

Effect of particle size upon catalytic and electronic properties of supported Ag catalysts: combined catalytic, ^{109}Ag NMR and quantum chemistry studies

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Abstract

The rate of ethylene epoxidation over Ag/Al₂O₃ supported catalysts demonstrates the drastic increase at a mean size of Ag particles about 400–500 Å. The integral intensity of the ^{109}Ag NMR line from Ag metal particles of the same catalysts increases in the same range of particle sizes. This is due to the large line broadening of the signal from the Ag particles of which the sizes are less than 400–500 Å. The self-consistent calculations of the electronic structure of semi-infinite Ag(111) crystal show the large deviation of the local density of electronic states and ^{109}Ag NMR Knight shifts for the first surface layers of Ag compared with Ag bulk.

Keywords: ^{109}Ag NMR; Nuclear magnetic resonance; Silver; Small metal particles; Surface electronic structure

1. Introduction

The effect of the size of metal particles upon their electronic structure is of fundamental importance for the variety of their properties including adsorption and catalysis [1].

The ^{109}Ag NMR spectroscopy recently has been successfully applied for studies of supported Ag catalysts [2–5]. The results obtained in these studies show that ^{109}Ag NMR line width depends upon the size of supported Ag particles, thus demonstrating the effect of surface on the electronic properties of metal particles (quantum size effect). For the detailed study of this phenomenon one needs to deal with monodispersed metal par-

ticles or at least with samples which have a distinct distribution of particle size.

In this paper, we present the results of the catalytic, ^{109}Ag NMR and quantum chemistry studies of silver particles supported on Al₂O₃ and SiO₂ and having distinct distributions of their sizes. We are reporting the data on the change of catalytic activity in ethylene epoxidation and the ^{109}Ag NMR spectra integral intensity as function of particle size, which we attribute to change of the electronic properties of the surface and subsurface layers compared with those for Ag bulk. The self-consistent calculations of the local density of electronic states and of the Knight shifts performed for semi-infinite Ag(111) crystal show the large deviation of these parameters for surface and subsurface layers in relation to the Ag bulk.

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2. Experimental

The samples of catalysts were synthesized by impregnation of supports (Al_2O_3 or SiO_2) with the amino complex of silver. Drying was performed by a low temperature contact method. Reduction of the silver to a metal state was carried out in vacuum at 90°C under rotation conditions. Reduced samples were washed with doubly distilled water and dried at 100°C . To obtain the samples with different Ag particle sizes the variation of the concentration of impregnating solution as well as the repeated impregnation procedure were employed.

The statistical size distribution of the Ag particles was measured with electron microscope JEOL-100CX (5\AA point to point resolution). The typical, near log-normal distributions of the particle sizes of the series of the Ag catalysts are presented in Fig. 1.

The catalytic activity was determined with the use of a flow-recycling reactor at a pressure of gas mixture 1 atm, temperature 230°C at an ethylene conversion of 15%. The reaction mixture contained 2 vol.% of ethylene, 7 vol.% of oxygen and 91 vol.% of nitrogen. The reaction products were analyzed by chromatography.

The ^{109}Ag NMR spectra were measured on Bruker MSL-400 NMR spectrometer at frequency 18.717 MHz. The frequency range was 10 kHz, the duration of radio-frequency pulse 18 μs , the pulse repetition time 0.15 s. The chemical shifts were measured relative a signal of Ag powder with particle size about 10^4\AA . Magic angle spinning

was performed in a cylindrical ZrO_2 rotor, frequency 2–3 kHz.

The electronic structure of a semi-infinite face Ag(111) of Ag single crystal has been calculated by a tight-binding version of linearized muffin-tin orbitals method (LMTO-TB) [6]. The s-, p- and d-states of crystal atoms were taken into account. The crystal surface was considered by the Green function method [7]. The surface and subsurface Ag planes were treated self-consistently.

The XPS data obtained on VG Escalab HP spectrometer demonstrated that an Ag $3d_{5/2}$ line (367.9 eV) and its shape as well as a position of valence band (4.5 eV) were the same for all the samples, indicating that the silver in metallic state was presented on support surface.

