



Budapest University of Technology and Economics

Department of Chemical Technology

Octane reforming over modified catalyst by adsorbed metals

PhD theses

Ákos Fürcht

MSc in Chemical Engineering

Consultant:

Prof. Dr. Antal Tungler

Head of Department

Budapest

2002.

Introduction

The PhD study was made in co-operation of MOL Plc. and the Department of Chemical Technology of Budapest University of Technology and Economics. The industrially used reforming catalyst was modified and tested under industrial conditions. The modification technology, the metal adsorption, was not used formerly in industrial research. The advantage of the technology is the close contact between the platinum and the modifying metal, since the modifying metal is adsorbed directly on the platinum surface. After the test reactions we can conclude the metals, that are advantageous regarding the following research objectives:

- Utilisation of metal adsorption in industrial scale conditions.
- Testing the modified catalysts under industrial conditions.
- The reformat amount should not decrease significantly.
- The reformat octane should not decrease significantly.
- The aromatic content of the reformat should alter in advantageous direction.
- The multiple regeneration should not influence the catalyst behaviour; the catalyst should remain stable.

Summary

The industrial bimetallic platinum-tin/ γ -alumina catalyst was modified by palladium, gold, iridium, tin, tellurium and bismuth. The theory of the metal adsorption is the following: The catalyst is treated with hydrogen (the platinum is saturated with hydrogen), then under inert atmosphere the solution of the modifying ions is contacted with the catalyst. The adsorbed hydrogen reduces the metal ions into metal. This way the theoretical amount of adsorbed modifying metal equals the amount of adsorbed hydrogen.

It revealed after the modification, during the characterisation of catalysts, that the adsorption takes place differently of that mentioned in the literature. We cannot displace all ions from the catalyst, some solution remains in the pores of the catalyst. During the drying step these ions are impregnated on the surface of the support. The hydrogen spill-over also has its influence on the “over-modification”. The introduced metal above the theoretical maximum has its impact during the catalytic reactions. However, independently of this impact, the metal placed selectively on the platinum surface by adsorption has its own impact (there are direct contact between the platinum and the modifying metal).

The metal content of the catalysts was measured by atom adsorption and X-ray fluorescent spectroscopy methods. Other methods to characterise the catalysts were chemisorption and X-ray photoelectron spectroscopy. Reforming test reactions were performed at 480 and 510 °C using octane as raw material. The reaction products were analysed by capillary gas chromatography. The activity and selectivity of the catalysts were calculated from the chromatograms.

In the first series the reference and the modified catalysts were tested under industrial conditions (space velocity, pressure, temperature, hydrogen/hydrocarbon ratio). I concluded, that the majority of the catalysts couldn't be characterised correctly. Since the reference, and the palladium-, gold-, iridium-, and tin-modified catalysts produced nearly 100% conversion, the secondary reactions have significant impact on the reformat composition. The primary and secondary products cannot be separated.

The conversion was convenient in the case of tellurium and bismuth modified catalysts. The most significant impact of the modifiers were the decrease of the catalyst. This is normal, since both metals are known for its poisonous character. Indeed, according to literature data, positive impact was awaited. The positive impact was realised on the selectivity hand, since the aromatic content of the liquid product decreased significantly, while the isoparaffins increased. From the industrial point of view these catalysts have low activity and their liquid yield is small, therefore they cannot be used in industrial applications. Their mechanism is the adsorption on the platinum surface, so they selectively block the metallic sites of the catalyst. Reactions taking place on the acid sites of the catalyst become dominant among the possible reaction pathways (hydrocracking, isomerisation).

The above-mentioned very active catalysts should be tested with decreased conversion to be really comparable. To achieve a comparable conversion level another series of measurements were carried out. The space velocity was increased. I concluded, that the maximal space velocity, i.e. 4 h^{-1} , that can be used in the reactor is suitable to compare the modified catalysts.

The impact of palladium, gold, iridium and tin was measured beside increased space velocity. I concluded, that as the impact of iridium and gold the reforming catalyst became more active than the reference one: the conversion was higher. After the comparison of the liquid yield and gas amount at different temperature it came to truth that the gas producing selectivity of the modified catalysts is just slightly dependent on the temperature, while with the reference catalyst produced significantly less liquid product at higher temperature. The inactive gold splits the platinum surface into smaller clusters, so the selectivity is pushed

toward the non-destructive reactions. Both metal increase the aromatic and decrease the isoparaffin content of the reformat. This result is the reverse of the basic objectives, so the industrial usage cannot be advised in either case.

The other two modifier, tin and palladium, have a positive impact on the catalyst selectivity. As the result of tin, introduced by adsorption, I experienced higher liquid yield at higher temperature, than with the reference catalyst. From composition point of view positive alteration was found at lower temperature (while a small negative alteration at higher temperature), since the aromatic content of the reformat decreased, and the isoparaffin content increased. The interpretation is the hindered metallic function that is supported by the amount of the naphthenic hydrocarbons (twice as the reference). The palladium modified catalyst produced similar amount of liquid product as the reference one. However, the isoparaffin/aromatic ratio increases at higher temperature, while at lower temperature it remains practically unchanged. At higher temperature the advantageous selectivity change is more significant from industrial point of view.

