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CA 2079164 C 2002/11/26

(11)(21) 2 079 164

(12) BREVET CANADIEN
CANADIAN PATENT

(13) C

(22) Date de dépôt/Filing Date: 1992/09/25

(41) Mise à la disp. pub./Open to Public Insp.: 1993/04/16

(45) Date de délivrance/Issue Date: 2002/11/26

(30) Priorités/Priorities: 1991/10/15 (776,031) US;
1991/10/15 (776,937) US

(51) Cl.Int.^{5}/Int.Cl.^{5} C07C 15/02, C07C 6/12

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(54) Titre : UNE METHODE DE DEMARRAGE DE LA DISMUTATION DU TOLUENE ASSURANT UNE MEILLEURE SELECTIVITE

(54) Title: A START-UP PROCESS FOR IMPROVED SELECTIVITY IN TOLUENE DISPROPORTIONATION

(57) Abrégé/Abstract:

A start-up procedure for use in the disproportionation of co-fed hydrogen and toluene feedstock over a nickel mordenite catalyst containing between 1.0 - 1.5 weight per cent nickel and having a silica to alumina molar ratio of between 16.1 and 22.1. At reaction start-up, the hydrogen to toluene molar ratio is maintained at an unconventionally low level of between 0.5 and 1.7. With an initial temperature of 250°C and under pressure of 550 psig or greater, toluene disproportionation is effected resulting in desirably high selectivity to benzene product and simultaneously low selectivity to undesirable non-aromatic compound by-product.

ABSTRACT

A start-up procedure for use in the disproportionation of co-fed hydrogen and toluene feedstock over a nickel mordenite catalyst containing between 1.0 - 1.5 weight per cent nickel and having a silica to alumina molar ratio of between 16.1 and 22.1. At reaction start-up, the hydrogen to toluene molar ratio is maintained at an unconventionally low level of between 0.5 and 1.7. With an initial temperature of 250°C and under pressure of 550 psig or greater, toluene disproportionation is effected resulting in desirably high selectivity to benzene product and simultaneously low selectivity to undesirable non-aromatic compound by-product.

2079184

PATENT

Docket #COS-604\605

A START-UP PROCESS FOR IMPROVED SELECTIVITY IN TOLUENE DISPROPORTIONATION

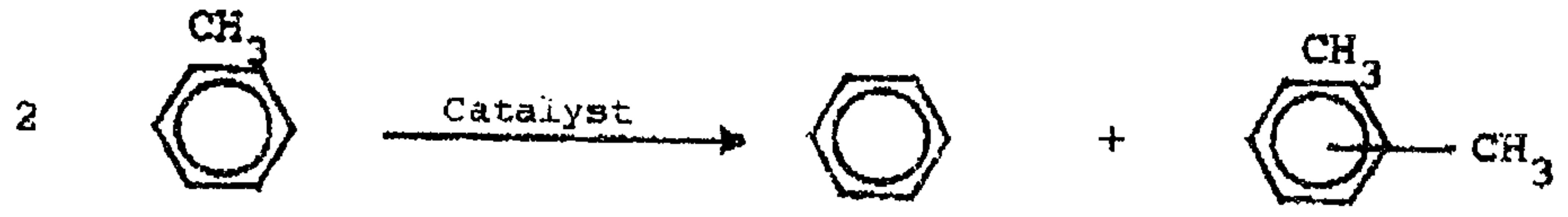
BACKGROUND OF THE INVENTION

Field of the Invention

This invention relates to a start-up procedure for use in the disproportionation of alkylaromatic feedstreams and, more particularly, in the disproportionation of toluene containing feedstocks employing mordenite catalysts of relatively high aluminum content.

Description of the Related Art

The disproportionation of toluene involves a well known transalkylation reaction in which toluene is converted to benzene and xylene in accordance with the following reaction:



(1)

Reaction (1) is mildly exothermic.