3. Results

3.1. Rate of the ethylene epoxidation

Fig. 2 demonstrates the dependence of the logarithm of the rate of ethylene epoxidation R upon the average size of Ag particles for Ag/ Al_2O_3 and Ag/ SiO_2 samples. It follows from Fig. 2, that within the wide range of Ag crystal sizes (from 500 to 2000 \AA) the epoxidation rate only slightly increases its value both for Ag/ Al_2O_3 and Ag/ SiO_2 catalysts. However, the drastic decrease of R was found for the catalysts with the mean particle sizes smaller than about 500 \AA . For the particles of 160 \AA in diameter the decrease of the

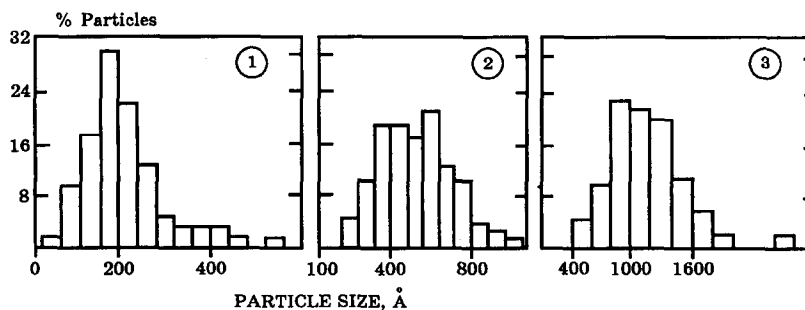


Fig. 1. The typical particle size distributions in studied Ag/ Al_2O_3 catalysts: (1) sample with mean particle size 160 \AA ; (2) sample with mean particle size 400 \AA ; (3) sample with mean particle size 1000 \AA .

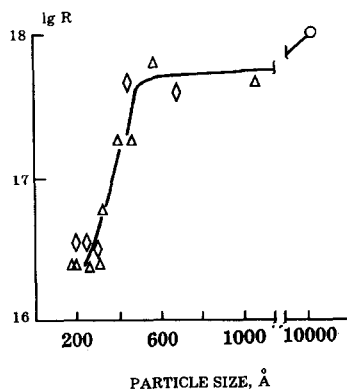


Fig. 2. The logarithm of the rate of ethylene epoxidation, C_2H_4 molecules $cm^{-2} s^{-1}$, as function of average particle size ($P = 1$ atm, $T = 230^\circ C$). (Δ) Ag/Al_2O_3 ; (\diamond) Ag/SiO_2 ; (\circ) Ag powder.

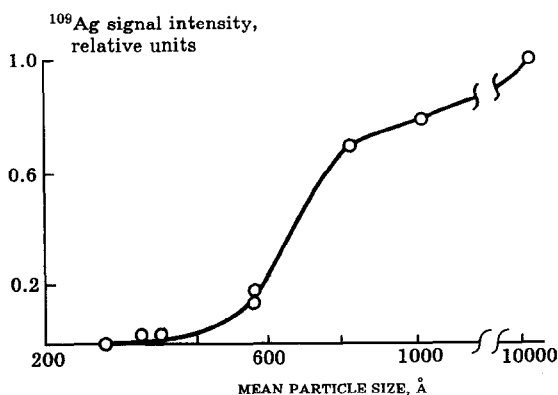


Fig. 3. The dependence of ^{109}Ag NMR signal intensity (per 1 g of supported Ag) upon the mean particle size of Ag/Al_2O_3 catalysts relative to the intensity of signal from bulk metal (particles ≈ 10000 Å).

reaction rate was found to be about two orders of magnitude compared with Ag powder particles (≈ 10000 Å). It seems this is the first unambiguous demonstration of the catalytic size effect for Ag supported catalysts, e.g., the dependence of reaction rate upon the crystal size. It becomes possible due to the use of the samples with narrow distribution of particle sizes. This dependence clearly demonstrates the impact of the Ag particle sizes upon their catalytic activity in ethylene epoxidation.