In general the palladium was found to be more effective modifying metal, because its liquid yield decreased just a little, its selectivity was similar to the reference one at 480 °C, while at 510 °C its isoparaffin/aromatic ratio increased. After its behaviour it would be potentially applicable to industrial use, therefore I conducted detailed research with this catalyst.

During the detailed research the octane raw material was changed to industrial raw material. It was investigated, if the formerly found positive effects take place under industrial conditions. According to the results, the positive effects are similar, however to a bit less extent.

The final series of test were realised to find out the applicability of the sixth objective. I was interested to the behaviour of the catalysts after multiple oxidation-reduction cycles. According to the results, the tin- and iridium-modified catalysts endure the regeneration without noticeable activity or selectivity change. Unfortunately, in the case of the other two metal, gold and palladium, we cannot talk about stable regeneration-enduring ability. The first cycle has just a little effect on the catalysts yet, however the following oxidation-reduction cycles –pronouncedly on the palladium modified catalyst–, caused significant platinum-palladium (-gold) relocation. As the effect of relocation the activity of the catalysts decreased significantly. Finally this decrease prevents the industrial application even in the case of the palladium-modified catalyst.

Briefly summarising the results of the research I should conclude that I couldn't prepare an industrially applicable catalyst with the applied metal adsorption method. However, as the result of the PhD study it became obvious that the method is applicable for the modification of supported catalysts. There are some interfering circumstances. Because of the porous nature of the support parallel with the adsorption in most cases impregnation also takes place. However, besides the impregnated modifying metal the adsorbed metal clearly demonstrates its effect. The hindered, partly deactivated metallic function of the catalyst is to be thanked to the adsorbed metal.

Theses

The modification of the industrial Pt-Sn/Al₂O₃ reforming catalyst by different adsorbed metals, the physical-chemical measurements and the catalytic tests revealed the following scientific results:

1. Using alumina supported platinum catalyst the metal adsorption do not takes place alone, but because of the hydrogen spill-over and the porous nature of the support the alumina also adsorbs some modifying ions (impregnation).
2. During the modification of industrial catalyst by adsorption the amount of the deposited tellurium, bismuth, iridium, gold and palladium is more than the equivalent amount of adsorbed hydrogen.
3. The adsorbed tellurium and bismuth selectively blocks the metallic sites of the catalyst, therefore the reactions taking place on acidic sites become more dominant (hydrocracking, isomerisation).
4. The temperature dependence of the hydrocracking activity of the iridium- and gold-modified catalysts decreased compared to the reference one, meanwhile the liquid yield values changed just a little with the reaction temperature.
5. Because of the metallic function hindrance the adsorbed tin –due to the interference with the platinum–causes the isoparaffin/aromatic ratio increase, besides of the minimal activity decrease of the catalyst.
6. In the case of gold and –mainly– palladium the repeated oxidation-reduction caused an alteration in the interference of platinum and the modifying metal (alloying, surface relocation). Due to this alteration the catalyst permanently loses activity, while the selectivity of the destructive reactions increases (the liquid yield decreases).

Publications

Publications, oral presentations and posters concerning the PhD study:

1. **Ákos Fürcht**, Antal Tungler, Sándor Szabó, Antal Sárkány, *n-Octane reforming over modified catalysts I. The role of Sn, Te and Bi under industrial conditions*, Applied Catalysis A: General 226 (2002) 155-161.
2. **Ákos Fürcht**, Antal Tungler, Sándor Szabó, Zoltán Schay, László Vida, Iván Gresits, *n-Octane reforming over modified catalysts II. The role of Au, Ir and Pd*, Applied Catalysis A: General 231 (2002) 151-157.
3. **Ákos Fürcht**, Antal Tungler, Sándor Szabó, *n-Octane reforming: Conversion and selectivity dependence on space velocity*, Reaction Kinetics and Catalysis Letters, 72 (2001) 269-275.
4. **Ákos Fürcht**, Antal Tungler, Sándor Szabó, *n-Octane reforming over modified catalysts: Effect of regeneration on the catalyst performance*, Reaction Kinetics and Catalysis Letters, 76 (2002) 227-233.
5. **Ákos Fürcht**, Antal Tungler, Sándor Szabó, *Modification of reforming platinum catalysts by metal adsorption*, Oral presentation, Catalysis and Adsorption in Fuel Processing and Environmental Protection, Kudowa Zdrój, Poland, 1999.
6. **Ákos Fürcht**, Antal Tungler, Sándor Szabó, *Modification of reforming platinum catalyst by adsorbed metals*, Poster, 5th Pannonian International Symposium on Catalysis, Kazimierz Dolny, Poland, 2000.

Other publications:

7. Antal Tungler, **Ákos Fürcht**, Zsolt Pál Karancsi, Gábot Tóth, Tibor Máthé, László Hegedüs, Ákos Sándi, *Diastereoselective and enantioselective heterogeneous catalytic hydrogenation of aminocinnamic acid derivatives*, Journal of Molecular Catalysis A: Chemical, 139 (1999) 239-244.
8. Antal Tungler, László Hegedüs, Karina Fodor, Gabriella Farkas, **Ákos Fürcht**, Zsolt Pál Karancsi, *Reduction of dienes and polyenes*, in Zvi Rappoport (ed.), The chemistry of dienes and polyenes, Vol 2, John Wiley & Sons, Chichester, 2000, p. 991-1028.