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(54) **Immobilisation of vanadia deposited on catalytic materials during the conversion of oil that contains coke precursors and heavy metals.**

(57) Crude oils or residual fractions from the distillation of petroleum containing substantial amount of metals such as Ni, V, Fe, Cu, Na and high Conradson carbon values are converted to liquid transportation and distillate heating fuels by contacting with a zeolitic containing catalyst containing a metal additive to immobilize the vanadium oxides deposited on the catalyst. As the vanadium oxide level builds up on the catalyst, the elevated temperatures encountered in the regeneration zone cause the vanadia to melt and liquid vanadia to flow. Among other things this vanadia enters the zeolite structure leading to neutralization of acid sites and more significantly to irreversible destruction of the crystalline structure to less active amorphous material (see attached graphs). In addition this melting and flowing of vanadia can, at high levels and for materials with low surface area, also coat the outside of the microscope with liquid, thereby causing coalescence between catalyst particles adversely affecting its fluidization properties. The select metal additives of this invention were chosen so as to form compounds or complexes with vanadia which have melting points above the temperatures encountered in the regeneration zone, thus avoiding zeolite destruction, surface sintering and particle fusion.

These select additives were also chosen with a view of immobilizing vanadia while simultaneously avoiding neutralization of acidic sites. Many additional additives which do affect the melting point of vanadia were eliminated due to this negative effect on catalyst activity. Titania and zirconia, in combination with silica, are known to form acidic catalysts with cracking activity in their own right. Alkaline earth metals can be used to immobilize vanadia but are somewhat detrimental to acidic sites. Selection of additives to immobilize vanadia on RCC catalysts is much more confined in comparison but dealing with the same problem as vanadia deposited on sorbent materials.

The method of addition of the metal additive can be during manufacture, after spray drying or at any point in the reduced crude processing cycle.

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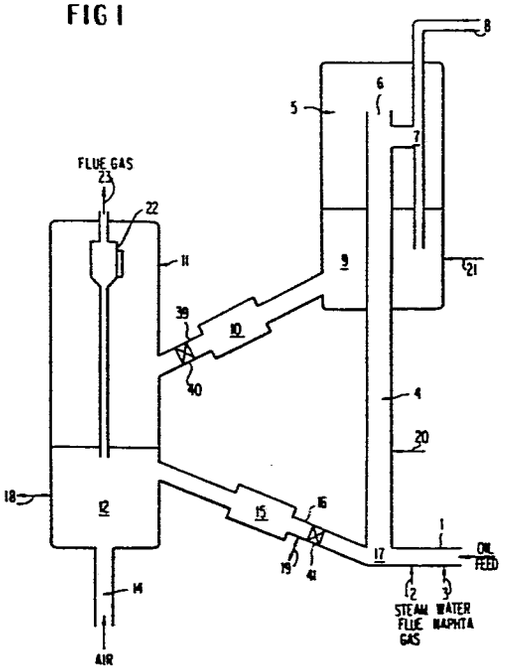
EP 0 073 874 A1

FIG 1


8
6
5
7
FLUE GAS
23
22
11
9
21
39
10
40
4
20
18
12
15
16
1
OIL FEED
19
41
17
2
3
STEAM FLUE GAS
WATER NAPHTA
14
AIR

## BACKGROUND OF THE INVENTION

This invention relates to an improved catalyst, one or more methods for its preparation, one or more methods for treatment, and a process for its use in the conversion of reduced crude or crude oil to liquid transportation and/or heating fuels. More particularly, the invention is related to a catalyst composition comprising a catalytically active crystalline aluminosilicate zeolite uniformly dispersed within a matrix containing a metal additive as a select metal, its oxide or salts to immobilize the vanadium oxide deposited on the catalyst during processing. A further embodiment of this invention is the addition of the metal additive for vanadia immobilization during catalyst manufacture, after spray drying by impregnation, or at any point in the reduced crude processing cycle.

The introduction of catalytic cracking to the petroleum industry in the 1930's constituted a major advance over previous techniques with the object to increase the yield of gasoline and its quality. Early fixed bed, moving bed, and fluid bed catalytic cracking FCC processes employed vacuum gas oils (VGO) from crude sources that were considered sweet and light. The terminology of sweet refers to low sulfur content and light refers to the amount of material boiling below approximately 1,000-1,025°F.

The catalysts employed in early homogeneous fluid dense beds were of an amorphous siliceous material, prepared synthetically

or from naturally occurring materials activated by acid leaching. Tremendous strides were made in the 1950's in FCC technology as to metallurgy, processing equipment, regeneration and new more-active and more stable amorphous catalysts. However, increasing demand with respect to quantity of gasoline and increased octane number requirements to satisfy the new high horsepower-high compression engines being promoted by the auto industry, put extreme pressure on the petroleum industry to increase FCC capacity and severity of operation.

A major breakthrough in FCC catalysts came in the early 1960's, with the introduction of molecular sieves or zeolites, which were incorporated into the matrix of amorphous and/or amorphous/kaolin materials constituting the FCC catalysts of that time. These new zeolitic catalysts, containing a crystalline alumino-silicate zeolite in an amorphous, amorphous/kaolin, matrix of silica, alumina, silica-alumina, kaolin, etc. were at least 1,000-10,000 times more active for cracking hydrocarbons than the earlier amorphous, amorphous/kaolin containing silica-alumina catalysts. This introduction of zeolitic cracking catalysts revolutionized the fluid catalytic cracking process. New innovations were developed to handle these high activities, such as riser cracking, shortened contact times, new regeneration processes, new improved zeolitic catalyst developments, etc.

The overall result (economic) of these zeolitic catalyst developments was to give the petroleum industry the capability

of greatly increasing throughput of feedstock with increased conversion and selectivity while employing the same units without expansion and without requiring new unit construction.

The newer catalyst developments revolved around the development of various zeolites such as type X, Y, faujasite; increased thermal-steam stability through the inclusion of rare earth ions or ammonium via ion-exchange techniques and the development of more attrition resistant matrices.

After the introduction of zeolitic containing catalysts the petroleum industry began to suffer from crude availability as to quantity and quality accompanied by increasing demand for gasoline with increasing octane value. The world crude supply picture changed in the late 1960's - early 1970's. From a surplus of light-sweet crudes the supply situation changed to a tighter supply with an ever increasing amount of heavier crudes with higher sulfur contents. These heavier and high sulfur crudes presented processing problems to the petroleum refiner in that these heavier crudes invariably also contained much higher metals and Conradson carbon values, with accompanying significantly increased asphaltic content.

Fractionation of the total crude to yield cat cracker charge stocks also required much better control to ensure that metals and Conradson carbon values were not carried overhead to contaminate the FCC charge stock.

The effects of metals and Conradson carbon on a zeolitic

containing FCC catalyst have been described in the literature as to their highly unfavorable effect in lowering catalyst activity and selectivity for gasoline production and their equally harmful effect on catalyst life. In particular, we have shown that vanadia, at high concentrations in the feed, is especially detrimental to catalyst life.

As mentioned previously, these heavier crude oils also contained more of the heavier fractions and yielded less or a lower volume of the high quality FCC charge stocks which normally boils below 1025°F, and usually is so processed, as to contain metal contents below 1 ppm, preferably 0.1 ppm and Conradson carbon values substantially below 1.

With this increasing supply of heavier crudes, which meant lowered yields of gasoline and the increasing demand for liquid transportation fuels, the petroleum industry began a search for processing schemes to utilize these heavier crudes in producing gasoline. Most of these processing schemes have been described in the literature. These include Gulf's Gulfining and Union Oil Unifining processes for treating residuum, UOP's Aurabon process, Hydrocarbon Research's H-Oil process, Exxon's Flexicoking process to produce thermal gasoline and coke, H-Oil's Dynacracking and Phillip's Heavy Oil Cracking (HOC). These processes utilize thermal cracking or hydrotreating followed by FCC or hydrocracking operations to handle the higher content of metals (Ni-V-Fe-Cu-Na) and high Conradson carbon values of 5-15. Some of the drawbacks of this type of

processing are as follows: Coking yields thermally cracked gasoline which has a much lower octane value than cat cracked gasoline and is unstable due to the production of gum from diolefins and requires further hydrotreating and reforming to produce high octane product; gas oil quality is degraded due to thermal reactions to produce a product containing refractory polynuclear aromatics, high Conradson carbons are highly unsuitable in catalytic cracking; hydrotreating requires expensive high pressure hydrogen, special alloy multi-reactor system, costly operations, and a separate costly facility for the production of hydrogen.

To better understand the reasons why the industry has progressed along the processing schemes described, one must understand the known and established effects of contaminant metals (Ni-V-Fe-Cu-Na) and Conradson carbon on the zeolitic containing cracking catalysts and the operating parameters of a FCC unit. Metal content and Conradson carbon are two very effective restraints on the operation of a FCC unit or a Reduced Crude Conversion unit towards obtaining maximum conversion, selectivity and life. As metals and Conradson carbon increase, the operating capacity and efficiency of a FCC unit is greatly and finally adversely affected or made impossible, although there is enough hydrogen in the feed to produce only toluene and pentane, if a highly selective catalyst could be devised.

The effect of increasing Conradson carbon is to increase that portion of the feedstock converted to carbon deposited on the catalyst. In typical VGO operations employing a zeolite containing catalyst in a FCC unit, the amount of coke deposited on the catalyst averages around about 4-5 wt% of feed. This coke production has been attributed to four different coking mechanisms, namely, contaminant coke (from metal deposits), catalytic coke (acid site cracking), entrained hydrocarbons (pore structure adsorption - poor stripping) and Conradson carbon. In the case of processing higher boiling fractions, e.g., reduced crudes, residual fractions, topped crude, etc., the coke production based on feed is the summation of the four types present in VGO processing plus the higher Conradson carbon value, higher boiling unstrippable hydrocarbons and coke associated with high nitrogen containing molecules which irreversibly adsorb on the catalyst. Thus, coke production on clean catalyst, when processing reduced crudes, is approximately 4 wt% plus the Conradson carbon value of the feedstock. Thus, there has been postulated, two other types of coke formers present in reduced crudes in addition to the four present in VGO andthey are: 1) adsorbed and absorbed high boiling hydrocarbons not removed by normal-efficient stripping and, 2) high molecular weight nitrogen containing hydrocarbon compounds adsorbed on the catalyst's acid sites. Both of thse two new types of coking producing phenomena add greatly to the complexity of resid processing.

