

III INTERNATIONAL CONFERENCE “CATALYSIS: FUNDAMENTALS AND APPLICATIONS”

Effect of Electron Beam Irradiation on the Formation of Active Sites in the Pt/H Pentasil Catalyst

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Received October 18, 2007

Abstract—The influence of preirradiation with an electron beam from a linear resonance electron accelerator in flowing argon on the structure and properties of the 1% Pt/H pentasil catalyst was studied. The support structure was studied by x-ray diffraction and low-temperature nitrogen adsorption. No changes in the crystal structure and pentasil specific surface area were observed in the irradiation dose range from 120 to 900 Mrad at an average electron energy of 7.7 MeV. The electron beam treatment resulted in a considerable increase in the catalytic activity of the Pt/H pentasil in gas-phase toluene hydrogenation as a model reaction. The results obtained by IR spectroscopy of adsorbed CO and X-ray diffraction data suggested that the increase in the catalyst activity after electron beam irradiation is due to changes in the size and charge of the Pt particles.

DOI: 10.1134/S0023158408050236

INTRODUCTION

Unconventional activation methods using low-temperature plasma, microwave radiation, and high-energy electron beams along with standard thermal treatment are of considerable interest from the standpoint of active site formation in heterogeneous catalysts. Irradiation with accelerated electrons seems most promising because, during catalyst irradiation, the joint physical and chemical action of the beam of accelerated electrons can produce new active sites with unusual catalytic properties. However, the data available on the effect of electron irradiation on the catalytic properties of supported metallic catalysts are scarce. Earlier, we studied the catalytic properties of the irradiated 1% Pd/C catalyst [1]. The purpose of this work is to study the influence of the electron beam effect on the activity of the 1% Pt/H-TsVM catalyst in the gas-phase hydrogenation of toluene and to investigate the changes in the active phase of the catalysts using X-ray diffraction and IR spectroscopy.

EXPERIMENTAL

Catalyst Preparation

Zeolite of the pentasil type (trade mark TsVM, SiO₂/Al₂O₃ = 35, ZAO Nizhegorodskie Sorbenty, Russia) was used as the support. The 1% Pt/H-TsVM catalyst was prepared by the ion exchange method from a solution of the [Pt(NH₃)₄]Cl₂ · H₂O complex using a procedure described earlier [2]. After the ion exchange,

the sample was calcined in flowing air at 500°C for 2 h (the temperature was increased at a rate of 0.5 K/min).

The catalysts were irradiated with an electron beam from an LU-10-20 linear resonance electron accelerator in flowing argon. The temporal structure of the electron beam consisted of macropulses with a duration of 3.8 μs and a repetition frequency of 1000 Hz. The average electron energy was 7.7 MeV. The irradiation dose was varied by changing the duration of the electron action. The catalysts irradiated with a dose of 120–900 Mrad were studied. The irradiation dose on the catalyst surface was monitored as the accelerator current value.

Toluene Hydrogenation

The activity of the initial and irradiated catalysts was studied in a flow-type installation at atmospheric pressure in the temperature interval from 100 to 200°C. The catalyst sample weight was 500 mg, and the catalyst grain size was 0.20–0.63 mm. Before the reaction, the catalysts were reduced with hydrogen at 200°C for 1 h.

Hydrogen was purified to remove the O₂ and H₂O traces by passing it through a column filled with MnO/Al₂O₃ and over zeolite 5A. Next, H₂ was directed to a mixing evaporator to saturate it with toluene vapor. The resulting hydrogen–toluene mixture was fed into a heated reactor with the catalyst; the hydrogen feed rate was 40 ml/min, and the toluene feed rate was 0.53 ml/min (0.15 ml/h of liquid toluene). The reaction

