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Dispersive XAFS Study on on Structural Transformations of [Ru_6C] Clusters Attached on MgO Surface under Vacuum and CO/H_2

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Introduction

I have succeeded in monitoring time-dependent ruthenium-carbido cluster structures at a MgO surface in a molecular scale by DXAFS. The preliminary results were reported, summarizing the information on how and when the cluster structure changes during the processes of CO adsorption and desorption. This chapter reports novel issues found by in-situ characterization of the active metal clusters dispersed on the surface, namely, the time scale and sequence of dynamic bond rearrangements in ruthenium-carbido clusters on MgO by DXAFS[1].

Experimental

DXAFS measurements were carried out at BL-9C in KEK-PF. A Si(311) bent-crystal polychromator (Bragg-type) to achieve an elliptical optics for focusing incident X-rays at the sample. A self-scanning photodiode array was used as a position-sensitive linear detector.

Results and Discussion

The structural transformations of a MgO-attached [Ru_6C] cluster catalyst during carbonylation under CO/H_2 and decarbonylation under vacuum were studied by energy dispersive X-ray absorption fine structure (DXAFS). The DXAFS study revealed that the carbonylation of [Ru_6C]/MgO to [$Ru_6C(CO)_{11}$]/MgO proceeded via two intermediates with the same composition [$Ru_6C(CO)_6$] with different Ru-Ru bond distances (0.265 nm and 0.269 nm). At first six CO molecules coordinate to a [Ru_6C] framework and secondly the Ru-Ru length expands from 0.265 to 0.269 nm. Finally five CO molecules coordinate to the [$Ru_6C(CO)_6$] cluster to produce [$Ru_6C(CO)_{11}$] species, where the Ru-Ru distance is further elongated to 0.271 nm. In the decarbonylation process the [$Ru_6C(CO)_6$]/MgO is partially decarbonylated to form [$Ru_6C(CO)_{11}$]/MgO accompanied with a decreace of Ru-Ru length from 0.271 to 0.269 nm. Then the complete decarbonylation occurs to form [Ru_6C] species, keeping the Ru-Ru distance at 0.269 nm. Finally, the cluster framework shrinks to recover the original [Ru_6C]/MgO with the Ru-Ru distance of 0.265 nm. There were definite time lags between the first carbonylation and the cluster framework expansion (2-4 s, depending on the temperature) and between the last decarbonylation and the cluster framework shrinkage (3-5 min, depending on the temperature). The activation energies for the structural changes in the Ru cluster framework in every transformation step under CO/H_2 (423-523 K) and vacuum (573-623 K) were estimated by the time-resolved DXAFS analysis. This sort of study is the first to provide structural kinetics of catalytically active metal sites at oide surfaces.

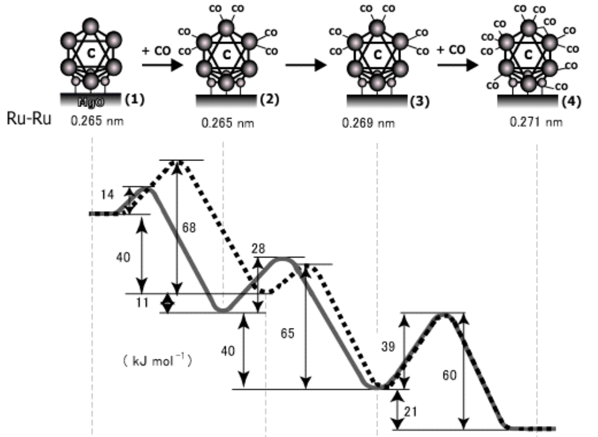

Figure 4.9 The energy profiles for the structural changes in the steps (**1**) → (**4**) and (**4**) → (**1**) determined by DXAFS.

Reference

[1] A. Suzuki, A. Yamaguchi, T. Chihara, Y. Inada, M. Yuasa, M. Abe, M. Nomura, Y. Iwasawa, *J. Phys. Chem. B*,**108(18),** 5609-5616 (2004).