

QUANTUM CHEMICAL STUDY OF PHYSICAL CHARACTERISTICS OF Co- AND Ni-FAUJASITES

Stanislav BERAN

*J. Heyrovský Institute of Physical Chemistry and Electrochemistry,
Czechoslovak Academy of Sciences, 121 38 Prague 2*

Received June 17th, 1981

The CNDO/2 method was used for a physico-chemical characterization of faujasite zeolites, modelled by $T_6O_6(OH)_{12}$ clusters containing Ni^+ , Ni^{2+} , $Ni(OH^+)$, Co^{2+} , Co^{3+} , $Co(OH^+)$ cations localized in the S_{II} and S_I cationic positions. It is shown that the cations are bound preferentially to the oxygen atoms of the zeolite skeleton by a strong electron donor-acceptor bond. As the consequence of the bond formation, the electron charge is significantly shifted from a skeleton to the cation. The charge densities calculated on the cations ($Ni^+ \sim 0.3$, $Ni^{2+} \sim 0.35$, $Co^{2+} \sim 0.4$, $Co^{3+} \sim 1.1$ respectively) show that with uni- and bivalent cations the positive charge is in main part compensated by donation of electrons from the skeleton, while with trivalent cations the compensation is only partial. The Ni^+ cation possesses significant electron donor properties whereas the Co^{3+} cation has a strong electron acceptor character. For both cations bivalency appears to be the most stable valent state. Both studied cations show great affinity to hydration, however, their corresponding hydroxyl adducts — the $Ni(OH^+)$ and $Co(OH^+)$ cations exhibit substantially less acid properties, compared with the hydroxyl groups of the skeleton.

The metal cations compensating the negative charge of the zeolitic skeleton determine to a large extent the physical, chemical and catalytic zeolite properties^{1,2}. While cations of the non-transition metals effect the electrostatic field of the zeolite, the acidity of hydroxyl groups (*i.e.* zeolite Brönsted centres) or they act as Lewis centres, cations of the transition metals may act in addition as zeolitic redox sites. The transition metal cations localized in the cationic positions of the zeolite (so as randomly localized cations and metallic or oxide clusters) can be found in different oxidation states, depending on the zeolite pretreatment. The properties of these cations are also influenced by a type of the cation position, as well as by the fact that together with the skeletal oxygen atoms other ligands (H_2O , OH , O) can be coordinated to the cation.

The cations of Co and Ni appear in the zeolites in cationic positions as Co^{2+} and Ni^{2+} cations and they can be reduced down to the metal². For Ni-zeolites the existence of the Ni^+ cation was described³, on the other hand Co^{3+} and Ni^{3+} cations were not observed^{2,3}. Both last cations can be found in various hydroxy and aquo complexes^{4,5}.

Calculations of the electronic structure of the zeolites by means of quantum chemistry methods represent one of the direct approaches providing information on physico-chemical properties of various forms of zeolites on a molecular level. Theoretical study of the different forms of Co and Ni faujasites is the main object of this paper.

The Model and Method

The quantum chemistry models suitable to study properties of the solid phase can deal only with a limited number of atoms. As a result, the models do not fully describe the simulated solid phase, especially for such properties which depend on a majority or all atoms of the real crystal. In case of zeolites belonging to the group of ionic (or partially ionic) crystals, their cluster models do not take full account of the electrostatic field of the zeolitic crystal. However, a number of calculations of the physico-chemical properties of zeolites, based on cluster models provided at least qualitatively reasonable information on a character of the zeolite crystals⁶⁻²³.

