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Platinum nanoparticles as active sites for C–C bond activation in high-silica zeolites ☆

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ABSTRACT

Density functional theory (DFT) was applied to investigate the structure and reactivity of Pt_6 particles encapsulated in silicalite as well as in sodium and hydrogen ZSM-5 zeolites. Incorporation of a metal particle in silicalite or sodium zeolite leads to the formation of a negatively charged metal cluster with stabilization energies close to 9 and 16 kcal/mol, respectively. Interaction of a platinum cluster with hydrogen zeolite and extra-framework aluminum species is characterized by energies as high as 45–50 kcal/mol and yields an electron-deficient metal particle. This positively charged metal cluster stabilized in the zeolite channel can function as active site in alkane transformations. The formation of the active site is accompanied by suppression of both Brønsted and Lewis acidities. An alternative mechanism of alkane cracking and isomerization avoiding the direct participation of acid sites has been proposed.

1. Introduction

Platinum zeolites are important catalysts in current processes of petrochemistry and oil refining. A great contribution to the development of new catalytic systems was made by the pioneering works of the outstanding Russian scientist, Professor Khabib Minachev, whose 100th anniversary will be celebrated by the scientific community on December 24, 2008. Minachev's first scientific publications were presented in 1939; the last one was presented in 2001 – more than 60 years of productive research work. Professor Minachev is known for his numerous works on metal-containing catalysts. However, his major work was devoted to zeolite catalysis. Kh. Minachev was one of the first to recognize the importance of zeolite systems, and he initiated extensive studies on the structure and catalytic properties of new metal-containing zeolite catalysts at the N.D. Zelinsky Institute of organic chemistry (Moscow). This work was the foundation of the systematic study of new promising metal–zeolite systems, which resulted in the development of processes effective in one-step synthesis of many technically important products such as components of high-quality fuels, lubricant oils and many other products. Professor Minachev had the satisfaction of seeing the results of much of his research work transferred to industrial practice.

Professor Minachev's devotion to his beloved science was unique. A rare combination of knowledge, tolerance and equanimity radiated from him, making every contact with him a pleasant and fruitful experience. Many generations of young scientists from various countries worked in his laboratory as Ph.D. students, guest researchers and invited professors. He was a coordinator of USA–USSR collaboration in catalysis. Professor Minachev contributed to the book "Zeolite chemistry and catalysis", edited by Jule Rabo and published in 1976. He edited the book "Catalysis on zeolites", published in 1988 in Budapest. Khabib Minachev frequently attended international meetings on catalysis.

Our admiration of this man is based not only on the success of his scientific work but also on the wonderful balance between his experimental and theoretical achievements. It was characteristic of Minachev's keen perception that, during his efforts to find novel catalysts, he remained conscious of the need to use sophisticated tools for studying the surface chemistry such as photoelectron spectroscopy and quantum chemistry. With his associates, he discovered the strong effect of the support and the reaction environment on electronic structure and geometry of supported metal particles. He was one of the first to discover the important role played by hydrogen spillover in catalytic transformations over metal–zeolite systems [1]. In the course of his research using XPS, Professor Minachev was able to show that the state of platinum in

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☆ This paper is dedicated to the memory of Professor Khabib Minachev (1908–2002).

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platinum-supported zeolites drastically changes upon interaction with surface hydroxyl groups. He initiated theoretical and experimental studies to shed some light on the nature of metal-support interaction and its impact on catalytic activity.

Sachtler, together with Professor Minachev's associates, used X-ray photoelectron spectroscopy and showed that metal clusters supported on acid oxides are electron-deficient [2], and the deficiency increases with acidity [3]. The increase in positive charge on metal particle observed on increasing local concentration of Brønsted acid sites (BAS) allows identifying BAS as electron-accepting sites of the support. The increase in electron deficiency of palladium particles leads to a drastic increase of catalytic activity in C–C bond cleavage [4].

Moreover, Freund [5,6] presented evidence that, when rhodium particles are introduced on the alumina surface, the concentration of the surface hydroxyls decreases, whereas Rh 3d-bands shift to higher binding energies. That results in the oxidation and stabilization of supported metal particles. The electron deficiency of metal particles is also confirmed by the frequency shift in the infrared spectra of adsorbed CO [7–9]. Recently, Murzin [10,11] reported the relation between changes in the electronic structure of supported platinum particles and the acid site strength of zeolites. In the presence of platinum, the concentration of acid sites decreases, and in some cases both Brønsted and Lewis acidity are completely suppressed. The DFT calculations by Rösch [12–15] provided evidence that the interaction between metal particles and the H-form of X zeolite leads to transfer of hydrogen atoms of hydroxyls onto the metal surface and to the oxidation of the metal particle. The density functional theory [16] indicates that interaction of platinum atom with HZSM-5 zeolite results in transfer of electron density from oxygen to metal atom.