3.2. ^{109}Ag NMR data

We have found that the integral intensity of the ^{109}Ag NMR signal calculated per 1 g. of supported

Ag shows the dependence upon the mean particle size (Fig. 3). For the catalyst with particle sizes lower than 200 Å no ^{109}Ag NMR signal has been detected. The signal of very small intensity has been found for the samples containing Ag particles of 240 and 300 Å in diameter. The increase of the signal intensity took place for the particles larger than 400–500 Å.

Another interesting feature of the ^{109}Ag NMR spectra was found to be the asymmetry of the line for the samples which have the intermediate size of Ag particles. Fig. 4-A illustrates the ^{109}Ag NMR MAS spectrum of 8 wt.% Ag/Al_2O_3 catalyst. The use of the magic angle spinning removes the dipole–dipole broadening of the line (its value is about 100 Hz [3]), thus reducing the NMR line width. Formally, this spectrum could be deconvoluted upon two lines: a Gaussian line with the chemical shift and line width typically observed in the spectra of large Ag metal particles [3–5]

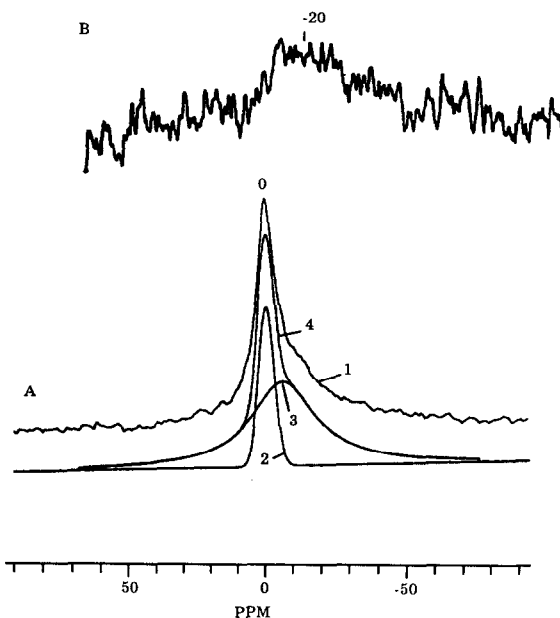


Fig. 4. The ^{109}Ag NMR MAS spectra of Ag-supported catalysts. The chemical shifts are referenced to the signal of Ag bulk metal ($\delta = 0$ ppm): (A) 8 wt.% Ag/Al_2O_3 (mean particle size 500 Å) with spectrum deconvolution on two components: (1) experimental spectrum; (2) narrow Gaussian component; (3) broad Lorentzian component; (4) sum of narrow and broad component; (B) 16 wt.% Ag/SiO_2 (mean particle size 240 Å), demonstrating the asymmetrical line shifted to high field.

Table 1

The population of s-states (n), densities of s-states near Fermi surface (σ) and the value of the Knight shift (δ) for the first 8 layers of Ag(111) crystal

Layer	n	σ	$\delta^a, \Delta H/H$	δ, ppm
1	0.734	1.359	1.120	5898
2	0.696	0.985	0.457	2406
3	0.705	0.582	-0.124	-653
4	0.698	0.576	-0.143	-753
5	0.696	0.651	-0.037	-195
6	0.695	0.668	-0.013	-67.9
7	0.695	0.673	-0.005	-26.3
8	0.695	0.666	-0.016	-82.7
bulk	0.693	0.679	0.0	0.0

^a Units of Knight shift for Ag bulk metal (5266 ppm relative to the aqueous solution of AgNO₃).

and a broad line shifted to high field. For the sample with a mean particle size 240 Å (16 wt.% Ag/SiO₂) the broad asymmetric line of small intensity shifted to high field indeed was detected in the spectrum (Fig. 4-B). These data show that the small Ag particles (less than 400–500 Å) have the ¹⁰⁹Ag NMR characteristics (line width, chemical shift and, most probably, also spin-lattice relaxation rate T_1) which are different from those for Ag bulk and do not contribute to the spectrum of catalysts which have the large particles; the latter have ¹⁰⁹Ag NMR parameters typical for Ag bulk.