Mordenite is one of a number of molecular sieve catalysts useful in the transalkylation of alkylaromatic compounds. As a crystalline aluminosilicate zeolite, mordenite exhibits a network of silicon and aluminum atoms interlinked by oxygen atoms within the crystalline structure. For a general description of mordenite catalysts, reference is made to Kirk-Othmer, Encyclopedia of Chemical Technology, 3rd Edition, 1981, under the heading "Molecular Sieves", Vol. 15, pages 638-643. Mordenite as found in nature or as synthesized to replicate the naturally occurring zeolite, typically exhibits a relatively low silica to alumina mole ratio of about 10 or less. Also known, however, are mordenite catalysts exhibiting a substantially lower alumina content. These aluminum deficient mordenite catalysts exhibit silica to alumina ratios greater than 10, ranging up to about 100, and may be prepared by direct synthesis as disclosed, for example, in U.S. Patent No. 3,436,174 to Sand or by acid extraction of a more conventionally prepared mordenite as disclosed in U.S. Patent No. 3,480,539 to Voorhies, et. al. Both the typical and the aluminum deficient mordenites are known to be useful in the disproportionation of toluene.

Disproportionation of toluene feedstock may be performed at temperatures ranging from about 200°C to about 600°C or above and at pressures ranging from atmospheric to perhaps 100 atmospheres or above. The specific catalyst, however, may impose constraints on reaction temperatures thus affecting catalyst activity and aging character. In general, the prior art suggests the use of relatively high temperatures when employing the high aluminum mordenites (low silica to alumina ratios) and somewhat lower temperatures when employing the low alumina mordenites. Accordingly, where mordenite catalysts exhibiting high silica/alumina ratios have been employed in the transalkylation of alkylaromatics, it has been the practice to operate toward the lower end of the temperature range. U.S. Patent No. 4,665,258 to

Butler, et. al., however, discloses disproportionation of a toluene containing feedstock employing an aluminum deficient mordenite catalyst under relatively severe disproportionation conditions; involving a temperature range of 370°-500°C. The mordenite catalysts exhibit silica/alumina mole ratios of at least 30 and, more desirably, within the range of 40-60. The feedstock may be supplied to the reaction zone containing the mordenite catalyst at rates providing relatively high space velocities. The toluene weight hourly space velocity (WHSV) may be greater than 1. Hydrogen is supplied to the reaction zone at a hydrogen/toluene mole ratio within the range of 3-6. The hydrogen pressure may be 500 psi or more. The toluene feedstock need not be dried before supplying it to the reaction zone and the patent discloses toluene feedstocks exhibiting a water content in excess of 100 ppm.

Butler, et al. also discloses passing a hot preflush gas, nitrogen or hydrogen, to the reaction zone prior to initiating the disproportionation reaction. The preflush gas is heated to a temperature sufficient to substantially dehydrate the catalyst by the time the toluene feed is started. This measure enables the disproportionation process to initially be performed at a somewhat lower temperature and without reduction in toluene conversion. As the disproportionation proceeds, temperature progressively increases to maintain toluene conversion at the desired level, typically about 80 percent of theoretical.

U. S. Patent No. 4,723,049 to **Menard et al.** discloses toluene disproportionation carried out over aluminum deficient mordenite of the type disclosed in the aforementioned patent to Butler. In this process, preferably carried out at a reaction zone temperature of 370°-500°C, and more preferably at a temperature of 400°-500°C with an unmodified aluminum deficient mordenite catalyst, the supply of toluene to the reaction zone is interrupted while the supply of hydrogen is continued. Preferably the period of interruption during which hydrogen supply is continued is for at least one day prior to reinstating the supply of toluene feedstock to the reaction zone. This mode of operation is disclosed to enhance the aging quality of the catalyst and show a reduction in reactor zone temperature without a corresponding decrease in toluene conversion.

It is also a common practice to promote an aluminum deficient mordenite catalyst with a catalytically active metallic content. For example, U.S. Patent No. 3,476,821 to **Brandenburg et al.** discloses disproportionation reactions employing mordenite catalysts having silica/alumina ratios within the range of 10-100 and preferably within the range of about 20-60. The mordenites are modified by the inclusion of a sulfided metal selected from the Group VIII metals. The metal may be included in the mordenite by well known ion exchange or impregnation techniques. The especially preferred sulfided Group VIII metals are cobalt and nickel present in a concentration of 0.5-10 weight percent. When compared with nickel oxide, nickel sulfide is said to provide less overactivity as indicated by gas and saturated hydrocarbon yield. Here the desired temperature ranges are said to be from about 400°-750°F and preferably 450°-640°F. The metal promoters are said to substantially increase activity and catalyst life, as indicated by runs extending over several hours or days.

