OBSERVATIONS ON CATALYSTS FOR CRACKING
AND HYDRO-CARBON CONVERSION

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X-Ray Examinations

Synthetic magnesium silicates have a montarillonite structure, like terrana.

Synthetic aluminum silicates are amorphous under x-rays.

Magnesium silicate catalysts of various manufacture show various sizes of crystallites; the finest crystallites are the most active.

Heavy Metal in Cracking Catalysts

Heavy metal in splitting catalysts produces much gas under cracking conditions, which, as a rule, consists of about 80% H_2. At the same time the splitting deteriorates.

Zinc

Zinc (abt. 10%) on Mg-silicate catalyst already produces considerable gas (90% H_2) at 400-430°C. However, the product is little dehydrogenated; rather, a corresponding part of the oil is coked. Small zinc additions tend to retard the splitting to low-boiling (C_3C_4).

Iron

Terrana produces less splitting than super-filterol, but more gas: iron content.

Alkali Addition to Cracking Catalysts

When alkali (K) is added, the split product contains less low-boiling constituents.

Isomerizing in Cracking

Cracked gasoline from Elwerather oil over Mg-silicate has a motor method octane number of 72-74 @ 25% aromatics and little unsaturated (1% according to H_2SO_4 method, abt. 10% according to iodine number). This causes isomerization.

Nitrogen Sensitivity

Mg-silicate is resistant against 0.1% aniline.

Non-Silicate Catalysts in Cracking

Activated alumina splits considerably less than silicates, but is important for splitting of paraffin to unsaturated middle oils.

Activated carbon splits about as super-filterol, but yields less low-boiling (C_3C_4).

It yields a greater gas volume and in this respect resembles terrana and catalysts containing heavy metals.

Synthetic Carriers for Aromatization

Silicates: While silicates (Al or Mg) precipitated with ammonia are inactive, precipitation with lime or, better still, with Mg-carbonate yielded active silicates, which were improved by the addition of Fe and Mn.

Activated Alumina: yields catalysts which are superior in the processing of products containing cresol, and probably also nitrogen, because the silicate catalysts polymerize compounds containing oxygen and nitrogen too rapidly.

Combined Results of the Study of Catalysts for the Conversion of Hydro-Carbons

The studies of catalysts in various fields, such as splitting, dehydrogenation, isomerization, cyclization and polymerization, may be summarized about as follows:

a). Splitting

The most active basic catalysts (mono-substance catalysts) are silicic acid and carbon. Both indicate almost a pure splitting reaction (without additions), as e.g. the decomposition of a paraffin molecule of average chain length into paraffin + olefin of shorter chain. With these catalysts, the splitting takes place about the middle of the chain and, with the use of a gas oil fraction (mol - wt. = 200), yields gasoline (mol - wt. = 100), which is half paraffinic and half olefinic (iodine number = 100). There is very little gasification here. The new formation of aromatics could not be determined.

By activating SiO_2, or carbon with Al or Mg, the splitting capacity is increased considerably, i.e. with the same conversion either the thruput may be increased, shortening the contact time and yielding the same reaction products as before (paraffin + olefin from paraffin), or the conversion may be increased with the same thruput, yielding other products of reaction. Instead of about equal quantities of paraffin + olefin a parafinnic gasoline (iodine number = 30-60) is produced in this case, because the SiO_2 catalysts activated

with Al or Mg not only split the paraffin but also polymerize the olefin. Both reactions take place successively, splitting as primary and polymerization secondary. Gasification is higher here than in a pure splitting reaction.

In Al or Mg activated SiO_2 catalysts the increased splitting is combined with an isomerization of the split products, which preferably occurs in the shorter split fragments (C_4 and gasoline components to about 150° C). The butane formed in splitting is 80-90% by vol. iso-butane. Isomerization disappears almost entirely above 150° C and the split B-middle oil shows no further indication of a new formation of isomers (good diesel oil).

Natural Fuller's Earth (Bleicherde) (Al or Mg-silicate), activated with acid, behaves like SiO_2-Al or SiO_2-Mg, but is much weaker.

If the Al or Mg in the SiO_2-catalysts is replaced by Fe, gaseous split fragments appear in large volume facilitating the separation of the C atoms formed.

Al_2O_3 is much less active as a splitting catalyst than SiO_2 or C. Al_2O_3 entirely free of alkali will split better than one containing alkali, but the split fragments are gaseous. No appreciable isomerization is noticeable in the split products obtained over Al_2O_3.

b). Dehydrogenation

When operating with a deteriorating catalyst, Al_2O_3 has proved to be the best component in combination with Mo.

The preparation of an especially active form of Al_2O_3 is dependent upon certain conditions, which are being investigated at the present time in cooperation with Dr. V. Füner. Besides precipitation and washing, heating presumably plays an important part.

Al_2O_3 entirely free of alkali will produce high splitting to gaseous products with relatively little formation of aromatics.

Al_2O_3 catalysts formed in an extrusion press show a distinct reduction in activity compared to individual pieces. (Presumably because of their lower contact surface; longer compared to shorter pieces-?).

Partial replacement of Al_2O_3 by Fe_2O_3 will produce distinctly inferior dehydrogenation catalysts. The same is true of catalyst containing MgO instead of Al_2O_3. Both catalysts produce gasoline of high iodine number.

When dehydrogenating with a deteriorating catalyst, heavy gasoline is split, dehydrogenated and cyclizated. Isomerization probably takes place at the same time, even though to a lesser degree. Furthermore, low anti-knock, paraffinic, heavy gasoline components are removed by gasification and olefinic, split gasoline components are saturated at the end of the catalyst layer by weak hydrogenation.

In testing various charges of alumina it was found that strong displacements may occur within the given reactions. When using variously prepared alumina for the 7360 dehydrogenation catalyst, dehydrogenation gasolines were produced from the same feed gasoline, which differed very much from each other, not only in aromatic content, but also in the iodine number. If suitable alumina are used, it should be possible to produce high performance fuels with an iodine number < 4 without further refining.

Pure dehydrogenation of naphthenes to aromatics is least affected by the quality of the alumina. This reaction is comparatively simple. On the contrary, cyclization is very much dependent upon modification of the alumina. This has been shown in experiments with n-heptane, which may be converted into toluene by catalytic cyclization.

c). Cyclization

After many experiments, together with Dr. V. Püner, a combination of Al_2O_3 and Cr has been found to be by far the most active catalyst. These experiments clearly showed that the alumina best suited for n-heptane cyclization are also the best components of dehydrogenation catalysts. They also showed that various modifications of alumina may be vastly different in their cyclization properties.

d). Polymerization

The polymerization properties of SiO_2-Al_2O_3-catalysts have already been mentioned under the heading of "Splitting", which properties may markedly influence the nature of the split products in catalytic cracking. SiO_2-Al_2O_3 may also be used for the polymerization of gaseous olefins into polymer gasoline, instead of the normally used catalysts based on H_2SO_4 or Cupyrophosphate. Compared to the latter catalysts, the polymerization takes place without pressure, although the position of the polymerides in the boiling curve differs from those obtained over P-catalysts; they contain more components in the middle-oil range.