

PHYSICAL
CHEMISTRY

⁹⁹Tc NMR of Supported Technetium Nanoparticles

V. P. Tarasov*, Yu. B. Muravlev*, K. E. German**, and N. N. Popova**

Presented by Academician Yu.A. Buslaev November 23, 2000

Received December 5, 2000

The properties of metals are related to their electronic structure and crystal structure. Small clusters of metal atoms exhibit extraordinary physical and electronic properties, caused by size effects, namely, by the surface-to-volume ratio and discreteness of electronic levels [1]. Bulk technetium metal has a hexagonal close-packed lattice with parameters $a = 2.735 \text{ \AA}$ and $c/a = 1.6047$; technetium films less than 150 \AA thick are characterized by a fcc lattice with $a = 3.68 \text{ \AA}$ [2, 3]. One of the most important characteristics of the metal electronic structure is the density of states at the Fermi level $N(E_F)$. For the two most probable states of technetium, ($4d^65s^1$) and ($4d^55s^2$), the calculated $N(E_F)$ values are 12.25 and 11.87 states/(Ry atom), respectively [4]. The experimental characteristics that reflect the metal electronic state and structure are NMR parameters, such as the Knight isotropic shift (K), its anisotropy (K_{an}), spin–lattice relaxation time (T_1), line width ($\Delta\nu$), quadrupole coupling constant (C_Q), and asymmetry parameter η of the electric field gradient tensor. We have recently determined these parameters for a technetium metal powder with a grain size of $50\text{--}100 \text{ \mu m}$: $K = 6872 \text{ ppm}$, $K_{an} = -400 \text{ ppm}$, $(T_1 \times T)^{-1} = 3.23 \text{ s}^{-1} \text{ K}^{-1}$, $C_Q = 5.74 \text{ MHz}$, and $\eta = 0$ [5]. We are interested in comparing these characteristics with those for technetium nanoparticles. As is known, small technetium particles on different supports are active catalysts [2]. In this paper, we reported on the NMR parameters of technetium small particles on supports with different crystal structures and specific surfaces.

EXPERIMENTAL

Three types of supports with basic properties were used, namely, $\gamma\text{-Al}_2\text{O}_3$, MgO, and TiO_2 (supports are conventionally classified into acid, basic, and neutral supports [6]). The structure, specific surface S_{sp} , and pore size of these supports are presented in Table 1. The dispersity and particle size of technetium metal were determined on an EM-301 transmitting electron micro-

scope with a resolution of 3.5 \AA [7, 8]. The bar diagrams of size distribution of particles indicate that on a $\gamma\text{-Al}_2\text{O}_3$ support with the highest specific surface, the size of technetium particles ranges from 10 to 80 \AA (the average particle size is 23 \AA for a 1% Tc/ Al_2O_3 catalyst). This distribution is skewed toward larger particles with an increase in technetium concentration. For the MgO and TiO_2 supports with a smaller specific surface, size distribution is wider, the average particle size being above 40 \AA .

Catalysts were prepared by procedures described elsewhere [7, 8]: support samples¹ were impregnated with an aqueous solution of NH_4TcO_4 , dried at $80\text{--}90^\circ\text{C}$, and reduced in a hydrogen flow for 2–12 h at 700°C . The calculated amount of the deposited metal was $\sim 0.01\text{--}20 \text{ wt } \%$. Catalysts (0.7–0.8 g) were placed in Teflon tubes 10 mm in diameter and 30 mm in length for recording NMR spectra. ⁹⁹Tc NMR spectra were recorded at 293 K on a Bruker MSL-300 spectrometer in a magnetic field of 7.04 T at a frequency of 67.55 MHz. The spin echo pulse sequence was used. The width of the first exciting pulse was 3.22 \mu s , repetition time was 0.5 s, and the number of scans was 64000 to 250000. Chemical shifts were referenced to a 0.1 M KTcO_4 solution as the external standard.

