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Investigation of co-hosted basic and metal nanoparticles in Pt/Cs-BEA zeolites

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Abstract

Various acido-basic BEA zeolites having different Cs contents and containing supported Pt particles were prepared using two acidic parent BEA supports with same framework Al content but with strongly different morphology of the zeolite crystallites. In spite of highly different exchange capacities in aqueous solution, the two parent BEA supports behaved similarly towards formation of Cs-oxide like nanospecies. Thus, the addition of a similar amount of Cs was necessary in the two samples to extinguish all Brønsted acidic sites and a further introduction of Cs led to the presence of highly dispersed Cs_2O like species with strong basic character as shown by the adsorption of CO_2 followed at 293 K by FT-IR spectroscopy. FT-IR experiments were also conducted at 100 K and 293 K using CO as probe molecule to give further insights on the Cs and reduced Pt species, respectively. In the presence of co-hosted Cs-oxide like, highly dispersed Pt^0 nanoparticles are formed with sizes close to 1 nm as observed by TEM. Both the high dispersion of the Pt^0 nanoparticles in the more basic samples and the phenomenon of electro-donation by the basic support contribute to the changes in electronic behaviour of the Pt^0 particles shown by FT-IR of adsorbed CO.

Keywords: Basicity; BEA zeolite; Caesium; Platinum; Nanoparticles

1. Introduction

In the field of metal supported heterogeneous catalysts, one advantage of zeolites among classical aluminosilicate supports is to have a high specific area with strongly organized microporous channel systems in which both a high dispersion and a regular distribution of metal nanoparticles can be obtained. Another interest of these supports is the possibility to tune their acid–base properties by simply changing their chemical composition, by both exchange of the countercations and/or occlusion in the microporosity of other phases (e.g., sulfides, oxides), thus possibly modifying the characteristics of the dispersed metal particles through metal–support interaction effects. This is exemplified in this work in which increasing amounts of caesium, in the form of both Cs^+ exchanged ions and Cs-oxide like nanospecies, were introduced into the porosity of two Pt-containing BEA zeolites with the aim to vary their basic properties [1]. The use of FT-IR spectroscopy in the presence of adsorbed CO and CO_2, complemented by TEM and N_2 physisorption experiments, allows us to characterize both the state and location of caesium and to show how the particle size and the electronic properties of dispersed platinum vary when the basicity of the Cs-containing BEA support increases.

2. Experimental

2.1. Materials

The two parent acidic BEA zeolites, henceforth abbreviated as H-BEA_{ENI} (Si/Al = 13) and H-BEA_{RIPP} (Si/Al = 16), were provided by Polimeri Europa S.P.A (Italy) and the Research Institute for Petroleum Processing (China), respectively. As illustrated elsewhere [2], these two samples exhibit X-ray diffractograms typical of the BEA structure with, however, slightly less intense and broader diffraction peaks in the case of H-BEA_{ENI} that is made of very small nanocrystallites with a

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mean size of *ca.* 80 nm, whereas the crystallites in H-BEA$_{RIPP}$ are quite regular in shape and sizes (between 200 and 500 nm), as shown by SEM. Related to these textures, the microporous volume is slightly smaller in H-BEA$_{ENI}$ than in H-BEA$_{RIPP}$ (0.20 and 0.25 mL g^{-1}, respectively).

Before their use, both samples were calcined at 823 K in flowing air to ensure full template removal and surface cleaning. Then, they were ion exchanged at 323 K under stirring for 2 h in a 0.5N aqueous solution of CsCl (100 mL g^{-1} zeolite); the procedure was repeated three times using each time a fresh CsCl solution and the Cs-exchanged solids were washed in deionized water. Next, platinum was added by preparing a stirred aqueous suspension containing the zeolite (100 mL g^{-1} of zeolite) and adding dropwise a given volume of a 2.5×10^{-2} M [Pt(NH$_3$)$_4$Cl$_2$] solution calculated as to introduce a nominal content of about 1.0 wt% of Pt in the zeolite (weight of Pt per weight of TO$_2$ (T = Si or Al) framework in the suspension, in %). After exchange, the sample was thoroughly washed in deionized water and then dried overnight in an oven at 80 °C. In order to increase further the Cs contents, parts of the above Pt containing samples were submitted to an incipient wetness impregnation with a CsOH solution containing 0.6 Cs atom per Al atom in the zeolite. Before characterizations, the exchanged (Pt/Cs-BEA$_{RIPP}$ and Pt/Cs-BEA$_{ENI}$) and impregnated (Pt/Cs*-BEA$_{RIPP}$ and Pt/Cs*-BEA$_{ENI}$) samples were calcined at 723 K for 2 h in order to decompose the NH$_3$ ligands of the parent Pt tetraammine complex. A low heating rate (50 K h^{-1}) and a high air flow (800 mL min^{-1}) were used in order to prevent any autoreduction process [3].