The Co- and Ni-zeolite were modelled by means of the earlier successfully used $T_6O_6(OH)_{12}$ clusters, representing six-member windows of the zeolite facing a large cavity (cluster A, Fig. 1) or a prisma (cluster B, Fig. 1). The cations Co^{3+} , $Co(OH)^+$,

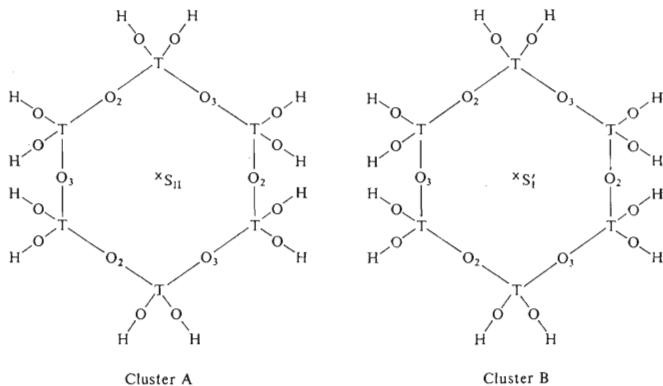


FIG. 1
Co- and Ni-zeolite cluster models used for the calculations

Co^{2+} , Ni^{2+} , $\text{Ni}(\text{OH})^+$ and Ni^+ were localized in a S_{II} position (cluster A) or a S'_I position (cluster B). With $\text{Co}(\text{OH})^+$ and $\text{Ni}(\text{OH})^+$, the metallic ion was localized in the S_{II} or S'_I position and the hydroxyl group was located on a three-fold axis of the zeolitic crystal, facing large cavity (cluster A) or the cub-octahedron (cluster B). The $\text{Co}-\text{O}(\text{Ni}-\text{O})$ and $\text{O}-\text{H}$ bond length equaled $2.0 \cdot 10^{-10}$ and $1.08 \cdot 10^{-10}$ m respectively. Geometry of the zeolite skeleton was obtained from X-ray data of the Co-zeolites²⁴ and Ni-zeolites²⁵ and it was not adapted for different Al-O and Si-O lengths, for reasons given in reference²⁰. The zeolite clusters were terminated by the hydrogen atoms⁶⁻⁹.

Cluster calculations were performed by the CNDO/2 method extended for transition metals, parametrized by Clark²⁶ and coworkers and using the s, p basic set of AO's for Si and Al atoms²⁰.

RESULTS AND DISCUSSION

The effect of Co^{2+} , $\text{Co}(\text{OH})^+$, Co^{3+} , Ni^{2+} , $\text{Ni}(\text{OH})^+$ and Ni^+ cations on the faujasite zeolite skeleton is evident from charge densities and bond orders, given for individual cluster types in Table I and Table II. It shows that in analogy with other cationic forms of faujasites^{8,18-23}, the atom charge densities of the zeolite skeleton are practically not influenced by coordination of the cobalt or nickel cations. An exception can be found with the skeletal oxygen atoms participating in the cation coordination (O_2 for the S_{II} , O_3 for the S'_I position). Much more affected by the cation coordination are the T-O bond strengths of skeletal oxygen atoms coordinating the cations, which are weakened (Table I and II). The relative extent of T-O bond weakening can be expressed for individual cations as a sequence: $\text{Co}^{3+} > \text{Co}^{2+} > \text{Co}(\text{OH})^+$ for cobalt and $\text{Ni}^{2+} > \text{Ni}^+ > \text{Ni}(\text{OH})^+$ for nickel. This trend is connected with the ability of individual cations to withdraw electron charge from the zeolite skeleton.

The bond between individual cations and the zeolite skeleton has, in analogy with other cationic forms of zeolites^{8,18-23}, a character of the electron donor-acceptor bond and due to formation of this bond, the electron charge from a lone electron pair of the skeletal oxygen atom is donated to the coordinated cation. The electron donor-acceptor bond is in Co and Ni zeolites relatively quite strong, similarly to other faujasite zeolites containing aluminium or transition metal cations^{8,23} (see the Wiberg's bond orders $p_{\text{Co}-\text{O}}$ and $p_{\text{Ni}-\text{O}}$, Table I and II). As the consequence of formation of these new cation-skeletal bonds, the structure of the zeolite is stabilized and the destabilizing effect of the coordination of cations (reflected in weakening of T-O bonds in the zeolitic skeleton) is thus compensated.