The spent-coked catalyst is brought back to equilibrium activity by burning off the deactivating coke in a regeneration zone in the presence of air and recycled back to the reaction zone. The heat generated during regeneration is removed by the catalyst and carried to the reaction zone for vaporization of the feed and to provide heat for the endothermic nature of the cracking reaction. The temperature in the regenerator is normally limited because of metallurgy limitations and the thermal-steam stability of the catalyst.

The thermal-steam stability of the zeolite containing catalyst is determined by the temperature and steam partial pressure at which the zeolite begins to rapidly lose its crystalline structure to yield a low activity amorphous material. The presence of steam is highly critical and is generated by the burning of adsorbed carboneceous material which has a high hydrogen content. This carboneceous material is principally the high boiling adsorbed hydrocarbons with boiling points as high as 1500-1700°F or above that have a modest hydrogen content and the high boiling nitrogen containing hydrocarbons as well as related porphyrins and asphaltenes.

As the Conradson carbon value of the feedstock increases, coke production increases and this increased load will raise the regeneration temperature; thus the unit is limited as to the amount of feed that can be processed, due to the Conradson carbon content. Earlier VGO units operated with the regenerator at 1150-1250°F. A new development in reduced crude processing,

namely, Ashland Oil's "Reduced Crude Conversion Process" (pending application USSN 094,216) can operate at regenerator temperatures in the range of 1350-1400°F. But even these higher regenerator temperatures place a limit on the Conradson carbon value of the feed at approximately 8. This level is controlling unless considerable water is introduced to further control temperature, which addition is practiced in the RCC process.

The metal containing fractions of reduced crudes contain Ni-V-Fe-Cu, present in porphyrins and asphaltenes. These metal containing hydrocarbons are deposited on the catalyst during processing and are cracked in the riser to deposit the metal or carried over by the spent catalyst as the metallo-porphyrin or asphaltene and converted to the metal oxide during regeneration. The adverse effects of these metals as taught in the literature are to cause non-selective or degradative cracking and dehydrogenation to produce increased coke and light gases such as hydrogen, methane and ethane which affects selectivity, resulting in and poor yield and quality of gasoline and light cycle oil. The increased production of light gases, while impairing the yield and selectivity structure of the process, also puts an increased demand on compressor capacity. The increase in coke production, in addition to its negative impact on yield, also affects catalyst activity-selectivity, greatly increases regenerator air demand and compressor capacity and uncontrollable and dangerous regenerator temperature.

These problems of the prior art have been greatly minimized by the development at Ashland Oil, Inc. of the Reduced Crude Conversion Process, see pending applications 094,092 and 094,216. This new process can handle reduced crudes or crude oils containing high metals and Conradson carbon values previously not susceptible to direct processing. Normally, these crudes require expensive vacuum distillation to isolate suitable feedstocks, and producing as a by product, high sulfur containing vacuum still bottoms. The RCC process avoids all of this.

It was early noted that reduced crudes with high nickel to vanadium levels presented less problems as to catalyst deactivation at high metal on catalyst contents, e.g., 5,000-10,000 ppm, at elevated regenerator temperatures. However, when reduced crudes with high vanadium to nickel levels are processed over zeolite containing catalysts, especially at high vanadium levels on the catalyst, rapid deactivation of the zeolite containing catalyst is noted. This deactivation manifests itself as a rapid loss of the zeolite structure at vanadium levels, above 5,000 ppm approaching 10,000 ppm at elevated regenerator temperatures. Published accounts report that it is impossible to operate at vanadium levels higher than 10,000 ppm because of this factor. To date, this rapid vanadium deactivation at high vanadium levels has only been retarded by lowering regenerator tempertures and increasing the addition rate of virgin catalyst.

## SUMMARY OF THE INVENTION

The problems of the prior art are now overcome in a process employing the catalyst and select metal additive of this invention which allows the processing of a reduced crude or crude oil of high metals - high vanadium to nickel ratio and Conradson carbon value. A reduced crude or crude oil having a high metal and Conradson carbon value is contacted with a zeolitic containing catalyst of high area at tempertures above about 950°F. Residence time of the oil in the riser is below 5 seconds, preferably 0.5 - 2 seconds. The particle size of the catalyst is approximately 20 to 150 microns in size to ensure adequate fluidization properties.

The reduced crude - crude oil is introduced at the bottom of the riser and contacts the catalyst at a temperature of 1200-1400°F to yield a temperature at the exit of the riser in the reactor vessel of approximately 950-1100°F. Along with the reduced crude or crude oil, water, steam, naphtha, flue gas, etc., may be introduced to aid in vaporization and act as a lift gas to control residence time and provides other benefits described in applications #094,216.

Spent catalyst is rapidly separated from the hydrocarbon vapors at the exit of the riser by employing the vented riser concept developed by Ashland Oil, Inc. U. S. Patent No. 4,066,533. During the course of the reaction in the riser, the metal and Conradson carbon compounds are deposited on the catalyst.

After separation in the vented riser, the spent catalyst is deposited as a dense but fluffed bed at the bottom of the reactor vessel, transferred to a stripper and then to the regeneration zone. The spent catalyts is contacted with an oxygen containing gas to remove the carboneous material through combustion to carbon oxides to yield a regenerated catalyst containing less than 0.1 wt% carbon, preferably less than 0.05 wt% carbon. The regenerated catalyst is then recycled to the bottom of the riser where it again joins high metal and Conradson carbon containing feed to repeat the cycle.

At the elevated temperatures encountered in the regeneration zone, the vanadium deposited on the catalyst is converted to vanadium oxides, in particular, vanadium pentoxide. The melting point of vanadium pentoxide is much lower than temperatures encountered in the regeneration zone. Thus, it can become mobile, flow across the catalyst surface, cause pore plugging, particle coalescence, and more importantly, enter the pores of the zeolite, where our studies have shown that it catalyzes irreversible crystalline collapse to an amorphous material.

This application describes a new approach to offsetting the adverse effect of vanadium pentoxide by the incorporation of select metals, metal oxides or their salts into the catalyst matrix during manufacture, by impregnation techniques after spray drying, or added during processing at select points in the unit to affect vanadium immobilization through compound or

complex formation. These compounds or complexes of vanadia with metal additives, serve to immobilize vanadia by creating high melting point complexes or compounds of vanadia which are higher than the temperatures encountered in the regeneration zone.

DESCRIPTION OF PREFERRED EMBODIMENTS

The select catalysts of this invention will include solids of high catalytic activity such as zeolites in a matrix of clays, kaolin, silica, alumina, smectites, and other 2-layered lamellar silicates, silica-alumina, etc. The surface area of these catalysts would preferably be above 100 $m^2/g$, have a pore volume in excess of 0.2 cc/g and a micro-activity or conversion value as measured by the ASTM test method No. D3907-80 of at least or greater than 60, and preferably above 65.

To an aqueous slurry of the raw matrix matrix material and zeolite is mixed the metal additive to yield approximately 1-20 wt% concentration on the finished catalyst. The metal additive can be added in the form of a water soluble compound such as the nitrate, halide, sulfate, carbonate, etc., and/or as the oxide or hydrous gel. This mixture is spray dried to yield the finished promoted catalyst as a microspherical particle of 10-200 microns in size with the active metal additive deposited within the matrix and/or the outer surface of the catalyst particle. Since the concentration of vanadia on the spent catalyst can be as high as 4 wt% of particle weight, the concentration of metal additive will be in the range of 1-6 wt% as the metal element to maintain at least a one to one atomic ratio of vanadium to metal additive at all times. The catalyst can be impregnated with the metal additive after spray drying, employing techniques well known in the art, or as metioned above, an active gelatinous precipitate, such as titania or zirconia gel,

or other gels can be added to the matrix gel prior to spray drying.

It is not proposed to define the exact mechanism for the immobilization of vanadia but the metal additives of this invention will form compounds or complexes with vanadia that have higher melting points than the temperatures encountered in the regeneration zone. The one to one atomic ratio was chosen as minimum, although initially, the metal additive may be considerably above this ratio if it is incorporated in the catalyst prior to use, after which the ratio of additive to vanadia will decrease as vanadia is deposited on the catalyst. Thus, at this one to one ratio (50% vanadium - 50% metal additive) the melting point of the binary reaction product is generally well above operating conditions. Alternatively, the metal additive may be added at the same rate as the metal content of the feed to maintain a one to one atomic ratio. This experimental approach was employed as a practical matter to uncover and confirm suitable metals - metal oxides which can form binary reaction mixtures with vanadium pentoxide so as to yeild a solid compound that has a melting point of approximately 1800°F or higher at this one to one ratio. Search for this high melting point reaction product was initiated to help ensure that vanadia would not melt, flow and enter the zeolite cage structure to cause destruction of the zeolite's crystalline structure as previously described. The metal-metal oxides of this invention include the following groups and their active elements from the Periodic chart of the elements:

TABLE A

| | | M.P. of 1/1 Mixture - °F |
|---|---|---|
| Group IIA | Mg, Ca, Sr, Ba | 1740-1900 |
| Group IIIB | Sc, Y, La | 1800-2100 |
| Group IVB | Ti, Zr, Hf | 1700-2000 |
| Group VB | Nb, Ta | 1800-2000 |
| Group VIIB | Mn | 1750 |
| Group VIII | Fe, Co, Ni | 1600-1800 |
| Group IIIA | In, Tl | 1800 |
| Group VA | Bi | 1800 |
| Group VIA | Te | 1500 |
| Lanthanide Series | Ce, Pr, etc. | 2100 |
| Actinide Series | Th, U, etc. | - |

The reaction of the metal additive with vanadia generally yields a binary reaction mixture. This invention also recognizes that mixtures of these additive metals with vanadia can occur to form high melting ternary and quaternary reaction mixtures, e.g., Barium vanadium titanate, and in addition, these ternary and quaternary reaction mixtures can occur with metals not covered in the Groups above. Further, in this invention we have covered the lower oxidation states of vanadium as well as vanadium pentoxide. However, in processing a sulfur containing feed and regeneration in the presence of an oxygen containing gas vanadium will also likely form such compounds as vanadium sulfides, sulfates, and oxysulfides which can also form binary, ternary, etc., reaction mixtures with the metal additives of this invention as mixed oxides and sulfides.

If the metal additive is not added to the catalyst during manufacuture then it can be added by impregnation technques to the spray dried microspherical catalyst particles. In

addition, the metal additive can be added as an aqueous or hydrocarbon solution or volatile compound during the processing cycle at any point of catalyst travel in the processing unit. This would include but not be limited to addition of an aqueous solution of the inorganic metal salt or a hydrocarbon solution of organo-metallic compounds at the riser wye 17, along the riser length 4, the dense bed 9 in the reactor vessel 5, stripper 10 and 15, regenerator inlet 14, regenerator dense bed 12, or regenerated catalyst standpipe 16.

