

## REJUVENATION OF SPENT ACID CATALYST RESINS

This invention relates to the use of cation exchange resins as acid catalysts, and more particularly to the rejuvenation and re-use of spent acid catalyst resins.

Cation exchange resins are frequently used to catalyze reactions, including such etherification reactions as the formation of methyl *t*-butyl ether (MTBE) from methanol and isobutylene, or formation of *t*-amyl methyl ether (TAME) from isoamylene and methanol. Because of the importance of MTBE as a gasoline additive, and the large quantities of this material that are produced, large quantities of cation exchange resins are used in catalyzing this reaction. In use, catalyst resins become fouled by polymeric materials and catalyst-inhibiting materials such as metal ions and nitrogen-containing materials present in feedstreams. This fouling is thought to reduce the porosity and surface area of the catalyst, which in turn would reduce the availability of acid catalysis sites. The presence of the nitrogen-containing materials tends to reduce the activity of acid catalyst resins, a condition referred to as "nitrogen poisoning." The catalyst resins also undergo some limited desulfonation, although this appears not to be the primary cause of catalytic activity loss. The catalyst resins thus undergo a gradual deterioration of their catalytic effectiveness until they are no longer suitable for use in the processes in which they are employed, at which time they have been regarded as waste materials.

It would be economically and environmentally advantageous to reduce the amount of waste cation exchange resin generated, as for example that generated by the MTBE industry, and one way to do this would be to recover the resin and rejuvenate it into a catalyst resin which has sufficient activity to be useful in the original catalytic process.

We have discovered a process for rejuvenating spent acid catalyst resin which comprises treating a spent acid catalyst resin with an effective amount of a sulfonating reagent under sulfonating conditions, and subsequently separating the catalyst resin from the sulfonating reagent.

We have further discovered a preferred embodiment of the process wherein the catalyst resin is a sulfonic-acid-functionalized cation exchange resin, and a particularly preferred embodiment wherein the sulfonating reagent is sulfuric acid having a concentration of at least 85 weight percent.

We have discovered another particularly preferred embodiment of the process wherein the sulfonating reagent is oleum having a sulfur trioxide content

of from 10 to 40 weight percent, and the spent catalyst resin is rejuvenated as a polysulfonated catalyst resin.

In a particularly preferred embodiment of the present invention, we have discovered a process for rejuvenating spent etherification catalyst resin which comprises treating a sulfonic-acid-functionalized catalyst resin which has been used as an etherification catalyst resin until its activity is such that it is no longer useful to catalyze the etherification reaction, with a sulfonating reagent at a temperature of from 60°C to 140°C for one-half to six hours.

A particularly advantageous aspect of the present invention is that existing equipment and procedures for sulfonating copolymers to cation exchange resins may be employed in rejuvenating the catalyst resin. This is surprising in view of the limited loss of sulfonic acid groups during extensive catalysis, as for example etherification catalysis; the observed loss of from a few percent up to ten percent, by weight, of sulfonic acid groups would not be expected to account for the observed, extensive loss of etherification catalytic activity. Conversely, treatment of the catalyst resin under sulfonation conditions would not be expected to do more than restore that few percent of lost sulfonic acid groups, and would be expected neither to add more sulfonic acid groups to the already sulfonated aromatic nuclei of the copolymer, nor to have other beneficial effects upon the catalytic activity of the cation exchange resin in such catalyzed reactions as etherification.

The catalyst resins useful in the present invention are spent acid catalyst resins, preferably strong-acid catalyst resins, and include those prepared by monosulfonation or polysulfonation of macroporous, crosslinked, styrenic copolymers to form sulfonic-acid-functionalized catalyst resins. These catalyst resins have been employed in catalyzing organic chemical reactions, preferably etherification reactions, as for example the etherification of methanol and isobutylene to MTBE, or etherification of methanol and isoamylene to TAME, until they have lost a sufficient fraction of their catalytic activity that their continued use is no longer practical. Such catalyst resins typically have reduced catalytic capacity, which is believed to result from fouling by polymer, contaminants in the feedstock, and other materials, and to a lesser extent from loss of a minor amount of sulfonic acid groups, and are referred to herein as "spent" catalyst resins.

