

XPS and IR characterization of manganese ions deposited on alumina

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Abstract

By application of XPS and FTIR spectroscopy of adsorbed CO the effect of preparation conditions on the state and localization of manganese ions deposited on η -Al₂O₃ is studied. Both Mn²⁺ and Mn³⁺ ions are observed on the impregnated sample. The sample obtained by ion exchange contains only Mn³⁺ ions. The adsorbed CO species are identified. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Manganese containing oxides are used for obtaining valuable products such as ethane and ethene [1], mixtures of methanol and higher alcohols [2] and nitrosobenzene [3]. Recent investigations have also shown that manganese based catalysts can be used for catalytic removal of NO_x [4–6]. For this reason it is important to study the surface properties of these catalytic materials.

The structure of the active phase of the supported oxides depends strongly on the preparation conditions. The widely used method for synthesis is dispersion of the active component(s) by impregnation. However, the catalysts prepared by ion-exchange are especially interesting because of their high activity as well as from a commercial viewpoint owing to the low content of the active phase.

In this article an attempt was made to elucidate the

effect of preparation conditions on the oxidation state of manganese ions and their dispersion on the surface of η -Al₂O₃. Two different preparation techniques, impregnation and ion-exchange from an aqueous solution of Mn²⁺ ions, were used. The state and localization of the deposited manganese ions were studied by XPS and FTIR spectroscopy of adsorbed CO.

2. Experimental

The support η -Al₂O₃ was obtained by dehydration of AlOOH at 500°C. The latter was prepared by hydrolysis of aluminum isopropoxide. The ion exchanged sample was prepared by suspending the support powder in 0.2 M aqueous solution of MnCl₂ for 2 h followed by alkalization (pH = 13) of the mixture with aqueous ammonia (1 : 1) and immediate filtration. The product was then washed with deionized water, dried in air at 110°C, and calcined for 1 h at 350°C and for the same time at 450°C. This sample will be denoted by MnAl-IE. The impregnated sample was obtained by incipient wetness technique

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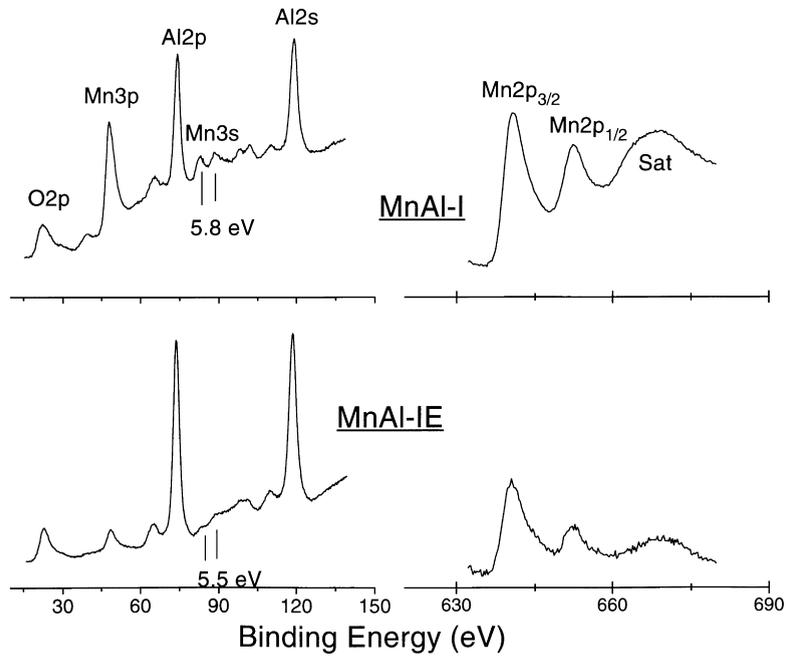


Fig. 1. Valence and Mn2p regions of the XPS spectra of the two samples.