The selective catalyst of this invention with or without the metal additive is charged to a Reduced Crude Conversion (RCC) type unit as outlined in Figure 1. Catalyst particle circulation and operating parameters are brought up to process conditions by methods well known to those skilled in the art. The equilibrium catalyst at a temperature of 1100-1400°F contacts the reduced crude of high metals and Conradson carbon values at riser wye 17. The reduced crude can contain steam and/or flue gas injected at point 2, water and/or naphtha injected at point 3 to aid in vaporization, catalyst fluidization, and controlling contact time in riser 4. The catalyst and vaporous hydrocarbons travel up riser 4 at a contact time of 0.5-5 seconds, preferably 1-2 seconds. The catalyst and vaporous hydrocarbons are separated in vented riser outlet 6 at a final rection temperature of 950-1100°F. The vaporous hydrocarbons are transferred to cyclone 7 where any entrained catalyst fines are separated and the hydrocarbon vapors are sent to the fractionator via transfer line 8. The spent catalyst is then

transferred to stripper 10 for removal of entrained hydrocarbon vapors and then to regenerator vessel 11 to form dense bed 12. An oxygen containing gas such as air is admitted to the bottom of dense bed 12 in vessel 11 to combust the coke to carbon oxides. The resulting flue gas is processed through cyclones and exits from regenerator vessel 11 via line 13. The regenerated catalyst is transferred to stripper 15 to remove any entrained combustion gases and then transferred to riser wye 17 via line 16 to repeat the cycle.

At such time that the metal level on the catalyst becomes intolerably high such that catalyst activity and selectivity declines, additional catalyst can be added and the deactivated catalyst withdrawn at addition-withdrawal point 18 into dense bed 12 and at addition-withdrawal point 19 into regenerated catalyst standpipe 16. Additions point 18 and 19 can also be utilized to add metal additive promoted catalyst. In the case of a non-promoted catalyst, the metal additive as an aqueous solution or an organo-metallic compound in aqueous or hydrocarbon solvents can be added at addition points 18 and 19 as well as at addition points 2 and 3 on feed line 1, addition point 20 in riser 4, addition point 21 to the bottom of vessel 5 into dense bed 9. The addition of the metal additive is not limited to these locations but can be practiced at any point in the reduced crude - catalyst processing cycle.

The regenerator vessel, as illustrated in Figure 1, is a simple one zone-dense bed type. The regenerator section is not limited to this example but can exist of two or more zones, stacked or side by side arrangement, with internal and/or external circulation transfer lines from zone to zone.

In some of the previous reduced crude processes, acceptable catalyst life and selectivity could be obtained with reduced crude feedstocks containing low levels of metal contamination, and having a high nickel to vanadium ratios. However, as the vanadium content on the catalyst increased or with high vanadium to nickel ratio reduced crude catalyst activity and selectivity decrease rapidly and can only be corrected by economically unacceptable increased catalyst addition rates. Having thus described the observed detrimental effects of vanadium and nickel, the catalyst, metal additive promoters and process of this invention, the following examples are provided to illustrate the effect of vanadia flowing and causing catalyst deactivation through destruction of the zeolite's crystalline structure and steps taken to prevent its occurence.

EXAMPLES

The determination that vanadia deposited on a fluid catalytic cracking catalyst would, under the conditions of elevated temperatures in the regenerator zone, enter the zeolite and catalyze the destruction of its crystalline structure to the less active amorphous material, with subsequent low activity and selectivity, was noted in our reduced crude demonstration unit.

This phenomenum was then evaluated in the laboratory by depositing vanadium and nickel, singly on a specially chosen canadidate catalyst to study its resistance to severe thermal and steaming conditions. As noted in Figure 2 through 5, and Tables 1 and 2, the overall effect of nickel is to neutralize acid sites, and increase coke and gas production but little or no destruction of the zeolite crystalline cage structure was observed. Vanadium on the other hand, was irreversibly destructive. At suitably severe conditions, as the vanadia content was increased, zeolite content decreased proportionally to the point that at approximately the 1 wt% vanadium level the zeolite crystalline structure was completely destroyed after 5 hours at 1450°F in steam leading to a completely deactivated catalyst.

The determination that vanadia deposited on a catalyst would flow and cause coalescence between catalyst particles at regenerator temperatures, and what elements and their salts would

prevent this processs were studied by three methods; namely, the clumping or lump formation technique, vanadia diffusion from or compound formation with a metal additive in a alumina-ceramic crucible, and through spectroscopic studies and differential thermal analyses of vanadia-metal additive mixtures.

CLUMPING TEST

A clay, spray dried to yield microspherical particles in 20-150 micron size, had vanadia deposited upon it in varying concentrations. The clay, free of vanadia, and those containing varying vanadia concentrations were placed in individual ceramic crucibles and calcined at 1400°F in air for two hours. At the end of this time period the crucibles were withdrawn from the muffle furnace and cooled to room temperature. The surface texture and flow characteristics of these samples were noted and the results are reported in Table 3.

TABLE 3

| $V_2O_5$ Concentration - ppm | Surface Texture | Flow Characteristics |
|---|---|---|
| 0 | Free | Free flowing |
| 1,000-5,000 | Surface Clumped | Broke crust-free flowing |
| 5,000-20,000 | Surface Clumped | Total clumping-no flow |

As shown in Table 3, the clay free of vanadia does not form any crust or clumps or fused particles at temperatures encountered in the regenerator section of the process described in this

invention. At vanadia concentrations above 5,000 ppm the clay begins to clump and bind badly and does not flow at all. While liquid at operating temperature, manifestation of this phenomenum is demonstrated by the finding that solidification point in a crucible, or the operating unit is cooled down in order to facilitate entrance to the unit for cleaning out plugged diplegs and other repairs. This phenomenum also makes a turn-around timely and complex, as this material must be chipped out.

CRUCIBLE DIFFUSION - COMPOUND FORMATION

An extension of the clumping test is the use of a ceramic-alumina crucible to determine whether vanadia react with given metal additive. If vanadia does not react with the metal additive or only a small amount of compound formation occurs, then the vanadia has been observed to diffuse through and over the porous alumina walls and deposit as a yellowish to orange deposit on the outside wall of the crucible. On the other hand, when compound formation occurs, there is little or no vanadia deposits on the outside of the crucible wall. Two series of tests were performed. In the first series shown in Table 4, a 1/1 mixture by weight of vanadia pentoxide and the metal additive was placed in the crucible and heated to 1500°F in air for 12 hours. Compound formation or vanadia diffusion was noted.

TABLE 4

1 Part $V_2O_5$ + 1 Part Metal Additive

1500°F - Air - 12 Hours

| Metal Additive | Diffusion of Vanadium | Compound Formation |
|---|---|---|
| Titania | No | Yes |
| Manganese Acetate | No | Yes |
| Lanthanum Oxide | No | Yes |
| Alumina | Yes | No |
| Barium Acetate | No | Yes |
| Copper Oxide | Yes | Partial |

In the second series of tests a vanadia containing material was tested in a similar manner. A one to one ratio by weight of the vanadia containing material and the metal additive were heated to 1500°F in air for 12 hours. The results are shown in Table 5.

TABLE 5

1 Part $V_2O_5$ - Catalyst + 1 Part Metal Additive

1500°F - Air - 12 Hours

| Vanadia Concentration, ppm | Metal Additive | Particle Formation |
|---|---|---|
| 24,000 | None | Yes |
| 24,000 | Calcium Oxide | No |
| 24,000 | Magnesium Oxide | No |
| 24,000 | Manganese Oxide | No |

The study of the capability of certain elements to immobilize vanadium pentoxide was extended to DuPont differential thermal analyses (DTA), X-ray diffraction (XRD) and scanning electron microscope (SEM) instruments. The metal additives studied on the DTA showed that titania, barium oxide, calcium oxide, iron oxide and indium oxide all were excellent additives for the formation of high melting metal vanadates, with melting points of 1800°F or higher. Copper and manganese gave intermediate results with compounds melting at approximately 1500°F. Poor results were obtained with materials such as lead oxide, molybdena, tin oxide, chromia, zinc oxide, cobalt oxide, cadimium oxide and some of the rare earths.

The material reported and produced in Table 5, namely 24,000 ppm vanadia on clay with no metal additive, was fired at 1500°F and then studied in the SEM. The fused particles initially gave a picture of fused particles. However, as the material was continuously bombarded, the fused particles separated due to the heat generated by the bombarding electrons. One was able to notice the melting and flowing of vanadia with the initial single fused particles separating into two distinct microspherical particles.

An example of our XRD work is the identification of the compound formed when manganese acetate reacted with vanadium pentoxide. This compound has been tentatively identified as $Mn_2V_2O_7$.

The matrix material for the catalyst of this invention should possess good hydro-thermal stability. Examples of materials exhibiting relatively stable pore characteristics are alumina, silica-alumina, silica, clays such as kaolin, meta-kaolin, halloysite, anauxite, dickite and/or macrite, and combinations of these materials. Other clays, such as montmorillonite, may be added to increase the acidity of the matrix. Clay may be used in natural state or thermally modified. The preferred matrix of U. S. Patent No. 3,034,994 is a semisynthetic combination of clay and silica-alumina. Preferably the clay is mostly a kaolinite and is combined with a synthetic silica-alumina hydrogel or hydrosol. This synthetic component forms preferably about 15 to 75 percent, more preferably about 20 to 25 percent, of

the formed catalyst by weight. The proportion of clay is such that the catalyst preferably contains after forming, about 10 to 75 percent, more preferably about 30 to 50 percent, clay by weight. The most preferred composition of the matrix contains approximately twice as much clay as synthetically derived silica-alumina. The synthetically derived silica-alumina should contain 55 to 95 percent by weight of silica ($SiO_2$), preferably 65 to 85 percent, most preferably about 75 percent. Although catalysts wherein the gel matrix consists entirely of silica gel are also to be included. After introduction of the zeolite and/or metal additive, the composition is preferably slurried and spray dried to form catalyst microspheres. The particle size of the spray dried matrix is generally in the range of about 5 to 160 microns, preferably 40 to 80 microns.

Generally speaking, the finished catalyst will also contain from 5 to 50% by weight of rare earth or ammonia exchanged sieve of both X or Y variety, preferably about 15-45% by weight and most preferably 20-40% by weight. To further enhance the catalyst, rare earth exchanged sieve may be calcined and further exchanged with rare earth or ammonia to create an exceptionally stable sieve.

