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Catalysis Today 106 (2005) 166–169

CATALYSIS TODAY

www.elsevier.com/locate/cattod

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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0920-5861/$ – see front matter
doi:10.1016/j.cattod.2005.07.177

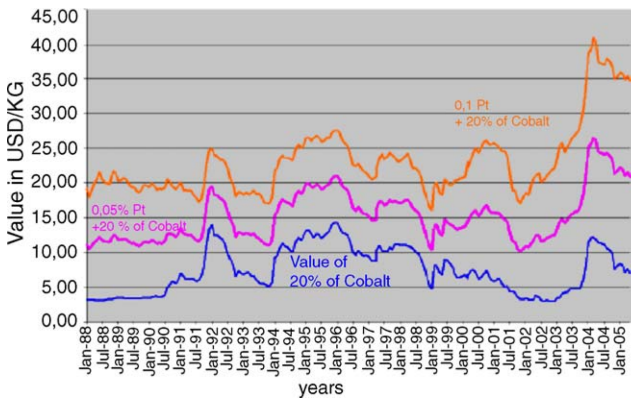

Fig. 1. Intrinsic metal value of the Co-Pt GTL catalyst during the last 17 years, with two different Pt contents (0.1 and 0.05%).

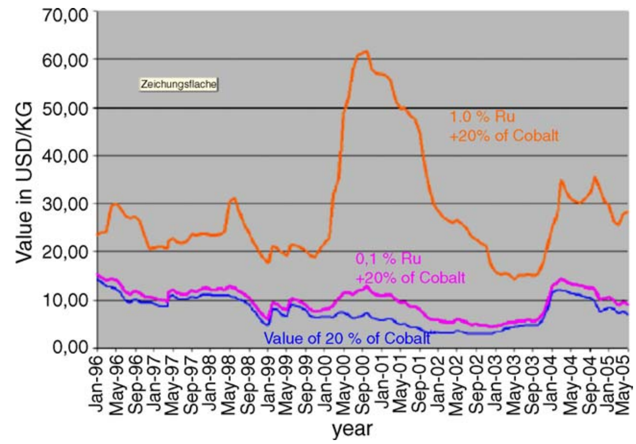

Fig. 3. Intrinsic metal value of the Co-Ru GTL catalyst during the last 9 years, with two different Ru contents (1.0 and 0.1%).

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.

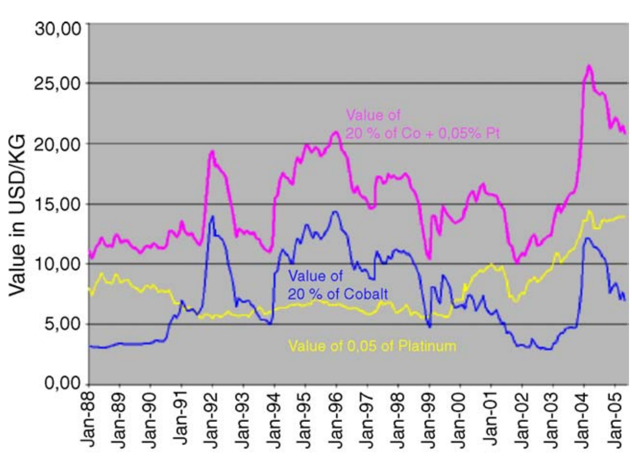

Fig. 2. Intrinsic metal value of the Co-Pt GTL catalyst (0.05% Pt) during the last 17 years.

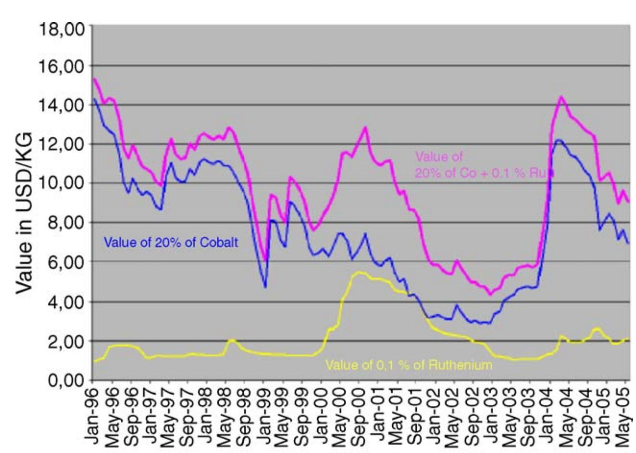

Fig. 4. Intrinsic metal value of the Co-Ru GTL catalyst (0.1%) during the last 9 years.

4. How recycling can decrease the influence of fluctuations in the prices of base metals and precious metals

Obviously, with increasing cobalt, platinum, and ruthenium prices, recovery of these metals becomes more interesting. However, even at lower price levels a positive return from recovery operations can be expected. If recovery were abandoned at all, the impact on the prices of those metals would even be higher.