RESULTS AND DISCUSSION

The ⁹⁹Tc NMR spectra of all the catalysts under consideration showed signals in the region of technetium metal shifts ($\sim 7000 \text{ ppm}$) and in the region of the external standard (ionic form). The integrated intensity of the low-field signal that arose from technetium metal was roughly one order of magnitude weaker than the intensity of the ionic form signal. The ⁹⁹Tc NMR shift and line shape for nanoparticles differ considerably from the bulk technetium sample (Fig. 1). The shift is 7406 ppm , which is about 600 ppm larger than the shift for the bulk sample. The line with a width at half-maximum of $\sim 1 \text{ kHz}$ has the Lorentzian shape and lacks the satellite structure caused by first-order quadrupole interactions, typical of the hexagonal close-packed lattice. The missing quadrupole structure clearly points to the cubic lattice of the nascent technetium phase. The considerable increase in the Knight shift can reflect a change in the density of states at the Fermi level, com-

¹ Support samples were spherical grains 1.5–2.0 mm in diameter.

* Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Leninskii pr. 31, Moscow, 117907 Russia

** Institute of Physical Chemistry, Russian Academy of Sciences, Leninskii pr. 31, Moscow, 117915 Russia

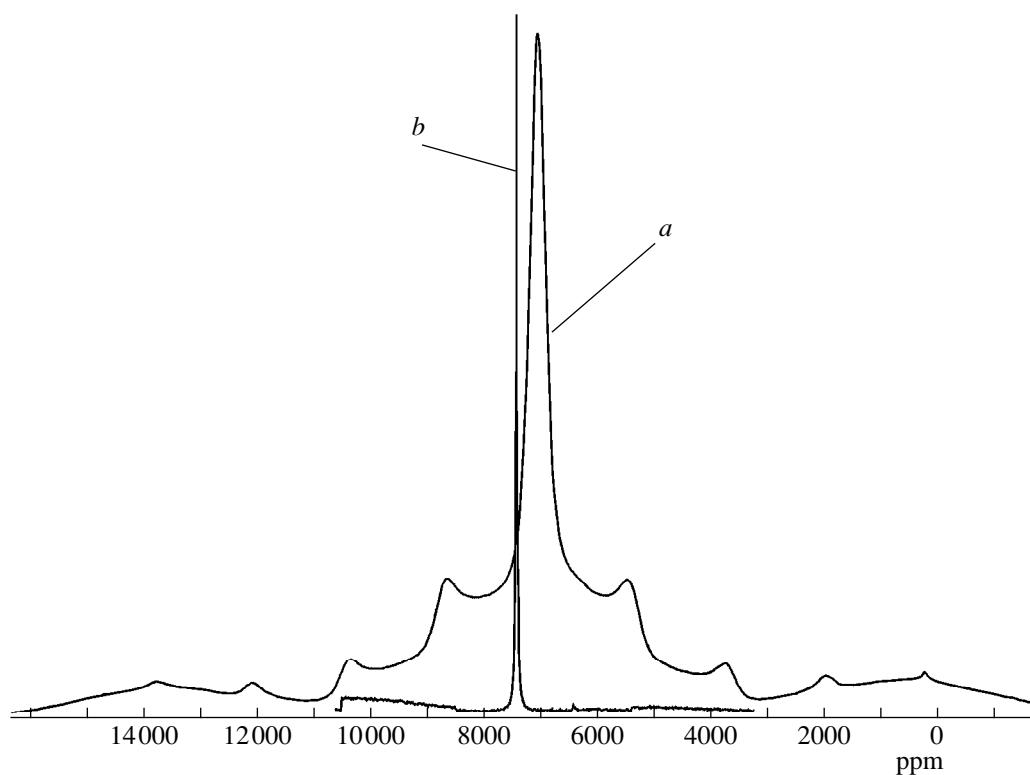


Fig. 1. ^{99}Tc NMR line shape and shift of (a) a bulk sample and (b) technetium metal nanoparticles.

pared to the bulk technetium sample with the hexagonal close-packed lattice [5].