2.2. Methods

Chemical compositions (contents of Cs, Al, Si and Pt) were measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) in the Central Analysis Service of the CNRS (France).

FT-IR measurements were performed on a Bruker IFS66 spectrometer (resolution 4 cm^{-1}). The self-supported wafers (*ca.* 15 mg of sample pressed at 5 tonnes cm^{-2}) were placed into a conventional IR cell equipped with KBr windows. Before adsorption of CO at 100 K (20 Torr, 1 Torr = 133.33 Pa) and of CO$_2$ at r.t. (100 Torr), the samples were previously dehydrated *in situ* for 3.5 h at 673 K (4 K min^{-1}) under dynamic vacuum (residual pressure $<10^{-5}$ Torr). The adsorption of CO at r.t. (30 Torr) was performed after *in situ* reduction of the samples in the FT-IR cell performed by, firstly, dehydrating the sample for 5 h at 773 K (5 K min^{-1}) in dynamic vacuum, then, admitting 100 Torr of H$_2$ into the IR cell and keeping it in contact with the sample for 5 h. The reduced wafer was finally evacuated for 1 h at 773 K and cooled down to room temperature under dynamic vacuum. All gases employed were high-purity grade and were used without further purification.

Porosities were characterized by N$_2$ physisorption on a Micromeritics ASAP 2010 instrument. The adsorption–desorption isotherms were registered at 77 K after preliminary evacuation of the samples at 573 K under vacuum. The microporous volumes were determined using the *t*-plot method. They were normalized per g of zeolite TO$_2$ framework (where T = Si or Al), *i.e.* by considering solely the mass of dehydrated Si$_x$Al$_y$O$_2$ support but not that of heavy Cs, the content of which changes from one sample to another.

Transmission electron microscopy (TEM) was used to evaluate the size and distribution of the Pt particles after reduction performed *ex situ* in flowing H$_2$ (50 mL min^{-1}) at 773 K (5 K min^{-1}) for 4 h. The micrographs were registered on a JEOL 2010 instrument (200 kV) equipped with a LaB$_6$ filament. In order to ensure presence of the Pt particles in the core of the zeolitic grains, the observations were made on samples previously embedded in an epoxy resin and cut in microtome slices thinner than 60 nm. The histograms of metal particle sizes were established by considering at least 1000 particles and the data were used to evaluate an average diameter of the particles as $d = \sum n_i d_i / \sum n_i$, where n_i is the number of particles with d_i diameter.

3. Results and discussion

3.1. Chemical contents and remaining acidity

Table 1 reports the chemical contents of the four samples, expressed as atomic ratios and Pt wt%. As indicated in Section 2.1, both the H-BEA$_{ENI}$ and H-BEA$_{RIPP}$ zeolites have close Al contents, as it is still the case after the exchange and impregnation treatments, the samples of the BEA$_{ENI}$ series being only slightly richer in Al (Si/Al ≈ 12.6) than those of the BEA$_{RIPP}$ series (Si/Al ≈ 16.5). Also, the Pt content is similar in all samples, close to 1 wt%, which indicates that all the metal ions of the Pt(NH$_3$)$_4$Cl$_2$ solution were introduced into the zeolite during the exchange procedure.

Besides these similarities, a main difference takes place with respect to the Cs contents after exchange in solution. Thus, in Pt/Cs-BEA$_{ENI}$, the atomic Cs/Al ratio is only 55% of that obtained in Pt/Cs-BEA$_{RIPP}$. Furthermore, if considering the ratio (Cs + 2Pt)/Al, *i.e.* the overall countercations/Al ratio that takes into account the fact that two Cs$^+$ cations were removed from the solid for each (divalent) tetraammine platinum complex introduced during the step of exchange in the Pt(NH$_3$)$_4$Cl$_2$ solution, it is seen that the exchange was completed in Pt/Cs-BEA$_{RIPP}$ (ratio equal to 0.96) whereas the ratio remains as low as 0.56 for Pt/Cs-BEA$_{ENI}$, confirming the low exchange capacity of this sample.

Low exchange levels in zeolites are often related to the presence of a significant amount of extra-framework Al atoms that do not generate any framework negative charge. In a previous paper reporting FT-IR data of adsorbed NH$_3$ [4], we showed that H-BEA$_{ENI}$ contains a low amount of extra-framework Al with Lewis acid character, and we demonstrated that the lack of about 40% of the exchange capacity in aqueous solution of this zeolite is rather due to a process of reversible opening of part of the framework Si–O–Al bonds when this sample with nanosized zeolite crystallites is put in presence of water. Upon dehydration, both the tetrahedral framework environments and their "associated" protons were recovered, and we could demonstrate that the content in protons