As noted previously, hydrogen is supplied along with toluene to the reaction zone. While the disproportionation reaction (1) does not involve chemical consumption of hydrogen, the use of a hydrogen cofeed is generally considered to prolong the useful life of the catalyst, as disclosed, for example, in the above mentioned patent to **Brandenburg**. The amount of hydrogen supplied, which is normally measured in terms of the hydrogen/toluene mole ratio, is generally shown in the prior art to increase as temperature increases.

Bhavikatti et al., "Toluene Disproportionation Over Aluminum-Deficient and Metal-Loaded Mordenites. 1. Catalytic Activity and Aging", Ind. Eng. Chem. Prod. Res. Dev. 1981, 20, 102-105, discloses toluene disproportionation at 400°C over mordenite catalysts having silica/alumina mole ratios ranging from 12 to 61 at atmospheric pressure and a space velocity (WHSV) of 1. As the silica/alumina mole ratio is increased, catalyst activity is substantially decreased while aging quality is increased. That is, the aging rates were lower. Based upon short term aging studies, the best silica/alumina mole ratio appeared to be 23. Catalyst decay was also suppressed by loading the mordenites with nickel. Mordenites having a silica/alumina ratio of 12, 16 and 23 were modified by the inclusion of nickel by a procedure involving ion exchanging ammonium mordenite with an aqueous solution of nickel nitrate. After ion exchange, the catalyst was activated under a hydrogen environment for two hours. The best activation temperature for nickel modified mordenite having a silica/alumina ratio of 23 was indicated to be about 550°C. The nickel modified mordenite having a silica/alumina ratio of 12 showed significantly lower activity when compared to the nickel loaded mordenite of a silica/alumina ratio of 23.

U.S. Patent No. 3,562,345 to **Mitsche** discloses the use of molecular sieves such as mordenite catalysts in the disproportionation of toluene. The catalysts are characterized by a silica/alumina mole ratio from about 6 to about 12, pore openings of from about 3 to about 18 angstroms and the incorporation of catalytically active metallic materials in the oxidized or reduced state, particularly Group VIB and Group VIII metals including molybdenum, tungsten, chromium, iron, nickel, cobalt, platinum, palladium, ruthenium, rhodium, osmium, and iridium. **Mitsche** discloses transalkylation at temperatures from about 200°C to about 480°C and gives specific examples of transalkylation of toluene at temperatures of 420°C and 450°C.

U.S. Patent No. 3,677,973 to **Mitsche** et. **al.**, discloses the use of mordenite catalysts composited with an alumina salt providing a silica/alumina mole ratio of about 10 to about 30 in the disproportionation of toluene. The reaction conditions proposed in this patent appear similar to those set forth in the aforementioned Mitsche patent and, like the former patent, **Mitsche et al.**, discloses incorporating Group VIB and Group VIII metals into the catalyst.

U.S. Patent No. 4,151,120 to **Marcilly** discloses a process for the manufacture of a hydrocarbon conversion catalyst involving incorporating cobalt, nickel, silver or palladium in a mordenite catalyst having a silica/alumina mole ratio within the range of 10-100. Following incorporation of the metal into the mordenite, the catalyst is dried and subjected to a dry calcination procedure at a temperature within the range of 300-700°C in the presence of an inert or oxidizing gas having a moisture content of less than 1 percent. **Marcilly** discloses various examples of the dismutation of toluene under reaction conditions 420°C, 30 bars, a space velocity (WHSV) of 5 and a hydrogen/hydrocarbon mole ratio of 5.

