Electron paramagnetic resonance studies on silver atoms and clusters in regularly interstratified clay minerals

Hirohisa Yamada,
Jaroslaw Sadlo,
Kenji Tamura,
Shuichi Shimomura,
Janusz Turek,
Jacek Michalik

Abstract The formation and stabilization of reduced silver species in the regularly interstratified clay minerals, trioctahedral smectite/chlorite (tri-Sm/Ch) and dioctahedral smectite/mica (di-Sm/M), have been studied by electron paramagnetic resonance (EPR) spectroscopy. Both minerals loaded with Ag^+ cations after degassing and dehydration were γ-irradiated at 77 K and monitored by EPR as the temperature increased. Some samples were exposed to water or methanol vapor after dehydration. In both hydrated and dehydrated samples only the doublets assigned to Ag^0 atoms were observed with no evidence of the formation of Ag clusters. However, the EPR parameters of silver atoms in both matrices are different. In tri-Sm/Ch the narrow anisotropic EPR lines overlap with the broader isotropic lines, whereas in di-Sm/M only broad lines are recorded. The hyperfine splitting $-A_{iso}(Ag^0)$ is larger in tri-Sm/Ch than in di-Sm/M. Also the stability of Ag^0 in both clay minerals is distinctly different. Ag^0 doublet in di-Sm/M disappears completely above 230 K, whereas in tri-Sm/Ch it is still recorded at 310 K. It is proposed, basing on the EPR results that Ag^0 atoms appear at different sites in both matrices: – in tri-Sm/Ch in the middle of smectite interlayer and in hexagonal cavities in the silicate sheets of tetrahedron layer and in di-Sm/M in hexagonal cavities only. When samples had been exposed to methanol before irradiation, the silver clusters become stabilized in the interlayer sites. In tri-Sm/Ch matrix the silver dimer Ag_2^+ formed by γ-irradiation at 77 K is transformed to tetrameric cluster, Ag_4^{3+} at 150 K. In di-Sm/M the radiation-induced silver agglomeration proceeds in a similar way, but with a slower rate and Ag tetramer is formed only above 190 K. In both clay minerals, Ag_4^{3+} clusters decay above 250 K.

Key words EPR spectroscopy • regularly interstratified clay minerals • silver atoms • γ-irradiation

H. Yamada✉, K. Tamura, S. Shimomura
Ecomaterials Center,
National Institute for Materials Science,
Namiki 1-1 Tsukuba, Ibaraki 305-0044, Japan,
Tel.: +81-29-860-4667, Fax: +81-29-860-4667,
e-mail: YAMADA.Hirohisa@nims.go.jp

J. Sadlo, J. Turek, J. Michalik
Institute of Nuclear Chemistry and Technology,
16 Dorodna Str., 03-195 Warsaw, Poland

Introduction

Although the monovalent silver cations are not paramagnetic, they can be easily reduced by ionizing radiation to silver atoms which, due to their magnetic properties, are excellent paramagnetic probes of the local environment. Both the silver isotopes, [107]Ag and [109]Ag, have nuclear spin ½ and a relatively large splitting constants of free atoms. Therefore, the EPR lines of Ag atoms as well as of Ag clusters are located far away from $g = 2$ region where the resonance signals of radicals and paramagnetic centers are usually observed [2].

The local environment of silver atoms in γ-irradiated montmorillonite [3, 6], fluorohectorite and beidellite [6, 9] have been studied by Kevan and co-workers using EPR and electron spin echo envelope modulation (ESEEM) spectroscopies. The modulation of electron spin envelope is due to dipolar electron-nuclear spin interaction and geometry of the molecules surrounding Ag^0 can be determined by ESEEM analysis.

In some matrices, Ag^0 atoms generated radiolytically at 77 K become mobile when temperature increases and in the reaction with unreduced Ag^+ ions form discrete cationic Ag clusters. It was proved that ESEEM data can be also used to solve structure of molecules coordinated by cationic Ag clusters [6]. The earlier studies on reduced silver species in zeolites brought new information on the

mechanism of silver agglomeration and the conditions of effective stabilization of cationic clusters inside zeolite framework [4, 9–14, 20, 21]. It has been proved that suitable size of framework cavities is not sufficient for the stabilization of small silver clusters. Other factors like silica to alumina ratio in the framework, the type of co-cations at exchangeable positions and the type of solvating molecules play also an important role. For example, in the smectite clays, in both hydrated and dehydrated forms, silver atoms only were stabilized after γ-irradiation. However, when methanol was present in the interlayer, the trimeric and tetrameric clusters were observed [15, 16].

