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Recycling GTL catalysts—A new challenge

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Abstract

The Fischer Tropsch synthesis of motor fuel from natural gas on a large scale may become significant in the near future for economic and environmental reasons. This process requires solid-phase catalysts containing large amounts of cobalt (catalyst) and traces of platinum group metals or rhenium (promoter). The economic data presented in this paper shows why recycling of those metals will be mandatory. Several recycling processes will be presented along with their technical challenges, most of which can be handled by Umicore using its know how and experience in the recycling of cobalt and the precious metals.

Keywords: Catalysts; Recycling processes; Fischer Tropsch; GTL

1. Introduction

Considerable investments are currently being assigned to convert natural gas into very pure diesel in order to fuel motorized vehicles without further depletion of oil reserves. The process of liquefaction the gas is known as gas to liquid (GTL). As large gas reserves – partly stranded or flared – are in regions where pipeline transportation is difficult or even not feasible, GTL will facilitate easier energy supplies. Furthermore, cars driven with ‘‘synthetic fuel’’ (i.e. the products of GTL plants) will burn cleaner and will contribute to a cleaner environment, e.g. in very large cities.

The GTL process consists of four steps that all require catalysts: (1) gas cleaning, (2) reforming of the gas into a mixture of carbon monoxide and hydrogen (Syngas), (3) Fischer Tropsch (FT) synthesis, and (4) hydrocracking.

The Fischer Tropsch synthesis is rather new to large-scale production plants, it was developed 80 years ago in Germany. The catalyst consists of a ceramic support (e.g. alumina), a considerable amount of a base metal (cobalt or iron) as the catalytically active metal, and traces of a platinum group metal (PGM, e.g. platinum, ruthenium, palladium, or rhodium) or rhenium as a promoter (PGMs and rhenium are also referred to as ‘precious metals’ in this paper). Rhenium, a transition metal, is known to have catalytic activity and can also be used for steel reinforcement, e.g. in turbine blades for aircrafts.

2. Availability of base and precious metals

The amounts of catalysts required for the planned GTL plants are fairly high, and may thus influence the availability and pricing of the constituent metals concerned. In the coming years, the GTL capacity might reach 1 million barrels per day (bpd), which requires approximately 25,000 t of FT catalysts containing around 5000 t of cobalt. Over a period of 10 years, this would mean some 500 t/year. Assuming a worldwide cobalt supply of 45,000 t/year, the use of cobalt in GTL catalyst would represent around 1% of the total cobalt demand.

A world-class 100,000 bpd GTL plant employing a 20% cobalt catalyst with 0.1% PGM or rhenium as promoter would require ~500 t of cobalt and 2.5 t of PGM or rhenium. At an annual production of more than 200 t of platinum and palladium, the effect on the market of these metals would be minor. However, considering an annual production of just over 20 t of ruthenium and 45–50 t of rhenium (most of

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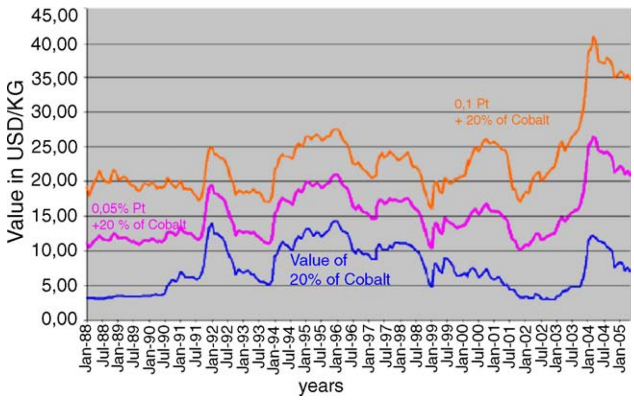

Fig. 1. Intrinsic metal value of the Co-Pt GTL catalyst during the last 17 years, with two different Pt contents (0.1 and 0.05%).

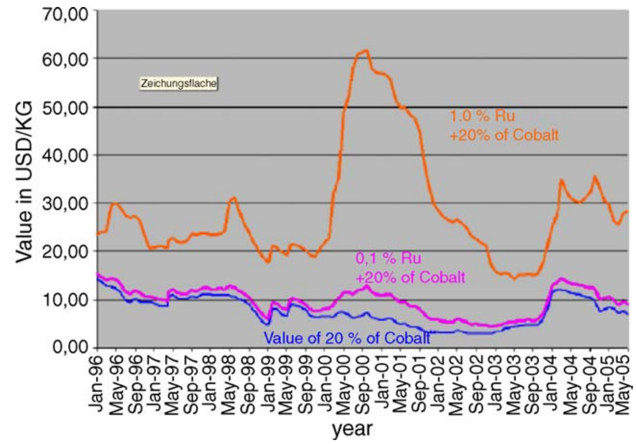

Fig. 3. Intrinsic metal value of the Co-Ru GTL catalyst during the last 9 years, with two different Ru contents (1.0 and 0.1%).

