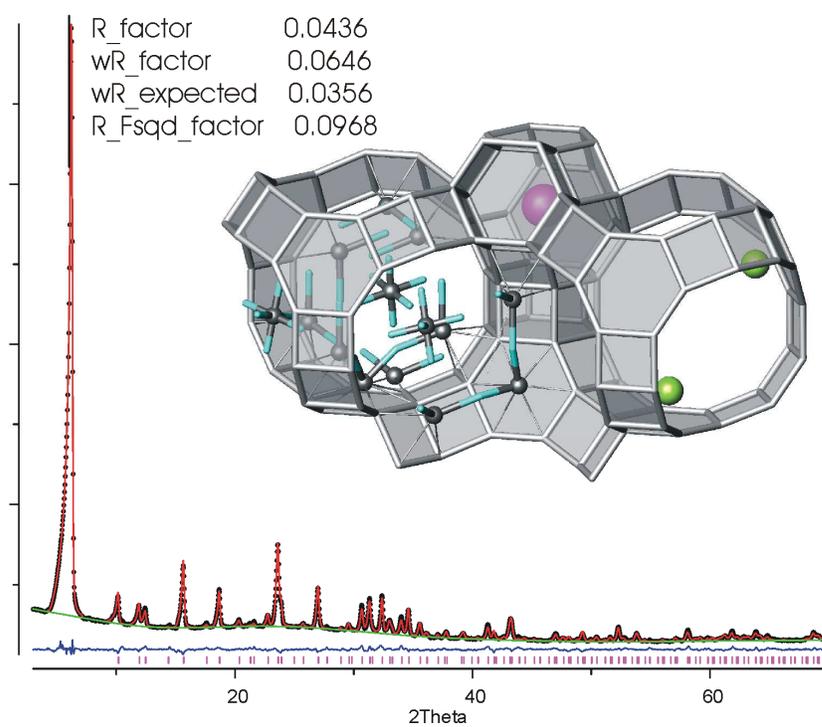
BaNaY des



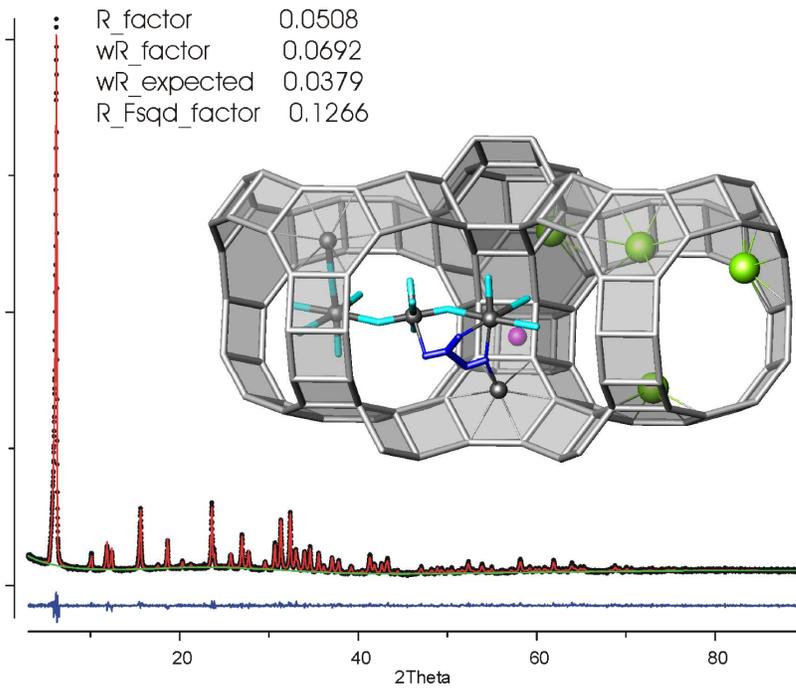
RuBaNaY ads



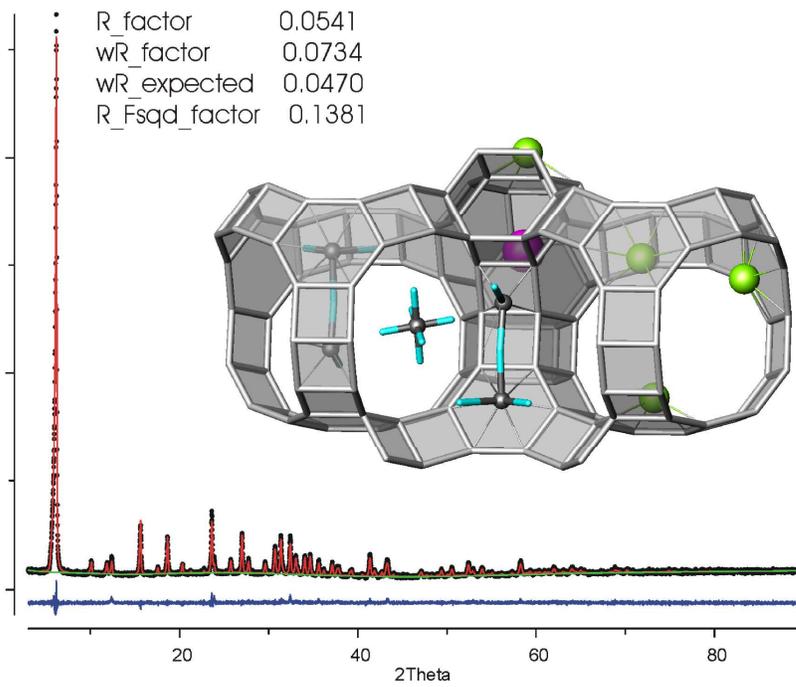
RuBaNaY des



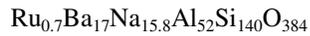
RuBaNaY 2 exch ads



RuBaNaY 2 exch des

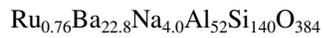


Occupation numbers of cations and water



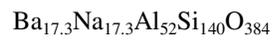
			des		ads	
sii	ba	32	0.31	9.92	0.31	9.91
si	ba	32	0.22	6.88	0.22	6.97
sii'	ba	32				
siii na	na	48	0.16	7.84	0.16	7.82
sv	na	16	0.16	2.63	0.17	2.7
sii	na	32	0.16	4.99	0.16	5.03
sum	ba			16.8		16.9
sum	na			15.5		15.6
sum cations				49.1		49.3
	OW5	96	0.16	15.7	0.17	16.1
	Ow23	96	0.17	16.3	0.17	15.9
	Ow3a	96			0.16	15.5
	Ow3b	96			0.17	16.2
sum water				32.1*		63.7

*determined by TG: 31



			ads		des		
sii	ba	32	0.28	9	0.29	9.21	
si	ba	32	0.21	6.69	0.21	6.69	
sii'	ba	32	0.21	6.72	0.21	6.81	
siii na	na	48	0.04	1.96	0.04	1.96	
sv	na	16	0.06	1	0.06	1	
sii	na	32	0.06	2	0.06	2	
sum	ba			22.4		22.7	
sum	na			4.96		4.96	
sum cations				49.8		50.4	
	OW53	96	0.06	6.16	OW53	0.04	3.46
	Ow3	96	0.04	3.65	Ow5a	0.02	2.02
	Ow23	96	0.04	4.09	OW5b	0.02	2.21
		96			OW2	0.05	5.09
sum water				13.9		12.8	

Occupation numbers of cations and water (cont.)