Although the data in favor of Sachtler's suggestion on the important role of metal–acid site interaction were reported more than 15 years ago, the majority of research shares the concept of bifunctional catalysis. According to this concept, dehydrogenation and hydrogenation steps occur on a metal particle, whereas isomerization and C–C bond cleavage proceed on an acid site. This implies the presence of independent active sites of two types [17–19]. However, we have shown recently [20,21] that the introduction of a platinum particle into the zeolite channel results in the specific metal–acid site interaction and the transfer of a Brønsted proton onto the metal surface. As a result, the platinum cluster oxidizes and stabilizes in the zeolite channel, while the acidity of the support is suppressed. It seems that this metal particle can function as an active site in alkane transformations. In this connection, a number of questions arise. In particular, the relation between the state of the metal and the zeolite composition and its impact on catalytic activity remain unclear. In a metal–zeolite catalyst, metal particles can interact with neighboring exchangeable cations, BAS, Lewis acid sites (LAS) and framework oxygen anions. For example, catalysts without BAS (Pt/NaZSM-5 or Pt/silicalite) exhibit a low catalytic activity in alkane transformations [22]. Based on the conventional interpretation, a low activity can be explained by the absence of sites active in isomerization (BAS). The role of extra-framework aluminum species (EFAL) also remains to be understood. It is supposed that EFAL can be either hydrated Al^{3+} cations or oxo-species containing coordinatively unsaturated aluminum atoms [23]. The EFAL can play the role of LAS. It appears that active sites can be formed by interaction of a metal particle with LAS.

It is therefore interesting to trace the relation between the electronic structure and the reactivity of platinum particles in different zeolite matrices. A convenient approach to the study can be to develop model catalytic systems such as Pt/ZSM-5 (silicalite), Pt/HZSM-5, and Pt/NaZSM-5 as well as EFAL using cluster approximation. In this work, density functional theory was used to study the electronic structure of a Pt_6 cluster localized in the channels of ZSM-5 type zeolites and their reactivity in alkane transformations. In addition, it appeared interesting to trace the effect of framework composition and the ratio of framework and extra-framework aluminum atoms on the activity of Pt-containing zeolites.

2. Computational details

To model the fragments of zeolite systems, the cluster approach was used. The cluster electronic structure was computed at the density functional theory (DFT) level using a B3LYP exchange-correlation functional [24–26]. The SBKJC effective core potential [27] and corresponding basis set augmented with polarization functions were used. All clusters were fully optimized without symmetry constraints. Transition state structures were verified by performing normal mode analysis. Calculations were performed with the PC GAMESS program package [28,29]. Analysis of natural populations was carried out with the help of the NBO program [30].

Cluster modeling the fragment of ZSM-5 zeolite framework consists of two ten-membered rings located at the intersection of straight and sinusoidal channels. Cluster modeling the silicalite fragment with the structure of ZSM-5 zeolite includes 15 silicon atoms, and that of HZSM-5 and NaZSM-5 contain 14 silicon atoms and one aluminum atom. The cluster broken bonds (Si–O and Al–O) were saturated with hydrogens, placed at the 1.6 and 1.5 Å along Al–O and Si–O bonds, respectively. All terminal hydrogens were fixed during the geometry optimization. The excessive negative charge of the framework was compensated by a proton of BAS and that of the sodium form by a sodium cation. The obtained clusters have the following stoichiometry: $Si_{15}O_{18}H_{24}$, $AlSi_{14}O_{18}H_{25}$ and $NaAlSi_{14}O_{18}H_{24}$. The extra-framework aluminum species was modeled by the $Al_2O_2(OH)_2$ cluster.

3. Results and discussion

The optimized structures modeling a Pt_6 particle incorporated in ZSM-5 (silicalite), HZSM-5 and NaZSM-5 zeolites are shown in Fig. 1a–c. The figures are complemented with the principal Pt–Pt and Pt–O (Å) distances. Table 1 contains the stabilization energies and the main parameters characterizing electronic structure. The isolated Pt_6 cluster has the ground state with spin multiplicity of 9 (electronic configuration $5d^{9.41}6s^{0.55}$) and the geometry of distorted octahedral (Pt–Pt distances are 2.63, 2.66 and 2.97 Å). Stabilization energy for a Pt_6 nanoparticle in silicalite is as low as 9 kcal/mol. The shape of the metal cluster was found to be significantly modified: the particle stretches along the zeolite channel whereby the corresponding Pt–Pt bond lengths increase by 0.9–1.4 Å (Fig. 1a). The changes in the shape are due to the interaction of the platinum cluster with the basic oxygen anions of zeolite framework. As result the metal cluster becomes negatively charged. Thus adsorption on basic sites favors the formation of electron enriched metal particles due to the incoming electronic density from the adjacent silicon atoms through the oxygen anions. The Pt_6/ZSM-5 system has the triplet ground state and the singlet–triplet splitting reaches the value of 10 kcal/mol. It appears that the silicalite supported Pt_6 cluster is characterized by essentially lower ionization potential and electron affinity as compared to an isolated particle. The chemical potential and the hardness [31] also decrease by 1.1 and 0.2 eV, respectively.

The presence of BAS in the vicinity of the platinum cluster dramatically changes the pattern of the metal–zeolite interaction (Fig. 1b). In this case the transfer of a Brønsted proton on the platinum surface is thermodynamically favorable, and an electron-deficient metal particle is formed. This process is of an exothermic nature ($\Delta E \approx -35$ kcal/mol), and it proceeds with a negligible low