which is used for turbine blade alloys), the GTL processes may affect the market dynamics of these two metals. Current prices are US$ 1250–1400/kg for rhenium, US$ 2000/kg for ruthenium, US$ 6000/kg for palladium, over US$ 25,000/kg for platinum and more than US$ 40,000/kg for rhodium, the most expensive PGM metal. An overview of PGM price development and demand/supply patterns with respect to lifecycles of oil refining catalysts is given in [1].

3. Development of the intrinsic metal value of GTL catalysts

Obviously, the intrinsic value of a GTL catalyst fluctuates depending on the price and content of cobalt and precious metals. Fig. 1 shows the intrinsic metal value of a typical GTL cobalt-platinum catalyst over the past 17 years. The platinum content is 0.05 or 0.1%, the cobalt content is 20% throughout (see [2] and related patents).

Taking the catalyst containing 0.05% platinum (500 ppm), there is a rather large fluctuation of the intrinsic value with a minimum of US$ 10/kg in the first quarter of 1988 and in January 1999 (see Fig. 2). At the beginning of 2004, there was a 25-year high in the platinum price. When this is combined with cobalt prices that were nearly as high in 2004 as in 1992 and 1996, this results in peak values of over US$ 25/kg for the GTL catalyst. Currently, intrinsic values are above US$ 20/kg, which makes recovery of both cobalt and platinum worth considering. Also note that the platinum makes a larger contribution to the price than the cobalt.

In addition to platinum, ruthenium can also be used as promoter for FT catalysts although likely at somewhat higher contents, e.g. 0.1 or up to 1.0%. Fig. 3 shows the impact of ruthenium (0.1 or 1%) on the intrinsic value over the past 9 years. The major influence of the promoter content is obvious. In Fig. 4, the intrinsic value of a catalyst with 0.1% ruthenium is shown, together with separate curves for ruthenium and cobalt prices. In contrast to the platinum-cobalt catalysts, the cobalt has the higher value in the cobalt-ruthenium catalysts. In view of the rather small ruthenium market, it might become crucial to recover and recycle the ruthenium, which is an even bigger technical challenge than for platinum.

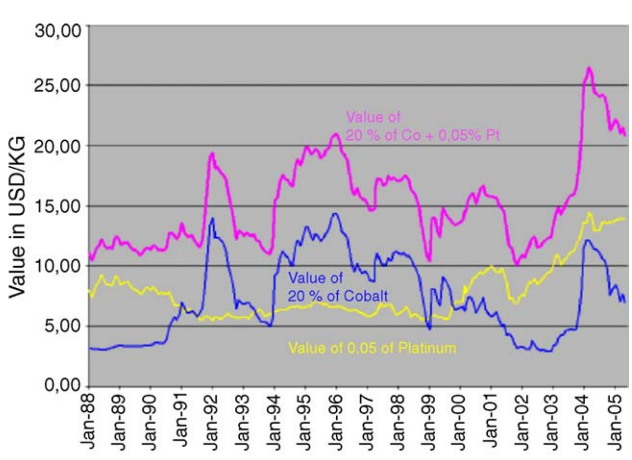

Fig. 2. Intrinsic metal value of the Co-Pt GTL catalyst (0.05% Pt) during the last 17 years.

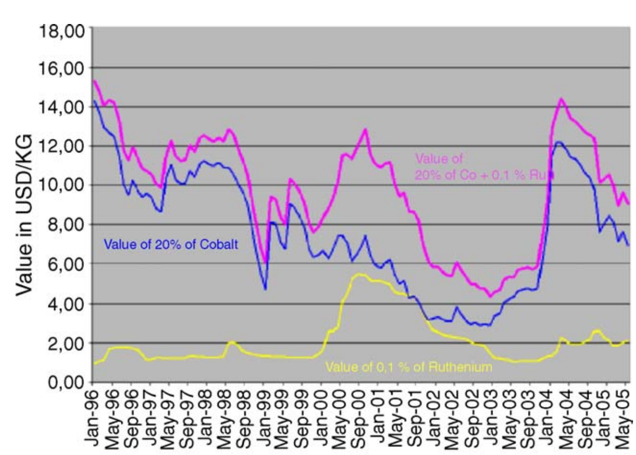

Fig. 4. Intrinsic metal value of the Co-Ru GTL catalyst (0.1%) during the last 9 years.