The above stabilizing effect follows for individual cations the same trend as the effect of destabilization: the extent of stabilization (given by a strength of cation-skeleton bond) decreases for cobalt cations in the order $\text{Co}^{3+} > \text{Co}^{2+} > \text{Co}(\text{OH})^+$ and for nickel cations in the order $\text{Ni}^{2+} > \text{Ni}^+ > \text{Ni}(\text{OH})^+$.

TABLE I
CNDO/2 charge densities q and Wiberg bond orders p in the zeolite models containing Co^{2+} , Co(OH)^+ and Co^{3+} cations localized in S_{II} and S_I positions, for a 1:1 and ∞ Si:Al ratio

Values	S_{II}						S_I					
	Co^{2+}		Co(OH)^+		Co^{3+}		Co^{2+}		Co(OH)^+		Co^{3+}	
	1:1	∞	1:1	∞	1:1	∞	1:1	∞	1:1	∞	1:1	∞
q_{Si}	1.57	1.68	1.55	1.70	1.55	1.70	1.56	1.67	1.54	1.69	1.56	1.56
q_{Al}	1.37	—	1.39	—	1.34	—	1.37	—	1.39	—	1.34	1.34
q_{O2}	-0.67	-0.70	-0.64	-0.68	-0.70	-0.68	-0.69	-0.69	-0.69	-0.68	-0.69	-0.69
$q_{\text{O3(4)}}$	-0.70	-0.72	-0.70	-0.71	-0.72	-0.71	-0.64	-0.68	-0.63	-0.66	-0.67	-0.67
q_{Co}	0.46	0.57	0.34	0.41	0.34	0.41	0.29	0.40	0.10	0.12	1.04	1.04
q_{O}	—	—	-0.51	-0.55	—	—	—	—	-0.49	-0.50	—	—
q_{H}	—	—	0.02	0.07	—	—	—	—	0.00	0.07	—	—
$p_{\text{Si-O2}}$	0.73	0.62	0.82	0.69	0.67	0.69	0.95	0.79	0.96	0.80	0.94	0.94
$p_{\text{Al-O2}}$	0.48	—	0.52	—	0.45	—	0.54	—	0.56	—	0.54	0.54
$p_{\text{Si-O3(4)}}$	0.96	0.78	0.98	0.80	0.94	0.80	0.68	0.58	0.76	0.63	0.59	0.59
$p_{\text{Al-O3(4)}}$	0.55	—	0.57	—	0.54	—	0.44	—	0.47	—	0.40	0.40
$p_{\text{Co-Si}}$	0.10	0.09	0.09	0.09	0.10	0.10	0.10	0.09	0.09	0.08	0.10	0.10
$p_{\text{Co-Al}}$	0.11	—	0.11	—	0.11	—	0.11	—	0.10	—	0.10	0.10
$p_{\text{Co-O2}}$	0.49	0.47	0.38	0.36	0.58	0.36	0.08	0.08	0.06	0.06	0.11	0.11
$p_{\text{Co-O3(4)}}$	0.08	0.08	0.07	0.07	0.12	0.07	0.60	0.57	0.50	0.47	0.73	0.73
$p_{\text{Co-O}}$	—	—	0.63	0.69	—	—	—	—	0.74	0.83	—	—
$p_{\text{O-H}}$	—	—	0.98	0.98	—	—	—	—	0.99	0.98	—	—

TABLE II

CNDO/2 charge densities q and Wiberg bond orders p in the zeolite models containing Ni^{2+} , $\text{Ni}(\text{OH})^+$ and Ni^+ cations localized in S_{II} and S'_{I} positions, for 1:1 and ∞ Si:Al ratio