Figure 2 shows the temperature dependences $K(T)$ of Knight shifts for the bulk sample and technetium

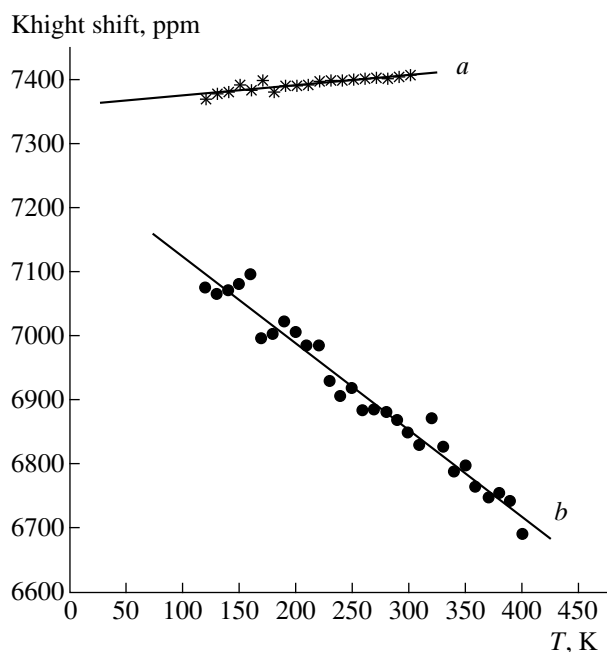


Fig. 2. Knight shift vs. temperature for (a) technetium nanoparticles and (b) bulk technetium.

nanoparticles. Compared to the $K(T) = 7268 - 1.35T$ for the bulk sample, the temperature dependence of the Knight shift for nanoparticles is noticeably weaker, $K(T) = 7360 + 0.16T$, and has the opposite sign. For the bulk technetium sample, $K(T)$ is determined by d -polarization interaction on the background of temperature-independent contact and orbital terms [5]. We may assume that for the cubic lattice also, a temperature change in d -polarization contribution dictates a change in the Knight shift. Since the density of d -states for nanoparticles is smaller than for bulk samples [9], the contribution of K_d to the total shift is also smaller in absolute value. However, the reasons behind such a weak temperature dependence $K(T)$ and its reverse sign for nanoparticles, as compared to the bulk technetium sample, are not conclusively established.

Table 2 presents the ^{99}Tc NMR parameters (Knight shifts for the metal, chemical shifts δ for the ionic form, line widths, and the metal-to-ionic form content ratio) we measured. These data permit the following conclusions:

(1) The K shifts are independent of the type of a support, within the experimental error; in all the samples technetium metal has a cubic structure.

(2) The line widths for the metal and technetium ionic form are 1–5 kHz; the lowest values are observed for the $\gamma\text{-Al}_2\text{O}_3$ support, and the highest values, for TiO_2 .

Table 1. Characteristics of supports

Support	Structure	Specific surface S_{sp} , m ² /g	Pore size, Å
γ -Al ₂ O ₃	Spinel	189	320 and 40
MgO	fcc	46	20
TiO ₂	Tetragonal (60% rutile + 40% anatase)	7	–

(3) The shifts for the ionic technetium form are slightly different for the three supports.

(4) The metal-to-ionic form ratio slightly depends on the initial technetium concentration, the largest ratio being observed for the TiO₂ support.