U.S. Patent No. 4,723,048 to **Dufresne** et al. discloses a process for the dismutation of toluene employing a zeolite catalyst modified by the inclusion of metals. The catalyst is described as a sodium containing mordenite in the nature of so-called "wide pore" mordenite, i.e., mordenite with main pores exhibiting a diameter of 7-10 Angstroms or "small pore" mordenite, mordenites with main pores exhibiting a diameter of 4-6 Angstroms. The mordenites are treated to extract sodium therefrom to provide not more than 1 percent by weight sodium ions and preferably not more than 0.5 percent by weight sodium ions. Dufresne discloses mordenites having silica/alumina ratios of 10.6 (catalyst A), 14.6 (catalyst B), 25.2 (catalyst C), and 58.6 (catalyst D) modified by the inclusion of nickel ranging from 0.43 weight percent to 2.11 weight percent and by the inclusion of nickel with certain other metals. Dufresne discloses activities of the nickel modified catalysts before and after an accelerated aging procedure at conversion rates of 10 percent and 45 percent. Catalyst C containing 1.1 percent nickel showed the best activity with catalyst B containing 2.11 percent nickel and catalyst D having 0.43 percent nickel showing slightly lower activities. The poorest activity was with respect to catalyst A having a nickel content of 1.81 percent.

The representative prior art discussed above reveals that much of the experimental and investigative work conducted in regard to alkylaromatic disproportionation employing metal promoted mordenite catalysts has been directed toward either achieving a higher level of alkylaromatic conversion or extending catalyst life (ie: controlling catalytic deactivation).

As distinguished from the extant art, the present invention is directed to a start-up procedure for use in the disproportionation of alkylaromatics which results in greater selectivity to desirable benzene product from the very inception of the reaction with a simultaneous and appreciable decrease in by-production of undesirable compounds (hereinafter non-aromatic compounds) due to hydrogenation of the aromatic feed material.

Practical benefits of the instant invention are essentially twofold. Specifically, as an aromatic solvent of comparatively high commercial value and virtually continuous demand, there exists sound economic rationale for increasing the efficiency of the means by which benzene is produced. In addition, and with respect to refining operation, the distillation separation of benzene from undesirable non-aromatic compounds of comparable boiling point range is markedly enhanced due to the significant decrease in non-aromatic by-production, which is the object of the instant invention.

As indicated, common, albeit undesirable, by-products of aromatic hydrogenation (which results when hydrogen is co-fed with an alkylaromatic under disproportionation conditions), including toluene disproportionation, are principally non-aromatic compounds such as methylcyclohexane and, to a lesser extent, other paraffinic and cyclic compounds. Formation of these compounds is particularly observed in association with the presence of a metal promoted mordenite catalyst and, additionally, low reaction temperature. The level of non-aromatic by-production, however, is known to decrease in direct relation to catalyst age. Accordingly, the selectivity to benzene and xylene(s) in toluene disproportionation is dependent upon the by-production level of non-aromatic compounds which, until stabilized, prevent optimum selectivity to the aforesaid desirable products. Applicants have discovered that by controlling the amount of hydrogen cofeed during reaction start-up, the level of non-aromatic production can be limited thereby resulting in greater reaction selectivity to benzene product.

Because it is believed to enhance reaction stability and catalyst aging character, it is generally known that it is desirable to employ a hydrogen cofeed in the disproportionation of alkylaromatics. As disclosed by Marcilly (U.S. 4,151,120), Butler, et. al. (U.S. 4,665,258) and Bhavikatti (Ind. Eng. Chem. Prod. Res. Dev. 1981, 20, 102-105), for example, the prior art generally teaches a hydrogen to toluene molar ratio greater than 3. Applicants' invention, to the contrary, teaches a hydrogen to toluene molar ratio below 3.0 and, preferably, about 1.0 to 2.0.

In view of the above, there exists, accordingly, a need in the art for a start-up process of disproportionating alkylaromatic feedstreams which yields an appreciably desirable and stable concentration of benzene and simultaneous reduction in the by-production of undesirable non-aromatic compounds.

