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On the nature of the sites of dihydrogen molecular and dissociative adsorption in ZnHZSM-5.

II. Effects of sulfidation

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The nature of zinc ions in ZnHZSM-5 zeolite prepared by incipient wetness impregnation was studied by DRIFT spectroscopy using dihydrogen adsorbed at low temperature as a molecular probe. The results obtained indicate the appearance of low-coordinated zinc ions following dehydroxylation at high temperature. It is concluded that the ions that most strongly perturb adsorbed hydrogen are localized on the surface of nanometric ZnO clusters that are formed in the channels of the zeolite framework upon high temperature pretreatment. This was demonstrated by the inhibition of dihydrogen adsorption by high temperature sulfidation of the zeolite with H₂S. The latter presumably converts ZnO particles into ZnS clusters. This was also confirmed by UV diffuse reflectance spectra of the sulfided samples. By contrast, sulfidation did not influence DRIFT spectra of hydroxyl groups in either HZSM-5 or HY zeolites, indicating that substitution of framework oxygen by sulfur does not occur in these materials.

KEY WORDS: ZSM-5 zeolite; DRIFT spectra; nanometric ZnO clusters; sulfidation; ZnS; activation of paraffins

1. Introduction

In our previous papers the state of zinc in ZnZSM-5 zeolite was tested using adsorption of dihydrogen or carbon monoxide as molecular probes [1,2]. It was concluded that modification with zinc resulted in the formation of low-coordinated Zn²⁺ ions. These species were formed either on the surface of nanometric zinc oxide clusters localized inside the channels of the zeolite framework or were stabilized on the walls of the channels at α sites, according to the classification proposed by Mortier and Wichterlova [3,4]. Unfortunately, the final choice between these two alternatives was not possible. It was also concluded that such low-coordinated Zn²⁺ ions strongly perturbed dihydrogen upon adsorption at 77 K and dissociatively adsorbed propane or hydrogen at elevated temperature [2]. This most likely indicated that the low-coordinated zinc ions were the active sites for dehydrogenation of paraffins.

The present study is a continuation of the aforementioned work. Below we present the results of a diffuse reflectance IR Fourier transform (DRIFT) study of ZnHZSM-5 zeolite prepared by incipient wetness impregnation of the ammonium form of the zeolite. As in [2] adsorbed dihydrogen was used as a molecular probe. The extent of perturbation of H₂ by adsorption sites was measured by DRIFT spectroscopy. In order to discriminate between the aforementioned possible types of Zn²⁺ sites, experiments were also performed in which the samples were pretreated with hydrogen sulfide at elevated temperature. Such treatment eliminates the sites connected with small zinc oxide nanoclusters as these are rather easily transformed into zinc sulfide particles. In this

way we were able to discriminate between zinc ions on the surface of the nanometric ZnO clusters and those at cationic positions in the zeolite framework.

2. Experimental

The ammonium form of the ZSM-5 zeolite (Si/Al ratio in the framework equal to 41) was prepared from the sodium form by triple ion-exchange with 1 M aqueous solution of NH₄NO₃ at room temperature as reported earlier [2]. The degree of exchange was determined to be equal to 95% from AAS measurements of the remaining Na⁺ content.

Zinc-containing samples were prepared from the ammonium form by incipient wetness impregnation using 1 M aqueous Zn(NO₃)₂ solutions. After impregnation the zeolite was dried at 390 K in flowing nitrogen for 45 min followed by calcination at 820 K for 4 h in flowing artificial air. The actual zinc content was also measured by AAS analysis and was equal to either 1.0 or 2.0 wt%.

Thermovacuum pretreatments of both the ammonium and the Zn-containing forms of the ZSM-5 zeolite were performed in the same sapphire ampoules used for DRIFT measurements. The ampoule-encapsulated samples were heated in vacuum for 2 h at either 570, 670, 770, 870 or 920 K. Sample temperatures were increased from room temperature at a rate of 5 K/min.

For sulfidation the zeolites were treated at 673 K and atmospheric pressure in a flow of hydrogen that contained 3 vol% of hydrogen sulfide. The samples were then transferred to sapphire ampoules for DRIFT measurements with-

out contact with the atmosphere and were preheated in vacuum for 1 h at different temperatures. Pretreatment of non-sulfided samples in vacuum was carried out in a similar way in either sapphire ampoules or in ampoules made of fused quartz.