The conditions affecting the stabilization of cationic metal clusters in clay minerals are much less known than in zeolites. For that reason we decided to extend our earlier works [15, 16] for a different type of clays – phyllosilicates, regularly interstratified clay minerals.

Phyllosilicates are composed of two or more kinds of layers stacked in fixed vertical sequence [17–19]. The schematic representations of regularly interstratified clay minerals – smectite-chlorite (Sm/Ch) and smectite-mica (Sm/M) are shown in Fig. 1. Sm/Ch smectite units alternate regularly with chlorite unit while Sm/M with mica units. Both smectite and mica units consist of two oxygen-coordinated tetrahedral sheets occupied by Al(III) and Si(IV) and one octahedral sheet containing Mg(II) and Al(III). They are denoted hereafter as the 2:1 layers (tetrahedral-octahedral-tetrahedral). The amount of interlayer cations is different in smectite and mica sheets corresponding to the amount of negative lattice charge originating from the isomorphous lattice substitution in the 2:1 layers: 0.25–0.60 monovalent cations for a half unit cell formula of smectite and one cation for mica. Octahedral sheets are occupied predominantly by Mg(II) in trioctahedral clay and by Al(III) in dioctahedral clay (where only two-thirds of the octahedral sites are filled). Chlorite unit consists of negatively charged 2:1 layers and positively charged octahedral sheets. The occupancy of cations in octahedral and tetrahedral sheet of chlorite is similar to those in smectite. Half unit cell formulas of different sheets are the following: smectites – beidellite $Na_{0.33}Al_2(Si_{3.67}Al_{0.33})O_{10}(OH)_2$ and saponite $Na_{0.33}Mg_3(Si_{3.67}Al_{0.33})O_{10}(OH)_2$; trioctahedral chlorite $Mg_3(Si_3Al)O_{10}(OH)_8(Mg_2Al)$, and dioctahedral mica $NaAl_2(Si_3Al)O_{10}(OH)_2$.

Many types of interstratified clay minerals, mica/smectite, chlorite/smectite, etc., have been found in nature. Interstratification can be organized according to various periodic stacking schemes. The most common ordering involves a regular alternation of two layer to produce the ABABAB sequences.

Experimental

Sample preparation

The regularly interstratified clay minerals were synthesized by hydrothermal reaction using homogeneous quenched glasses. For regular trioctahedral smectite/chlorite (tri-Sm/Ch) interstratified clays, the glass with dehydrated Na-smectite composition corresponding to $Na_{0.6}Mg_{5.7}Si_{8.0}O_{22}$ was prepared from a mixture of Na_2CO_3 and Al_2O_3, MgO, and SiO_2 oxides. For regular dioctahedral smectite/mica (di-Sm/M) interstratified clays, the glass with a composition of $Na_{0.6}Al_{3.9}(Al_{0.6}Si_{7.4})O_{22}$ was synthesized. The oxide mixture in a Pt-crucible was fused in an electric furnace at 1600°C and then quenched into water. The glass was crushed and fractionated at <10 μm by hydraulic elutriation and then used as starting material.

Hydrothermal experiments were performed using a rapid-quench type hydrothermal apparatus [22]. 200 mg of pulverized glass and 200 mg of distilled water were sealed in a gold tube. The mixture of glass and water was heated under the pressure of 100 MPa at a temperature of 325°C for 10 days for the synthesis of tri-Sm/Ch while at 400°C for 20 days to synthesize di-Sm/M matrix.

The products of synthesis were examined after quenching by powder XRD. Three different samples were prepared for that purpose following the method described by Yamada *et al.* [23]: compression-free (CF) sample, ethylene glycolated (EG) sample and a sample treated by the Greene-Kelly test (GK) [5, 8]. The CF sample was obtained by crushing and mounting the sample on a "back-ground less" quartz plate without compression to reduce the influence of preferred orientation. The EG sample was prepared as follows: the product was oriented by sedimentation in water onto a glass slide, dried at room temperature, placed in a sealed container with ethylene glycol and then heated overnight at 60°C. For the GK test, the product was dispersed in 1M LiCl solution. Then the sample was isolated from the suspension by centrifugation and the process was repeated four times in order to reach a complete exchange of Na^+ cations for Li^+. The Li-exchanged sample was washed three times with 90% ethanol to remove the excess of cations and chlorides. This material was oriented on a pure silica glass slide by sedimentation, heated overnight at 300°C, placed in a sealed container with glycerol and then heated overnight at 90°C.