Various processes may be used in preparing the synthetically silica-alumina, such as those described in U. S. Patent No. 3,034,994. One of these processes involves gelling an alkali metal silicate with an inorganic acid while maintaining the pH

on the alkaline side. An aqueous solution of an acidic aluminum salt is then intimately mixed with the silica hydrogel so that the aluminum salt solution fills the silica hydrogel pores. The aluminum is thereafter precipitated as a hydrous alumina by the addition of an alkaline compound.

As a specific example of this method of preparation, a silica hydrogel is prepared by adding sulfuric acid with vigorous agitation and controlled temperature time and concentration conditions to a sodium silicate solution. Aluminum sulfate in water is then added to the silica hydrogel with vigorous agitation to fill the gel pores with the aluminum salt solution. An ammonium solution is then added to the gel with vigorous agitation to precipitate the aluminum as hydrous alumina in the pores of the silica hydrogel, after which the hydrous gel is processed, for instance, by separating a part of the water on vacuum filters and then drying, or more preferably, by spray drying the hydrous gel to produce microspheres. The dried product is then washed to remove sodium and sulfate ions, either with water or a very weak acid solution. The resulting product is then dried to a low moisture content, usually less than 25 percent by weight, e.g., 10 percent to 20 percent by weight, to provide the finished catalyst product.

The silica hydrogel slurry with or without alumina in hydrous form may be filtered and washed in gel form to affect purification of the gel by the removal of dissolved salts.

This may enhance the formation of a continous phase in the spray dried microspheric particles. If the slurry is prefiltered and washed and it is desired to spray dry the filter cake, the latter may be reslurried with enough water to produce a pumpable mixure for spray drying. The spray dried product may then be washed again and given a final drying in the manner previously described.

The metal additives to immobilize vanadia includes the metals, their oxides and salts, or organo-metallic compounds of such metals as Mg, Ca, Sr, Ba, Sc, Y, La, Ti, Zr, Hf, Nb, Ta, Mn, Fe, In, Tl, Bi, Te, the rare eaths, and the actinide and Lanthanide series of elements. These promoters or metal additives in the metal element state, may be used in concentration ranges from about 0.5 to 20 percent, more preferably about 1 to 5 percent by weight of finished catalyst.

The catalytically active promoter in the preferred catalyst composition is a crystalline aluminosilicate zeolite, commonly known as molecular sieves. Molecular sieves are initially formed as alkali metal aluminosilicates, which are dehydrated forms of crystalline hydrous siliceous zeolites. However, since the alkali form does not have appreciable activity and alkali metal ions are deleterious to cracking processes, the aluminosilicates are ion exchanged to replace sodium with some other ion such as, for example, ammonium and/or rare earth metal ions. The silica and alumina making up the structure of the zeolite are arranged in a definite crystalline pattern

containing a large number of small uniform cavities interconnected by smaller uniform channels or pores. The effective size of these pores is usually between about 4A and 12A.

The zeolites which can be employed in accordance with this invention include both natural and synthetic zeolites. The natural occurring zeolites include gmelinite, clinoptilolite, chabazite, dechiardite, faujasite, heulandite, erionite, analcite, levynite, sodalite, cancrinite, nepheline, lcyurite, scolicite, natrolite, offertite, mesolite, mordenite, brewsterite, ferrierite, and the like. Suitable synthetic zeolites include zeolites Y, A, L, ZK-4B, B, E, F, H, J, M, Q, T, W, X, Z, ZSM-types, alpha, beta and omega. The term "zeolites" as used herein contemplates not only aluminosilicates but substances in which the aluminum is replaced by gallium and substances in which the silicon is replaced by germanium and also the so called pillared clays more recently introduced.

The zeolite materials utilized in the preferred embodiments of this invention are synthetic faujasites which possess silica to alumina ratios inthe range from about 2.5 to 7.0, preferably 3.0 to 6.0 and most preferably 4.5 to 6.0/ Synthetic faujasites are widely known crystalline aluminosilicate zeolites and common examples of synthetic faujasites are the X and Y types commercially available from the Davison Division W. R. Grace and Company and the Linde Division of Union Carbon Corporation. The ultrastable hydrogen exchanged zeolites, such as Z-14XS and Z-14US from Davison, are also particularly suitable. In addition to faujasites, other preferred types of zeolitic materials

are mordenite and erionite.

The preferred synthetic faujasite is zeolite Y which may be prepared as described in U. S. Patent No. 3,130,007 and U. S. Patent No. 4,010,116, which patents are incorporated hereby by reference. The aluminosilicates of this latter patent have high silica ($SiO_2$) to alumina ($Al_2O_3$) molar ratios, preferably above 4, to give high thermal stability.

The following is an example of a zeolite produced by the silication of clay. A reaction composition is produced from a mixture of sodium silicate, sodium hydroxide, and sodium chloride formulated to contain 5.27 mole percent $SiO_2$, 3.5 mole percent $Na_2O$, 1.7 mole percent chloride and the balance water. 12.6 parts of this solution are mixed with 1 part by weight of calcined kaolin clay. The reaction mixture is held at about 60°F to 75°F for a period of about four days. After this low temperature digestion step, the mixture is heated with live steam to about 190°F until crystallization of the material is complete, for example, about 72 hours. The crystalline material is filtered and washed to give a silicated clay zeolite having a silica to alumina ratio of about 4.3 and containing about about 13.5 percent by weight of $Na_2O$ on a volatile free basis. Variation of the components and of the times and temperatures, as is usual in commercial operations, will produce zeolite having silica to alumina mole ratios varying from about 4 to about 5. Mole ratios above 5 may be obtained by increasing the amount of $SiO_2$ in the reaction mixutre. The sodium form of the zeolite is then exchanged with polyvalent cations to reduce

the $Na_2O$ content to less than about 5 percent by weight, and preferably less than 1.0 percent by weight. Procedures for removing alkali metals and putting the zeolite in the proper form are well-known in the art as described in U. S. Patent Nos. 3,293,192; 3,402,996; 3,446,727; 3,449,070; and 3,537,816; which patents are incorporated herin by reference.

The zeolites and/or the metal additive can be suitably dispersed in matrix materials for use as cracking catalysts by methods well-known in the art, such as those disclosed, for example, in U. S. Patent Nos. 3,140,249 and 3,140,253 to Plank, et al.; U. S. Patent No. 3,660,274 to Blazek, et al.; U. S. Patent No. 4,010,116 to Secor, et al.; U. S. Patent No. 3,944,482 to Mitchell, et al.; and U. S. Patent No. 4,079,019 to Scherzer, et al.; which patents are incorporated herein by reference.

The amount of zeolitic material dispersed in the matrix based on the final fired product should be at least about 10 weight percent, preferably in the range of about 25 to 50 weight percent, most preferably about 35 to 45 weight percent.

Crystalline aluminosilicate zeolites exhibit acidic sites on both interior and exterior surface with the largest proportion to total surface area and cracking sites being internal to the particles within the crystalline micropores. These zeolites are usually crystallized as regularly shaped, discreet particles of approximtely 0.1 to 10 microns in size and, accordingly, this is the size range normally provided by commercial

catalyst suppliers. To increase exterior (portal) surface area, the particle size of the zeolites for the present invention should preferably be in the range of less than 0.1 to 1 micron and more preferably in the range of less than 0.1 micron. The preferred zeolites are thermally stabilized with hydrogen and/or rare earth ions and are steam stable to about 1,650°F.

An example of the effectiveness of the metals of this invention to immobilize vanadium and reduce its destructiveness towards the crystallinity of the zeolite structure is shown in Table 6. A standard FCC catalyst was steamed with and without vanadia, as shown in Run 1 and 2. The presence of vanadium reduces the zeolite content from an intensity of 9.4 down to 3.1. Runs 3 and 4 illustrate the effectiveness of titania and the need for the titania to be present as the vanadia is being deposited on the catalyst. As shown in runs 4, the titanium and vanadium are deposited as organo-metallics, oxidized to remove th hydrocarbon portion of the organo-metallic compound and oxidize the elements to their corresponding oxides. This is then followed by steaming at 1450°F - 5 hrs. During the oxidation and steaming, the titanium is present in at least a one to one ratio for the formation of titanium vanadate which is a high melting solid (see Table A).

TABLE 6

Steaming Performed at 1450°F - 5 Hrs.

V as Vanadium Naphthenate

Ti as Tripropyltitanate

| Standard Catalyst Run # | V ppm | Ti ppm | Ti Addition | Zeolite Intensity |
|---|---|---|---|---|
| 1 | 0 | 0 | - | 9.4 |
| 2 | 5500 | 0 | - | 3.1 |
| 3 | 5500 | 5500 | Ti added after V regeneration | 3.5 |
| 4 | 5500 | 5500 | Ti added with V compound Then regenerated | 8.2 |

We Claim,

1) A process for the conversion of reduced crude or crude oil to liquid transportation and light heating oil fuels having a substantial metal and Conradson carbon content, the improvement of which comprises contacting said feedstock with a metal additive promoted catalyst to immobilze vanadium compounds, having a catalytic cracking micro-acitivty value of at least 50, preferably above 60, at elevated temperatures in a riser fluidized transfer zone followed by rapid separation of the gaseous products and spent catalyst, subjecting said spent catalyst to regeneration in the presence of an oxygen containing gas, with recycle of the regenerated catalyst to the riser transfer zone for conversion of fresh reduced crude or crude oil.

2) The process of Claim 1 wherein the reduced crude or crude oil contains 200 ppm or less of metals consisting of nickel, vanadium, iron and copper and the Conradson carbon value is 10 wt% or less.

3) The process of Claim 1 wherein said catalyst consists of 10-40 wt% of a crystalline alumino-silicate zeolite dispersed in an amorphous inert solid oxide matrix containing a metal additive to immobilize vanadium compounds.

4) The process of Claim 1 wherein the metal additive is a water soluble inorganic metal salt or a hydrocarbon soluble organo-metallic compound.

5) The process of Claim 1 wherein the metal additive to immobilize vanadium compounds deposited on the catalyst will include the following elements: Mg, Ca, Sr, Ba, Sc, Y, La, Ti, Zr, Hf, Nb, Ta, Mn, Fe, In, Tl, Bi, Te, the lanthanide and actinide series of elements.

6) The process of Claim 1 wherein the metal additive can react with vanadium compounds to form binary metal vanadates and their mixtures to form ternary and quaternary compounds or complexes.

