

INVESTIGATION OF SURFACE CHEMISTRY PROPERTIES OF Ga₂O₃/Al₂O₃ CATALYSTS BY FT-IR SPECTROSCOPY

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Abstract

Currently mixed oxide catalysts are widely applied in the ecological field of catalysts. High surface area alumina has been widely used as a catalyst as well as support for metal and metal oxide catalysts. It is known that in both applications, surface Al-OH groups and coordinatively unsaturated (cus)Al³⁺ sites play key roles. Recently, it has been shown that Ga₂O₃-Al₂O₃ and Pt/ Ga₂O₃-Al₂O₃ systems exhibit high catalytic activity in the selective reduction of NO_x by hydrocarbons.

The Lewis and Bronsted acidic properties of the surface sites of a high surface Ga₂O₃-Al₂O₃ were investigated in previous research by CO adsorption at room temperature using FT-IR spectroscopy. The pressure of CO was 50 mmHg. Under certain conditions Lewis (electron acceptor) acid sites (LAS) Al³⁺cus and Ga³⁺cus on the surface were not detected by CO. Linearly bonded CO on the Ga³⁺cus was visible only on Pt/ Ga₂O₃-Al₂O₃ at 2193 cm⁻¹. After CO adsorption the intensity of some OH groups (3799 cm⁻¹, 3685 cm⁻¹) and 3669 cm⁻¹ decreased more significant than others (3720 cm⁻¹, 3690 cm⁻¹). In the literature these are frequency shifts of the OH stretching mode to lower frequencies induced upon CO adsorption due to OH-CO H-bonding interactions. It is not only a frequency shift but there are correlations between the decreasing intensity of OH bands and the increasing intensity of some carbonate and bicarbonate bands.

Introduction

Gallia containing catalysts has been reported to have catalytic activity in catalytic combustion, CO oxidation, NO_x's selective reduction. They are also used to operating gas sensors in hydrocarbon combustion. Aim of our work is to study the adsorption of CO on the active sites of Ga₂O₃-Al₂O₃ and platinum containing Ga₂O₃-Al₂O₃ catalyst system likely responsible for catalytic activity. Carbon monoxide is a suitable probe molecule to reveal and characterise the Lewis acidic sites (LAS's) on the high surface area metal oxide systems. The formation of these species was monitored by Fourier Transform InfraRed spectroscopy (4000-1000 cm⁻¹ region). Various pretreatment was done before CO adsorption. Oxidized samples were heated up in O₂ flow (100ml/min) to 473 (573, 673, 773) K with the heating rate of 5 K/min, then they were flushed and held on the appropriate temperature for 2h. Evacuation of the sample was done at the same temperature for 30 min to the residual pressure of 10⁻⁵ – 10⁻⁴ mmHg then it was cooled to room temperature under vacuum. At the end of every single pretreatment IR spectrum of the pretreated sample was recorded.

The CO adsorption was done at room temperature and low pressure (25 mmHg) for 30 min. All spectra were measured under these circumstances of *in situ* pre-treatment of the sample.

Methods

Samples (**Table 1.**) were prepared by impregnation of alumina with aqueous solution of gallium-nitrate $\text{Ga}(\text{NO}_3)_3 \cdot 9(\text{H}_2\text{O})$ (Aldrich) as precursor salt in aqueous solution.

Table 1. BET surface of the samples

Catalysts	BET surface (m^2/g)
$\gamma\text{-Al}_2\text{O}_3$	108
$\text{Ga}_2\text{O}_3(2,42\%)/\text{Al}_2\text{O}_3$	105
$\text{Ga}_2\text{O}_3(17\%)/\text{Al}_2\text{O}_3$	88
$\text{Pt}(0,4\%)/\text{Ga}_2\text{O}_3(3,2\%)/\text{Al}_2\text{O}_3$	99

After impregnation, the catalysts were dried at 393 K overnight and calcined at 773 K for 8 hours in air flow (1.1 L/h), heating rate 0.5 K/min. The gallia content was 17 and 2,4 m/m %. The $\text{Pt}(0,4\%)/\text{Ga}_2\text{O}_3(3,2\%)-\text{Al}_2\text{O}_3$ was prepared from alumina-supported gallium oxide obtained before and impregnated by aqueous solution of chloroplatinic acid (Strem Chemicals). The impregnated sample was dried for 18 h at 393 K and calcined in air flow (1,1 L/h) with a heating rate 0,5 K/min and 24h at 773 K. IR spectra were collected using Bio-Rad FTS 175 FT-IR spectrometer with air cooled DTGS detector. All spectra were recorded after 512 scans, at resolution of 8 cm^{-1} . Spectra were measured using a specially designed quartz cell to be suitable for the highest temperature of the oxidation (473, 573, 673, 773 K) under even ultrahigh-vacuum. The cell was mounted with CaF_2 windows and attached to a glass gas handling / ultrahigh-vacuum system. The sample was mounted in the cell. Oxygen (99.6 %) was passed through drying cartridge of CaCl_2 and MgClO_4 prior to use for calcination. Hydrogen of ultrahigh purity was passed through drying cartridge of CaCl_2 and MgClO_4 and purified by the diffusion through an equipment with silver-palladium diffuser load. The carbon-monoxide of 99.7 % purity was passed through a liquid nitrogen cooled freezer prior to use. Self-supporting wafer were prepared of both the catalyst and the γ -alumina support.