SUMMARY OF THE INVENTION

In accordance with the present invention, there is provided a process for the disproportionation of a substantially pure toluene feedstock over a metal promoted mordenite catalyst in which the yield of desirable benzene product is enhanced during start-up of the process concurrently with suppression of undesirable non-aromatic product(s), by employing a comparatively low concentration of hydrogen, cofeed. In practicing the invention, the toluene feedstock is supplied to the reaction zone containing a metal promoted, mordenite catalyst exhibiting a silica to alumina molar ratio of about 16:1 to 22:1 and containing an amount of nickel within the range 1.0 - 1.5 weight percent. The reaction zone is operated at a starting temperature of 250°C which is subsequently increased incrementally to within the range of about 320° to 330°C and at a pressure of at least 550 psig. The feedstock is supplied to the reaction zone at a rate sufficient to provide a toluene LHSV of about 2. Hydrogen gas is co-fed at a rate sufficient to achieve a hydrogen to toluene molar ratio of between about 0.5 and 2.5 and, most preferably, about 0.5 to 1.7. Following the disproportionation of the toluene to benzene and xylene, the disproportionation product is withdrawn from the reaction zone.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a graph illustrating product selectivity to non-aromatic compounds as a function of catalyst age in conjunction with a toluene disproportionation process carried out over a nickel-modified mordenite catalyst wherein hydrogen is co-fed with toluene in molar relationships of 0.5, 1.7 and 3.3.

Figure 2 is a graph illustrating product selectivity to benzene as a function of catalyst age in conjunction with a toluene disproportionation process carried out over a nickel-modified mordenite catalyst wherein hydrogen is co-fed with toluene in molar relationships of 0.5, 1.7 and 3.3.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

As evidenced in the foregoing discussion, the use of hydrogen in the disproportionation of toluene over a metal modified zeolite catalyst is well known in the art. The present invention, however, provides an improved mode of starting toluene disproportionation over a nickel-modified mordenite catalyst under relatively low temperature conditions providing for desirably low yields, such as less than 0.5%, of non-aromatic product and resulting in desirably high yields of desirable benzene, between 39-40% by weight.

A distinct advantage of the present invention is graphically illustrated in Figure 1 shown herein which indicates that, in utilizing a nickel promoted mordenite catalyst, a toluene conversion level of about 48% can be achieved with minimal formation of non-aromatic compounds in the product stream by reducing the concentration of hydrogen cofeed during reaction start-up. This measure results in a higher yield of desirable benzene product. Although the precise point of optimum hydrogen to toluene ratio was not determined, it was determined that the most significant improvements are achieved between about 0.5 - 2.5 and, more preferably, between about 1.0 - 2.0.

In accordance with the present invention there is provided a toluene disproportionation process employing a catalyst of the mordenite type modified by the inclusion of a metallic hydrogenation component, more specifically nickel, in which a dramatic decrease of non-aromatic by-product is achieved in conjunction with: toluene conversion of about 48%; relatively low temperature; and a desirably low rate of catalyst deactivation.

The mordenite catalyst employed in the present invention preferably exhibits a silica to alumina molar ration of between about 16:1 and 22:1, preferably between about 18:1 to 22:1, and more preferably about 18:1. The mordenite catalyst is, additionally, modified by the inclusion of nickel. Applicants' experimentation suggests that the best results are obtained by utilizing a catalyst made up of no less than 1.0 weight per cent nickel. While it is generally known in the art that low nickel content mordenite catalysts are useful in converting toluene and assist in selectivity to benzene and xylenes, they have generally demonstrated poor aging quality (character). Experimentation has demonstrated that, while greater amounts of nickel can be employed without corresponding significant benefit, one preferred nickel content in the catalyst is within the range of about 1.0 to 1.5 weight percent, preferably between about 1.2 to 1.4 weight percent, and more preferably about 1.25 weight percent.

The present invention resulted from a study conducted using three different hydrogen to toluene molar ratios utilizing a laboratory reactor. In each case, the catalyst was pre-dried by heating at a suitable temperature, preferably 250°C, under the flow of hydrogen gas.

Thereafter, a substantially pure toluene feedstock was passed over the reaction zone at a starting temperature of 250°C which was subsequently raised incrementally to within the range of about 320°C-330°C, and at a pressure of 600 psig and feedstock liquid hourly space velocity (LHSV) = 2.0. The hydrogen to toluene molar ratio varied at 0.5, 1.7 and 3.3. Reactor temperature was incrementally increased in an effort to maintain the desired 48% conversion.