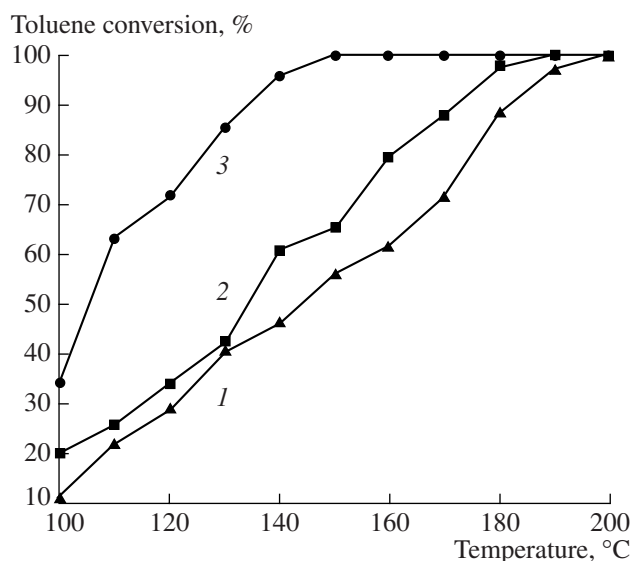


Fig. 1. Influence of the irradiation dose on the activity of the Pt/ZSM-5 catalyst in the gas-phase hydrogenation of toluene: (1) nonirradiated Pt/ZSM-5, (2) and (3) Pt/ZSM-5 irradiated with doses of 120 and 900 Mrad, respectively.

products were identified on a VLKhM-80 chromatograph equipped with a flame-ionization detector and a PONA chromatographic capillary column (length of 50 mm, SE-54 phase, nitrogen as the carrier gas). The only detectable reaction product was methylcyclohexane.

Determination of the Specific Surface Area

In order to determine the specific surface area of the catalyst, a 5% nitrogen + helium mixture was continuously passed through a quartz reactor with a fixed catalyst bed pre-heat-treated at 350°C for 30 min in flowing helium to remove the adsorbed water. The nitrogen concentration in the flow was measured with a thermal-conductivity detector. The specific surface area was measured as the amount of nitrogen adsorbed on the sample at -195.8°C.

X-Ray Diffraction

X-ray diffraction was carried out on a DRON-3M diffractometer using $\text{CuK}\alpha$ radiation. Scanning was performed in the interval $2\theta = 15^\circ\text{--}100^\circ$ with 0.5° increments. Peak positions in X-ray diffraction patterns were determined relative to the line of the internal standard, which was cerium oxide introduced into the sample before the analysis.

For determination of the phase composition, the set of interplanar spacings was compared to data from the ASTM-JCPDS International Standard Material Database.

From X-ray diffraction data, the unit cell parameters and volumes of the pentasil lattice were derived using a standard procedure [3, 4].

IR Spectroscopy

Diffuse reflectance IR spectroscopy was used to study the structural OH groups of the zeolite and the state of the supported platinum particles. The measurements were carried out on a Nicolet Protégé 460 spectrophotometer with a diffuse reflectance attachment.

Before recording a spectrum, the sample was evacuated at 500°C for 1 h to a residual pressure of 10^{-4} Torr.

The electronic state of the metal was determined by analysis of the vibration frequencies of adsorbed CO. For this purpose, CO (10 Torr) was adsorbed on the sample surface at room temperature and the spectrum was recorded after pumping at 20°C (30 min) and at 100°C (1 h).

RESULTS AND DISCUSSION

Toluene Hydrogenation

The temperature dependences of the toluene conversion for the initial Pt/H-TsVM sample and for the catalysts irradiated with doses of 120 and 900 Mrad are shown in Fig. 1.

The toluene conversion on the sample irradiated with a dose of 120 Mrad is higher only by 10–20% throughout the temperature interval. By contrast, an increase in the irradiation dose to 900 Mrad appreciably affects the catalyst activity: the toluene conversion at 150°C reaches 100%, whereas it is only 55% on the initial catalyst.

The changes in the zeolite structure and in the supported metal phase were studied to reveal the causes of the increase in catalytic activity.

Changes in the Support Structure

X-ray diffraction and specific surface area data.

The diffraction patterns from the H-TsVM sample, the nonirradiated Pt/H-TsVM catalyst, and the catalyst treated with an electron beam are shown in Fig. 2.