Similar to [2] DRIFT spectra of the powdered zeolites were measured using a Nicolet Impact 410 spectrophotometer equipped with a home-made DR unit and an MCT detector. Spectra of hydroxyl groups were recorded at room temperature. Spectra of physisorbed molecular hydrogen were measured at 77 K using a quartz Dewar vessel filled with liquid nitrogen for cooling of the samples. In both cases measurements were done in the presence of gaseous H₂. All DRIFT spectra were recorded at 4 cm⁻¹ resolution by co-adding 100 scans and were transformed into Kubelka-Munk units assuming that the reflectability of the samples at 5000 cm⁻¹ was equal to 0.9 units.

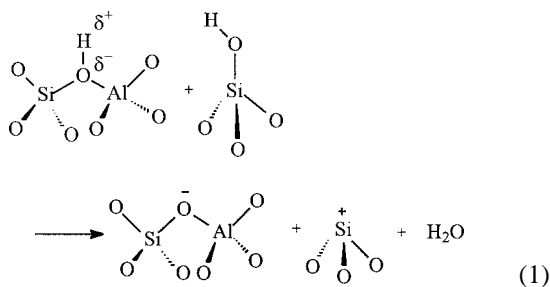
Diffuse reflectance UV spectra of sulfided *in situ* treated samples were recorded by means of a Specord M-40 spectrophotometer equipped with a commercially available diffuse reflectance Carl Zeiss R 8⁰/d unit.

Molecular hydrogen was adsorbed at 77 K at an equilibrium pressure of 100 Torr (1.33 × 10³ Pa).

3. Results

3.1. DRIFT spectra of dihydrogen adsorbed on hydrogen and on zinc-hydrogen forms of ZSM-5

In agreement with numerous literature reports, high temperature vacuum pretreatment of the ammonium form of ZSM-5 zeolite resulted in the decomposition of NH₄ ions. This was accompanied by the appearance of narrow IR bands due to bridging hydroxyl groups with an O–H stretching frequency equal to 3607 cm⁻¹ and of bands from silanol groups with a maximum at 3740 cm⁻¹. With increasing vacuum pretreatment temperature, the intensities of both these bands decreased in parallel by about 30–50%. This most likely indicates that water is formed upon high temperature vacuum pretreatment due to recombination of bridging hydroxyls with the more basic silanol groups according to the following equation:



This well-known process results in formation of the low-coordinated Si⁺ ions [6,7]. Reaction (1) could be also followed by dealumination of the zeolite yielding AlO⁺ ions