Results

Table 2., OH vibrations on the surface of $\text{Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$ catalysts

	Wavenumber (cm^{-1}) of different OH bands
Terminal OH on different type of Al	3760-3800
Bridging OH between two different Al (octahedral, tetrahedral)	3740-3745
Bridging OH between two octahedral Al	3730-3735
Threefold OH group on Al octahedral interstices	3700-3710
Terminal OH groups on Ga	3740
Bridging OH as Ga-OH-Al	3680-3688
Bridging OH's of β , γ - Ga_2O_3	3668-3672
Hydrogen bonding OH---CO interaction	3550-3570

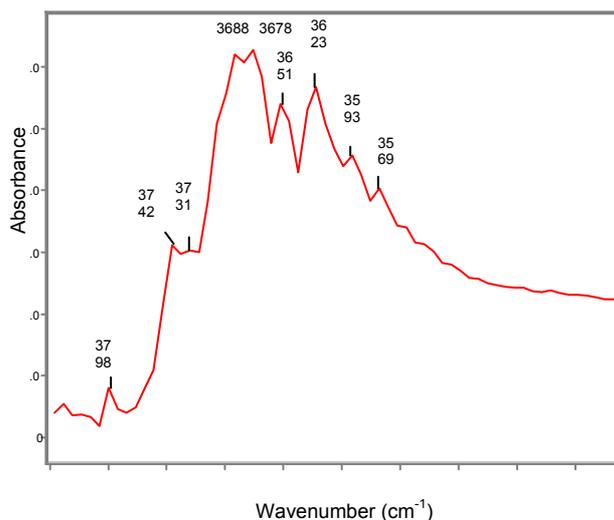


Fig. 1. OH vibrations on the surface of Ga₂O₃-Al₂O₃ catalysts

IR bands of hydroxyl groups on metal oxide catalysts surface are depend on the chrystalline modification and chrystallographic orientation of the surface (**Fig.2.**). The investigation of surface OH groups can provide several information on coordination symmetry and the structure of the nearest neighbours of surface cations.

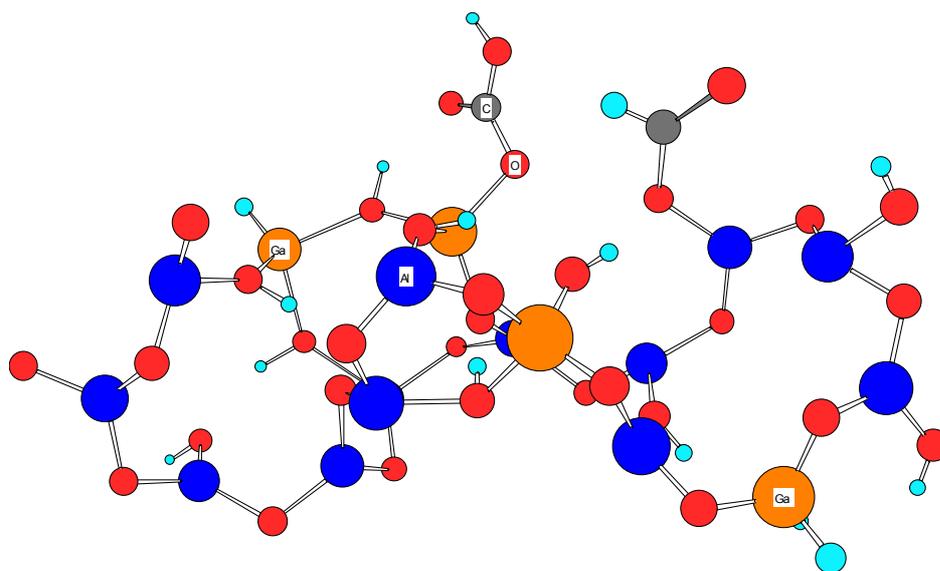


Fig. 2. Surface species of Ga₂O₃-Al₂O₃ system

These OH groups are only perturbed in some processes (e.g., CO adsorption), but participates actively in several other surface reactions. These particular OH groups certainly plays an important role also as electron donor sites, since several author shown that electron transfer occurs from surface OH groups to adsorbed molecules of sufficiently high electron affinity. The most basic OH groups bearing the highest net negative charge are most likely the best electron donor groups [1].

Partially hydroxylated γ - Ga₂O₃'s main OH stretching bands are at 3637 and 3668 cm⁻¹ (**Fig.1.**). These OH bands are significantly perturbed by adsorbed CO, thus show Brønsted acid characters. Lewis acidity was not assigned the $\nu(\text{C-O})$ stretching mode of CO adsorbed on

(cus) Ga^{3+} ions. $\nu(\text{C-O})$ stretching was found only in the case of Pt content catalyst. OH groups on Ga_2O_3 are more acidic and has more interaction with adsorbed CO.

