A SURVEY OF LITERATURE FOR THE PREPARATION, ACTIVATION AND TESTING OF PRECIPITATED IRON FISCHER-TROPSCH CATALYSTS

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I.   INTRODUCTION

Catalyst preparation and activation has been more of an art than a science. For widely used catalysts, preparative techniques have been developed by an empirical approach. In many instances, there is little agreement about the properties and facets of the product which contribute to and define its quality.

Because of ease of operations and cost considerations, precipitation from an aqueous solution of an appropriate metal salt has become the most widely used method for preparing metal oxide catalysts. This is frequently true even when the oxide form of the catalyst will not be utilized under reaction conditions. For instance, the Mo or W based hydrotreating catalyst is first obtained in the oxide form and then converted to the sulfide form during activation. Likewise, a common approach for the preparation of iron based Fischer-Tropsch Synthesis (FTS) catalysts is to prepare the metal oxide and to then convert the material partially or completely to a carbide form during activation and/or use. For these catalysts many procedures have become widely accepted even though, in many cases, the basis for acceptance is not well founded. More importantly, these commonly followed practices frequently do not provide a reliable pathway that permits one to produce at will a catalyst with specified properties.

Waldram (I.1) reported results for a study that was designed to define the relationships between key catalyst production variables and the physical properties of the catalyst end product. These studies were performed on the ICI 52-8LT shift catalyst. This is a co-precipitated, copper oxide/zinc oxide/alumina catalyst, supplied

as a cylindrical pelleted particle 5.4 mm diameter and 3.6 mm long. The

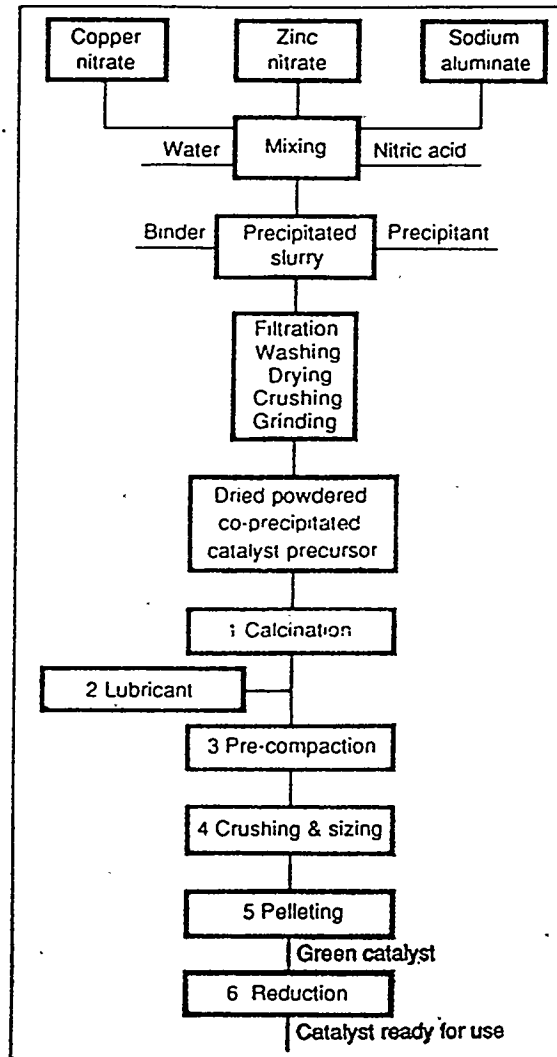manufacturing route for the catalyst is outlined in Figure I.1.

Figure I.1. **Schematic of the process route used to manufacture ICI's 52-8LT shift catalyst (from reference I.1).**

Waldram focused upon six key variables in his study:

- temperature where the calcination process was carried out,
- amount of lubricant added to the powdered catalyst before pre-compaction,
- pre-compaction load,

I.2

- particle size range of the ground pre-compacted catalyst selected for pelleting,
- pellet density, and
- reduction conditions to activate the catalyst.

The catalyst was characterized in terms of physical properties alone.

The 52-8LT catalyst is normally quoted (I.2) as having a pore volume of 0.25 cm^3g^{-1}, a BET surface area of 75 m^2g^{-1} and a mean pore radius of 6.7 nm. Five measures were used to define the physical properties of the catalyst:

- porosity,
- BET surface area,
- tensile strength of the pellet,
- permeability of the porous compact, and
- effective diffusivity within the pellet.

