

Recent Developments in Rh Heterogeneous Catalysts

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Rh-based catalysts successfully catalyze bond making and bond breaking reactions in most cases. Rhodium (Rh) has been one of the focuses of catalyst research from industrial and environmental points of view from the middle of seventies. This ascertainment is valid even nowadays, which is reflected in this Special Issue, too. Rh is one of the most important components of three-way catalysts [1,2]. A three-way catalyst oxidizes exhaust gas pollutants—both hydrocarbons (HC) and carbon monoxide (CO)—and reduces nitrogen oxides (NO_x) into harmless components, such as water (H₂O), nitrogen (N₂) and carbon dioxide (CO₂). Therefore, the mechanism of the reaction of NO with CO was extensively studied on oxide supported Rh catalysts, and it was established that isocyanate (NCO) surface complex is a real reaction intermediate [3–6]. The CO and CO₂ hydrogenation with hydrogen and methane is also an important issue from the past to the present. These reactions may result in reducing the poisoning and in producing compounds that are more valuable. Significant attention has been paid to the relations between catalytic activity, reaction mechanism and intermediates [7–11]. Furthermore, it was revealed that supported Rh was a promising catalyst for carrying out the transformation of oxo-hydrocarbons (alcohols, aldehydes) producing hydrogen as a potential fuel. It is an important conclusion that Rh plays an important role in the dissociation of carbon–carbon bonds [12,13].

Despite the high cost of rhodium metal, its superior catalytic properties at low temperature still make it indispensable to understand the interaction between the metal and the support, to check the surface compounds formed during the reaction, and to show the elementary steps of the reaction, and as additives appear to be unavoidable for the development of an effective and stable catalyst. Considering this economic demand, several important attempts are made to reduce the expenses. These efforts are reflected in the recent studies and in this Special Issue, too. Firstly, the amount and the size of the Rh catalyst can be minimized with the optimal preparation circumstances; secondly, the applied second adatom may increase the catalytic efficiency of the Rh nanoparticles. Finally, the new generation support materials for Rh may increase the catalytic performance in many cases. Following these efforts, methods are developed for the deposition of Rh, which results in nanosized distribution of the metal on the supports; the thermal stability and reactivity of Rh nanoclusters were studied, especially on CeO₂ and on an ultrathin alumina film [14,15]. The infrared study of carbon monoxide adsorption greatly helps in the mapping of morphology and oxidation states of Rh nanoparticles prepared on supports [16]. Very recently, it turned out, in several cases, that the adatom, similar to cobalt, significantly enhanced the Rh activity in the steam reforming of ethanol. The catalytic activity of 0.1% Rh + 2% Co on ceria exceeded the activity of 5%Rh/CeO₂ catalysts [17]. A similar promoting effect was observed in the dry reforming of methane using alumina supported Rh-Co bimetallic catalysts [18]. The physical–chemical properties and the morphology of the support may determine the nature of the interaction between rhodium and the support. It has been



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recently demonstrated, by several examples in the literature, including the papers in the present Special Issue, that different nanostructured supports, such as titania, may modify the activity and selectivity of rhodium in CO₂ hydrogenation, water–gas shift reactions and in ethanol transformation [19,20]. Furthermore, it was demonstrated in two reviews that different oxide supports changed not only the conversion, but the selectivity and the mechanism of CO₂ hydrogenation and the dry reforming of methane when Rh-based catalysts were used [21,22]. The numerical simulation of methane and other reforming alkanes was carried out over the Rh/Al₂O₃ catalyst in stagnation flows, emphasizing the importance of the impact of internal and external mass transfer [23]. The study of catalytic reactions of hydrogenation, including hydrodeoxygenation, was extended to several aromatics in the gas phase [24] and in liquid medium on Rh-based catalysts [25].

Very recently, it was demonstrated that titanate nanotubes influenced the reaction path in CO₂ hydrogenation in the presence of sodium. A significant amount of formic acid (HCOOH) was produced [26]. Several studies were published on the importance of formic acid recently [27–29]. It turned out that HCOOH is an important chemical for renewable energy systems and H₂ can be applied for fuel cell vehicles; formic acid is a good candidate as a H₂ storage compound. The importance of HCOOH for fuel cell application can nowadays be demonstrated by an increased number of patents. Due to this direction, the investigations of catalytic decomposition and surface chemistry of HCOOH on different catalysts, including Rh, are renewed [30,31].

In conclusion, this Special Issue clearly shows the importance of the optimization of size and chemical environment of Rh nanoparticles. It is demonstrated that the type of the support changes the conversion and the selectivity of the studied Rh catalyzed reactions. Finally, we would like to remember that Prof. Frigyes Solymosi was one of the great scientists who (with his research group) successfully took part in the research of Rh-catalyzed reactions from the early seventies up to very recently. Unfortunately, he passed away when we just started structuring this Special Issue. His 90th birthday would have fallen in March this year.

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