EPR characterization

The regularly interstratified clay minerals were loaded with silver cations by stirring overnight with an aqueous solution
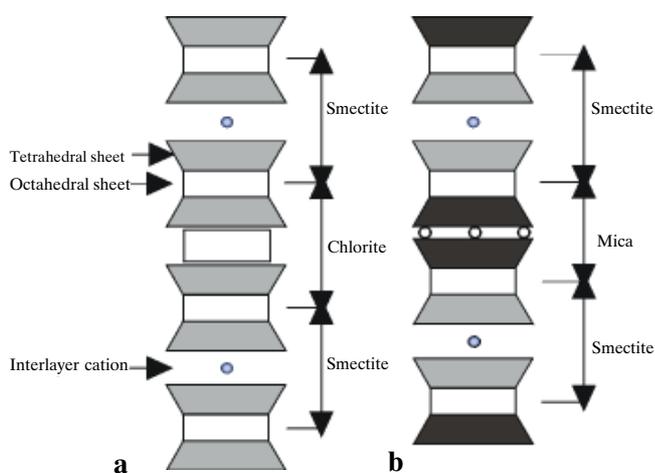

Fig. 1. Schematic representation of regularly interstratified clay minerals: (a) smectite-chlorite (Sm/Ch) and (b) smectite-mica (Sm/M). In Sm/Ch smectite units alternate regularly with chlorite units and in Sm/M with mica units. Interlayer cations are denoted by circles.
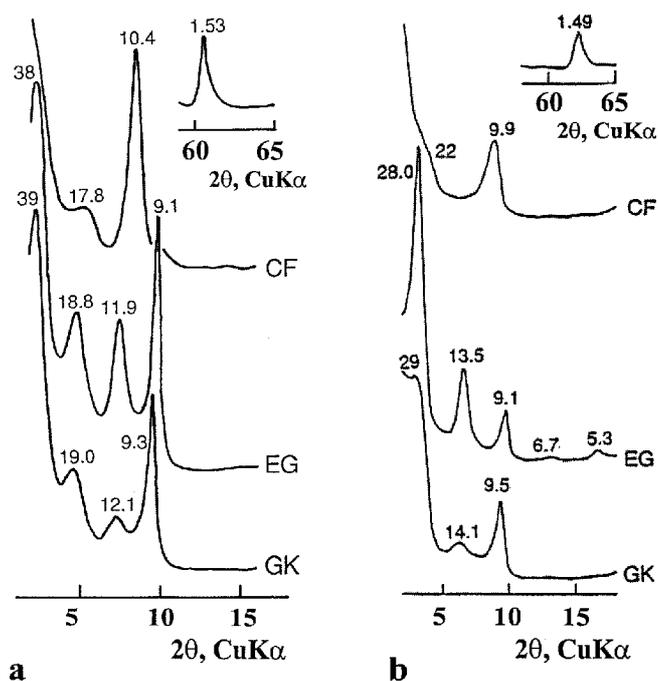
Fig. 2. XRD patterns of synthetic regularly interstratified clay minerals. a – Regularly interstratified trioctahedral smectite/chlorite (tri-Sm/Ch). b – Regularly interstratified dioctahedral smectite/mica (di-Sm/M). CF: compression-free sample; EG: ethylene-glycole sample; GK: sample after the Greene-Kelly test. The numbers indicate the observed d-value in Å. The (060) reflections are presented in the insert.

of silver nitrate at room temperature. Next, the samples were filtered and washed with distilled water several times. After drying at room temperature, the samples were placed into 2 mm i.d. by 3 mm o.d. Suprasil quartz tubes and dehydrated under vacuum with gradually increasing temperature till 200°C. Some clay samples were exposed in the vacuum line to water or methanol under their vapor pressure at room temperature.