Values	S_{II}						S'_{I}					
	Ni^{2+}		$\text{Ni}(\text{OH})^+$		Ni^+		Ni^{2+}		$\text{Ni}(\text{OH})^+$		Ni^+	
	1:1	∞	1:1	∞	∞	∞	1:1	∞	1:1	∞	1:1	∞
q_{Si}	1.58	1.69	1.56	1.71	1.62	1.62	1.55	1.67	1.53	1.58	1.61	1.61
q_{Al}	1.38	—	1.40	—	—	—	1.37	—	1.39	—	—	—
q_{O2}	-0.65	-0.68	-0.63	-0.66	-0.68	-0.68	-0.69	-0.68	-0.68	-0.68	-0.70	-0.70
$q_{\text{O3(4)}}$	-0.70	-0.71	-0.70	-0.71	-0.72	-0.72	-0.64	-0.67	-0.63	-0.65	-0.67	-0.67
q_{Ni}	0.31	0.41	0.18	0.24	0.34	0.34	0.29	0.41	0.10	0.12	0.34	0.34
q_{O}	—	—	-0.56	-0.58	—	—	—	—	-0.53	-0.53	—	—
q_{H}	—	—	0.03	0.09	—	—	—	—	0.04	0.10	—	—
$p_{\text{Si-O2}}$	0.69	0.59	0.78	0.66	0.61	0.61	0.94	0.79	0.96	0.80	0.76	0.76
$p_{\text{Al-O2}}$	0.46	—	0.50	—	—	—	0.54	—	0.56	—	—	—
$p_{\text{Si-O3(4)}}$	1.00	0.78	0.98	0.80	0.76	0.76	0.67	0.58	0.75	0.63	0.51	0.51
$p_{\text{Al-O3(4)}}$	0.55	—	0.56	—	—	—	0.44	—	0.48	—	—	—
$p_{\text{Ni-Si}}$	0.10	0.10	0.09	0.08	0.12	0.12	0.10	0.10	0.09	0.09	0.12	0.12
$p_{\text{Ni-Al}}$	0.11	—	0.11	—	—	—	0.11	—	0.11	—	—	—
$p_{\text{Ni-O2}}$	0.57	0.55	0.46	0.44	0.51	0.51	0.08	0.08	0.06	0.06	0.07	0.07
$p_{\text{Ni-O3(4)}}$	0.08	0.08	0.06	0.06	0.07	0.07	0.59	0.57	0.49	0.48	0.51	0.51
$p_{\text{Ni-O}}$	—	—	0.62	0.68	—	—	—	—	0.62	0.68	—	—
$p_{\text{O-H}}$	—	—	0.98	0.98	—	—	—	—	0.99	0.98	—	—

The influence of the Si : Al ratio on stability of the zeolitic ring is apparent from comparison of the Wiberg's bond orders $p_{\text{Si-O}}$ and $p_{\text{Al-O}}$ (Table I and II). Stability of the zeolitic skeleton goes down with increasing content of Al, since Al—O bonds are substantially weaker than the Si—O bonds. The effect of a changing Si : Al ratio on stability of the zeolites was discussed in detail recently¹⁹.

The charge densities on the Co atom are for formally bivalent Co^{2+} and $\text{Co}(\text{OH})^+$ ions quite low (Table I and II), in accordance with Cu^{2+} , Fe^{2+} , $\text{Fe}(\text{OH})^+$ and Li^+ cations coordinated in other faujasites^{18,22}. The low values are caused by donation of electrons from the zeolite skeleton to the coordinated cations. The lower charge value at the cobalt atom with the $\text{Co}(\text{OH})^+$ cation, compared to Co^{2+} , is due to additional donation of electron density from the hydroxyl group. The charge on the cobalt atom is for the formally trivalent Co^{3+} cation much higher than for the Co^{2+} cation (Table I and II), similarly to Fe^{3+} cations coordinated in corresponding zeolites¹⁸. The zeolite skeleton possesses evidently limited electron donor properties, (*i.e.* it is able to donate only a limited amount of electron density to the coordinated cation).