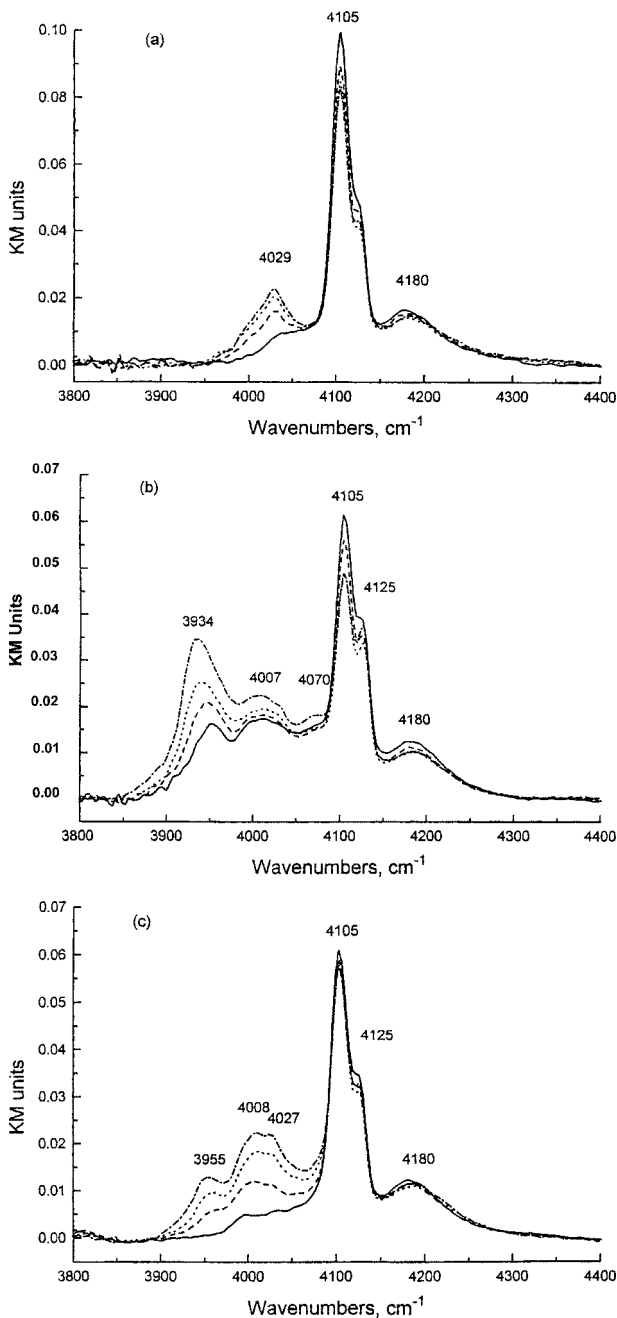


Figure 1. DRIFT spectra of molecular hydrogen physisorbed at 77 K and an equilibrium pressure of 13.3 kPa on (a) HZSM-5 and (b) ZnHZSM-5 dehydrated in vacuum at 670 (—), 770 (---), 870 (···) or 920 K (----). (c) DRIFT spectra of molecular hydrogen physisorbed at 77 K and an equilibrium pressure of 13.3 kPa on the sulfided ZnHZSM-5 sample evacuated at 670 (—), 770 (---), 870 (···) or 920 K (----).

or microcrystallites of aluminum oxide inside channels of the zeolite framework. In the present work, the formation of such new Lewis sites was investigated via DRIFT measurements following low temperature adsorption of dihydrogen at 77 K.

Indeed, in accordance with our earlier results [1,2], dihydrogen adsorption on HZSM-5 zeolite at 77 K resulted in the appearance of two bands due to H–H stretching vibrations perturbed by adsorption (figure 1(a)). The first band has a

maximum at 4105 cm^{-1} and a shoulder at 4125 cm^{-1} and is due to hydrogen molecules interacting with bridging hydroxyl groups or silanol hydroxyl groups, respectively. The intensities of both of these bands decrease upon dehydroxylation of the zeolite at higher temperatures. Simultaneously, a new, more strongly red-shifted band due to adsorbed dihydrogen appears at 4019 cm^{-1} . Upon dehydroxylation of the zeolite at higher temperatures, the intensity of this band increases. This most likely indicates adsorption of dihydrogen on coordinatively-unsaturated Si^+ or AlO^+ ions resulting from dehydroxylation of the HZSM-5 according to equation (1).

Modification of the zeolite with zinc results in the appearance of two new sites of low temperature dihydrogen adsorption with the stretching frequencies of adsorbed H_2 at 3934 and 4007 cm^{-1} indicating stronger perturbation of H–H stretching vibrations (figure 1(b)). Both of these bands are obviously connected with H_2 adsorption on modifying Zn^{2+} ions. It has been also demonstrated in [2] that the sites connected with the more strongly red-shifted H–H stretching vibrations became blocked by dissociative adsorption of hydrogen or propane at elevated temperatures resulting in disappearance of the corresponding DRIFT band arising from dihydrogen adsorbed at 77 K .

3.2. DRIFT spectra of dihydrogen adsorbed on the sulfided samples of ZnO and on ZnHZSM-5 and ZnY zeolites

Firstly we will discuss the DRIFT spectra resulting from adsorption of dihydrogen on sulfided samples of massive zinc oxide.

It is known from the literature that low temperature adsorption H_2 on ZnO results in the appearance of a H–H stretching band with a perturbed stretching frequency equal to 4016 cm^{-1} . As the temperature is increased to room temperature, dihydrogen is dissociatively adsorbed resulting in the formation of surface hydroxyls and hydrides with stretching frequencies equal to 3495 and 1708 cm^{-1} , respectively [8–11]. We reproduced these data for ZnO powder (the corresponding spectrum of dihydrogen adsorbed on ZnO at 77 K is shown in figure 2(a)) and then studied the influence of preliminary sulfidation of zinc oxide on adsorption of dihydrogen at high temperature.

