

Formation and thermostability of Ni⁺ cations in NiZSM-5. Testing by DRIFTS of adsorbed N₂, H₂, D₂ and EPR spectroscopy

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Introduction

High-silica zeolites modified by transition metal cations possess interesting catalytic and adsorption properties. Cobalt and copper modified ZSM-5 for example, are active for selective reduction of NO_x by hydrocarbons in excess oxygen. Copper-modified ZSM-5 zeolites have also attracted significant attention due to their activity in the direct decomposition reaction of NO_x. FeZSM-5 - which is active SCR catalyst - is very stable under reaction conditions. It was reported that microwave discharge greatly enhance the conversion of NO to N₂ over NiZSM-5 reaching almost 100% conversion [1]. ZSM-5 zeolite can stabilize Ni⁺ [2] and Co⁺ [3] ions in the presence of CO. Co²⁺/Co⁺ and Ni²⁺/Ni⁺ redox couples probably operate in the HC-SCR [3]. In the present study we have examined the formation and thermal stability of Ni⁺ cations in ZSM-5 zeolite by means of DRIFT spectroscopy of adsorbed N₂, H₂ and D₂ molecules and EPR spectrometry.

Materials and Methods

The starting material was the hydrogen form of ZSM-5 zeolite (Alsi-Penta, Si/Al=22). Nickel-containing samples were prepared by triple wet ion exchange of this material with 0.1 M nickel acetate aqueous solution. After the third exchange the material was washed in distilled water, dried at 380 K and calcined in flowing oxygen at 673 K for 1 h. Diffuse-reflectance measurements were performed using a home-made diffuse-reflectance attachment. The spectra were recorded both at room temperature and at 77 K using a Nicolet "Impact-410" spectrophotometer. Reduction of the samples by CO was conducted in the IR ampoule at a pressure of 7 kPa. The DRIFT spectra of adsorbed N₂ were recorded at ambient temperature while the spectra of adsorbed H₂ and D₂ were measured at 77 K. EPR spectra were recorded at ambient temperature in X band with a Bruker EPR-200 spectrometer.

Results and Discussion

A NiZSM-5 sample reduced in CO at 550 K and evacuated at 600 K was tested by adsorption of dinitrogen at ambient temperature (Fig.1a). A band observed at 2250 cm⁻¹ was assigned to N₂ adsorbed on Ni⁺ cations while a band at 2339 cm⁻¹ was assigned to N₂ adsorbed on Ni²⁺ cations. Ni⁺ cationic sites are of low thermal stability and can be destroyed by evacuation at high temperatures (Fig.1b) due to disproportionation reaction $2\text{Ni}^+ \rightarrow \text{Ni}^{2+} + \text{Ni}^0$. Prolonged heating of the sample in CO results in the restorations of Ni⁺ sites: $\text{Ni}^{2+} + \text{Ni}^0 + 4\text{CO} \rightarrow 2\text{Ni}^+(\text{CO})_2$. NiZSM-5 was also tested for the adsorption of H₂ and D₂ molecules at 77 K. Fig.2 shows DRIFT spectra of H₂ adsorbed on NiZSM-5. The bands at 4105 cm⁻¹ and 4125 cm⁻¹ belong to H₂ adsorbed on acidic and silanol hydroxyls respectively [4]. The bands at 3965, 3926 and 3963 cm⁻¹ can be assigned to H₂ adsorbed on Ni²⁺ cations. Finally, the band at 3430 cm⁻¹ which appears after prolonged treatment with CO was ascribed to H₂ adsorbed on Ni⁺ cationic sites which appear due to reaction: $\text{Ni}^{2+} + \text{Ni}^0 + 4\text{CO} \rightarrow 2\text{Ni}^+(\text{CO})_2$.

The Ni⁺ sites are also characterized by EPR signals at g_{||}=2.513 and g_⊥=2.114.

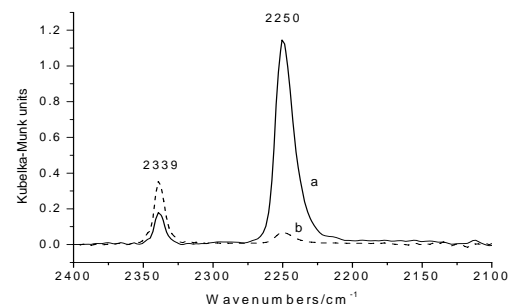


Figure 1. DRIFT spectra of N₂ adsorbed at room temperature at the equilibrium pressure of 6.5 kPa on NiZSM-5 reduced in CO at 400K: after removal of CO at 600 K (a); after consequent evacuation at 823 K for 2 h (b).

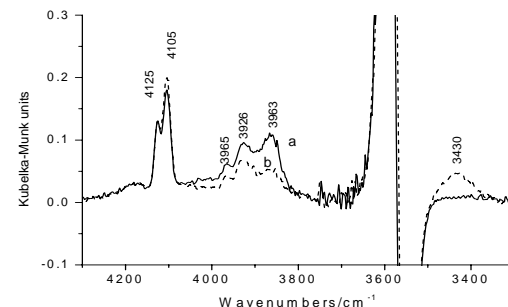


Figure 2. DRIFT spectra of H₂ adsorbed at 77 K and at the equilibrium pressure of 13.3 kPa on NiZSM-5 reduced in CO: followed by high temperature evacuation at 823 K (a); after consequent prolonged treatment with CO at 400 K for 2 h and removal of CO at 600 K (b).

Significance

The presence of Ni⁺ cations was confirmed in NiZSM-5 samples following characterization by DRIFTS and EPR spectroscopy. The thermal stability of these cations was also examined.

References

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