All samples were irradiated at 77 K in a ^{60}Co source with a dose of 4 kGy. The EPR spectra were recorded with a Bruker ESP-300e spectrometer in the temperature range 110–310 K using a Bruker variable temperature unit.

Results

Powder X-ray diffraction

The XRD patterns of the synthetic materials are shown in Fig. 2. The phases encountered in this study were identified using the same criteria as described previously [23]. The spacing of (060) reflection of the CF sample determines the dioctahedral (e.g., beidellite) or trioctahedral (e.g., saponite) phase. The d(060) of 1.48–1.50 Å indicates the dioctahedral phase, and the spacing of 1.53–1.55 Å is due to the trioctahedral phase [1]. The EG test enables to distinguish the identification of smectites which have the negative charge in tetrahedral sheets – beidellite and saponite, from those having the charge in octahedral sheets – montmorillonite. For beidellite and saponite, the spacing from GK test is 18 Å, whereas for montmorillonite 9.6 Å.

In X-ray diffractograms of the samples obtained from a glass with the composition $Na_{0.6}Mg_{5.7}Si_{8.0}O_{22}$, the large spacings of 38 Å for EG and 39 Å for GK were found (Fig. 2a). The d(060) = 1.53 Å indicates that the phase is the trioctahedral one. The phase that has a long spacing and the value of d(060) = 1.53 Å has been identified as a regularly interstratified trioctahedral smectite/chlorite (tri-Sm/Ch). Based on GK test, the smectite layer in tri-Sm/Ch was assigned to saponite – the smectite which has the negative charge in tetrahedral sheets.

In X-ray diffractograms of the EG samples obtained from a glass with the composition corresponding to the formula $Na_{0.6}(Al_{3.9})(Al_{0.6}Si_{7.4})O_{22}$, the large spacings of 28 Å and 29 Å for GK were measured (Fig. 2b). The d(060) = 1.49 Å indicates that the phase was the dioctahedral one. So, the phase was recognized as a regularly interstratified dioctahedral smectite/mica (di-Sm/M). The GK test indicated that the smectite layer in di-Sm/M was beidellite – another smectite with negative charge in tetrahedral sheets.

Electron Paramagnetic Resonance

The EPR spectra of dehydrated Ag-tri-Sm/Ch and Ag-di-Sm/M recorded after irradiation at 77 K and subsequently thermally annealed are shown in Fig. 3. Strong singlets L_1,
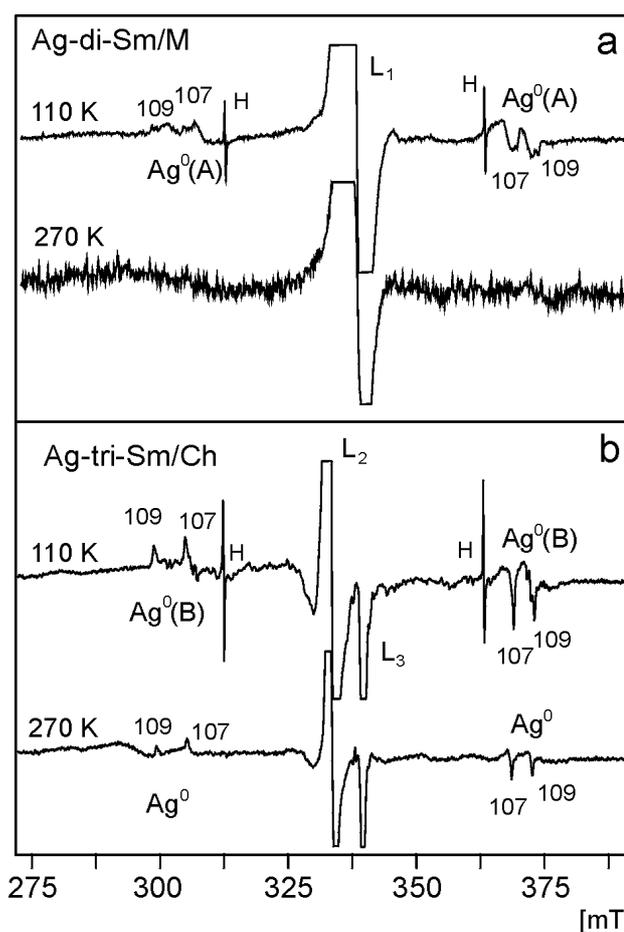

Fig. 3. EPR spectra of dehydrated interstratified clay minerals irradiated at 77 K and annealed at different temperature (a) dioctahedral Ag-smectite/mica, (b) trioctahedral Ag-smectite/chlorite.