As one can see from figure 2(b), after sulfidation the intensity of the H–H stretching band arising from adsorbed dihydrogen was about one hundred times less than that observed following adsorption on the nonsulfided ZnO. Thus, the preliminary sulfidation destroyed the sites for low temperature molecular hydrogen adsorption on the surface of zinc oxide. Moreover, those sites could not be regenerated, even after high temperature vacuum treatment at 623 K .

In addition, the position of the much weaker DRIFT band at 4084 cm^{-1} was shifted towards higher frequency by about 70 cm^{-1} relative to that observed following adsorption on the nonsulfided sample. This indicated a weaker perturbation of adsorbed H_2 and confirmed modification of the adsorption sites by sulfur.

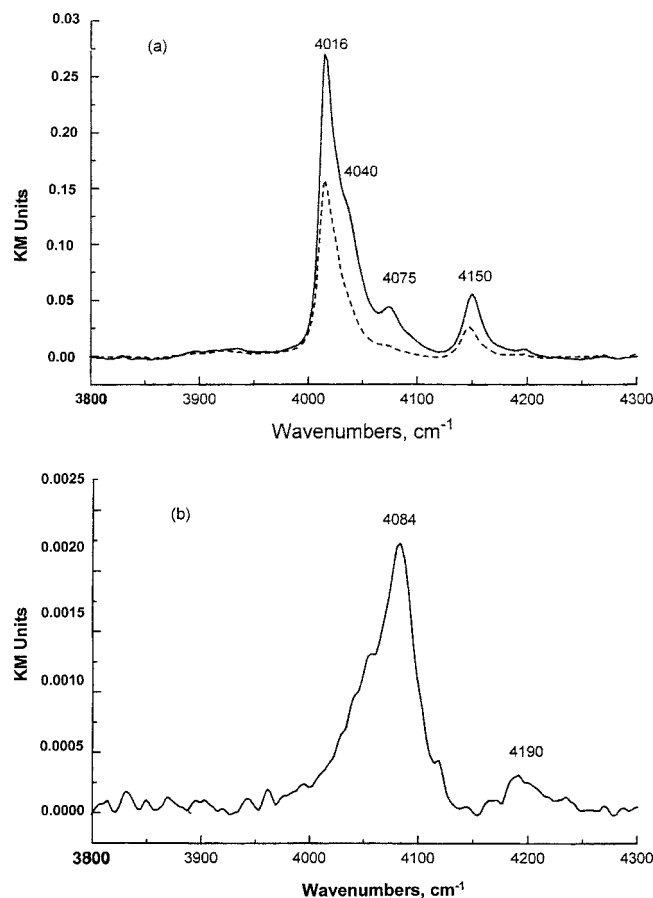


Figure 2. (a) DRIFT spectra of molecular hydrogen adsorbed at 77 K and an equilibrium pressure of 13.3 (—) or 1.33 kPa (---) on ZnO dehydrated in vacuum at 670 K . (b) DRIFT spectra of molecular hydrogen adsorbed at 77 K and an equilibrium pressure of 13.3 kPa on ZnO sulfided by $\text{H}_2\text{S}/\text{H}_2$ mixture (3% H_2S) at 670 K and evacuated at 670 K .

In contrast to the behavior of bulk zinc oxide, the sulfidation did not affect the low temperature molecular hydrogen adsorption on Zn^{2+} ions at S_{II} cationic sites of the ZnHY zeolite. This is illustrated by comparison of figure 3 (a) and (b), which show the development of the H–H stretching bands of dihydrogen adsorbed on nonsulfided and sulfided samples of ZnY at 77 K after vacuum treatment at different elevated temperatures. Evolution of the spectra for both sulfided and nonsulfided samples is practically identical indicating the absence of oxygen substitution by sulfur in the framework of ZnY zeolite. In addition, sulfidation did not influence the DRIFT spectra of hydroxyl groups in either HZSM-5 or in HY zeolites. This also definitely indicates that the high temperature pretreatment with hydrogen sulfide did not result in sulfidation of the framework of either the hydrogen or the zinc forms of this zeolite.