The reflection intensities characteristic of the pentasil crystal structure are similar in all three diffraction patterns, indicating that the zeolite crystal retains its structure under electron beam irradiation. The appearance of the low-intensity peak at 39.8° in the diffraction pattern of the nonirradiated catalyst is discussed below.

After Pt was supported on the zeolite, the specific surface area remained unchanged (350 m^2/g). In turn, the treatment of the Pt/H-TsVM sample with a dose of 900 Mrad insignificantly decreases (less than 10%) the specific surface area (to 320 m^2/g).

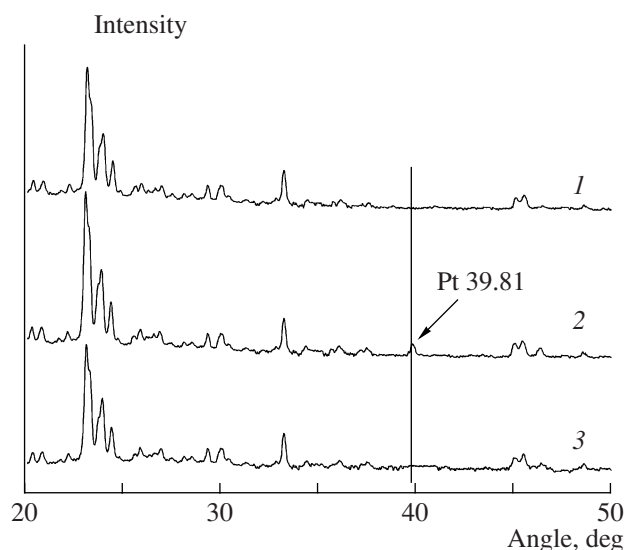


Fig. 2. X-ray diffraction patterns from the (1) initial H-TsVM-5, (2) nonirradiated Pt/H-TsVM-5, and (3) Pt/H-TsVM-5 irradiated with a dose of 900 Mrad.

Thus, these results suggest that no considerable destruction of the zeolite framework occurred during the electron beam treatment.

IR Spectroscopy of the OH Groups of H-TsVM

The IR spectra of the initial and irradiated samples (Fig. 3) contain absorption bands at 3744 and 3610 cm^{-1} . The first band is due to the silanol OH groups, and the second is due to the bridging OH groups (of Brønsted acid sites). Because the silanol hydroxyl groups are more stable than the bridging OH groups, the intensities of the spectral bands presented in Fig. 3 were normalized to the intensity of the band at 3744 cm^{-1} .

A comparison of the spectra shows that the electron beam treatment with doses of 120 and 900 Mrad considerably decreases the intensity of the absorption band at 3610 cm^{-1} , which is similar for both irradiated samples. This fact likely indicates the partial dealumination of the zeolite lattice or the replacement of a portion of the protons in the cationic positions of the zeolite by the metal cations.

Changes in the Supported Metal Phase

X-ray diffraction data. As mentioned above, the diffraction pattern from the nonirradiated Pt/H-TsVM catalyst exhibits a low-intensity peak at $2\theta = 39.8^\circ$ corresponding to platinum metal particles larger than 2 nm (Fig. 2). These large Pt particles likely form on the outer zeolite surface at the metal precursor (platinum ammine) decomposition stage. This peak disappeared after the catalyst was treated with an electron beam with a dose of 900 Mrad, possibly indicating a decrease in the platinum particle size down to a value character-