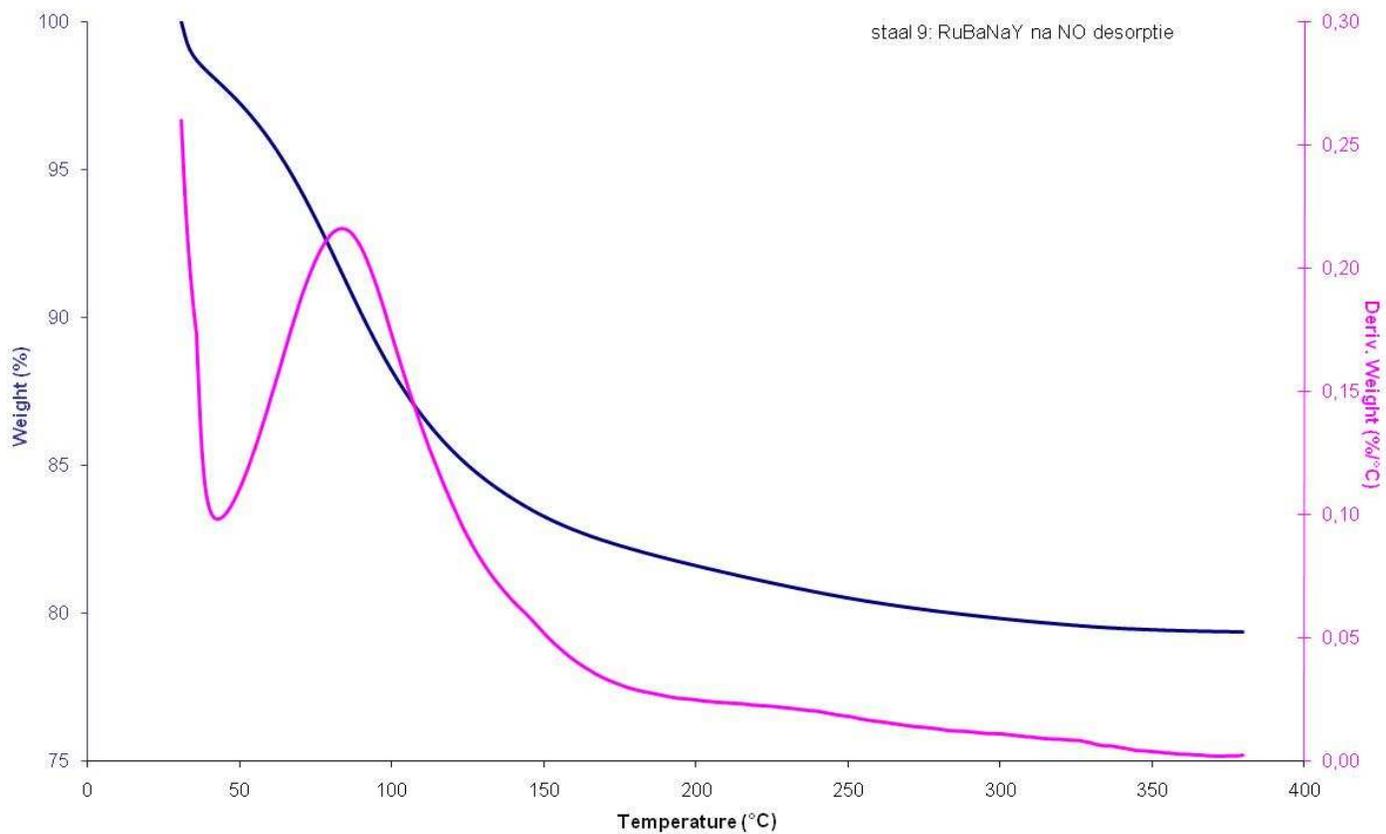


			ads		des	
sii	ba	32	0.28	8.8	0.28	8.99
si	ba	32	0.26	8.32	0.25	8.01
sii'	ba	32				
siii na	na	48	0.17	8.11	0.16	7.87
sv	na	16	0.51	8.1	0.49	7.87
sii	na	32				
sum	ba			17.1		17
sum	na			16.2		15.7
sum cations				50.4		49.7
	OW5a	96	0.17	5.41	OW53	0.49 47.2
	OW5b	96	0.17	16.2	OW3a	0.16 7.87
	Ow3a	48	0.17	8.11	OW3b	0.16 7.87
	Ow3b	96	0.17	16.2	OW3c	0.16 15.7
sum water				56.8		78.7

Bondlengths (Å) and angles (°) of framework

banads				banades				rubaads			
	O1	T1	1.64		O1	T1	1.60		O1	T1	1.66
	O2	T1	1.64		O2	T1	1.63		O2	T1	1.66
	O3	T1	1.62		O3	T1	1.57		O2	T1	1.66
	O4	T1	1.65		O4	T1	1.69		O3	T1	1.58
			1.64				1.63				1.64
T	O3	T	145.00	T	O3	T	144.03	T	O3	T	141.19
T	O1`	T	138.09	T	O1`	T	145.83	T	O1`	T	135.18
T	O2	T	143.65	T	O2	T	144.24	T	O2	T	144.62
T	O4	T	140.94	T	O4	T	142.61	T	O4	T	141.76
			141.92				144.18				140.69
O3	T	O1	112.55	O3	T	O1	109.35	O1	T	O2	112.04
O3	T	O2	108.24	O3	T	O2	113.19	O1	T	O4	105.60
O3	T	O4	109.56	O3	T	O4	108.99	O1	T	O3	118.55
O1	T	O2	112.38	O1	T	O2	110.77	O2	T	O4	106.98
O1	T	O4	106.81	O1	T	O4	110.90	O2	T	O3	105.07
O2	T	O4	107.13	O2	T	O4	103.53	O4	T	O3	108.07