For Ni^{2+} and $\text{Ni}(\text{OH})^+$ cations the charge densities at the nickel atom are comparable with corresponding charge densities of Co^{2+} and $\text{Co}(\text{OH})^+$ cations at the cobalt atom. Only for Co^{2+} and $\text{Co}(\text{OH})^+$ cations localized in the S_{II} cationic position are the electron densities found at the cobalt atom somewhat higher than with corresponding nickel cations at the nickel atom (Table I and II). This difference is consistent with the difference in the strength of the electron donor-acceptor bond

TABLE III

CNDO/2 energy HOMO and LUMO (eV) and charge density at the cation q_{C} in neutral zeolitic clusters containing different cations localized in S_{II} and S'_{I} positions

Cation	S_{II}			S'_{I}		
	E_{HOMO}	E_{LUMO}	q_{C}	E_{HOMO}	E_{LUMO}	q_{C}
Fe^{2+a}	-12.99	-1.62	0.42	-12.60	-1.33	0.40
Fe^{3+a}	-12.24	-2.98	1.38	-12.17	-3.33	1.16
Co^{2+}	-12.91	-1.94	0.50	-12.66	-1.41	0.33
Co^{3+}	-13.33	-5.50	1.27	-13.25	-5.13	1.04
Ni^{2+}	-12.91	-1.93	0.36	-12.16	-1.81	0.34
Ni^+	- 8.16	-1.75	0.33	- 7.84	-1.18	0.30
Cu^{2+b}	—	—	—	-12.55	-2.81	0.47
Cu^{+b}	—	—	—	- 6.61	-2.17	0.27
Al^{3+c}	-13.23	-5.67	0.84	-12.21	-5.57	0.76

From: ^a ref.¹⁸, ^b ref.²³, ^d ref.⁸.

between the cobalt (respectively nickel) cation and the skeleton and most probably it is related to a slightly different geometrical arrangement (the Co-O₂ bond is longer than the Ni-O₂ bond^{24,25}). The charge at the nickel atom for the case of Ni⁺ cation is practically identical with the charge of the Ni²⁺ cation (Table II), similarly to Cu⁺ and Cu²⁺ cations coordinated in comparable zeolites²³. This effect can be explained by compensation of the positive cation charge by electron donation from the zeolitic skeleton. In the case of formally uni- and bivalent Ni⁺, Ni²⁺, and Co²⁺ cations, most of the positive charge localized at the cation is compensated by the skeleton while with trivalent cations this is no longer possible.

The electron donor-acceptor properties of zeolitic clusters, containing different cations localized in cationic positions can be in first approximation described by the energy values of their highest occupied molecular orbital (HOMO) or by the values of the lowest unoccupied molecular orbital (LUMO). HOMO's of the cobalt - and nickel cations containing clusters are mostly localized at corresponding cations and from their values it follows that the electron donor properties of Co and Ni zeolites do not differ significantly from other cationic forms of zeolites^{8,18,19,22,23}. The Ni⁺ cation is an exception and similarly to the Cu⁺ cation (localized in comparable zeolites) it shows substantially stronger electron donor properties compared with other types of cationic zeolites (Table III); this suggests increased oxidizability of the ion. LUMO's of the cobalt- and nickel cations containing clusters are localized mostly at the corresponding cation. The LUMO energy values (Table III) indicate that zeolites with Co²⁺, Ni²⁺ and Ni⁺ cations do not possess (compared with other cationic forms of faujasites) very strong electron acceptor properties - on contrary to strong properties of the Co³⁺ forms of zeolites. The calculations thus indicate that Co³⁺ ions coordinated in cationic positions of faujasites very easily accept an electron (*i.e.* they are very easily reduced to Co²⁺ ions). This results into remarkable instability of Co³⁺ ions (localized in cationic positions of the zeolite), in agreement with the fact that the Co³⁺ ions were not observed in Co zeolites^{2,3}.