The ⁹⁹Tc NMR line shape for nanoparticles is represented by an asymmetric contour with a small shoulder at the high-field wing. The degree of asymmetry and line width change depend on the technetium concentration and annealing time of the catalyst. However, these changes are irregular (Table 2). The bar diagrams of distribution point to a wide size distribution of particles: from 10 to 80 Å for 1% Tc/Al₂O₃ (the average diameter is 23 Å) and from 10 to 200 Å for 2% Tc/MgO (the average diameter is 40 Å). The influence of nanoparticle size on the line shape and *K* has been found for rhodium and platinum [9–11]. Thus, we assumed that the experimental ⁹⁹Tc NMR line is a composite one because of the size effects of nanoparticles and decomposed this line into components. Simulation of a con-

Table 2. ⁹⁹Tc NMR parameters of catalysts on different supports, depending on the technetium concentration and annealing time

Technetium content	Annealing time at 700°C, h	NMR shift, ppm		NMR line width, Hz ± 5%		Integrated intensity ratio I_{Tc}/I_{TcO_4}
		Tc metal $K \pm 1.8$	TcO ₄ $\delta \pm 0.2$	Tc metal	TcO ₄	
On γ -Al ₂ O ₃						
0.01	12	7409.9	2.8	921.5	937.0	1/14
0.05	12	7411.7	3.6	1215.9	1015.1	1/7
0.1	12	7411.7	3.1	1361.8	898.0	1/4
1	6	7409.9	2.0	1361.8	1053.6	1/17
2	6	7411.7	1.3	1848.2	1443.9	1/12
3	6	7409.9	0.7	1614.7	775.1	1/16
5	12	7409.9	0.2	1653.6	1287.8	1/6
10	2	7408.1	0.5	1848.2	1639.8	1/13
10	6	7409.9	1.6	1365.7	771.2	1/10
20	2	7408.1	0.9	960	878.3	1/8
10% Ru – 10% Tc on γ -Al ₂ O ₃						
10	6	7410.2	0.9	2075.2	1281.7	1/4.5
Ha MgO						
1	12	7402.7	–6.0	1611.3	1171.3	1/8
2	12	7406.3	–2.2	2140.0	2420.6	1/13
3	6	7400.9	–8.8	1945.5	1834.1	1/12
4	12	7409.9	–3.8	1848.2	2498.7	1/11
10	12	7406.3	–5.2	3015.5	4060.5	1/8
Ha TiO ₂						
1	2	7431.6	–16.3	4863.7	3434.1	1/17
3	2	7401.2	–13.7	4873.2	3746.3	1/4.7
5	2	7402.7	–1.1	2727.7	1874.0	1/5.5
10	2	7408.1	–1.4	2343.7	1326.8	1/7.7
1% Ru–3% Tc on TiO ₂						
3	2	7395.5	–15.2	4263.8	3118.5	1/4.6

