Comment

Comment on Heterogeneous catalysis since Berzelius: some personal reflections

[by M.W. Roberts]

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As scientists who have been active in the field of catalysis and particularly in industrial catalysis for over 60 years, we have read M.W. Roberts' article on heterogeneous catalysis in Volume 67, No. 1 (2000) of *Catalysis Letters* with interest. While as stated it is a personal view reflecting the author's interests and prejudices, it is also a valuable contribution to the history of catalysis, a contribution which deserves a few additions, corrections and comments.

Eugene Houdry formed the Houdry Process Corporation in the US jointly with Sun Oil Company and Socony Mobil Oil Company. He contributed greatly to applied catalysis, stimulating much fundamental research and his work was a major driving force for many years. He pioneered the use of clay cracking catalysts and also the engineering of a continuous unit operation. It should also be mentioned that among many other inventions, he first proposed and demonstrated a platinum on support emission control catalyst for internal combustion engines.

The Houdry fixed bed (and later fluid bed) units produced a much higher octane number gasoline than other gasolines available at the time. Using acid-treated clays (very different from Bergius' coal hydrogenation catalysts), the Houdry units provided the large volume high octane base stock into which alkylate and to some extent cumene was blended. The resulting high octane aviation fuel contributed to the victory of the Royal Airforce during the crucial Battle of Britain in World War II. Given these accomplishments, a picture of Eugene Houdry would have been appropriate.

Catalytic reforming of naphtha, barely mentioned in the article, was another milestone which stimulated fundamental research and a picture of Vladimir Haensel would have been appropriate. Prior to the use of platinum–alumina catalysts naphthene dehydrogenation with supported molybdena catalysts had been in commercial operation. The dehydrogenation of methylcyclohexane was important during the war for toluene (and TNT) production. Almost simultaneously with Platforming, two other processes using platinum catalysts were introduced. Frank Ciapetta used a silica–alumina support to supply the needed acid function. Mills, Heinemann, Milliken and Oblad (Ind. Eng. Chem. 45 (1953) 130) demonstrated the concept of dual functional catalysts, possessing separate metal and acid sites, with reaction intermediates moving from one site to the other, permitting isomerization and aromatization as well as dehydrogenation to proceed. In contrast to Roberts' statement, a very substantial octane number boost was obtained which in fact justified the large scale application of Platforming, the major surviving process. As a valuable by-product large volumes of hydrogen were produced for such applications as hydrocracking and hydrodesulfurization. The latter is another important process not described in Roberts' industrial section. Many scientific advancements associated with the concept of multifunctional catalysis derived from these processes.

M.W. Roberts gives deserved credit to Charles Thomas (who at the time was at UOP, not Sun Oil Co.) for describing (in late 1949) the nature of the acidity of cracking catalysts. It can, however, be disputed whether he was the first person to do so. Milliken, Mills and Oblad presented pertinent similar information simultaneously or prior to Thomas at the San Francisco meeting of the American Chemical Society in April 1949 as well as at the 1949 Gordon Research Conference and at the Faraday Society meeting on Catalysis. Tamele described in 1950 extensive work done by Shell workers on using amines to define the acidity of silica–alumina catalysts. Hansford (in *Heterogeneous Catalysis*, ACS Symposium Series, Vol. 222, eds. B.H. Davis and W.P. Hettinger (1982) p. 247) notes that the structure proposed by Tamele gives "...a similar, but probably better picture..." of the reasons for acidity than Hansford's 1947 proposal. Some of the early concepts can be found in the above mentioned book *Heterogeneous Catalysis*.

In Roberts' discussion of shape selective catalysts no mention is made of ZSM-5, the most widely used shape selective zeolite which enabled the conversion of methanol to gasoline, improved xylene isomerization, ethylbenzene synthesis and many other reactions which again led to substantial fundamental work.

The chapter on "Industrial Developments" contains a valuable table (is it new or what is the reference?) which lists numerous developments which have not been discussed elsewhere in the article though they have driven much basic research. A notable omission from the table is polymerization with metallocenes or single site catalysts.

Overall the industrial importance and the often empirical first discovery of catalysts and of catalytic reactions appear to be somewhat shortchanged in Roberts' article. A more balanced picture of the interplay of empirical industrial and fundamental research would have been desirable.