The results obtained upon sulfidation of ZnHZSM-5 zeolite were quite different. Indeed, as one can see from a comparison of figure 1 (b) and (c), high temperature pretreatment of this zeolite with H_2S destroyed the sites of hydrogen adsorption with the lowest H–H stretching frequency of 3955 cm^{-1} . This should be considered as evidence that the corresponding adsorption sites are the low-coordinated

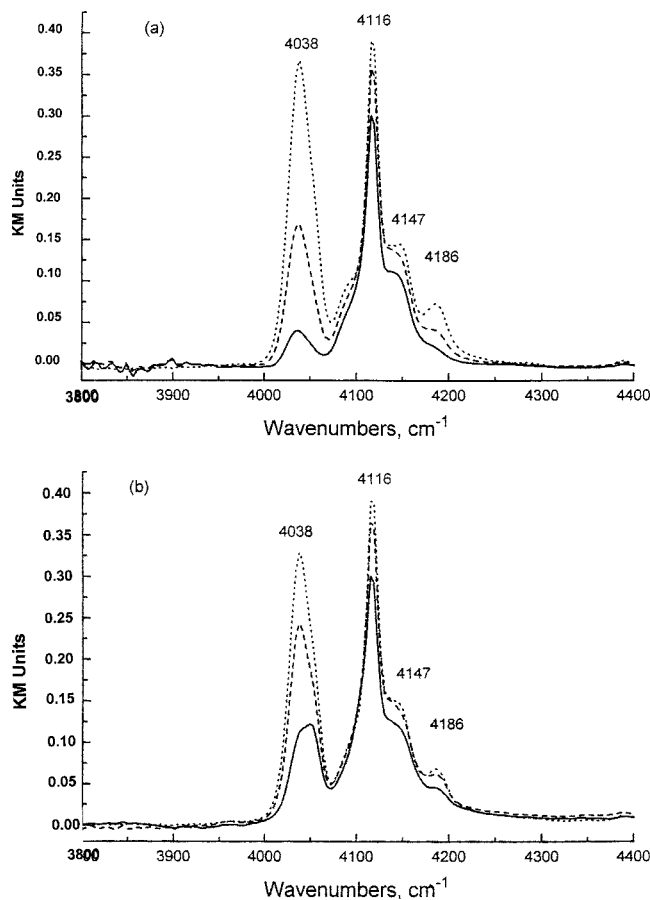


Figure 3. (a) DRIFT spectra of molecular hydrogen adsorbed at 77 K and an equilibrium pressure of 13.3 kPa on ZnY zeolite evacuated at 570 (—), 673 (---) and 770 (· · ·). (b) DRIFT spectra of molecular hydrogen adsorbed at 77 K and an equilibrium pressure of 13.3 kPa on sulfided ZnY zeolite evacuated at 570 (—), 670 (---) and 770 K (· · ·).

Zn^{2+} ions on the surface of nanometric zinc oxide clusters located outside the channels of the zeolite framework. Such clusters could be rather easily transformed into small zinc sulfide particles upon sulfidation with H_2S . In a manner similar to bulk ZnO, zinc sulfide particles adsorb dihydrogen less strongly than do ZnO particles. On the other hand, the adsorption sites that correspond to H–H stretching vibration of adsorbed hydrogen equal to 4007 cm^{-1} and are not influenced by sulfidation, are most likely connected with Zn^+ ions localized at cationic positions of the zeolite framework.

3.3. UV spectra of sulfided ZSM-5 samples

UV spectra of the nonsulfided ZnHZSM-5 samples were too weak to be recorded reliably. However, after sulfidation, due to the much higher extinction coefficient of ZnS_2 , the corresponding band connected with small zinc sulfide particles appeared in the UV region, as shown in figure 4.

The UV spectrum of 4(a) belongs to the nonsulfided ZnHZSM-5 sample. The very weak absorption at about 380 nm is due to the ZnO particles. Figure 4(b) corresponds to the sulfided sample pre-evacuated at 773 K that was recorded using nonsulfided ZnHZSM-5 as a reference.