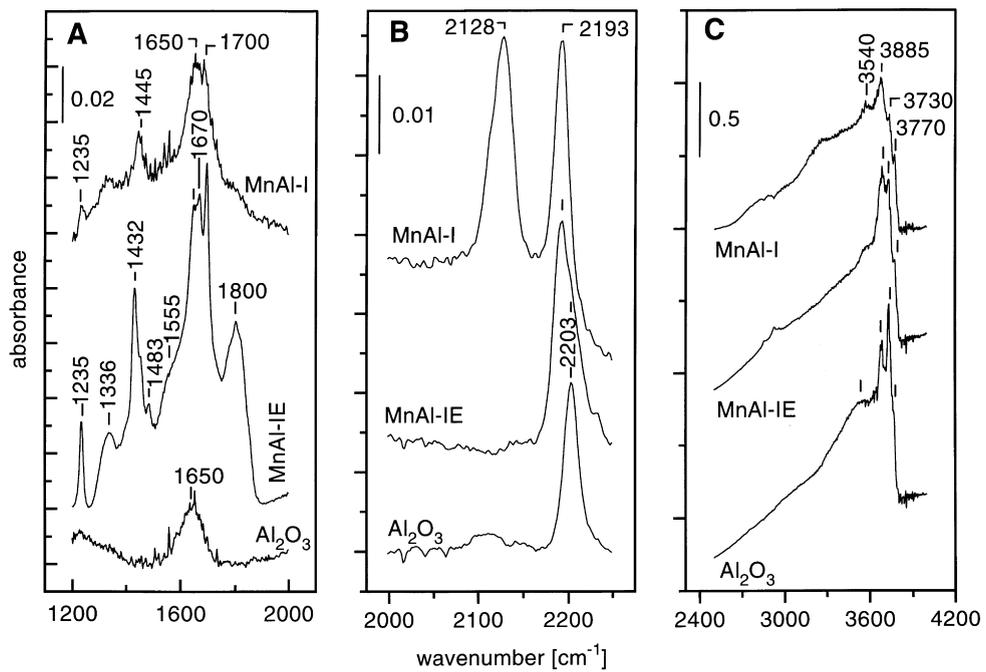


Fig. 2. FTIR spectra of: (A, B) adsorbed CO (30 Torr) at room temperature; (C) OH stretching region of the activated samples.

Table 1

Assignment of the IR bands observed in the carbonate–carbonyl region during adsorption of 30 Torr CO at room temperature on the samples studied

| Sample | Frequency (cm ⁻¹) and mode | Possible assignment | References |
|--|---|--|---|
| η -Al ₂ O ₃ | ~ 1350 (ν_s (CO)), 1650 (ν_{as} (CO)) 2203 (ν (CO)) | Formate species Al ³⁺ -CO | [9,10] [11] |
| MnAl-I | 1235 (δ (OH...O)), 1445 (ν_s (CO)) 1684 (ν_{as} (CO)) 1340 (ν_s (CO)), 1650 (ν_{as} (CO)) ~ 1800 (ν (CO)) 2128 (ν (CO)) 2193 (ν (CO)) | Bicarbonate species Formate species (HCO ₃)Mn ⁰ -CO and/or (CO ₃)Mn ⁰ -CO Mn ²⁺ -CO Mn ³⁺ -CO | [9] [9,10] This work This work |
| MnAl-IE | 1235 (δ -(OH...O)) 1432–1483 (ν_s (CO)) 1650–1700 (ν_{as} (CO)) 1336 (ν_s (CO)) 1550–1600 (ν_{as} (CO)) 1800 (ν (CO)) 2193 (ν (CO)) | Bicarbonate species Bidentate carbonate species (HCO ₃)Mn ⁰ -CO and/or (CO ₃)Mn ⁰ -CO Mn ³⁺ -CO | [9] [9,10] This work This work |

(5 wt.% of nominal manganese content) using MnCl₂ solution which was alkalized with ammonia to pH = 13 at the last stage of the preparation procedure. For this sample the notation MnAl-I will be used.