L_2 and L_3 represent radiation-induced paramagnetic centers in clay lattice; a doublet H is due to hydrogen atoms generated radiolytically in the EPR Suprasil glass tubes. The silver species, namely Ag atoms are represented by EPR doublets with hyperfine splittings larger than 60 mT. In di-Sm/M samples, the doublet lines of $^{107}Ag^0$(A): A_{iso} = 60.0 mT, g_{iso} = 2.002 and $^{109}Ag^0$(A): A_{iso} = 68.6 mT, g_{iso} = 2.002 are isotropic with a relatively large linewidth, ΔH_{pp} = 2.5 mT (Fig. 3a). They decay completely above 270 K without any evidence of silver cluster formation. In tri-Sm/Ch samples, the wide lines of Ag^0(A) doublets are partly overlapped with much narrower Ag^0(B) lines of asymmetric line shape which results from the anisotropy of hyperfine splittings: $^{107}Ag^0$(A): $A_\perp$ = 63.0 mT, g = 2.002 and $^{109}Ag^0$(A): $A_\perp$ = 72.6 mT, g = 2.002 (Fig. 3b). The parallel components of Ag lines are not very well defined making impossible to measure the values of $A_{||}$ and $g_{||}$ tensors. At 270 K, the Ag^0(A) doublets are not observed whereas Ag^0(B) lines with their characteristic anisotropy are still recorded, but with reduced intensity. They decay completely above 310 K. The EPR measurements clearly indicate that in tri-Sm/Ch the Ag^0 atoms are located at two different sites and only at one site in di-Sm/M clays. Silver atoms are formed during low temperature radiolysis as a result of electron capture by Ag^+ cations. The first EPR spectra were measured at low temperature (110 K) at which Ag^0 atoms remain still immobile. Thus, they can be considered as the magnetic probes indicating the preferential locations of silver cations in clay matrices.

When dehydrated Ag-tri-Sm/Ch and Ag-di-Sm/M samples are exposed to water vapor and then irradiated at 77 K, the EPR spectra recorded just after the radiation treatment and in the course of annealing are similar to those of dehydrated samples. On the contrary, the samples exposed to methanol vapor show completely different spectra after irradiation. In Fig. 4, the lines related to Ag species are denoted D and Q. D lines observed at low temperature (110 K) constitute a triplet with hyperfine splitting 28.5 mT and g = 1.979. The outer lines are additionally split to three components with an intensity ratio of 1:2:1 separated with 1.8 mT. We assigned the triplet D to the Ag_2^+ dimer. Then, the sub-structure on the outer lines can be explained by existence of the three silver isotopomers – $^{107}Ag_2^+$, $(^{107}Ag^{109}Ag)^+$ and $^{109}Ag_2^+$ having slightly different hyperfine splittings. At 110 K besides the Ag_2^+ triplet, the signals of the framework defects and H atoms – the triplet R of $^•CH_2OH$ (A_{iso} = 1.8 mT and g_{iso} = 2.003) radical is observed. This radical is formed by the reaction of primary radical cation with a methanol molecule in close vicinity [7]:

(1) $CH_3OH^+ + CH_3OH \rightarrow {}^•CH_2OH + CH_3OH_2^+$

It was reported earlier that $^•CH_2OH$ radicals attack Ag^+ cations forming $Ag^•CH_2OH^+$ silver hydroxymethylene radicals, represented by isotropic EPR doublet with hyperfine splitting in the range 9.6–18.0 mT [21]. However, in Ag-tri-Sm/Ch samples we were unable to observe these species. At 150 K after the decay of Ag_2^+ and $^•CH_2OH$ spectra, the quartet Q is only recorded. Its EPR parameters: A_{iso} = 13.9 mT and g_{iso} = 1.979 strongly support the view that it represents Ag_4^{3+} cluster which was earlier observed in γ-irradiated Ag-NaCs-rho zeolite even at room temperature. In the interstratified clays tetrameric clusters are less
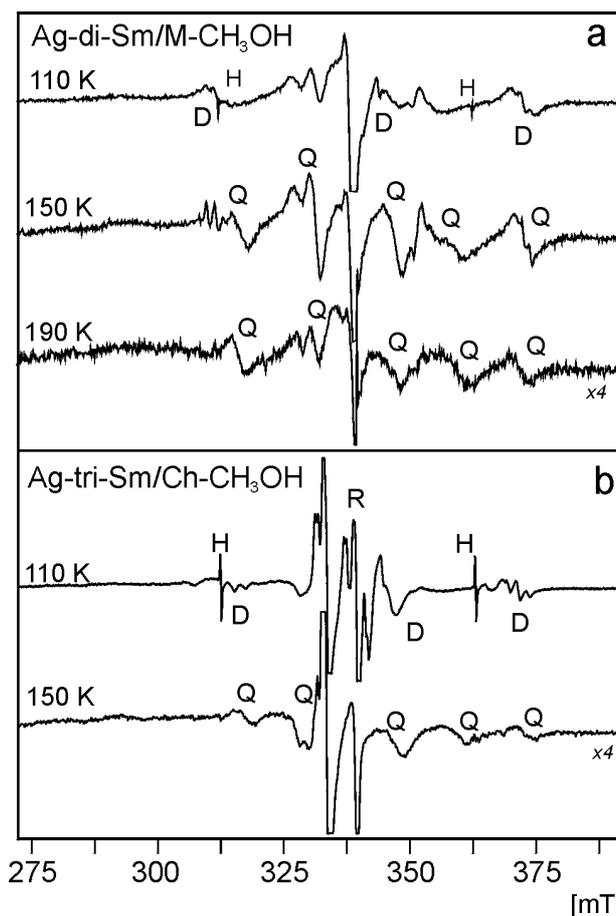

Fig. 4. EPR spectra of interstratified clay minerals exposed to methanol irradiated at 77 K and annealed at different temperature (a) dioctahedral Ag-smectite/mica, (b) trioctahedral Ag-smectite/chlorite.

stable – in Ag-tri-Sm/Ch they decay above 170 K and in Ag-di-Sm/M above 200 K, respectively.

Discussion

In hydrated and dehydrated samples of regularly interstratified clays, Ag-tri-Sm/Ch and Ag-di-Sm/M, only silver atoms are stabilized after γ-irradiation. No evidence for Ag-cluster formation was found. This is in agreement with earlier EPR studies on paramagnetic silver species in three smectites – montmorillonite, hectorite and saponite [15]. In dehydrated form, those clays exhibit different abilities for stabilization of Ag^0 atoms. In montmorillonite, Ag^0 could be observed even at room temperature whereas in hectorite and saponite they decay at 200 K. These differences were explained in terms of the clay structure. It was proposed that on dehydration at 250°C some of the Ag^+ ions become trapped in the so-called hexagonal cavities in clay lattice. It is well-known that the six-membered ring of silicon atoms with bridging oxygens in tetrahedral layers of clay lattice can strongly chelate cations of appropriate size [2]. The authors speculate that the size of hexagonal cavities, which has decisive impact on Ag^+ trapping and Ag^0 stabilization, depends on the composition of the octahedral lattice layer, and in montmorillonite the cavity size is optimal for trapping of Ag^+ cations.

To explain the differences in stabilization abilities of Ag^0 atoms in smectite/chlorite and smectite/mica clays, we adopted the concept described above postulating that the size of hexagonal cavity depends on the composition of the octahedral lattice. We propose that in the presence of larger Mg^{2+} cations in trioctahedral clays the size of hexagonal cavities is the most suitable for the effective trapping of Ag^+ cations, whereas in dioctahedral clays the cavities are too small to accommodate Ag^+ ions. Thus, in smectite/mica clay Ag^+ are only located in smectite interlayers. The EPR lines of Ag^0(A) in di-Sm/M are wide and show distinctly smaller hyperfine splitting than free Ag^0 atoms indicating a strong interaction of parent Ag^+ cations with lattice atoms, possibly with Al to balance directly the lattice negative charge. During the thermal annealing, the neutral Ag^0 atoms in the interlayer can easily migrate to the surface of microcrystallites where silver metallic particles are formed. However, in both clays – smectite/chlorite and smectite/mica, Ag^0(A) atoms located in the interlayers are not observed above 270 K. The Ag^0(B) atoms in smectite/chlorite samples representing silver atoms trapped in hexagonal cavities are still more stable and were recorded even above room temperature. When Ag^+ cation located in a cavity captures an electron as a consequence of radiation treatment the resultant Ag^0 atom, which is larger than the parent ion, should remain even more effectively trapped inside. The EPR spectra of Ag^0(B) atoms having narrow linewidths and large hyperfine splittings indicate that Ag^0 interact weakly with clay lattice possible because they are located in the middle of the cavity.

