Chapter 3
Palladium in Heterogeneous Oxidation Catalysis

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ABSTRACT

Palladium is one of the precious group metals mainly used in automobile catalytic converters. Besides, it has an importance in various catalytic processes. Although it is well known for hydrogenation reactions, various oxidations can also be catalyzed by palladium. This chapter gives an overview on the most common application of palladium catalysts in heterogeneously catalyzed acetoxylation, i.e. the acetoxylation of ethylene to vinyl acetate. Derived from this knowledge, the authors summarize in detail recently accumulated research results in acetoxylation of toluene to benzyl acetate that can be easily converted to benzyl alcohol. The chapter includes a detailed description of catalyst syntheses, gas phase oxidation runs, comprehensive characterizations and a deep understanding in catalyst-feed interaction. This development can turn away the manufacture of important petrochemicals from chlorine chemistry to oxidations using molecular oxygen.

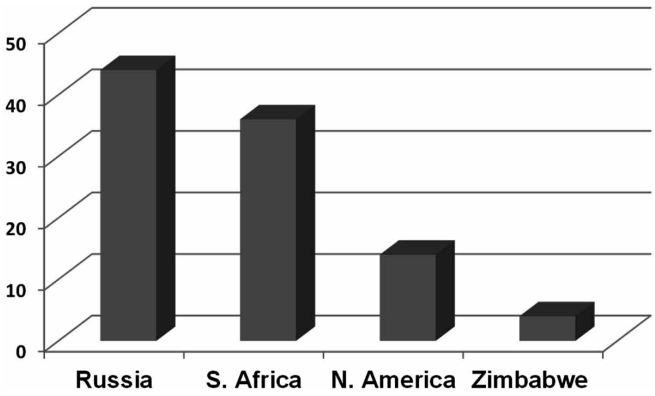
BACKGROUND

Palladium (Pd) is a silvery-shining metal discovered in 1803 by W.H. Wollastone. It is a member of the nickel group standing in group 10 (Ni, Pd, Pt) of the periodic table of elements and it is also a part of the platinum group metals (PGM) together with platinum, rhodium, ruthenium, iridium and osmium.

In general, metallic Pd and Pd ores are rare and often found together with other PGMs (e.g. alloyed with gold or platinum). However, the most commercial sources are deposits containing nickel and copper. The total Pd supply in 2012 was ca. 6.5 million oz.; 44% were extracted from Russian mines,

DOI: 10.4018/978-1-4666-9975-5.ch003

Figure 1. Palladium supply (%) by regions (Johnson Matthey, 2014)



36% in South Africa (Johnson Matthey, 2014; Stillwater Palladium, 2012). Other important producing regions are located in North America and Africa; Figure 1 depicts the shares of the four largest producing countries. In addition, Pd is also obtained from recycling of noble metal containing scrap, mainly catalytic converters from automobiles.

Most of the Pd is used for automotive catalysts (65%), electronic, dental and jewelry application consume ca. 20%, the remaining part is for investment and other applications including its use as catalysts or dopants in catalyst formulations (Figure 2) (Manhattan Gold & Silver, 2011). In automotive catalysts, it is combined with platinum or rhodium and removes over 90% of harmful carbon monoxide, unconverted hydrocarbons and nitrogen oxides into water vapor, nitrogen and carbon dioxide. Pd plays also a key role in fuel cell technology to produce electricity and heat.

Besides its use in automotive catalysts and fuel cell technology, palladium has a large number of applications in homogeneous and heterogeneous catalysis (Ugo, 1980). For example, finely dispersed Pd on several supports, in particular carbon is well known as hydrogenation or dehydrogenation catalyst in chemical industries (Coq, & Figueras, 2001; Mahata, &Vishwanathan, 2000) as well as petroleum cracking (Gallezot, 1979; Bradow, Grenoble, Foley, Murray, Winquist, & Milham, 2001). Pd is also widely

Figure 2. Palladium demand (%) by application fields; AC = Automotive catalysts, E = Electronics, D = Dental, I = Investment and J = Jewelry (Johnson Matthey, 2014)