Composition and morphology changes of Al₂O₃ and CeO₂ supported Rh and Co catalysts during preparation

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Hydrogen production is in the forefront of research nowadays. One viable route to produce hydrogen is heterogeneous catalysis using some kind of hydrocarbon or alcohol as raw material. The best catalysts for this purpose are oxide supported platinum metals, which are rather costly. So for the optimization of these materials, in terms of both catalytic properties and thrift, the thorough knowledge of catalyst characteristics is a must.

In the present paper the changes of the chemical composition and the surface morphology of alumina and ceria supported Rh catalyst with varying constituents during preparation are followed. The effect of Co promoter is also examined.

Photoemission spectra revealed that 1 wt% and 5 wt% Rh supported on CeO₂ can be reduced at much lower temperatures – around 400 K, depending on the Rh content – than what is mostly applied. IR spectra of adsorbed CO proved that the reductive agglomeration of the noble metal did not happen. Reduction at 773 K led to the dramatic decrease in the Rh 3d signal intensity. EDX data showed that the metal content did not change, only the metal surface decreased due to sintering. The addition of 2 wt% cobalt completely changed the catalyst's behavior by inhibiting the formation of large metal particles during heating. Some suggest that this is the consequence of the enrichment of the transition metal on the noble metal surface, but this cannot be always the case. After the low temperature reduction Co is still in oxidized form as justified by XPS, and neither DRIFTS, nor XRD or TEM could prove the formation of bimetallic species. We suppose that Rh and oxidized Co form separate particles which are in the close vicinity of each other to facilitate hydrogen spillover. The mobile oxygen of CeO₂ can contribute to the partial oxidation of Rh during heating. These oxygens also decrease the number of Ce³⁺ sites on the support surface.

Some catalysts with the same supports but with Co as the main metal and Rh as promoter were also studied. Even a minor amount of Rh had a considerable effect by downshifting the onset of reduction. Rh facilitates the dry reforming of methane. The noble metal also changed the intermediate Co oxidation state distribution upon reduction.

Using CeO₂ as support we found evidence for the enrichment of Rh in the surface layer, which along with metallic Co, contributed to the enhanced hydrogen selectivity in the steam reforming of ethanol.

References:

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