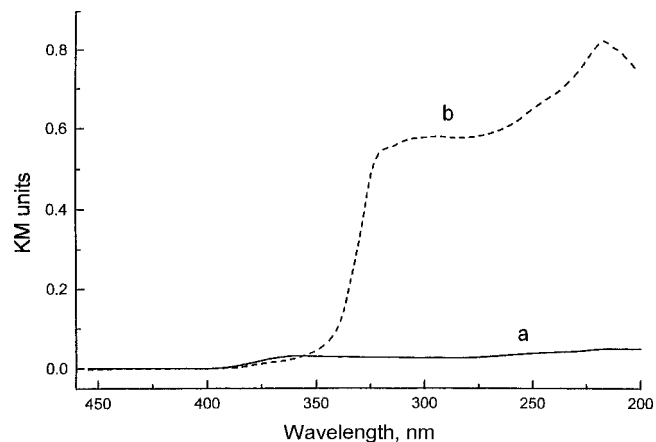


Figure 4. UV-VIS diffuse reflectance spectra of nonsulfided (a) and sulfided (b) ZSM-5 zeolite containing 2.0 wt% of Zn.

The position of an intense absorption edge at around 330 nm agrees with the spectrum of the bulk ZnS. Therefore it should be related to relatively large ZnS particles. A very strongly blue-shifted diffuse absorption edge in the region 200–250 nm should be attributed to very small nanoparticles of ZnS that are stable even after evacuation at 773 K. Similar blue-shifted absorption bands have been also earlier reported for ZnS and CdS nanometric particles in Zn- and Cd-loaded zeolites [12,13]. Thus, formation in ZnZSM-5 upon incipient wetness impregnation of small zinc oxide particles was also confirmed by UV diffuse reflectance spectra developed in this zeolite by high temperature sulfidation.

4. Discussion

The state of zinc in ZSM-5 zeolites has been the subject of several recent publications. It was studied by IR spectroscopy [14,15], by thermodesorption, or thermoreduction [15,17], and by EXAFS [15]. The models proposed that zinc exists in these materials as either exchangeable Zn^{2+} ions [15–17], as ZnOH^+ ions [16] or as Zn^{2+} that replaces two protons in the neighbouring aluminum–oxygen tetrahedra, resulting in the formation of binuclear ($\text{Al–O–Zn}^{2+}–\text{O–Zn}^{2+}–\text{O–Al}$) bridging fragments [15]. However, none of these models explains all of the available experimental data. For instance, the bands due to ZnOH^+ species have never been directly observed in IR spectra. In addition, the substitution of protons by Zn^{2+} ions does not agree well with the high concentration of bridging hydroxyl groups that remains in HZSM-5 zeolites after high temperature pretreatment [15]. Further, for ZSM-5 zeolites with high silica-to-aluminum ratios, the formation of binuclear structures is rather unlikely [19]. On the other hand, there is no doubt that at least part of modifying zinc can form nanometric zinc oxide clusters that are stabilized inside the channels of the zeolite framework.

We do not criticize or object to the conclusions of these papers. However, it should be emphasized in this connection, that none of these studies reported observation of the

sites responsible for nondissociative adsorption of molecular hydrogen at low temperature that were detected in the present work.

The results of the present study also clearly indicated that the sites of the strongest H₂ activation created in HZSM-5 using incipient wetness impregnation for its modification with zinc, are localized on the surface of the zinc oxide nanometric clusters that are formed inside channels of the zeolite framework. This conclusion was supported by the inhibition of dihydrogen adsorption upon sulfidation of ZnHZSM-5 zeolite that converts the small zinc oxide particles into zinc sulfide microclusters. Sulfided zinc oxide did not perturb dihydrogen upon adsorption as strongly as did zinc oxide.

By contrast, sulfidation of the ZnZSM-5 zeolite did not influence adsorption of dihydrogen on Zn²⁺ ions at cationic positions with H–H stretching frequency of adsorbed H₂ molecules at 4007 cm⁻¹. The high temperature pretreatment with H₂S of the ZnY zeolite prepared by ion-exchange did not also influence adsorption of dihydrogen on zinc ions at S_{II} cationic positions. It also had no influence on the DRIFT spectra of the hydroxyl groups in the HZSM-5 zeolite or on the Lewis sites in this material resulting from the high temperature dehydroxylation. This obviously indicates the absence of sulfidation of the ZSM-5 framework by the high temperature pretreatment with hydrogen sulfide. This should be explained by a much lower mobility of oxygen in the zeolite framework as compared with that in zinc oxide.

The results of our preliminary study also indicated that the adsorption properties of the nanometric zinc oxide particles in ZnHZSM-5 zeolite are substantially different from those of bulk zinc oxide. This difference will be studied and discussed in more detail in our following publications.

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