3.3. Electronic structure of surface and subsurface layers of Ag(111) crystal

Since the ¹⁰⁹Ag NMR spectra indicate the difference in ¹⁰⁹Ag NMR characteristics of small and large Ag particles and therefore the difference in the electronic structure of surface and subsurface layers of Ag crystal from those for bulk Ag, the electronic structure of the semi-infinite crystal Ag(111) has been calculated.

The populations of s-states – (n) and their densities near the Fermi surface – (σ) for the first eight layers of the Ag(111) surface and for the Ag bulk are collected in the Table 1, together with the values of Knight shifts δ in the units of the Knight shift $\Delta H/H$ for Ag bulk. The latter were calculated with the use of relation

$$\Delta H/H = (n\sigma - n_B\sigma_B) / n_B\sigma_B$$

where n and σ are populations of s-states and their densities near Fermi surface respectively; n_B and σ_B are those for Ag bulk.

The data in the Table 1 show that the populations of s-states, their densities near the Fermi level and the Knight shifts for the surface and subsurface layers are quite different from those for Ag bulk. Unexpectedly, the Knight shifts for the first two layers are larger than for bulk metal, while for the next layers they become smaller than the value for bulk metal. These results explain the large broadening of the ¹⁰⁹Ag NMR line from the surface and subsurface layers of Ag crystals as caused by the spread of the resonance over large frequency range.

4. Discussion

The results presented above show that the use of the Ag catalysts with sharp distributions of Ag particle sizes has allowed us to obtain the interesting information on the dependence of the properties of small Ag particles upon their size.

For the first time the effect of particle size upon the catalytic activity in ethylene epoxidation has been clearly demonstrated. The increase of the rate constant about two order of magnitude has been observed when going from particles of 160 to 10000 Å in diameter.

This effect is most pronounced for the particles up to about 500 Å and is caused by the influence of the surface upon the electronic state of Ag atoms. Indeed, ¹⁰⁹Ag NMR results show that the NMR characteristics and therefore the electronic properties of those Ag particles that are smaller than 400–500 Å are different from those for bulk metal. This follows directly from the drastic broadening of ¹⁰⁹Ag NMR line for samples having the Ag particles with diameters less than this value. The most evident explanation of this effect is the spread of the Knight shifts of the NMR lines from Ag atoms located in the surface and subsurface layers of Ag crystals. Indeed, the direct cal-

ulation of the Knight shifts for Ag nuclei in the surface and subsurface layers of Ag(111) crystal shows their large deviation from the value for Ag bulk. Although the model of semi-infinite crystal may need some corrections when going to the particles having 10^4 to 10^6 atoms it seems that at least qualitatively it explains the experimental ^{109}Ag NMR data.

It is remarkable that in the case of Ag particles the influence of surface propagates unexpectedly deep into the inner layers of Ag crystal (up to 200–250 Å, or 70–80 layers from surface). This behavior is quite different from that for Pt particles, where the signal from metal bulk was observed for considerably smaller average particle sizes [8]. In ^{195}Pt NMR spectra extremely broad lines (width ≈ 5 MHz) have been detected for the most fine Pt/ Al_2O_3 particles with the use of the special spin-echo methods. Due to about 100 times lower signal intensity compared with ^{195}Pt NMR resonance, the broad signal from the most fine Ag particles has not been found in present work. Only the asymmetry of the ^{109}Ag NMR line indicates the presence of the subsurface layers with electronic characteristics different from those for Ag bulk. Note that the line asymmetry was detected only in magic angle spinning spectra which decrease the dipole interaction between magnetic nuclei, thus allowing the detection of the inhomogeneously broadened line from those inner subsurface layers which have relatively moderate impact of surface.

The difference between Pt and Ag particles can be either due to the different contributions to the Knight shift from s- and d-states in the two cases,

or due to the presence in the Pt samples studied in [8] of small uncontrolled amounts of the crystals, which have relatively large diameters. The presence even of small amounts of the latter may produce a large contribution to the signal intensity since it is proportional to the particle volume.

5. Conclusion

Thus, combined catalytic, ^{109}Ag NMR and quantum chemistry studies of Ag supported catalysts have revealed the profound influence of particle size upon their catalytic and electronic properties.

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