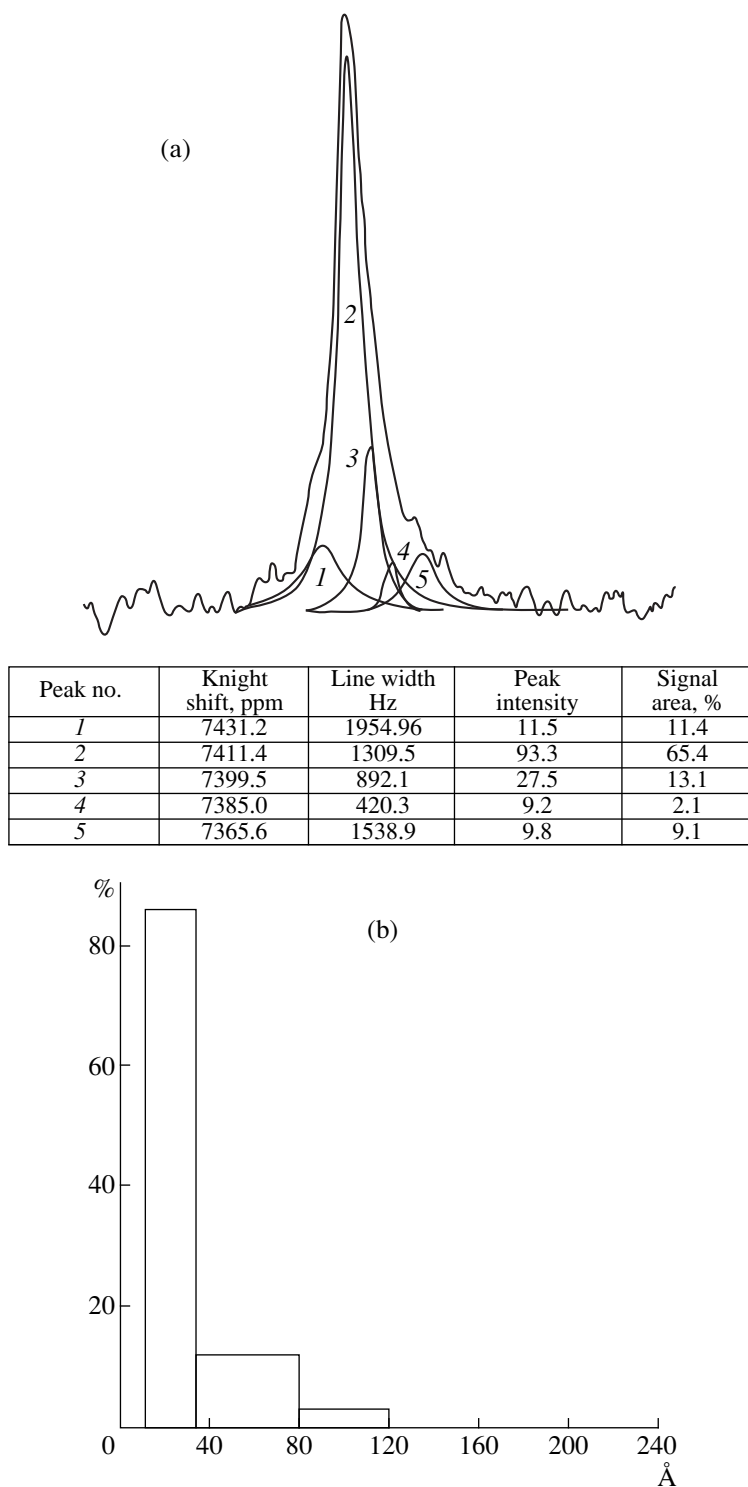
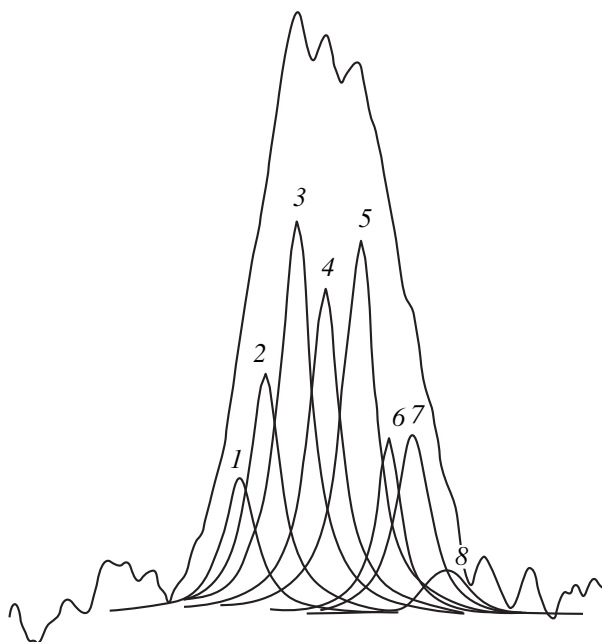


Fig. 3. (a) ^{99}Tc NMR spectrum of a 2% Tc/ $\gamma\text{-Al}_2\text{O}_3$ catalyst and its decomposition into Lorentzian components; the NMR parameters of the components and their intensities are given in the table. (b) bar diagram of the size distribution for this sample.