In practice, the user of catalyst resins decides that a catalyst resin is spent and must be replaced when the reaction conversion has decreased to the point that continued operation of the process with the current catalyst is no longer economical. The user will typically monitor the concentration of a reactant, for example, the reactive olefin in an etherification reaction, both before and after

the reactants pass through a bed of the catalyst resin; conversion is the percentage of reduction in the reactant concentration. One may, of course, choose to monitor the concentration of a reaction product exiting from the catalyst resin bed as an alternative to monitoring a reactant entering and exiting the bed.

By way of exemplifying how one might decide when a catalyst resin is spent, one may be operating the catalyst resin in a process which etherifies isobutylene and methanol to MTBE, and the feed concentration of isobutylene may be 16%. At the start of the run, with new catalyst resin, 95% conversion may be achieved, meaning that the isobutylene concentration at the reactor outlet would be only 0.8%. As the reaction continues, the catalytic activity of the catalyst resin will decrease, causing the isobutylene concentration at the reactor outlet to increase. For example, one may decide that, when the isobutylene concentration at the reactor outlet has increased to 1.92%, with a corresponding decline in conversion to 88%, the catalyst resin must be replaced.

The specific decision depends upon the user of the catalyst resin, and may be influenced by such considerations as the ability of downstream processing units to handle unconverted reactant, the cost of separating reactants from the product, and decreased purity of the final product. At some point, however, each user of an acid catalyst resin decides that the catalytic activity of that resin has declined to the point that replacing the resin is more economical than continuing to operate with it. That resin, when removed from the process equipment, is spent catalyst resin.

The term, "sulfonation conditions" as used herein is intended to mean reaction conditions, *e.g.* temperature, pressure and time, suitable for incorporating sulfonic-acid functional groups into the aromatic nuclei of a crosslinked, aromatic copolymer which has not previously been sulfonated, and includes the conditions suitable for monosulfonating such a copolymer, as for example treatment of the copolymer with concentrated sulfuric acid at elevated temperatures, and conditions suitable for polysulfonating such a copolymer, as for example treatment of the copolymer with oleum at elevated temperatures. The time for treatment of the spent catalyst resins is approximately the same as the time appropriate for sulfonation of a similar aromatic copolymer which has not previously been sulfonated. Such conditions are well known to a person having ordinary skill in the art. The treatment time for a selected set of sulfonating conditions may be more precisely determined by treating samples of the spent catalyst resin for progressively longer times, and determining the time required to restore catalytic activity to approximately that of the original catalyst resin prior to its use as a catalyst.

Where sulfuric acid is used to rejuvenate the spent catalyst resins of the present invention, the sulfuric acid has a concentration of at least 85% by weight. The temperature at which the spent catalyst resin is treated with the sulfuric acid includes the range from 60°C to 150°C, preferably from 80°C to 140°C, and more preferably from 110°C to 135°C. The pressure at which the spent catalyst resin is treated with the sulfuric acid includes the range from 100 to 200 kPa, and more preferably at atmospheric pressure. Treatment time is sufficient to restore the original catalytic activity of the catalyst resin, and is preferably from one half hour to six hours, more preferably from one to three hours.