7) The process of Claim 1 wherein the metal additive is present in the catalyst in about 1-20 wt%, preferably 1-6 wt% of finished catalyst.

8) The process of Claim 1 wherein the water soluble metal additive is a salt consisting of the halides, nitrates, sulfates, sulfites, carbonates.

9) The process of Claim 1 wherein the hydrocarbon soluble metal additives are alcoholates, esters, phenolates, naphthenates, carboxylates, dienyl sandwich compounds.

10) The process of Claim 1 wherein the metal additive to immobilize vanadium compounds is tetraisopropyl titanate.

11) The process of Claim 1 wherein the metal additive to immobilize vanadium compounds is titanium tetrachloride.

FIG. 1

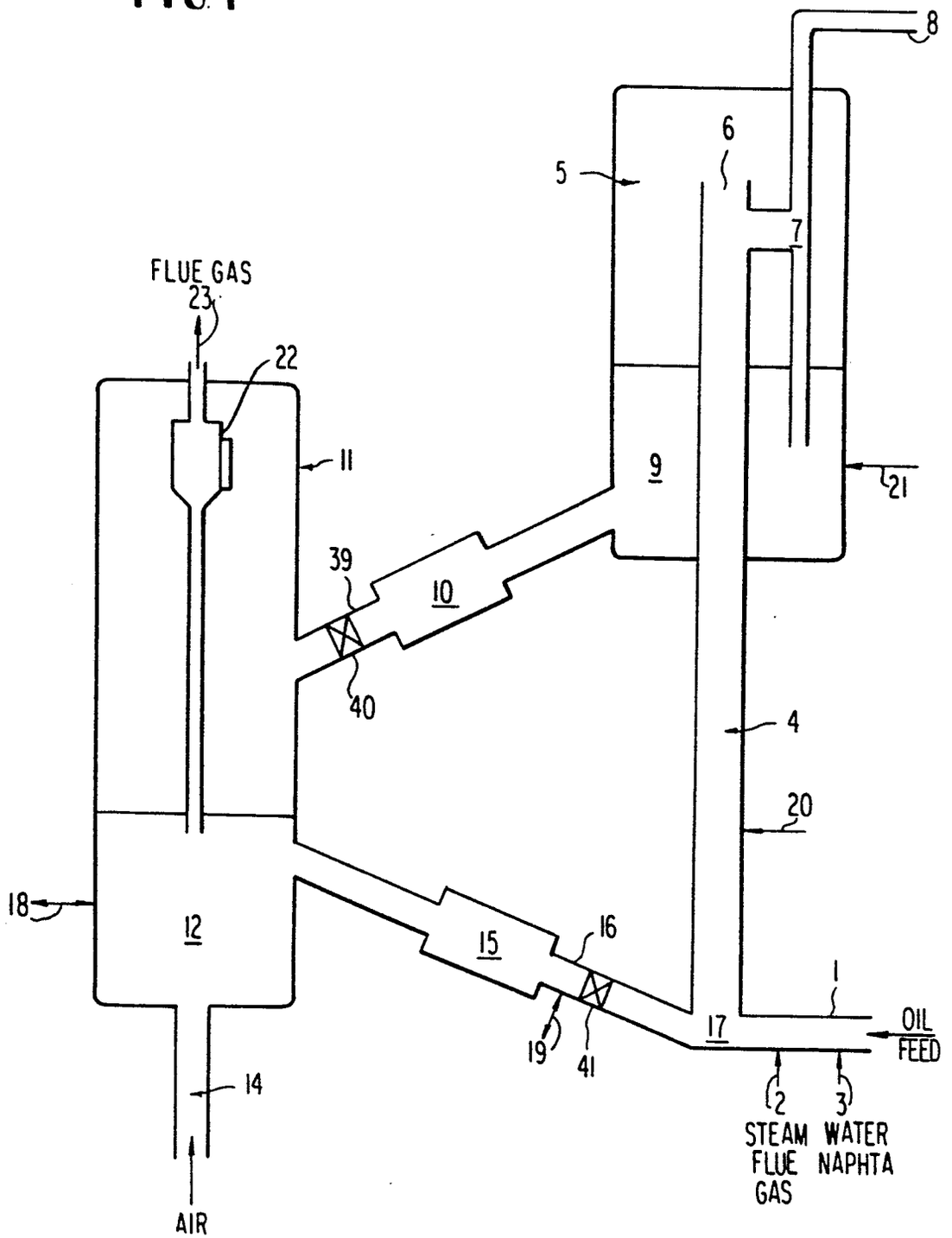

8
6
5
7
FLUE GAS
23
22
11
9
21
39
10
40
4
20
18
12
15
16
1
OIL
FEED
19
41
17
14
2
3
STEAM
FLUE
GAS
WATER
NAPHTA
AIR

FIG. 2

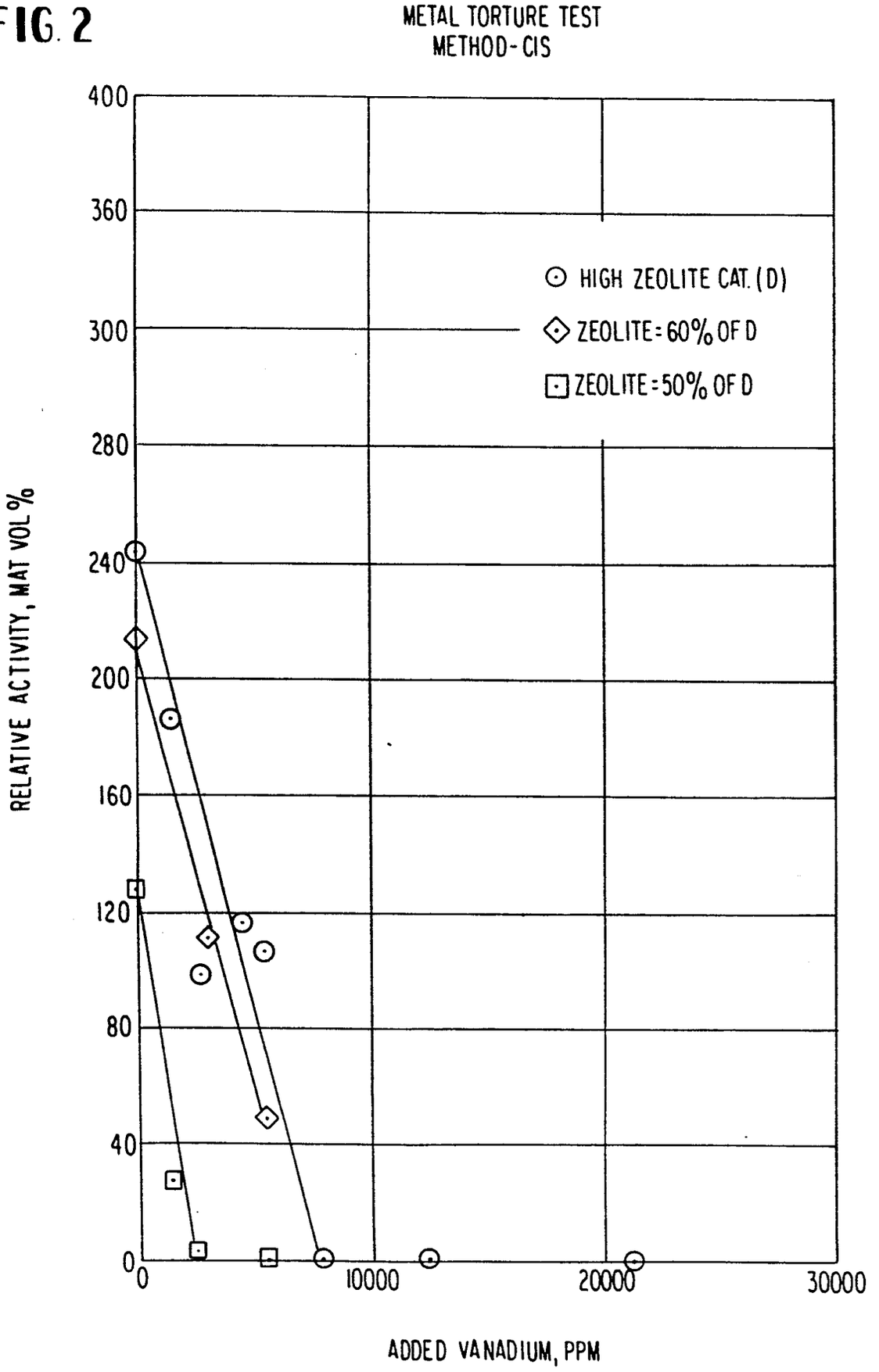

METAL TORTURE TEST
METHOD-CIS
HIGH ZEOLITE CAT. (D)
ZEOLITE=60% OF D
ZEOLITE=50% OF D
RELATIVE ACTIVITY, MAT VOL %
400
360
300
280
240
200
160
120
80
40
0
0
10000
20000
30000
ADDED VANADIUM, PPM