tour with the LineSim program² resulted in six components of the experimental line shape for the 1% Tc/ Al_2O_3 catalyst and in eight components for the

² The LineSim is built in the Aspect-3000 software.

bimetallic (3% Tc–1% Ru)/ TiO_2 catalyst. Figures 3 and 4 show the ^{99}Tc NMR spectra and the results of decomposition of experimental lines into components. Each of the components has a Lorentzian shape and a width of 0.5–1.0 kHz. The area under a component corre-



Peak no.	Knight shift, ppm	Line width, Hz	Peak intensity	Signal area, %
1	7427.3	885.1	22.3	7.1
2	7418.1	925.0	39.8	18.2
3	7408.2	872.1	65.5	20.6
4	7396.2	909.2	54.5	17.9
5	7384.8	909.8	62.2	20.4
6	7378.3	791.5	29.2	8.3
7	7364.1	916.8	29.9	9.9
8	7351.1	919.8	7.7	2.6

Fig. 4. ⁹⁹Tc NMR spectrum of a binary 1% Ru-3% Tc/TiO₂ catalyst and its decomposition into Lorentzian components; the NMR parameters of the components and their intensities are given in the table.

sponds to the relative concentration of a definite technetium metal form. Consideration of the size distributions of particles in combination with the intensities and shifts of resonance lines permits the tentative and qualitative conclusion that the smaller the technetium nanoparticles, the larger the Knight shift (downfield shift). In a small particle, the technetium positions are not equivalent, in contrast to the bulk sample where translational symmetry results in equivalent technetium positions.

Site nonequivalence implies that the densities of states N_s and N_d change in switching from one technetium position to another. In this case, N_s and N_d relate to the of local density of states [10]. Therefore, each technetium position gives rise to an individual relatively narrow (< 1 kHz) line, and the experimental spectrum is an unresolved superposition of these individual lines. The model for describing the Knight shift is based on the concept of layer nonequivalence of atoms [11]. Each technetium layer is treated as a spherical shell 2.5–3 Å thick. For the cubic lattice, the smallest particle con-

tains 13 atoms: one atom is at the center, and 12 atoms are at the surface. The next layer contains 42 atoms, etc. The overall number of atoms in a particle containing $(m + 1)$ layers is $N_T(m + 1) = N_T(m) + N_s(m + 1)$, where $N_T(m) = 10/3 m^3 - 5m^2 + 11/3m - 1$ is the number of atoms in the interior layers, and $N_s = 10m^2 + 2$ is the number of atoms at the surface of a layer [11]. For spherical technetium nanoparticles with an average diameter of 20 to 40 Å, the number of atoms is 100 to 2000, which corresponds to the number of layers from 4 to 8. For each layer, the Knight shift K_n is the same. The layer with $n = 0$ corresponds to the surface, the layer with $n = 1$ corresponds to the subsurface layer, etc. The Knight shift for the n th layer K_n is described by the formula [12]

$$K_n - K_\infty = (K_0 - K_\infty) \exp(-n/m),$$

where $K_\infty = 7350$ ppm is the limiting shift of the technetium position in the bulk, $K_0 = 7430$ ppm is the technetium shift at the surface of a particle with a given diameter, m is a dimensionless constant, which has the

meaning of the depth at which the layers have distinguishable Knight shifts. With allowance for these data, the Knight shifts K_n in the layers of a five-layer particle were estimated to be $K_1 = 7417$, $K_2 = 7410$, $K_3 = 7397$, $K_4 = 7384$, and $K_5 = 7365$ ppm, at the average value $m = 5$. The calculated K_n values are consistent with the data obtained upon decomposition of the experimental line shape (table to Fig. 4). Note that the layer model for a monodisperse sample implies that the most intense signal with the maximal shift K_0 should arise from the surface. The signals that arise from interior layers will be less intense. The real sample is polydisperse, which may lead to a change in K_0 depending on the particle size, so that the intensity distribution is disturbed. For the binary (3% Tc–1% Ru)/TiO₂, the experimental line shape points to the multicomponent character of the signal [Fig. 4]. A possible reason for this observation may be the narrower individual lines due to dilution of technetium with ruthenium. Since the width of each individual line is determined by dipole–dipole interaction between the magnetic moments of technetium spins, substituting ruthenium, characterized by low natural abundances of magnetic isotopes with small magnetic moments, for a fraction of technetium will lead to line narrowing.