Where oleum is used to treat the spent catalyst resins of the present invention, to create or rejuvenate polysulfonated catalyst resin, the oleum has a concentration of from 10 to 40 weight percent sulfur trioxide dissolved in 100% sulfuric acid. The temperature at which the spent catalyst resin is treated with the oleum includes the range from 40°C to 150°C, preferably from 60°C to 140°C, and more preferably from 80°C to 130°C. The pressure at which the spent catalyst resin is treated with the oleum includes the range from 100 to 200 kPa, and more preferably at atmospheric pressure. Treatment time is sufficient to create or restore the original catalytic activity of a polysulfonated catalyst resin, and is preferably from one half hour to six hours, more preferably from one to three hours. Polysulfonated catalyst resins are those having an average of more than one sulfonic acid group per available aromatic ring, that is, per aromatic ring which is available to sulfonation. As not all aromatic rings are available to sulfonation in highly crosslinked copolymers and resins, actual sulfonic acid functionality of a polysulfonated resin may be less than the theoretical maximum for a monosulfonated resin. A more detailed discussion of this may be found in Maroldo *et al.*, U. S. Patent No. 4,839,331

It is, of course, possible within the scope of the present invention to polysulfonate a monosulfonated spent catalyst resin, that is, a monosulfonated cation exchange resin which has been used as a catalyst resin in etherification reactions, simultaneously rejuvenating it of the fouling which had lowered its catalytic activity and converting it into a polysulfonated catalyst resin.

Once rejuvenated by treatment with a sulfonating reagent under sulfonating conditions, the catalyst resin is then separated from the sulfonating reagent. This may be done, for example, by washing the catalyst resin with water or another solvent to remove the sulfonating reagent. Techniques known to those having ordinary skill in the art, such as washing initially with dilute sulfonating reagent, either as a single wash or as two or more washes each containing progressively less sulfonating reagent in the water or other solvent, before washing with pure water or solvent, may be employed. The catalyst resin

may then be separated from the water or solvent by filtration, draining or other known techniques.

When spent catalyst resin is treated according to the present process, much of the effect of polymer fouling, fouling by nitrogenous substances and desulfonation is eliminated, and the spent catalyst is rejuvenated to a useful catalyst resin with a catalytic activity and lifetime in catalytic use approximately that of unused catalyst resin.

In the following examples, all reagents used are of good commercial quality unless otherwise indicated, and all percentages and ratios given herein are by weight unless otherwise indicated.

#### EXAMPLE 1

This example illustrates rejuvenation with sulfuric acid of a spent, monosulfonated acid catalyst resin used in preparation of MTBE.

To a reactor containing 8616 kg of 98% sulfuric acid was added 1524 kg of a spent sulfonic-acid-functionalized catalyst resin which had been used as an etherification catalyst resin in the production of MTBE. The mixture was heated to 122°C and held at that temperature for three hours, after which water was added at a rate to maintain the mixture temperature between 80°C and 110°C, until the sulfuric acid concentration was less than 10%. The rejuvenated sulfonic-acid-functionalized catalyst resin was then washed with deionized water in a backwash tower and packed out. The rejuvenated catalyst resin had a cation exchange capacity of 4.9 milliequivalents per gram (meq/g) compared to the cation exchange capacity of new catalyst resin of 4.8 meq/g, and to the cation exchange capacity prior to rejuvenation of 4.40 meq/g. The rejuvenated catalyst resin was dark brown to black in color, compared to tan for new catalyst resin.

#### EXAMPLE 2

This example illustrates rejuvenation of a different sample of spent catalyst resin, which had been used in etherification of a different feedstock to produce MTBE.

The procedure of Example 1 was followed. The rejuvenated catalyst resin had a cation exchange capacity of 4.8 meq/g, compared to the cation exchange capacity of new catalyst resin of 4.8 meq/g and to the cation exchange capacity prior to rejuvenation of 4.76 meq/g.

**EXAMPLE 3**

This example illustrates rejuvenation with oleum to a polysulfonated catalyst resin of a spent, monosulfonated acid catalyst resin used in preparation of MTBE.

The procedure of Example 1 was followed, except that the sulfuric acid was replaced with 15 kg of 20% oleum for every kg of spent catalyst resin and the mixture was heated to 130°C and maintained at that temperature for four hours. The resulting polysulfonated catalyst resin had a cation exchange capacity of 5.5 meq/g, compared to 5.4 meq/g for a new polysulfonated catalyst resin.