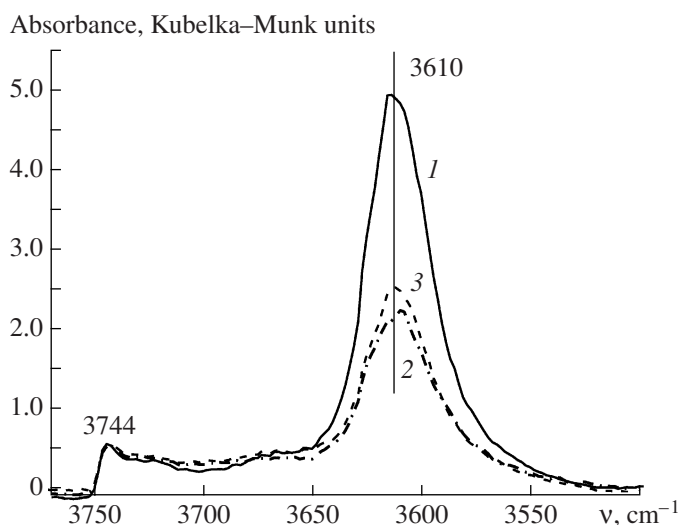


Fig. 3. Diffuse reflectance IR spectra of the (1) initial sample and 1% Pt/H-TsVM-5 catalysts irradiated with doses of (2) 120 and (3) 900 Mrad.

istic of the X-ray-amorphous state. It is likely that, in addition to getting smaller, the large metal particles can migrate inside the channels. This is indirectly indicated by the decrease in the specific surface area, which is probably caused by the blocking of part of the TsVM zeolite channels by platinum particles. Since the crystal lattice of zeolites with the pentasil structure has a two-dimensional system of relatively narrow channels (~ 0.5 nm), this blocking can make part of the porous structure of the zeolite inaccessible to molecules being adsorbed. From the decrease in the absorption intensity at 3610 cm^{-1} in the IR spectra of the irradiated samples (Fig. 3), it can be inferred that the platinum particles in the pentasil channels are located in cation-exchange sites. Substitution for the isolated platinum ions seems improbable because the vibrational spectra of adsorbed CO (see the discussion of the data presented in Fig. 4) suggest that no isolated platinum cations exist after the electron beam irradiation with a dose of 900 Mrad.

IR spectroscopy of adsorbed CO. The vibrational spectra of the CO molecules adsorbed on the initial Pt/H-TsVM catalyst and on the catalysts irradiated with doses of 120 and 900 Mrad (Fig. 4) were measured after evacuation at room temperature for 30 min.

The spectrum of the initial sample contains three absorption bands at 2149 cm^{-1} (shoulder), 2124 cm^{-1} , and 2092 cm^{-1} (broad). The last one likely consists of several absorption bands. Earlier [5], the absorption band at 2149 cm^{-1} was assigned to vibrations of the CO molecules in the $\text{Pt}^+(\text{CO})_3$ or $\text{Pt}^{2+}(\text{CO})_2$ complex and the low-frequency bands at 2124 and 2092 cm^{-1} were assigned to the stretching vibrations of the CO molecules of the dicarbonyl $\text{Pt}^+(\text{CO})_2$. The absorption bands at 2078 cm^{-1} were assigned to vibrations of the CO

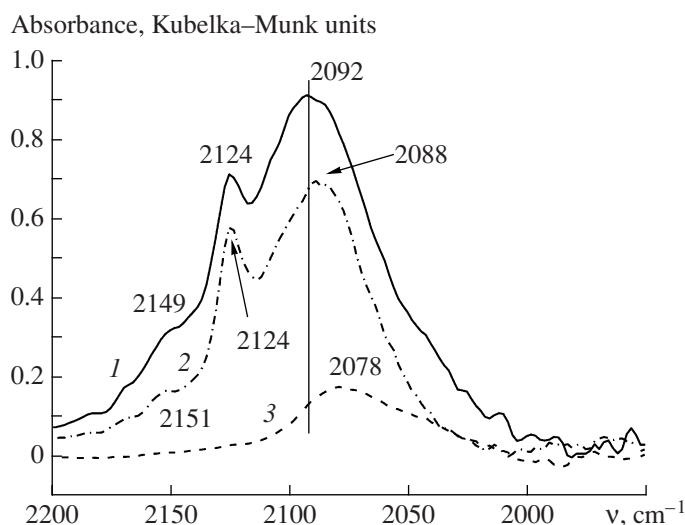


Fig. 4. Diffuse reflectance IR spectra of CO adsorbed on the (1) initial sample and Pt/H-TsVM-5 samples irradiated with doses of (2) 120 and (3) 900 Mrad after evacuation at room temperature.

molecules adsorbed in linear form on small Pt_n° or $\text{Pt}_n^{\delta+}$ particles (Pt_n is the metal cluster).