In a further aspect of the invention, it is possible to increase the concentration of hydrogen cofeed and hence the molar ratio of hydrogen to tolune to a value between 3 and 4 at such a time in the reaction, i.e. within 10 days of reaction start-up, that a desirably low and stable concentration of non-aromatic compounds is observed in the product stream. This post start-up increase in hydrogen concentration following stabilized production of non-aromatics is generally believed to enhance the aging character of the catalyst.

While the invention has been described with reference to particular embodiments thereof, it will be apparent to those skilled in the art that various changes and modifications can be made without departing from the spirit of the invention or from the scope of the appended claims.

WHAT IS CLAIMED IS:

1. A transalkylation start-up procedure for the process of disproportionating a toluene-containing feedstock over a metal promoted mordenite catalyst to produce benzene and xylene, the steps of said procedure comprising:

(a) passing a cofeed of substantially pure toluene and hydrogen gas into a reaction zone and contacting it with a mordenite catalyst modified by the inclusion of nickel within the reaction zone,

(b) conducting the disproportionation reaction within said reaction zone at a starting reaction temperature of about 250°C and a pressure of at least 550 psig;

(c) adjusting said cofeed to obtain a hydrogen to toluene molar ratio within a range of about 0.5 and 1.7 at reaction start-up; and

(d) withdrawing disproportionation product containing benzene and xylene from said reaction zone.

2. The process according to claim 1 wherein said reaction temperature is raised incrementally to around 320 - 330°C.

3. The process according to claim 1 wherein said toluene disproportionation is around 48% and is maintained by adjusting the reaction temperature.

4. The process according to claim 1 wherein said feedstock is being supplied to said reaction zone at a rate sufficient to provide a toluene LHSV of about 2.

5. The process according to claim 1 wherein said mordenite catalyst has a silica to alumina molar ratio in the range of about 16:1 to 22:1.

6. The process according to claim 1, wherein said hydrogen cofeed concentration is adjusted within 10 days of reaction start-up to result in a hydrogen to toluene molar ratio of between 3 and 4.

7. The process according to claim 1 wherein the level of non-aromatic compounds in said disproportionation product comprises a stable value of less than 0.5 wt. % of the disproportionation product(s).

8. The process according to claim 1 wherein the level of said produced benzene comprises a stable value of between 39 - 40% by weight of the disproportionation product(s).

9. The process according to claim 5 **wherein said mordenite catalyst exhibits a silica to alumina molar ratio of about** 18:1 **to 22:1.**

10. The process according to claim 1 wherein said mordenite catalyst exhibits a silica to alumina molar ratio of about 18:1.

11. The process according to claim 1 wherein the metal promoted mordenite catalyst exhibits a nickel concentration within the range 1.0 - 1.5 weight percent.

12. The process according to claim 1 wherein the metal promoted mordenite catalyst exhibits a nickel concentration within the range 1.2 - 1.4 weight percent.

13. The process according to claim 1 wherein the metal promoted mordenite catalyst exhibits a nickel concentration of about 1.25 weight percent.

14. A transalkylation start-up procedure for the process of disproportionating of a toluene-containing feedstock over a metal promoted mordenite catalyst to produce benzene and xylene, said procedure comprising a cofeed of substantially pure toluene and hydrogen gas into a reaction zone and contacting it with a mordenite catalyst modified by the inclusion of nickel within the reaction zone, said catalyst having a silica to alumina molar ratio in the range of about 16:1 to 22:1, said feedstock being supplied to said reaction zone at a rate sufficient to provide a toluene LHSV of about 2; and withdrawing disproportionation product containing benzene and xylene from said reaction zone, wherein the improvement comprises

(a) conducting the disproportionation reaction within said reaction zone at a starting reaction temperature of about 250°C and a pressure of at least 550 psig; and

(b) adjusting said cofeed to obtain a hydrogen to toluene molar ratio within the range of about 0.5 and 1.7 at reaction start-up.