A factorial experimental approach was adopted. Each variable was allowed to assume one of up to four values: these were defined as low, normal high and extra high. Catalyst pellet batches were produced for 50 different combinations of production conditions, and a representative sample from each batch was tested for the chosen physical properties.

For simplicity, only the results from experiments where only one processing variable at a time were allowed to deviate from its normal value are given here. Results for pellet porosity are shown in Figure I.2. The circle represents the mean porosity for a 52-8LT catalyst made under normal production conditions. Low, high and extra high values of each variable, indicated by the letters L, H and EH, affect pellet porosity in the manner illustrated. Ideally, the porosity for L and H should straddle the circle representing the normal conditions as, for example, in the case of powder size pellet density or amount of lubricant. However, because of experimental

I.3

inaccuracies and variation in pellet properties between different samples, there is

sometimes an offset in values as is the situation with calcination temperature. Ignoring

the effect of reduction, where porosity decreases by a factor of 2, the ratio of

maximum to minimum porosities shown in Figure I.2 is 1.5.
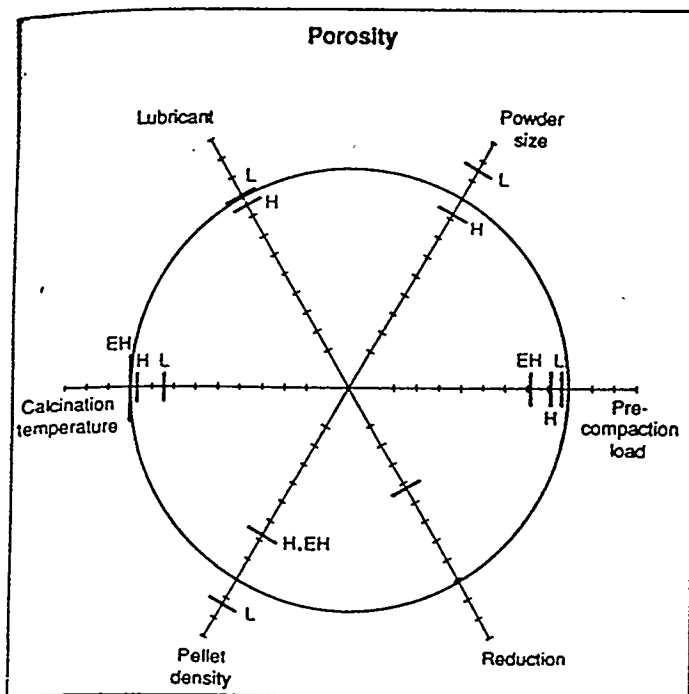
Figure I.2. **The relationship between pellet porosity and key production variables (from reference I.1).**

Alterations in pellet effective diffusivity are shown in Figure I.3. The magnitude

of these variations is 8.0 and requires a different scale of presentation. Comparison of

Figures I.2 and I.3 makes it clear that effective diffusivity is most influenced by

variations in the key processing variables.

This approach allows one to identify key variables provided one has performed

sufficient scoping studies to have identified the key variables. The following sections

identify key variables in the preparation of precipitated, promoted iron FTS catalysts.

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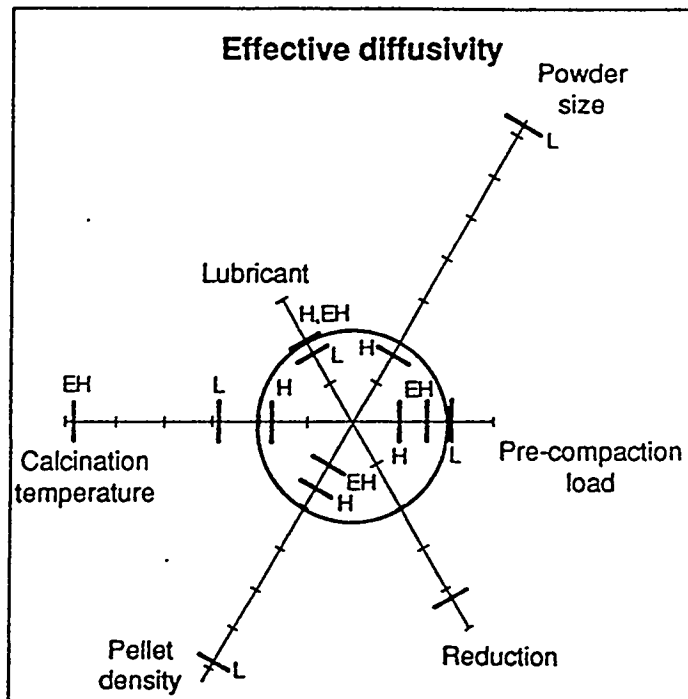
Figure I.3. The relationship between effective diffusivity and key production variables (from reference I.1).