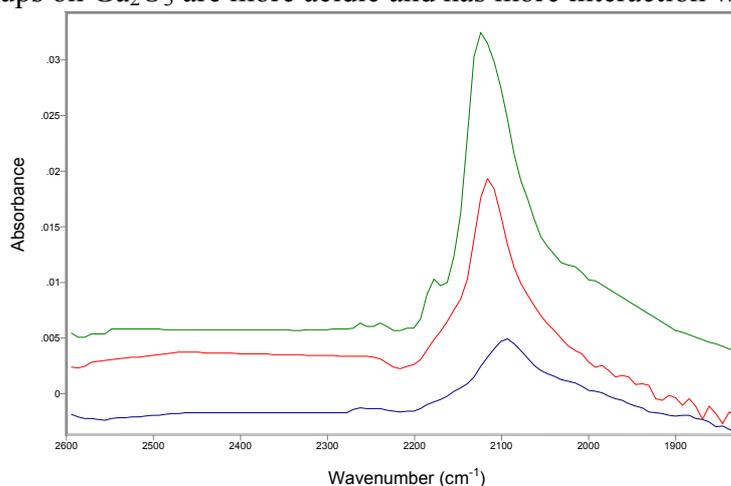


Fig.3. FT-IR difference spectra of adsorbed CO species on Pt sites after oxidation at a, 473, b, 573, c, 773 K and 25 mmHg of CO at RT.

Conclusions

The acidic properties of alumina supported Ga_2O_3 and Pt- Ga_2O_3 content catalysts were investigated focusing on the catalyst surface toward CO (**Fig.3, 4.**). Carbon monoxide is able to be adsorbed relatively easily on the catalyst surface. Alumina supported Ga_2O_3 catalyst had no assigned $\nu(\text{CO})$ on coordinatively unsaturated sites Ga^{3+} , but platinum containing catalyst systems had. The pressure of CO was very low. Therefore the CO was adsorbed on Brønsted acidic OH groups and the results of this interaction lead to increase the hydrogencarbonate and carbonate species (**Fig.5.**).

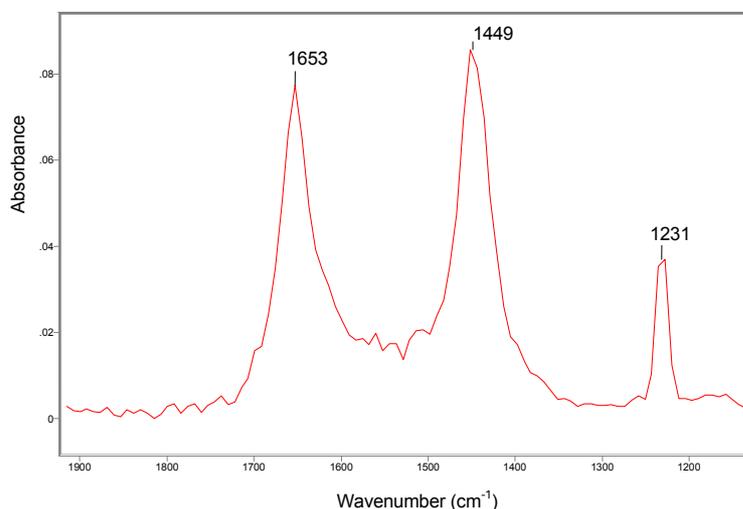


Fig.4. FT-IR spectrum of hydrogencarbonate and carbonate species on $\text{Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$ catalyst after oxidation at 773 K and CO exposure at room temperature

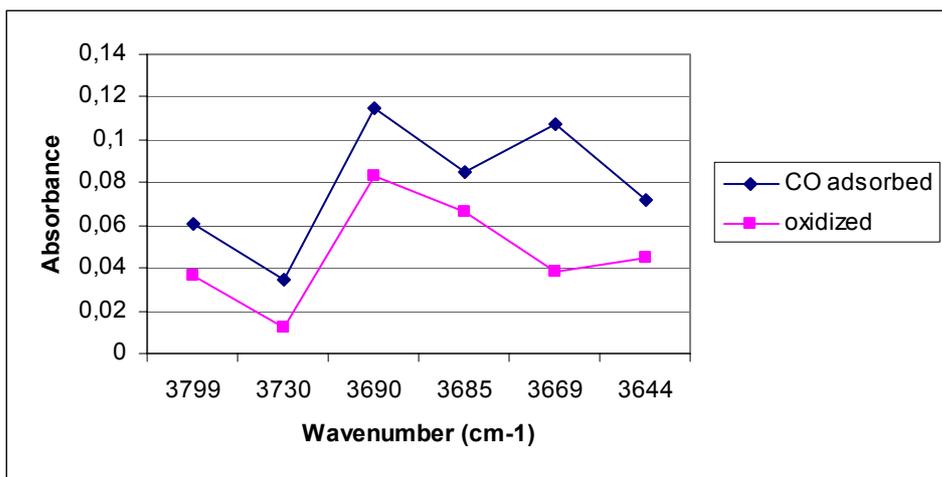


Fig 5. OH vibrations intensity changing of Ga_2O_3 catalysts after oxidation at 673 K and CO adsorption

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References

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