In the presence of methanol, silver tetramers are stabilized in both – dioctahedral and trioctahedral interstratified clays. Because neither chlorite layer in tri-Sm/Ch nor mica layer in di-Sm/M are able to expand, the silver clusters can be only formed in the smectite layers. Based on X-ray diffraction analysis, especially on the Green-Kelley test, it was proved that the smectite layers in tri-Sm/Ch and di-Sm/M are saponite and beidellite layers, respectively. The negative charge in both layers is situated in the tetrahedral sheets. So, after the ion exchange in solution, the hydrated silver cations should be located in the vicinity of negative charges of tetrahedral sheets of smectite layers. In the course of dehydration, Ag^+ can move closer to tetrahedral sheet to balance its charge more directly. Some of the cations may enter hexagonal cavities in which they are able to interact directly with adsorbate molecules and mobile silver species. Thus, the silver atoms formed by radiation reduction can be formed in interlayers as well as in the hexagonal cavities. The agglomeration process, however, can proceed only in interlayers because it requires mobility of the silver species. In clays exposed to water or methanol, silver atoms and cations have to move through interlayers filled up with frozen water or methanol molecules. Why silver tetramers are formed in the presence of methanol molecules but not water molecules is not an easy question to answer. We can only speculate upon the possible reasons. During radiolysis silver cations are not only reduced to Ag^0 atoms, but also oxidized to divalent silver Ag^{2+} which do not participate in agglomeration process. Methanol molecules scavenge effectively the primary positive holes which are the main reactive intermediates oxidizing Ag^+ cations. The experimental results indicate that in the presence of methanol Ag^+ cations show a lower tendency to occupy the hexagonal cavities which additionally increases the number of species participating in the agglomeration process. As a result, the density of Ag^0 atoms and Ag^+ cations in the smectite interlayers is higher in the presence of methanol than in the presence of water. Thus, the migration path of Ag^0 to the nearest silver cation is shorter, making the agglomeration process more effective in comparison to the reactions of silver atoms with the molecules and radicals which are present in the interlayer. The observation of silver dimers Ag_2^+ at 110 K in clays exposed to methanol supports this hypothesis (Fig. 4). At low temperatures Ag^0 atoms are unable to migrate and Ag_2^+ can be only formed when one of two very close Ag^+ cations is reduced. This might happen when two Ag^+ cations are located close to each other balancing the negative charge of two opposite tetrahedral layers. The bulky dimer blocking the interlayer may facilitate the next agglomeration stages. In the presence of water the reactions of Ag^0 atoms with radical products of water radiolysis are dominant and clusters are not formed.

Conclusions

This work clearly demonstrates that the combination of EPR spectroscopy with low temperature radiolysis can be very useful to probe the location of Ag^+ cations in regularly interstratified clay minerals. Owing to that methodology, it was proved that even small differences in tetrahedral and octahedral layers might influence the location of Ag^+ cations in the interlayers. In trioctahedral smectite/chlorite clay Ag^+ cations occupy sites in the middle of smectite interlayers and in hexagonal cavities of the upper and the lower silicate sheets, whereas in dioctahedral smectite/mica clays Ag^+ cations are located only in the interlayer sites.

Silver clusters, Ag_4^{3+}, are formed in the clays exposed to methanol but not in both dehydrated samples or samples exposed to water. The effective scavenging of positive holes by methanol molecules, which limits the geminate recombination and increases the number of Ag^0 atoms initiating the agglomeration process, is proposed to explain the experimental results.

The general conclusion of the present work is that small Ag clusters generated radiolytically can be stabilized in the interlayers of solvent-expandable layers of interstratified clay minerals making such systems catalytically attractive.