The classification by manufacturing route is the most comfortable and descriptive approach for the catalyst production person. It takes account of all types of natural materials, synthetics, aluminas, silicas, etc. Livingston (I.3.) spoke of this classification in a paper on hydrotreating catalysts, and he divides the manufacturing of catalysts into three general approaches (Table I.1):

- Precipitation or coprecipitation

- Impregnation

- Comixing or compounding

I.5

Table I.1

Process Classifications

Precipitation or Coprecipitation	Impregnation	Comixing or Compounding
Mixing of two or more solutions	Precipitation of support (i.e., Al_2O_3)	Precipitation of major component (i.e., Al_2O_3)
↓	↓	↓
Precipitation	Washing and drying	Washing and drying
↓ (splits to Forming and Drying)	↓	↓
Forming Drying	Forming of Support	Mixing with other metallic salts
↓ ↓	↓	↓
Washing Washing	Activation of support	Forming
↓ ↓	↓	↓
Drying Forming	Impregnation from metallic solutions	Drying
↓ (both to Final Activation)	↓	↓
Final Activation	Drying	Washing or decomposing
	↓	↓
	Washing or decomposing	Final activation
	↓	
	Final activation	

Higginson (I.4) provides a view on the selection of the order of the various process steps: "The manufacturing steps employed for any of the three routes are similar; differences show up in the order in which each of these steps is conducted. Each step has an effect on the final product, so that care must be exercised throughout the

process. For example, to make a nickel alumina catalyst by either the impregnation or comixing route, one would first have to obtain an alumina powder of the proper characteristics and chemical properties. This alumina would be precipitated from some kind of aluminum salt solution, such as sodium aluminate or an acid salt such as aluminum sulfate. Following precipitation, there would have to be extensive washing to remove the undesirable components (sodium present in the aluminate or the anion of the acids used in the solution). A drying step would undoubtedly follow, so that the alumina could be brought to the proper physical consistency for the operations that follow.

- In the impregnation route, the alumina would then be formed via extrusion or tableting into cylindrical shape, or by forming into spheres (beads). In the comixing route, the desired metallic salts would first be mixed with the alumina prior to the forming step.

- For the impregnation route, the formed and activated alumina would be immersed in a solution of the desired metal, while in the comixing route this would already have been accomplished.

- For both routes, a drying step is required, followed by some means of removing the undesired ion from the metal salt impregnating-solution or from the compound mixed in. By choosing the appropriate salt, this can sometimes be accomplished by thermal decomposition just prior to the final activation step."

"The coprecipitation route is in a sense not too dissimilar to the impregnation or comixing routes. From a manufacturing view, it appears to consolidate a number of steps from the other two routes, in that it mixes everything together right at the start; the precipitation is then carried out and the need for double washing and double drying (of the support and final catalyst) is eliminated."

"One of the problems in coprecipitation, however, is that with two or more components present, different rates of precipitation can exist, so that control of the mother liquor concentrations is difficult. Moreover, it is frequently very tough to remove the undesirable ions by washing without also losing some of the desired components in the precipitate."

"The choice of a manufacturing route should not be made solely on the basis of the minimum number of processing steps. One route can offer a much more difficult, if not impossible, manufacturing problem regardless of its apparent advantage in a flow diagram."

"Even more important: while it may be possible to make the chemically same product by all three routes, the final catalysts produced by each route probably will differ markedly in their physical or catalytic performance. While catalysts can all be classified as to their route of manufacture, the actual process selected is really set in the laboratory, where it is determined just how the catalyst must be made in order to yield a product with the desired performance."

REFERENCES - Section I

I.1.   S. Waldram, *Manufacturing Chemistry*, February 1991, pp 28-30.

I.2.   M. V. Twigg, "Catalyst Handbook", 2nd Edition, Wolfe, 1989.

I.3.   J. Y. Livingston, "Hydrotreating Catalyst Properties Do Affect Performance", AIChE meeting, March 12, 1973.

I.4.   G. W. Higginson, *Chem. Eng.*, Sept. 1974, pp 98-104.