XPS spectra were taken by KRATOS ES300 spectrometer equipped with a Mg K α radiation source. FTIR spectra were recorded with a Bomem-MB102 (Hartmann & Braun) FTIR spectrometer at a spectral resolution of 4 cm⁻¹ (320 scans).

Self-supporting discs of the samples were activated by heating in 100 T of oxygen for 1 h at 400°C and evacuation for 1 h at the same temperature.

3. Results and discussion

3.1. Oxidation state of the Mn ions (XPS)

Although assignment of the chemical state of many elements is straightforward using the measured binding energies by XPS, difficulties arise in the elements with variable valency such as Mn. In such cases additional features such as intensity ratios and/or the magnitude of the multiplet splittings can help in assignment [7]. Accordingly, Foord et al. measured and tabulated the Mn2p_{3/2} binding energies, the O1s : Mn2p_{3/2} intensity ratios as well as 3s multiplet splittings for all stable MnO_x species [8]. For example, although the Mn2p_{3/2} binding energies 640.9, 641.8 and 642.5 for MnO, Mn₂O₃ and MnO₂, respectively, are too close for differentiation, the 3s multiplet splittings which are 6.1 eV (for 2 +), 5.5 eV (for 3 +) and 4.5 eV (for 4 +) can easily be used to differ-

entiate between various valencies. In Fig. 1 we display a part of the XPS spectra of MnAl-I and MnAl-IE. On the basis of the observed 5.8 and 5.5 eV 3s multiplet splitting we can determine that a mixture of Mn²⁺ and Mn³⁺ ions are present on the surface of the impregnated sample and only Mn³⁺ ions on the ion-exchanged one, respectively.

3.2. Localization of the Mn ions on the oxide support (FTIR of adsorbed CO)

The spectra of adsorbed CO (30 Torr) at room temperature are shown in Fig. 2 (A) and (B) with their assignments in Table 1. Arguments supporting these assignments are following: (i). For all the samples studied a negative absorption in the region of isolated hydroxyl groups (3600–3800 cm⁻¹) (Fig. 2(C)) were observed which indicates their involvement in the formation of the adsorbed species. (ii). The formate structures on the impregnated sample, MnAl-I, are recognized by appearance of an absorption in the 2600–2900 cm⁻¹ region owing to CH stretching bands of the formate ion [9]. (iii). The bicarbonate structures were identified by the appearance of a band at 3615 cm⁻¹. This absorption is attributed to the ν (OH) band of bicarbonate species on metal oxide surfaces [9]. (iv). Assignment of the bands at 2128 and 2193 cm⁻¹ to Mn²⁺-CO and Mn³⁺-CO, respectively, is based on the XPS data.

The XPS data and the results of CO adsorption show that, depending on the way of sample preparation, manganese ions in two different oxidation states are stabilized on the surfaces of η -Al₂O₃. In the case

of the impregnated sample, both Mn^{2+} and Mn^{3+} ions are observed. The sample obtained by ion exchange contains only Mn^{3+} ions. The more basic OH groups of $\eta\text{-Al}_2\text{O}_3$ (band at 3730 cm^{-1}) are involved in the deposition process (Fig. 2(C)). As the Mn^{3+} -CO band on MnAl-IE sample contains a high-frequency shoulder at about 2203 cm^{-1} it could be concluded that coordinatively unsaturated (cus) Al^{3+} ions are not blocked by the deposited Mn^{3+} ions.

Formation of bicarbonate and carbonate species accounts for the existence of reactive surface oxygen which oxidizes CO to CO_2 . The higher concentration of CO_3 and HCO_3 species on the surface of the ion-exchanged sample indicates that it contains a larger amount of reducible Mn^{3+} ions than the impregnated one. This is probably associated with a better dispersion of the deposited manganese ions achieved by application of ion-exchange technique for the sample preparation.

4. Conclusions

Depending on the technique used for sample

preparation different oxidation states of manganese are stabilized on the surfaces of $\eta\text{-Al}_2\text{O}_3$. Adsorption of CO at room temperature is reactive leading to formation of bicarbonate, carbonate and formate structures.

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