

On the nature of catalytically active sites in GaMFI. High temperature XPS study and DFT modeling.

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Introduction

Gallium-containing MFI zeolites continue to attract interest as efficient system for dehydrogenation and aromatization of light paraffins [1-3] and the reduction of NO with methane [4]. A large number of experimental and theoretical investigations have been focused on the nature of the catalytically active sites and the mechanism of activation of hydrocarbon molecules in GaMFI. Most have conclude that the catalytically active sites are extraframework Ga^+ compensating cations which are formed under reduction conditions, as a result of the interaction of partially reduced gallium oxide with acidic protons of the MFI zeolite. Some results of theoretical studies suggested that GaH^{2+} or GaH_2^+ cationic hydride species can also be active sites. In this presentation we report XPS results which show that Ga^+ , Ga^{3+} cations and metallic gallium can simultaneously present in the reduced GaMFI at high temperatures.

Materials and Methods

GaMFI samples were prepared by impregnation of HMFI (Davison, Si/Al=15) with aqueous solution of gallium nitrate followed by drying and calcination at 773 K. XPS measurements were performed using of a KRATOS AXIS ULTRA DLD spectrometer with a monochromatized Al-K α source. An electron gun was used to neutralize surface charging occurring with insulating samples. Powdered GaMFI samples were pressed into a gold-covered copper sample holder. Reduction of the samples was performed in hydrogen at 823 K for 2 h in the sample preparation chamber of the spectrometer. After reduction the samples were cooled down to room temperature in hydrogen, evacuated and transferred to the analysis chamber of the XPS spectrometer. Background pressure in the analysis chamber at room temperature was approximately $2 \cdot 10^{-9}$ Torr. Upon heating the samples to 823 K the pressure increased to $2 \cdot 10^{-7}$ Torr and then gradually decreased. High temperature XPS spectra were collected after maintaining the samples at 823 K for 1h. The energetic positions of the XPS lines was determined with respect to Si 2p line (B.E.=103.4 eV)

A simulation of interaction of ethane molecule with Ga^{3+} sites of GaMFI was performed using GAUSSIAN-03 program. The calculations were carried out within the gradient corrected density functional theory (hybrid B3LYP functional).

Results and Discussion

Fig. 1 shows the XPS spectra (O 2s + Ga 3d region) of GaMFI samples subjected to different treatments. Trace (a) represents the spectrum of a freshly calcined sample. The band at 21.2 eV is typical for Ga^{3+} and characterizes Ga_2O_3 particles located on the top surface of the zeolite crystallines.

After reduction (Trace b) the intensity of this band decreases dramatically; in addition, a new weak band at 19.1 eV appears. The position of this band matches the position

of Ga 3d band of Ga_2O oxide [5]. Therefore this band can be assigned to Ga^+ intrazeolite cations. When the reduced sample was further heated to 823 K a new low-energy band appeared in the spectrum at approximately 18.5 eV (Trace c). This band continued to grow and shifted to lower energies upon cooling of the sample to room temperature (Trace d). Low energy bands below 18.5 eV are characteristic of Ga^0 [5]. The observed changes in the XPS spectrum of the reduced GaMFI can be attributed to the disproportionation of Ga^+ (i.e., $\text{Ga}^+ \rightarrow \text{Ga}^0 + \text{Ga}^{3+}$) upon heating under UHV. Zero-valent gallium subnanometer particles formed as a result of this reaction migrate out of the zeolite channels and sinter on the external surface of the zeolite crystallines. This results in the shift of Ga^0 peak to lower energies (particle size effect). The disproportionation reaction is reversible in the presence of hydrogen.

Based on the XPS results we can further suggest that at high temperatures Ga^+ , Ga^0 and Ga^{3+} species coexist in GaMFI. It is therefore reasonable to suggest Ga^{3+} compensating cations, which supposedly are strong Lewis sites, can catalyze different reactions.

DFT calculations were performed to simulate interaction of ethane molecule with Ga^{3+} sites in MFI. The results show that these sites can be responsible for the catalytic dehydrogenation of alkanes.

Significance

XPS evidence of the high-temperature disproportionation of Ga^+ cations in GaMFI was obtained for the first time. Our results further indicate that Ga^{3+} sites formed as a result of the disproportionation can be active for different catalytic reactions involving hydrocarbons.

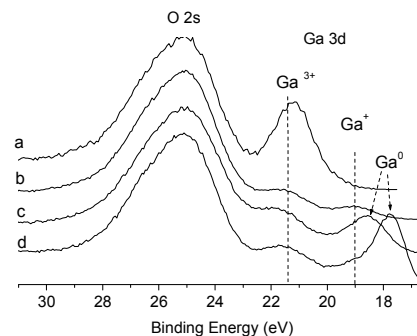


Figure 1. XPS spectra (O 2s + Ga 3d) of GaMFI: (a) calcined at 773 K; (b) reduced in hydrogen at 823 K and evacuated at room temperature; (c) heated in vacuum at 823K for 1 h; (d) cooled down to room temperature.

References

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