References

1. Brindley GW (1980) Order-disorder in clay mineral structure. In: Brindley GW, Brown G (eds) Crystal structures of clay minerals and their X-ray identification. Mineralogical Society, London, pp 126–195
2. Brown DR, Findlay TJV, Symons MCR (1976) Radiation mechanisms. Part 12. ESR studies of electron capture by silver(I) ions, nitrate ions and their ion pairs and clusters in methyl cyanide. J Chem Soc, Faraday Trans 72:1792–1798
3. Brown DR, Luca V, Kevan L (1991) Electron paramagnetic resonance and electron spin echo modulation analysis of silver atom environment in γ-irradiated silver-exchanged sodium montmorillonite and its Al_{13} pillared derivative. J Chem Soc, Faraday Trans 87:2749–2754
4. Brown R, Kevan L (1986) Comparative electron spin resonance and optical absorption studies of silver-exchanged

sodium Y zeolites: Silver centers formed on dehydration, oxidation, and subsequent γ-irradiation. J Phys Chem 90:1129–1133

5. Greene-Kelly R (1953) The identification of montmorillonoids in clays. J Soil Sci 4:233–237

6. Kevan L (1992) Applications of electron spin echo modulation to transition metal ions in smectite clays. Pure Appl Chem 64:781–788

7. Kevan L, Schlick S (1976) Spin trapping of radicals formed in gamma-irradiated methanol: effect of the irradiation temperature from 77 K to 300 K. Chem Phys Lett 38:505–509

8. Lim CH, Jackson ML (1986) Expandable phyllosilicate reactions with lithium on heating. Clays Clay Miner 34:346–352

9. Luca V, Brown DR, Kevan L (1991) Electron spin resonance and electron spin-echo modulation studies of silver ion solvation in silver-exchanged synthetic fluorohectolite and synthetic beidellite. J Phys Chem 95:10065–10070

10. Michalik J (1996) Silver atoms and clusters in molecular sieves and clays. Appl Magn Reson 10:507–537

11. Michalik J, Azuma N, Sadlo J, Kevan L (1995) Silver agglomeration in SAPO-5 and SAPO-11 molecular sieves. J Phys Chem 99:4679–4686

12. Michalik J, Kevan L (1986) Paramagnetic silver clusters in Ag-NaA zeolite: electron spin resonance and diffuse reflectance spectroscopic studies. J Am Chem Soc 108:4247–4253

13. Michalik J, Sadlo J, Kodaira T, Shimomura S, Yamada H (1998) ESR and optical studies of cationic silver clusters in zeolite rho. J Radioanal Nucl Chem 232:135–137

14. Michalik J, Sadlo J, Yu JS, Kevan L (1996) Tetrameric silver clusters in rho zeolite stable above room temperature – ESR studies. Colloids Surf A 115:239–247

15. Michalik J, Yamada H, Brown DR, Kevan L (1996) Small silver clusters in smectite clay interlayers. J Phys Chem 100:4213–4218

16. Michalik J, Yamada H, Wasowicz T, Kevan L (1995) Pulsed electron spin resonance studies of silver atoms and clusters in smectite clays. In: IS&T's Annual. Conf, Final Program Adv Print Pap, 48th:309–311

17. Newman ACD, Brown G (1987) Interstratified clay minerals. In: Newman ACD (ed) Chemistry of clays and clay minerals. Wiley, New York, pp 92–107

18. Reynolds RC (1980) Interstratified clay minerals. In: Brindley GW, Brown G (eds) Crystal structures of clay minerals and their X-ray identification. Mineralogical Society, London, pp 249–303

19. Reynolds RC, Hower J (1970) The nature of interlayering in mixed-layer illite-montmorillonite. Clays Clay Miner 18:25–36

20. Sadlo J, Wasowicz T, Michalik J (1995) Radiation-induced silver agglomeration in molecular sieves: a comparison between A and X zeolites. Radiat Phys Chem 45:909–915

21. Wasowicz T, Mikosz J, Sadlo J, Michalik J (1992) Organo-silver radicals in gamma-irradiated Ag-NaA zeolites with methanol adsorbate. J Chem Soc, Perkin Trans 2:1487–1491

22. Yamada H, Fujita T, Nakazawa H (1988) Design and calibration of a rapid quench hydrothermal apparatus. J Ceram Soc Jpn 96:1041–1044

23. Yamada H, Nakazawa H, Yoshioka K, Fujita T (1991) Smectites in the montmorillonite-beidellite series. Clay Minerals 26:359–369