Two business models can be applied; one is to sell the catalyst containing the base and precious metals to the recycler and the other is to toll refine, keeping the majority of the metals in a closed loop. In this case, only metals for additional capacity and for making up recovery losses in the loop have to be bought on the market. Therefore, the sensitivity to fluctuations in the prices of base metals and precious metals is minimized.

With this model, the catalyst can be considered as a fixed reactor asset, and its metals' price sensitivity and market volatility would be limited only to the small fraction of metal loss occurring during operation and recovery. There would be a temporary additional need for those metals during the metal recovery period that consists of the time required for bridging the metal refining and the fresh catalyst manufacturing time. Some of these metals can be leased, but here again for certain metals with lower liquidity it will be important to evaluate the impact carefully and consider the use of several small reactors with equally distributed reactor dumps against one single large reactor.

5. Recycling of both cobalt and PGM is a prerequisite

Recycling of the spent catalyst is not only required because of the value of the base and precious metals, but also might become mandatory to provide a sound, environmentally friendly solution for the large amounts of spent catalysts involved. Landfills should be the last recourse from both an environmental and an economic point of view.

The spent FT catalyst is a new challenge for the recycling industry for a number of reasons:

- the huge spent dumps with high contents of wax;
- the combination of recoverable base and precious metals;
- the different chemical compositions of the support materials;
- the different sizes of the catalyst particles, going down to a very fine powder;
- the different promoters used (platinum, ruthenium, palladium, rhodium, and rhenium each require different refining and separation technologies).

To cope with these challenges, Umicore has started a development program to deal with a broad range of spent FT catalysts by combining its know how in base and precious metals recycling technologies and by applying its extensive experience in hydro- and pyrometallurgy. Even though the spent catalyst will only be available some years from now, the GTL industry wants to obtain information on recycling feasibilities today. Therefore, the time is right to discuss the best interface between the GTL plant and the recycler. In this very early stage partnerships can be formed for developing solutions that optimize the value chain.

There are two major possible ways of treating GTL catalysts: (1) selective digestion and precipitation of the metals (the hydrometallurgical method) or (2) high temperature treatment of the material (the pyrometallurgical method).

- *Hyrometallurgy:* The hydrometallurgical method consists of partial or complete digestion of the entire catalyst including its carrier and subsequent separation of the carrier, PGM, and cobalt by selective precipitation. A process is known for dissolving the alumina in caustic soda or sulfuric acid from the recycling of platforming catalysts.

  However, a major obstacle of this method is its sensitivity to pollutants, primarily the high content of wax. An initial calcination/pyrolysis step must be applied to remove these hydrocarbons before hydrotreatment.

  In addition, the hydrometallurgial method is very carrier sensitive. Taking into account the large amount of possible different GTL catalyst supports, a single hydroroute might not be feasible.
- *Pyrometallurgy:* In the pyrometallurgical method, end-of-life catalysts are heated to high temperature in a furnace. The metals are melted out, and the ceramic support can be slagged off. This method is much less sensitive to pollutants, and it can handle several pollutants, such as carbon, sulfur, and hydrocarbons. Further developments are ongoing:
  - decrease carrier sensitivity further by an appropriate slag system adapted to the type of carrier used;
  - decrease or even avoid the presence of metals in the slag;
  - assure close control and management of the off gas treatment.

6. Summary

- Recycling of end-of-life GTL catalysts is required for economic and environmental reasons.
- Combined recycling of both metals used in a GTL catalyst (cobalt + precious metal) is preferred in order to provide a true environmentally sustainable solution.
- The wide variety of catalyst composition makes recycling very challenging. In addition, catalysts usually contain wax and other potential pollutants such as sulfur.
- A process aiming to recycle these catalysts should be extremely robust to cope with all possible intrinsic compositions.

- To assure complete control of the waste chain, recycling should be the responsibility of a reliable and sustainable company already recognized as a key player in the recycling world, with outstanding experience in handling precious metals and cobalt.
- Finally, Umicore is already proposing a specially developed, environmentally sustainable recycling solution able to cope with all possible compositions and pollutants. Umicore's integrated approach for recovering base and precious metals, also in the form of compounds ready to be used in the production of new catalysts, enables the GTL industry to retain most of the base and precious metals in a closed loop. Thus, the influence of the availability of base and precious metals and the fluctuation of their prices is strictly minimized.

References

[1] C. Hagelüken, A precious effort, Hydrocarb. Eng. 8 (July (7)) (2003) 48–53.
[2] C.H. Bartholomew, History of cobalt catalyst design for FTS, to be found among many other interesting literatures, www.Fischer-tropsch.org.