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K. Asakura, Y. Iwasawa, H. Kuroda. EXAFS AND XANES STUDIES ON THE LOCAL STRUCTURES OF METAL IONS IN METAL DOPED MgO SYSTEMS. *Journal de Physique Colloques*, 1986, 47 (C8), pp.C8-317-C8-320. 10.1051/jphyscol:1986862 . jpa-00226184

HAL Id: jpa-00226184

<https://hal.science/jpa-00226184>

Submitted on 1 Jan 1986

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EXAFS AND XANES STUDIES ON THE LOCAL STRUCTURES OF METAL IONS IN METAL DOPED MgO SYSTEMS

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*Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113, Japan*Abstract:

The local structures around the metals in metal-doped MgO catalysts were studied by EXAFS and XANES spectroscopies in connection with their catalysis which markedly depends on the kinds of doped metal ions. In the M-MgO samples ($M = \text{Ni}^{2+}$, Cu^{2+} , and Co^{2+}), the M ions occupied the octahedral sites of MgO lattice by replacement with Mg^{2+} . On the other hand, in the system of M-MgO samples ($M = \text{Fe}^{3+}$ and Cr^{3+}) the M ions existed as the cluster structure with a Koch-Cohen type M_4 -framework. The pair sites of the cation vacancy and basic oxygen atom derived from the cluster formation may be corrected with the specific catalysis for the cross-coupling reaction.

Introduction

Magnesium oxide (MgO) is known as a representative basic catalyst. When MgO is doped with Ni^{2+} or Cu^{2+} , the surface basicity increases¹⁾. In contrast, MgO doped with Fe^{3+} or Cr^{3+} ion is converted to be active catalyst for the cross-coupling reaction between methanol and acetonitrile or acetone to form unsaturated compounds²⁾. The local structures around the added metals play an important role for the catalytic feature of those modified MgO samples. In the present paper EXAFS and XANES spectra of the metals added to the MgO were measured and analyzed in order to find the correlation between the local structures of the doped metals and the catalytic properties.

Experimental

The metal-doped MgO was prepared by the impregnation of MgO (Soekawa Chemicals Co., 99.99 %) with the aqueous solutions of Cr^{3+} , Fe^{3+} , Cu^{2+} , Ni^{2+} and Co^{2+} nitrates, followed by the calcination at 873 K in a flow of N_2 . Ni^{2+} and Co^{2+} are known to form solid solutions with MgO in the whole range of metal concentrations. The amounts of added metals were 5 wt%. The X-ray diffraction patterns showed no separated metal oxide phase in all samples.

X-ray absorption spectra were measured at 80 K using synchrotron radiation on an EXAFS spectrometer installed at BL-10B of Photon Factory in National Laboratory for High Energy Physics (KEK-PF)³⁾. The EXAFS data were analyzed by a curve fitting techniques⁴⁾⁵⁾.

Results and Discussion

From the results of EXAFS and XANES, the samples were classified into two groups. The first group includes Ni^{2+} -, Co^{2+} - and Cu^{2+} -doped MgO catalysts (Group 1) where the increase of basicity by the addition of the metal ions has been observed. The second group includes Fe^{3+} - and Cr^{3+} -doped catalysts (Group 2) which have been found to show the high activities for the MgO system on the reaction. We describe EXAFS and XANES analyses of Ni^{2+} - and Fe^{3+} -doped MgO samples as the typical examples in each group.

Figures 1 and 2 show the XANES spectra of Ni and Fe K-edges of the Ni^{2+} -MgO and Fe^{3+} -MgO catalysts, respectively. The weak absorption peak observed in the pre-edge region in Fig.1 is assigned to 1s-3d transition. It is demonstrated that the transition is weak in intensity when metal atoms are located in an octahedral position⁶⁾. The pre-edge peak in the XANES spectrum of Fe K-edge in Fig. 2 was rather strong, suggesting that Fe^{3+} ions are located at tetrahedral sites without symmetry-centers⁶⁾.