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FIG.1

TOLUENE DISPROPORTIONATION: SELECTIVITIES TO NONAROMATICS, BENZENE, XYLENES, HEAVIES and C1-C5 GASES VS. CATALYST AGE at VARIOUS H2/TOL RATIOS

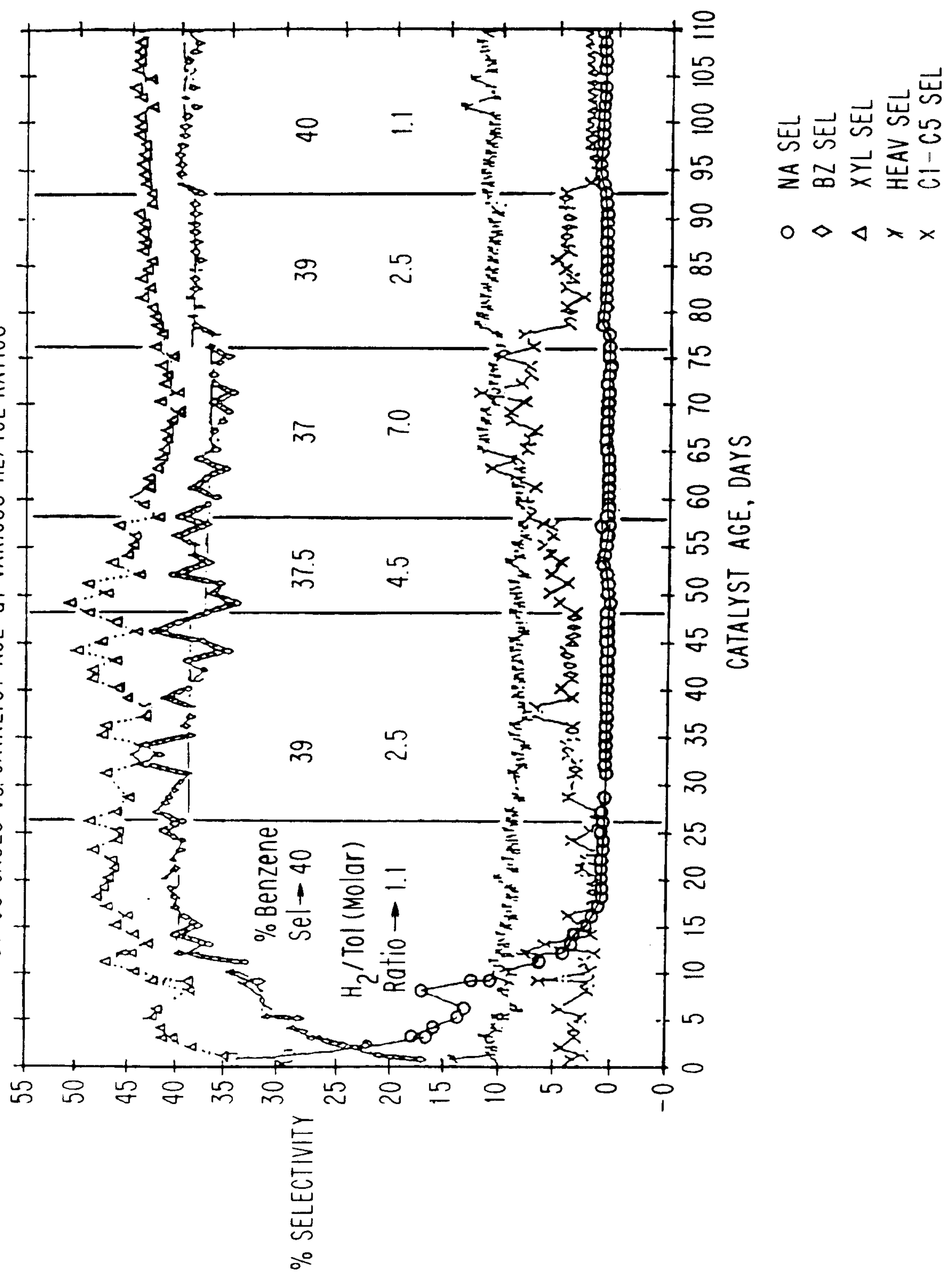