A similar spectrum was observed for the sample irradiated with a dose of 120 Mrad. However, the low-frequency shift of the band maximum at 2092 cm^{-1} ($2092 \rightarrow 2088\text{ cm}^{-1}$) should be mentioned. This shift is probably caused by the increase in the intensity of the absorption band at 2078 cm^{-1} , which is due to the increase in the fraction of the reduced forms of platinum.

The spectrum of the sample irradiated with a dose of 900 Mrad contains a single low-intensity broad band at 2078 cm^{-1} , which can be assigned to vibrations of CO adsorbed on small $\text{Pt}_n^{\delta+}$ or Pt_n° particles. These changes in the IR spectra of adsorbed CO suggest that raising the dose from 120 to 900 Mrad results in a more complete reduction of the isolated platinum cations to small Pt_n particles. This conclusion is confirmed by the fact that the absorption bands at 2149, 2124, and 2092 cm^{-1} , which arise from vibrations of the CO molecules adsorbed on the cationic forms of platinum, are absent from the spectra of the sample after irradiation with a dose of 900 Mrad.

After pumping at 100°C , the spectrum of adsorbed CO (not shown in Fig. 4) indicated a low-frequency shift of the absorption band corresponding to the linear CO complexes with the $\text{Pt}_n^{\delta+}$ platinum particles (2078 cm^{-1}), as well as a decrease in its intensity relative to the intensity of the vibrational band of the CO complex with the cationic form of platinum (2124 cm^{-1}). The absorption band at 2149 cm^{-1} disappeared from the spectrum.

The spectrum of the sample irradiated with a dose of 120 Mrad is characterized by similar changes, specifically, a 12-cm^{-1} shift of the absorption band at 2088 cm^{-1} to lower frequencies, a decrease in its relative intensity, and the disappearance of the band at 2151 cm^{-1} .

The spectra of CO adsorbed on the sample irradiated with a dose of 900 Mrad also exhibit a low-frequency shift of the absorption band at 2078 cm^{-1} by 16 cm^{-1} .

The absorption maximum at 2124 cm^{-1} remains unchanged with an increase in the evacuation temperature. This indicates the formation of stable linear CO complexes with the isolated Pt^+ cations. The formation of these complexes is possible if the metal cation is located in a cationic site in a zeolite cavity.

The spectra of the sample irradiated with a dose of 900 Mrad contain no absorption bands assignable to CO vibrations on the cationic forms of platinum. Since no chemical reduction of the metal was done during sample preparation for IR spectroscopy, it can be concluded that the platinum cations were reduced through their interaction with the electron beam. According to the data presented above, the degree of reduction depends, to a considerable extent, on the irradiation dose. The detailed mechanism of the reductive effect of accelerated electrons remains unclear, but two main processes can be hypothesized. The first process is the direct interaction of the supported platinum particles with electrons. In this case, the platinum particles likely interact with secondary, slower electrons, which can result from the interaction of primary electrons with the catalyst sample because direct capture of electrons with an energy of 7.7 MeV seems improbable. The second possible process is metal reduction by the products of radiolysis of adsorbed water, which is present in the zeolite pores in considerable amounts. As was shown earlier [6], the radiolysis of water can produce atomic and molecular hydrogen, which can readily interact with noble metal particles.

Thus, our data suggest that two processes occur during the treatment of the catalysts with an electron beam, namely, (1) a decrease in the size of comparatively large ($>2\text{ nm}$) particles of supported platinum and (2) the reduction of the Pt^+ cations to $\text{Pt}_n^{\delta+}$ or Pt_n° clusters, whose size is likely limited by the diameter of the pentasil channels ($0.5\text{--}0.6\text{ nm}$).

ACKNOWLEDGMENTS

The authors are grateful to I.V. Mishin for assistance in X-ray diffraction measurements and for valuable remarks in the discussion of this work.

This work was supported by the International Science Foundation, grant no. 1764.

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