FIG. 3

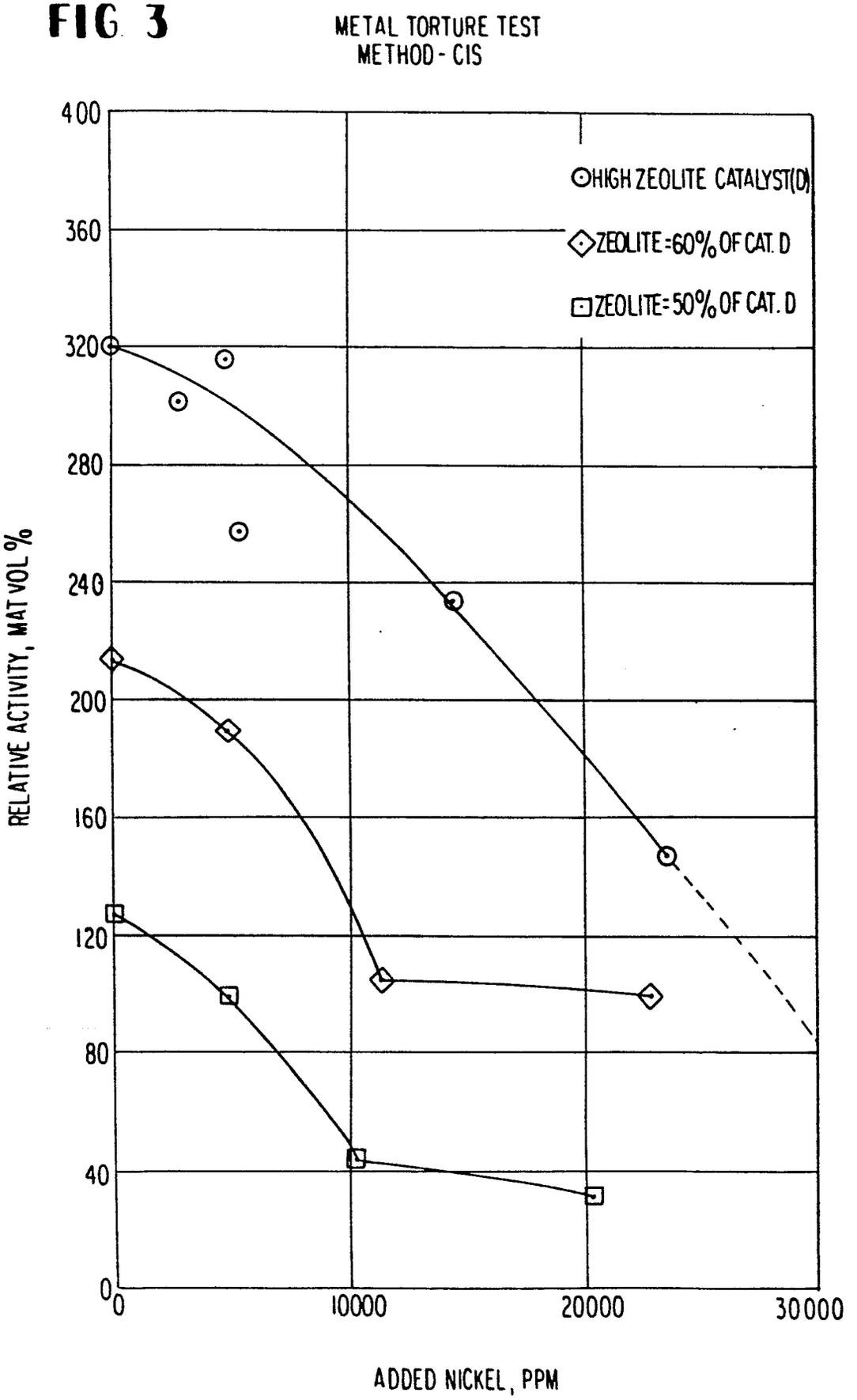

METAL TORTURE TEST
METHOD - CIS
HIGH ZEOLITE CATALYST(D)
ZEOLITE=60% OF CAT. D
ZEOLITE=50% OF CAT. D
RELATIVE ACTIVITY, MAT VOL %
400
360
320
280
240
200
160
120
80
40
0
0
10000
20000
30000
ADDED NICKEL, PPM

FIG. 4

METAL TORTURE TEST
METHOD- CIS
VANADIUM EFFECTS

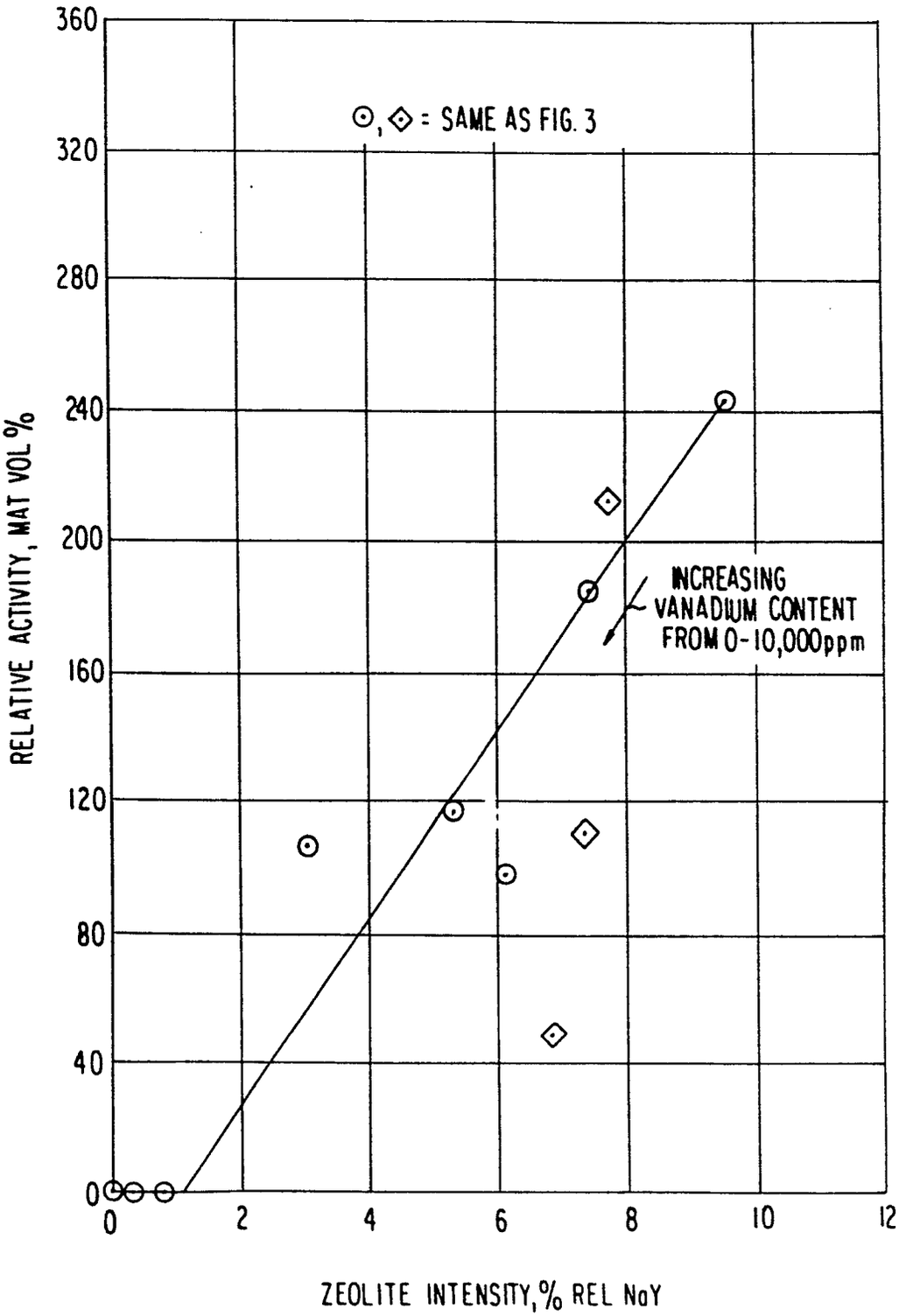
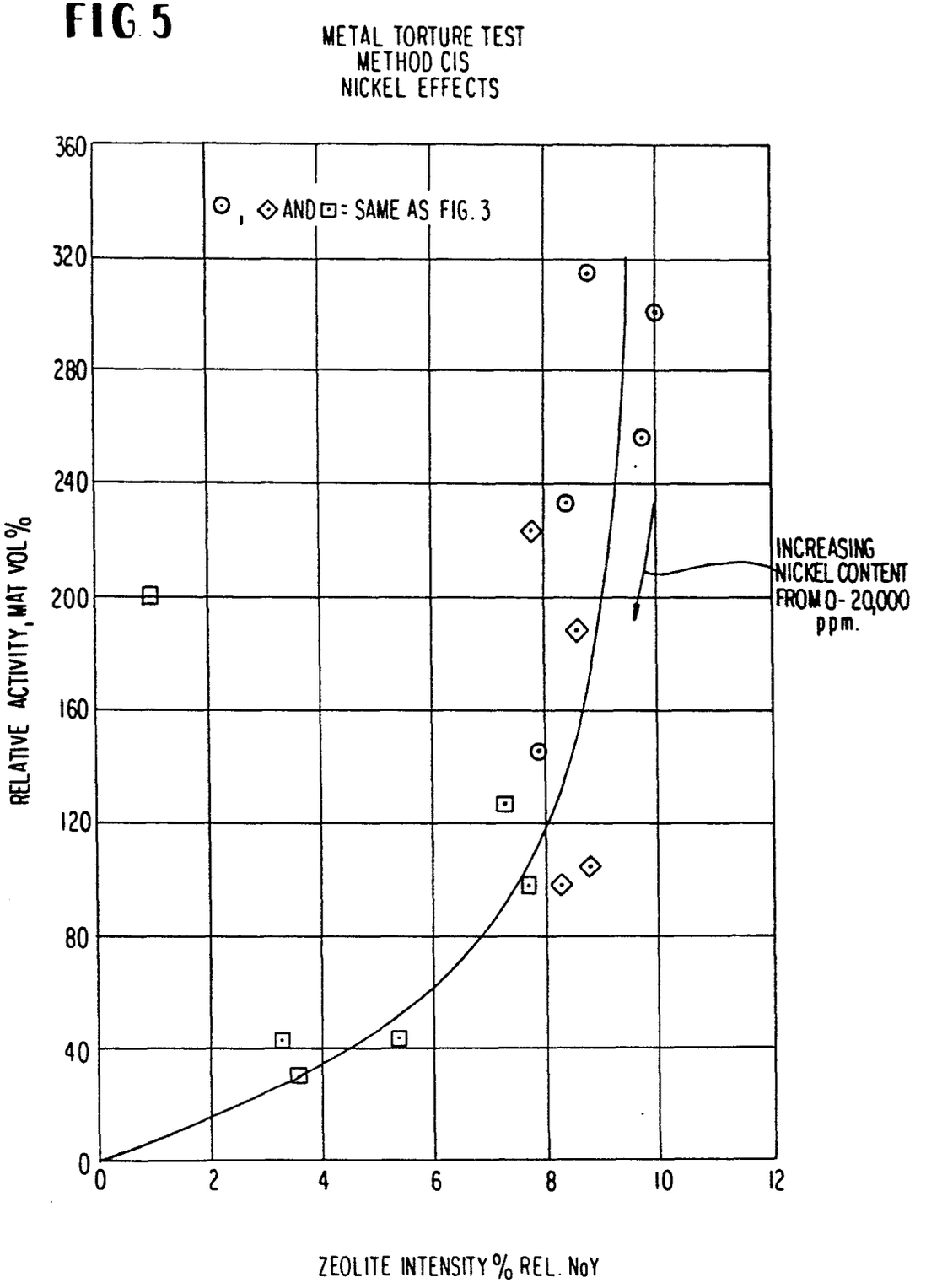


