



Experiment title: In-Situ Cu-Rh Catalysts under reaction condition.

Experiment number:
CH-282

Beamline:

ID-24

Date of experiment:

from: 29.1.97 to: 2.297

Date of report:

15.2.98

Shifts:

12

Local contact(s):

Dr. M. Hagelstein

Received at ESRF:

02 MAR. 1998

Names and affiliations of applicants (* indicates experimentalists):

* M. Fernandez-Garcia

Into Catalisis, CSIC, Campus Cantoblanco, 28049-Madrid, Spain

I. Rodriguez-Ramos

Idem

* P. Ferreira-Aparicio

Idem

* A. Guerrero-Ruiz

Dept. Quimica Inorganica, UNED, Senda de l Rey, 28040-Madrid, Spain

Report: Most of the recent advances in heterogeneous catalysis comes directly from the use of complex multicomponent bimetallic systems. However, the understanding of their properties *in "real" in-situ* conditions is strongly limited by the small number of techniques able to characterize a solid with only short-range order under the direct influence of a reactive mixture at elevated temperatures. XANES is one of these, although it can yield a variety of information depending of the type of analysis of the data performed. By applying a statistical analysis, known as Factor Analysis, to a set of XANES spectra taken during a treatment, the chemical state and phase behavior of a complex multicomponent catalyst can be obtained (1).

The Rh-Cu system is used in the production of synthesis gas (CO+H₂) from a CO₂+CH₄ mixture (2). The catalytic properties of Rh-Cu/Al₂O₃ catalysts depends notably on the Rh:Cu atomic ratio. To investigate this problem, we have studied the genesis (i.e., reduction process) of two RhCu specimens with Rh:Cu atomic ratios of 0.08 and 0.43 as well as Rh and Cu monometallic references. In both monometallic samples the active metal interacts strongly with the alumina support; Rh shares O²⁻ ions with alumina to complete its

coordination sphere yielding a short-range order close to that of Rh_2O_3 (3) while Cu forms mixed oxides with Al (superficial and bulk-like copper aluminates) (4). In the RhCu bimetallic catalysts, the oxidized state contains copper aluminates and Rhodium oxide, without appearance of mixed phases. In the RhCu0.08 system, Cu and Rh are coreduced yielding a Rh_xCu_y alloy and metallic Cu. The Rh-Cu phase diagram does not show the existence of any ordered phase and only a very small region of miscibility (giving disordered alloys) is observed close to the Rh abscissa. In small particles, the distribution of both metals is far from homogeneous and a surface enrichment in copper is expected. The surface characteristics of the zero-valent phases obtained are currently being investigated using IR-CO. The Rh-rich bimetallic system, RhCu0.43, shows completely different behavior; Cu and Rh are reduced independently (copper first) and no bimetallic phase is obtained.

When these RhCu reduced catalysts are left in contact with the reactive mixture, the presence of Rh^+ is detected on both samples while Cu does not change its oxidation state. In the RhCu0.08 catalyst Rh^+ coexists with the Rh_xCu_y alloy, while for RhCu0.43, the cationic Rh species coexist with metallic rhodium. This fact suggests, in both systems, that the surface of the Rh-containing phases is oxidized by CO_2 while the original, reduced phase is still in the core of the particle. Thus, the data described above suggest that the catalytic activity of the RhCu system is primarily governed by a geometrical effect induced by Rh dilution with Cu and that the electronic effects derived from alloy formation play only a minor role.

References

- (1) M. Fernandez-Garcia, C. Marquez, G.L. Haller J. Phys. Chem. 99, 12565 (1995); C. Marquez, I. Rodriguez-Ramos, A. Guerrero-Ruiz, G.L. Haller, M. Fernandez-Garcia J. Am. Chem. Soc. **119**, 2905 (1997).
- (2) F. Solymosi, J. Cerenyi *Catal. Letters* 34,343 (1995).
- (3) P. Ferreira-Aparicio, B. Bachiller-Baeza, I. Rodriguez-Ramos, A. Guerrero-Ruiz, M. Fernandez-Garcia *Catal. Letters* 49, 163 (1997).
- (4) M. Fernandez-Garcia, P. Ferreira-Aparicio, I. Rodriguez-Ramos, A. Guerrero-Ruiz (submitted).