The probability of hydration of the Co²⁺ and Ni²⁺ cations coordinated in cationic zeolite positions (*i.e.* the probability that these cations are found in the S₁₁ and S'₁ zeolite positions in tetrahedral symmetry of ligands) can be estimated from the Wiberg orders of Co-OH and Ni-OH bonds (Table I and II). These bond-order values indicate that the cation-hydroxyl group bond is quite strong (comparatively strong with cations Fe(OH)⁺, Al(OH)²⁺ and Al(OH)²⁺ (ref.^{8,18})). This indicates easy hydration of the Ni²⁺ and Co²⁺ cations (localized in cationic positions of the zeolite), eventually the existence of an additional, fourth ligand. Acidity of these hydroxyl groups can be characterized either by means of the Wiberg bond orders p_{O-H} value) or by the calculated positive charge at the H-atom q_H (the acidity increases with decreasing q_H value). The p_{O-H} and q_H values show (Table I and II) that the hydroxyl groups of the Co(OH)⁺ and Ni(OH)⁺ cations exhibit much lesser acidity than the skeletal hydroxyl groups ($p_{O-H} \cong 0.93$ and $q_H \cong 0.16$, ref.⁹).

REFERENCES

1. Jacobs P. A.: *Carboniogenic Activity of Zeolites*. Elsevier, New York 1977.
2. Haynes H. W. jr: *Catal. Rev.-Sci. Eng.* 17, 273 (1978).
3. Naccache C., Ben Taarit Y.: *Acta Phys. Chem.* 24 (1), 23 (1978).
4. Kubelková L., Wichterlová B.: *This Journal* 42, 2033 (1977).
5. Gallezot P., Imelik B.: *J. Phys. Chem.* 72, 652 (1973).
6. Mortier W. J., Geerlings P.: *J. Phys. Chem.* 84, 1982 (1980).
7. Sauer J., Hobza P., Zahradník R.: *J. Phys. Chem.* 84, 3318 (1980).
8. Beran S., Jírů P., Wichterlová B.: *J. Phys. Chem.* 85, 1951 (1981).
9. Beran S.: *J. Mol. Catal.* 10, 177 (1981).
10. Mikheikin I. D., Abronin I. A., Zhidomirov G. M., Kazanskii V. B.: *J. Mol. Catal.* 3, 135 (1978).
11. Mikheikin I. D., Abronin I. A., Zhidomirov G. M., Kazanskii V. B.: *Kinet. Katal.* 18, 1580 (1977).
11. Mikheikin I. D., Abronin I. A., Zhidomirov G. M., Kazanskii V. B.: *Kinet. Katal.* 18, 1580 (1977).
12. Lygin V. I., Smolikov V. V.: *Zh. Fiz. Khim.* 49, 1526 (1975).
13. Mortier W. J., Geerlings P., VanAlsenoy C., Figeas P.: *J. Phys. Chem.* 83, 885 (1970).
14. Tossel J. A., Gibbs G. V.: *J. Phys. Chem. Minerals* 2, 21 (1977).
15. Gibbs G. V., Mearcher E. P., Smith J. V., Pluth J. J.: *ACS Symp. Ser. No 40*, 19 (1977).
16. Grabovsky W., Moisono M., Yoneda Y.: *J. Catal.* 61, 103 (1980).
17. Sauer J., Fiedler K., Schirmer W., Zahradník R.: *Proc. IV Int. Conf. Molecular Sieves*, (L.V.C. Rees, Ed.), p. 501. Neapol 1980.
18. Beran S., Jírů P., Wichterlová B.: *Zeolites*, in press.
19. Beran S.: *Z. Phys. Chem. N. F.* 123, 129 (1980).
20. Beran S., Dubský J.: *J. Phys. Chem.* 83, 2538 (1980).
21. Beran S., Dubský J.: *Chem. Phys. Lett.* 71, 300 (1980).
22. Beran S.: *J. Phys. Chem. Solids* 43, 221 (1982).
23. Beran S.: *Chem. Phys. Lett.* 84, 111 (1981).
24. Gallezot P., Imelik B.: *J. Chim. Phys. Physicochim. Biol.* 71, 155 (1974).
25. Olson D. H.: *J. Phys. Chem.* 72, 4366 (1968).
26. Clack D. W., Hush N. S., Yandle J. R.: *J. Chem. Phys.* 57, 3503 (1972).

Translated by Z. Dolejšek.