Figures 3 and 4 show the Fourier transforms extracted from the EXAFS data for Ni^{2+} -doped and Fe^{3+} -doped MgO catalysts, respectively. Since the back-scattering powers as well as phase shift functions of Mg^{2+} and of Ni^{2+} or Fe^{3+} differ, these elements are indistinguishable in the fitting process in k-space. Thus the first peak of the Fig. 3 was assigned to Ni-O bond and the second one was due to Ni-Mg bond by the curve fitting analysis. No Ni-Ni bond was observed. The distances of Ni-O and Ni-Mg are 2.09 Å and 2.95 Å, respectively as shown in Table 1. The coordination numbers of O and Mg atoms around a Ni atom were 6 and 11, respectively. These distances and coordination numbers are in good agreement with those expected when the Ni^{2+} ions occupy the Mg^{2+} sites in MgO crystal as illustrated in Fig.5. The same conclusion was drawn with Co^{2+} -MgO and Cu^{2+} -MgO catalysts.

On the other hand, the Fe^{3+} -doped MgO sample showed the different Fourier transform in Fig.4. The curve fitting analysis showed that the first peak is attributed to Fe-O and the second one is made up by the superposition of Fe-Fe and Fe-Mg bonds. The determined Fe-O distance (1.90 Å) corresponded to the sum of the ionic radii of O^{2-} (1.40 Å) and tetrahedrally coordinated Fe^{3+} (0.49 Å)⁷⁾ and the coordination number of O atoms around a Fe atom was nearly 4. The EXAFS data also indicated that the Fe ions are situated in a tetrahedral position. The second remarkable point is the existence of Fe-Fe bonds at a distance of 2.99 Å, suggesting the cluster formation. The Fe-Mg distance is 3.31 Å which is much longer than that of Ni-Mg bond distance. We propose the Koch-Cohen-type structure as a model structure for the Fe^{3+} -MgO system as depicted in Fig.6. The structure has been postulated to exist in a non-stoichiometrical Fe_{1-x}O sample obtained from FeO contains Fe^{3+} ions and cation vacancies⁸⁾. In this structure 4 Fe^{3+} ions and the 13 cation vacancies gather to form the cluster structures, where Fe^{3+} ions are located in tetrahedral positions. In the Fe^{3+} -MgO catalyst the Fe_4 cluster structure may be dispersed in the MgO crystal (lattice constant : 4.20 Å) as shown in Fig.6. The bond distances for Fe-O, Fe-Fe, and Fe-Mg expected from this model are 1.86 Å, 2.98 Å and 3.42 Å, respectively. These values are in good agreement with those obtained from the EXAFS analyses as shown in Table 1. The small coordination number for Fe-Fe and Fe-Mg bonds observed in the EXAFS results may be due to the distortion of the ideal Fe_4 -cluster structure. The formation of similar Cr_4 -clusters were indicated for the Cr^{3+} -MgO system on the basis of the EXAFS and XANES studies.

The high catalytic activities of the Fe^{3+} -MgO and Cr^{3+} -MgO catalysts for the cross-coupling reaction may be related to the specific cluster formation. Acetone and acetonitrile adsorb at the cation vacancies and strongly interact with Fe^{3+} ions of the cluster.

Fig.1 Ni K-edge XANES spectrum

Fig.2 Fe K-edge XANES spectrum

Fig.3 Ni EXAFS Fourier transform

Fig.4 Fe EXAFS Fourier transform

Table 1 Curve fitting results of M-MgO

M-MgO	M-O		M-M		M-Mg	
	C.N.	r / Å	C.N.	r / Å	C.N.	r / Å
Co-MgO	5(1)	2.13(3)			11(2)	2.97(4)
Ni-MgO	6(1)	2.09(3)			11(2)	2.95(4)
Cu-MgO	3(1)	2.01(4)			10(2)	2.98(4)
Fe-MgO	4(1)	1.90(3)	2(1)	2.99(4)	4(2)	3.31(4)
Cr-MgO	3(1)	1.94(3)	2(1)	2.95(4)	3(2)	3.32(5)

Through the lone pair electrons of the ketone or nitrile groups so that the rupture of $C\alpha-H$ bond is promoted, while the ability of oxygen atoms located adjacently to the vacancies for hydrogen abstraction from methanol increases by the coordination unsaturation. Thus the pair sites of Lewis-acidic cation vacancy and basic oxygen atom produced from the clusterization of doped metal ions are likely to be the origin of the cross-coupling catalysis. The correlation between the increase of the surface base concentration and the structure of $M-MgO$ ($M = Ni^{2+}, Cu^{2+}, Co^{2+}$) systems is not clear, but this phenomenon must be related to the localization of d electrons of the transition metal embedded in the insulator MgO -crystal.

Fig.5 A model for Ni^{2+} - MgO .

Fig.6 A model for Fe^{3+} - MgO .

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