FIG. 5


METAL TORTURE TEST
METHOD CIS
NICKEL EFFECTS
⊙, ◇ AND ⊡ = SAME AS FIG. 3
INCREASING NICKEL CONTENT FROM 0-20,000 ppm.
RELATIVE ACTIVITY, MAT VOL %
ZEOLITE INTENSITY % REL. NoY
0
40
80
120
160
200
240
280
320
360
0
2
4
6
8
10
12

## METAL TOLERANCE
## TORTURE TEST METHOD/3-CIS

| SAMPLE NO. | ADDED METAL TYPE WT% IB | SURFACE ARE $m^2/g$ | ZEOLITE %NaY | MAT DATA | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | REL. ACT. | CONV. VOL.% | CONV. WT% | GAS WT% | COKE WT% | GASO. WT% | CPF | HPF |
| B600-159 | | | | | | | | | | | |
| 1 | Ni 0.48 | 115 | 7.7 | 98 | 74.8 | 73.4 | 16.6 | 7.1 | 49.6 | 2.5 | 17.0 |
| 2 | Ni 1.06 | 77 | 3.3 | 74 | 72 | 65.4 | 15.6 | 3.8 | 45.9 | 1.4 | 12.1 |
| 3 | Ni 2.06 | 66 | 3.6 | 55 | 70 | 62.1 | 13.5 | 3.0 | 45.6 | 1.3 | 15.1 |
| 4 | V 0.14 | 55 | 4.4 | 52 | 69 | 65.2 | 16.7 | 1.2 | 47.3 | 0.5 | 2.0 |
| 5 | V 0.24 | 35 | 2.2 | 8 | 52 | 49.9 | 12.2 | 0.5 | 37.2 | 0.4 | 2.5 |
| 6 | V 0.61 | 11 | 0.0 | 0 | 2 | 12.2 | 5.0 | 0.2 | 7.0 | 0.8 | 7.1 |
| 19 | V 1.79 | 11 | 0.0 | 0 | 3 | 9.5 | 5.2 | 0.4 | 3.9 | 1.4 | 10.3 |
| 21 | CONTROL | 73 | 5.4 | 44 | 68 | | | | | 0.9 | 0.4 |
| | CONTROL | 84 | 7.3 | 127 | 77 | 73.0 | 16.0 | 2.9 | 55.0 | 0.9 | 0.8 |

FIG 6

**FIG. 7**

METAL TOLERANCE
TORTURE TEST METHOD/3-CIS

| SAMPLE NO | ADDED METAL TYPE | WT% IB | SURFACE AREA m2/g | ZEOLITE %NaY | MAT DATA REL. ACT. | CONV. VOL.% | CONV. WT% | GAS WT% | COKE WT% | GASO. WT% | CPF | HPF |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| B600-159- | | | | | | | | | | | | |
| 10 | Ni | 0.49 | 240 | 8.6 | 456 | 88 | 78.3 | 17.6 | 5.7 | 55.0 | 1.3 | 11.5 |
| 11 | Ni | 1.13 | 239 | 8.8 | 188 | 81 | 75.0 | 19.2 | 4.9 | 50.8 | 1.5 | 13.8 |
| 12 | Ni | 2.27 | 219 | 8.3 | 186 | 81 | 74.4 | 16.9 | 7.2 | 50.2 | 2.1 | 28.0 |
| 13 | V | 0.13 | 238 | 8.1 | 341 | 86 | 80.5 | 22.6 | 3.6 | 54.3 | 0.9 | 2.7 |
| 14 | V | 0.34 | 213 | 7.4 | 192 | 81 | 75.5 | 20.4 | 3.0 | 52.0 | 0.9 | 9.7 |
| 15 | V | 0.55 | 211 | 6.9 | 97 | 74.7 | 68.7 | 15.2 | 4.6 | 49.0 | 1.7 | 16.6 |
| 20 | V | 1.11 | 159 | 3.5 | 27 | 63 | 58.4 | 11.8 | 4.6 | 42.0 | 2.3 | 31.9 |
| 22 | CONTROL | | 143 | 4.8 | | | | | | | | |
| | CONTROL | | 242 | 7.8 | 213 | 82 | 80.0 | 21.6 | 4.8 | 53.6 | 1.3 | 1.3 |

**FIG 8**

STEAMING PERFORMED AT 1450°F - 5 HRS.
V AS VANADIUM NAPHTHENATE Ti AS TRIPROPYLTITANATE

| STANDARD CATALYST RUN # | V ppm | Ti ppm | Ti ADDITION | ZEOLITE INTENSITY |
|---|---|---|---|---|
| 1 | 0 | 0 | - | 9.4 |
| 2 | 5500 | 0 | - | 3.1 |
| 3 | 5500 | 5500 | Ti ADDED AFTER V REGENERATION | 3.5 |
| 4 | 5500 | 5500 | Ti ADDED WITH V COMPOUND THEN REGENERATED | 8.2 |

FIG. 9

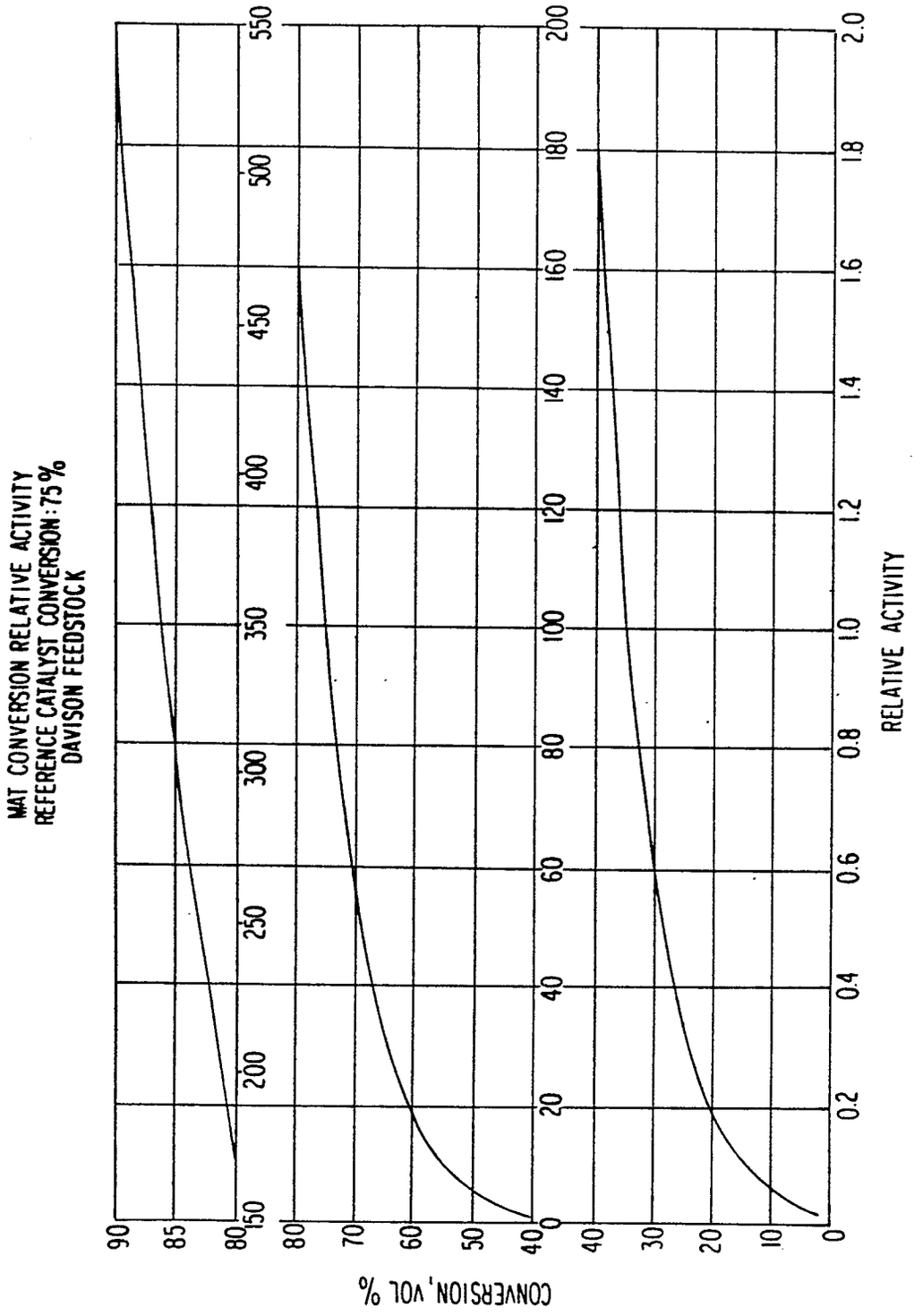

MAT CONVERSION RELATIVE ACTIVITY
REFERENCE CATALYST CONVERSION: 75%
DAVISON FEEDSTOCK
CONVERSION, VOL %
RELATIVE ACTIVITY
90
85
80
150
80
70
60
50
40
0
40
30
20
10
0
550
500
450
400
350
300
250
200
200
180
160
140
120
100
80
60
40
20
0
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0