As was mentioned above, the spectra show the signals of the ionic form, along with the signals due to the metal. The ⁹⁹Tc NMR chemical shift of this form corresponds to the shift of the pertechnetate ions, and the counterion may be ammonium or the positive charge of the support. To decide between these possibilities, we studied the ¹H and ¹⁴N NMR spectra of a 5%Tc/Al₂O₃ catalyst, depending on the annealing time in a hydrogen atmosphere.³ We found that the integrated intensities of ¹H and ¹⁴N NMR signals decreased with an increase in

annealing time from 2 to 12 h at 700°C. Therefore, we assigned the signal of the ionic form to residual unreduced ammonium pertechnetate. The smallest amount of unreduced NH₄TcO₄ was found for the TiO₂ support, which may be due to specific features of its surface (the pore number and size). For TiO₂, the specific surface is two orders of magnitude lower than for the remaining supports (Table 1). Therefore, the latter may exhibit the “encapsulation” effect when a fraction of the initial component (NH₄TcO₄) is caught in pores and, thus, is not reduced. As follows from Table 2, the content of unreduced technetium (ionic form) exceeds the content of the metal phase roughly tenfold.

REFERENCES

1. Halperin, W.P., *Rev. Mod. Phys.*, 1986, vol. 58, no. 3, p. 533.
2. Spitsin, V.I., Kuzina, A.F., Pirogova, G.N., and Bala-khovskii, O.A., *Itogi Nauki Tekh., Ser.: Neorg. Khim.*, 1984, vol. 10.
3. Golyanov, V.M., Elesin, L.A., and Mikheeva, N.M., *Zh. Eksp. Teor. Fiz.*, 1973, vol. 18, p. 572.
4. Faulkner, J.S., *Phys. Rev.*, 1977, vol. 16, no. 2, p. 736.
5. Tarasov, V.P., Muravlev, Yu.B., and Guerman, K.E., *J. Phys.: Condens. Matter* 2001 (in press).
6. Stakheev, A.Yu. and Kustov, L.M., *Appl. Catal. A*, 1999, vol. 188, p. 3.
7. Pirogova, G.N., Popova, N.N., Matveev, V.V., and Chalykh, A.E., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1990, no. 11, p. 2486.
8. Pirogova, G.N., Popova, N.N., Voronin, Yu.V., *et al.*, *Zh. Fiz. Khim.*, 1990, vol. 64, no. 11, p. 2933.
9. Tong, Y.Y., Yonezawa, T., Toshima, N., and Van der Klink, J.J., *J. Phys. Chem.*, 1996, vol. 100, no. 2, p. 730.
10. Vuissoz, P.A., Yonezawa, T., Yang, D., *et al.*, *Chem. Phys. Lett.*, 1997, vol. 264, p. 366.
11. Bucher, J.P., Buttet, J.J., and Van der Klink, J.J., *Surf. Sci.*, 1989, vol. 214, p. 347.
12. Makowka, C.D., Slichter, C.P., and Sinfelt, J.H., *Phys. Rev. B: Condens. Matter*, 1985, vol. 31, p. 5663.

³ A ¹H NMR signal was observed for all the catalysts and initial supports. The signal was a two-component line with a width of ~4 kHz. The signal became weaker after annealing a sample. The ¹⁴N NMR chemical shift was 300 ppm from the signal of ammonium in an aqueous NH₄NO₃ solution.