			109.45				109.46				109.39
rubades				ruba2exchads				ruba2exchdes			
	O1	T1	1.66		O1	T1	1.65		O1	T1	1.66
	O2	T1	1.65		O2	T1	1.61		O2	T1	1.69
	O3	T1	1.58		O3	T1	1.61		O3	T1	1.62
	O4	T1	1.69		O4	T1	1.65		O4	T1	1.61
			1.64				1.63				1.64
T	O3	T	142.57	T	O3	T	147.82	T	O3	T	144.70
T	O1`	T	134.98	T	O1`	T	150.52	T	O1`	T	140.90
T	O2	T	145.80	T	O2	T	141.49	T	O2	T	141.92
T	O4	T	142.08	T	O4	T	144.84	T	O4	T	135.19
			141.36				146.17				140.68
O1	T	O2	111.02	O3	T	O1	109.20	O3	T	O1	104.89
O1	T	O4	105.65	O3	T	O2	110.55	O3	T	O2	111.22
O1	T	O3	117.94	O3	T	O4	112.82	O3	T	O4	115.02
O2	T	O4	107.50	O1	T	O2	108.75	O1	T	O2	104.40
O2	T	O3	105.61	O1	T	O4	104.95	O1	T	O4	115.42
O4	T	O3	108.73	O2	T	O4	110.36	O2	T	O4	105.48
			109.41				109.44				109.41

Thermogravimetric analysis is Ru/Ba,NaY zeolite after NO_x release



The weight loss above 150°C corresponded to 31 water molecules in very good agreement with the 32 water molecules determined by Rietveld refinement. The earlier onset of dehydration during TG was caused by the dry environment while NO_x adsorption/desorption always occurred in presence of water.