FIG 10

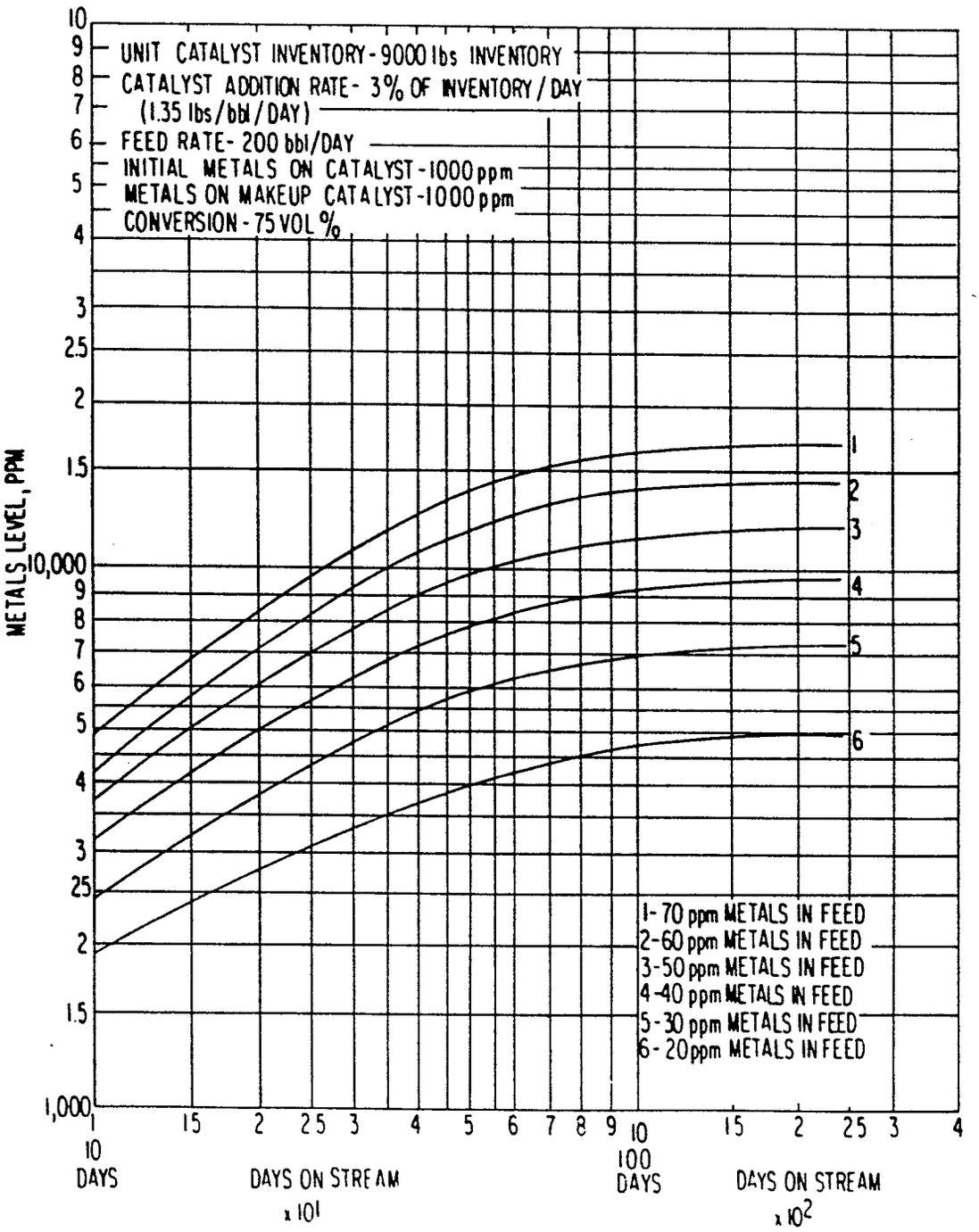
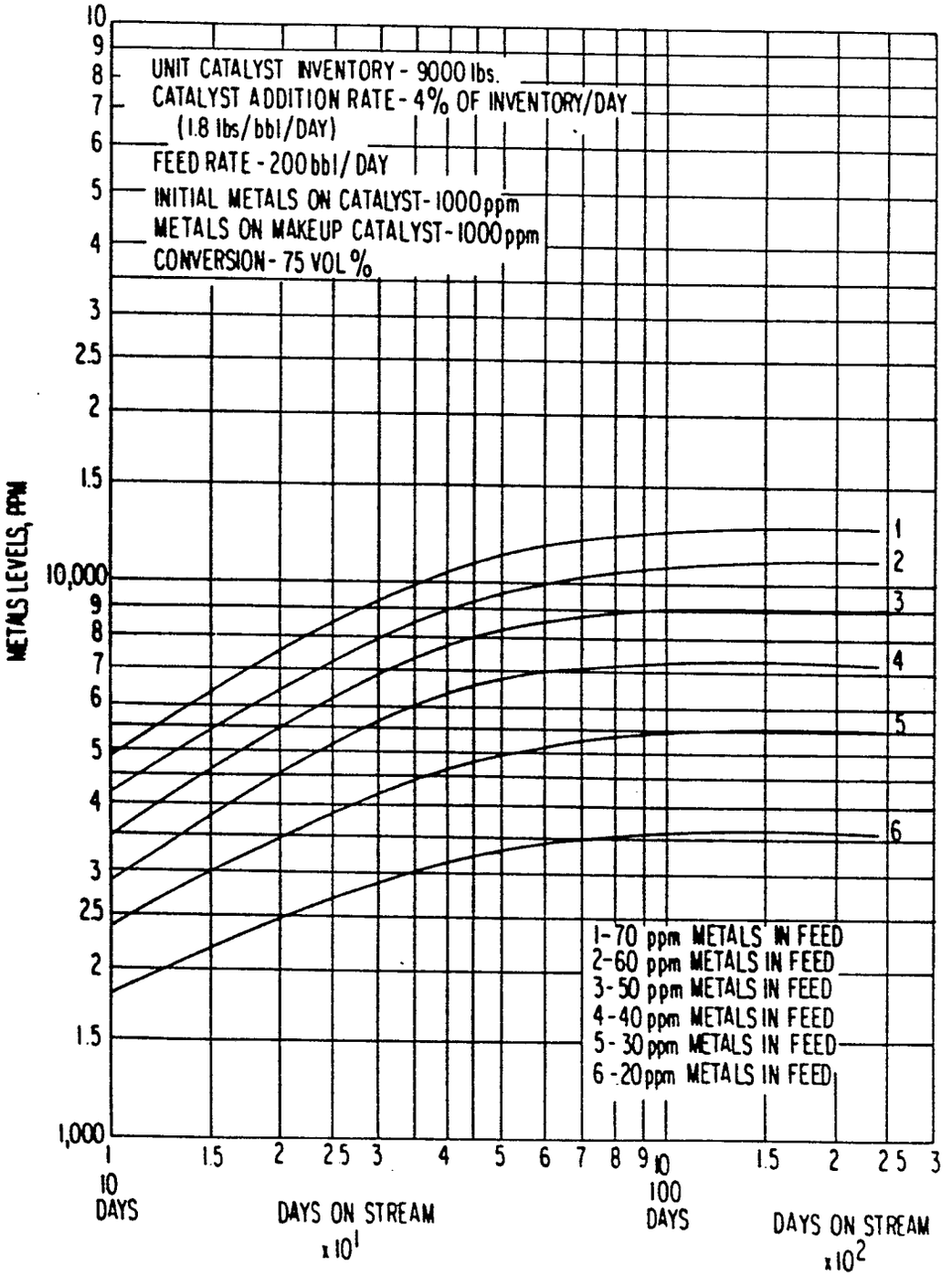

UNIT CATALYST INVENTORY - 9000 lbs INVENTORY
CATALYST ADDITION RATE - 3% OF INVENTORY / DAY
(1.35 lbs / bbl / DAY)
FEED RATE - 200 bbl/DAY
INITIAL METALS ON CATALYST - 1000 ppm
METALS ON MAKEUP CATALYST - 1000 ppm
CONVERSION - 75 VOL %
METALS LEVEL, PPM
1 - 70 ppm METALS IN FEED
2 - 60 ppm METALS IN FEED
3 - 50 ppm METALS IN FEED
4 - 40 ppm METALS IN FEED
5 - 30 ppm METALS IN FEED
6 - 20 ppm METALS IN FEED
10 DAYS
DAYS ON STREAM x 10¹
100 DAYS
DAYS ON STREAM x 10²

FIG II


UNIT CATALYST INVENTORY - 9000 lbs.
CATALYST ADDITION RATE - 4% OF INVENTORY/DAY
(1.8 lbs/bbl/DAY)
FEED RATE - 200 bbl/DAY
INITIAL METALS ON CATALYST - 1000 ppm
METALS ON MAKEUP CATALYST - 1000 ppm
CONVERSION - 75 VOL %
1 - 70 ppm METALS IN FEED
2 - 60 ppm METALS IN FEED
3 - 50 ppm METALS IN FEED
4 - 40 ppm METALS IN FEED
5 - 30 ppm METALS IN FEED
6 - 20 ppm METALS IN FEED
METALS LEVELS, PPM
10,000
1,000
10 DAYS
DAYS ON STREAM x 10¹
100 DAYS
DAYS ON STREAM x 10²

European Patent Office

# EUROPEAN SEARCH REPORT

0073874
Application number

EP 82 10 1625

## DOCUMENTS CONSIDERED TO BE RELEVANT

| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | CLASSIFICATION OF THE APPLICATION (Int Cl ³) |
|---|---|---|---|
| X,Y | WO-A-7 901 170 (PHILLIPS PETROLEUM) *Claims 1-7,10-12,22-28; page 4, lines 1-36; page 1, lines 6-13* | 1-4,6-9 | C 10 G 11/18<br>C 10 G 11/04<br>B 01 J 29/06<br>B 01 J 29/28 |
| X | US-A-4 218 337 (McKAY) *Claims 1-5* | 1-9 | |
| X | US-A-4 083 807 (McKINNEY) *Column 5, lines 14-24; claims 1-4* | 1-9 | |
| X | US-A-4 141 858 (McKAY) *Claims 1-9* | 1-3,6-8 | |
| X | US-A-4 256 564 (ROBERTS et al.) *Claims 1-17; column 2, lines 14-26; column 3, lines 43-59* | 1-9 | TECHNICAL FIELDS SEARCHED (Int. Cl. ³)<br>C 10 G |
| X | US-A-3 977 963 (READAL et al.) *Claims 1-12; column 1, lines 18-41; column 2, lines 3-44* | 1-9 | |
| X | EP-A-0 009 819 (PHILLIPS PETROLEUM) *Claims 1-10; page 4, lines 23-27; page 6, line 27 to page 8, line 15* | 1-9 | |

-/-

The present search report has been drawn up for all claims

| Place of search | Date of completion of the search | Examiner |
|---|---|---|
| THE HAGUE | 21-12-1982 | MICHIELS P. |

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO Form 1503 03.82

European Patent Office

# EUROPEAN SEARCH REPORT

0073874
Application number

EP 82 10 1625



## DOCUMENTS CONSIDERED TO BE RELEVANT

| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | CLASSIFICATION OF THE APPLICATION (Int. Cl. ³) |
|---|---|---|---|
| Y | FR-A-2 335 582 (STANDARD OIL) *Claims 1,5,7,10,14,15,17,18,26; page 8, line 26 to page 9, line 21, examples* | 1-11 | |
| Y | US-A-3 696 025 (CHESSMORE et al.) *Claims 1-3; column 3, lines 55-74* | 1,3,10-11 | |
| Y | GB-A-2 007 107 (GRACE) *Column 1, lines 5-12; claims 1-15* | 1-11 | |
| | | | TECHNICAL FIELDS SEARCHED (Int. Cl. ³) |

The present search report has been drawn up for all claims

| Place of search | Date of completion of the search | Examiner |
|---|---|---|
| THE HAGUE | 21-12-1982 | MICHIELS P. |

CATEGORY OF CITED DOCUMENTS

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T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

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