Structural and Catalytic Investigation of Rh Nanoparticles in Graphite

Ágnes Mastalir, Ferenc Notheisz
Department of Organic Chemistry, University of Szeged,
H-6720 Szeged, Hungary

Introduction
Graphite intercalation compounds (GICs) are synthetic metals formed by the insertion of layers of atoms or molecules of a guest species, the intercalate, between layers of the graphite host [1]. After intercalation, the overall morphology of the graphite host is retained in the product compound [2]. GICs have been widely employed in organic syntheses [3] and extensively studied in terms of their catalytic applications [4]. The graphite-transition metal systems are of particular importance because of their potential as hydrogenation catalysts [5]. The aim of the present work was to gain information on the location of the active species of Rh-graphimet, an efficient hydrogenation catalyst. Further, the effects of thermal treatment on the particle morphology, the surface heterogeneity and the active site distribution of Rh-graphimet were investigated.

Experimental
Rh-graphimet (1% Rh in graphite) was a product of Alfa Chemical Company. Thermal treatment of the sample (medium-temperature reduction, MTR) was carried out in a H₂ stream at 573 K for 1 h. The chemical state of the metal particles in Rh-graphimet was determined by XPS measurements. Further characterization was performed by N₂ adsorption, TEM, SAXS and H₂ titration. The active site distribution of Rh-graphimet was determined by 1-butene titration by applying the single turnover (STO) method developed by Augustine et al. [6]. Both the pristine and MTR samples were investigated.

Results and discussion
The results of XPS analysis gave evidence that the major amount of the total Rh content of both the pristine and MTR Rh-graphimet was present in the metallic state. Apart from a slight increase in the amount of Rh₂O₃, MTR had no significant effect on the chemical state of the metal. Ar⁺ etching increased the amount of Rh⁰ to an appreciable extent, indicating that a significant amount of elemental Rh was situated between the graphite layers.

TEM measurements of Rh-graphimet revealed the presence of a large number of small, monodispersed Rh particles on the surface of graphite. A narrow size distribution was obtained, with 44% of the particles less than 1 nm in diameter. After MTR, an increased number of 4-12 nm Rh particles and a fall in the amount of 1 nm crystallites were observed. Nevertheless, the average particle diameters were fairly close (3.15 nm and 3.65 nm for the pristine and MTR sample, respectively), which suggested that most of the surface Rh particles were resistant to sintering at 573 K.
The values of the SAXS parameters indicated that the distribution of the interlayer inhomogeneities in the MTR sample was similar to that in the pristine Rh-graphimet. Although the BET surface areas were fairly close, the relative inner surface area S/V for Rh-graphimet was substantially higher than that for pure graphite, which may be related to an increased interlayer distance of the host material, due to intercalation. Further, the close values of the surface fractal dimensions for the pristine and MTR Rh-graphimet suggested that both samples have non-planar fractal surfaces with similar degrees of irregularity.

![Logarithmic representations of SAXS scattering curves for graphite, Rh-graphimet and MTR Rh-graphimet](image)

Figure 1. Logarithmic representations of SAXS scattering curves for graphite, Rh-graphimet and MTR Rh-graphimet

Although no marked effect in the particle morphology and in the structural parameters of Rh-graphimet was experienced after MTR, thermal treatment was found to have a considerable influence on the active site distribution. The catalytically active sites of Rh-graphimet comprised hydrogenation (2\text{M}) and isomerization (3\text{M}) centres and the formation of both cis- and trans-2-butenes was observed. It was established that the 3\text{M} sites were more sensitive than the 2\text{M} centres to modifications of the surface metal content, including partial deintercalation of the interlayer Rh particles at 323 K. The catalytic activity of Rh-graphimet was mostly related to the presence of 1 nm surface Rh crystallites. Accordingly, the significant decrease in the number of active sites of MTR Rh-graphimet as compared with that of the pristine sample was mainly attributed to the joint effect of sintering and encapsulation of the active Pd particles in the graphite host.

**References**