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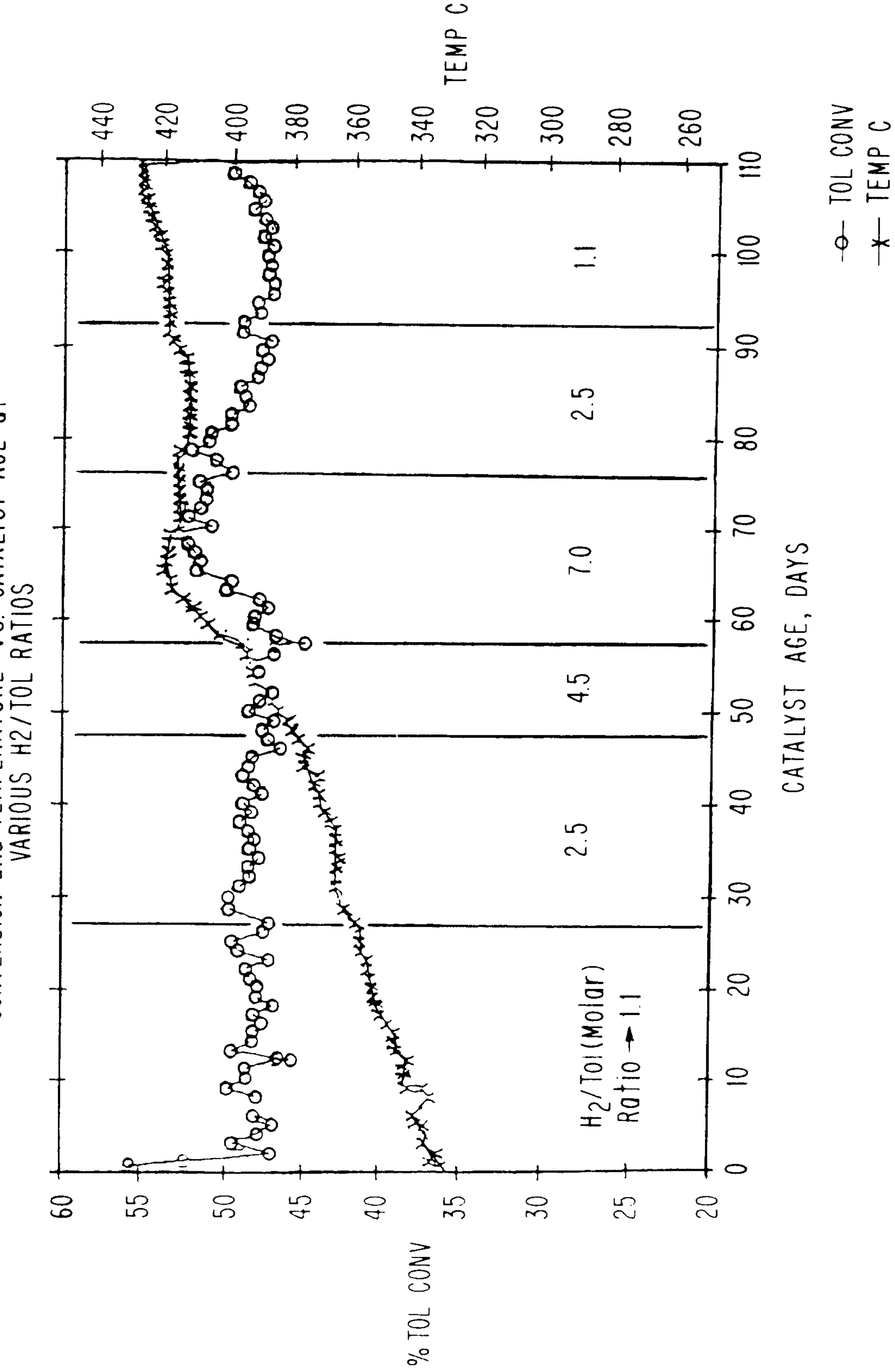
FIG. 2



TOLUENE DISPROPORTIONATION: PERCENT TOLUENE CONVERSION and TEMPERATURE vs. CATALYST AGE at VARIOUS H2/TOL RATIOS

Gowling, Strathy & Henderson