**EXAMPLE 4**

This example illustrates use of the rejuvenated catalyst resin of Example 1 for etherification of isobutylene and methanol to methyl *t*-butyl ether.

A sample of approximately 900 ml volume of the water-hydrated catalyst resin from the rejuvenation of Example 1 was saturated with methanol by slurring it in approximately two liters each of progressively more concentrated, aqueous methanol solutions, initially 10 weight percent methanol, then 20 and 30 weight percent methanol, respectively, and finally in pure methanol, decanting the excess liquid from the catalyst before adding the next methanol solution.

The catalyst resin was then packed as a slurry into two 152-cm reactor sections which were then connected in series and heated by circulating hot water through a water jacket around the reactor sections. The effective catalyst resin bed settled to a depth of about 274 cm after a short period of operation. Initially the reactor sections were heated to 55°C, and a feed having the composition shown in Table 1, below, was fed into the reactor inlet at a liquid hourly space velocity (i.e., volume of liquid feed per volume of catalyst per hour) of between 3.3 and 3.8. With a temperature rise to 75°C in the reactor (from the exothermic reaction) the conversion of isobutylene was  $94.6 \pm 1.50$ ,  $94.0 \pm 0.50$  and  $96.1 \pm 1.44$  mol percent, respectively, for three consecutive runs of approximately 80 kg total feed each. For each run the fractional selectivity (conversion to methyl *t*-butyl ether) was 0.996.

For comparison, under similar conditions fresh catalyst resin produces a conversion of isobutylene of about 92 mol percent, with the same fractional selectivity of 0.996. In typical operation, the catalyst resin may well be replaced when the conversion of isobutylene to methyl *t*-butyl ether has fallen to about 88 mol percent.

Table 1  
Feed Composition for Rejuvenated Catalyst Resin Evaluation

| Component   | Molecular Weight | Weight Percent | Mol Percent |
|-------------|------------------|----------------|-------------|
| n-Pentane   | 72.15            | 0.411          | 0.3165      |
| Propane     | 44.11            | 0.398          | 0.5013      |
| Methanol    | 32.04            | 5.249          | 9.0123      |
| Isobutylene | 56.11            | 8.021          | 7.9425      |
| Isobutane   | 58.12            | 42.678         | 40.7986     |
| n-Butane    | 58.12            | 43.243         | 41.3388     |
| Water       |                  | 20 ppm         |             |

#### EXAMPLE 5

This example illustrates the use of rejuvenated catalyst resin of the present invention to catalyze the etherification of isoamylene with methanol to form *t*-amyl methyl ether, and shows comparisons among new, spent and rejuvenated monosulfonated catalyst resin, and new and rejuvenated polysulfonated catalyst resin.

The catalyst resins of Examples 1 and 3, in new, spent, and rejuvenated form, were used in the *t*-amyl methyl ether etherification reaction. A feedstock containing isoamylene and methanol was reacted at elevated temperature over separate beds of new and spent, monosulfonated catalyst and the spent catalyst rejuvenated according to Example 1; and new polysulfonated catalyst and spent polysulfonated catalyst rejuvenated according to Example 3. Conditions for each synthesis run were approximately equivalent, so that comparisons among the several runs could be made. Total production of *t*-amyl methyl ether for each synthesis run with the individual catalysts was recorded at 30 and 60 minutes, and is shown below in Table 2.

Table 2  
Synthesis of *t*-Amyl Methyl Ether

| Time<br>Minutes | Example 1<br>New | Example 1<br>Spent | Example 1<br>Rejuvenated | Example 3<br>New | Example 3<br>Rejuvenated |
|-----------------|------------------|--------------------|--------------------------|------------------|--------------------------|
| 30              | 0.155            | 0.090              | 0.160                    | 0.220            | 0.225                    |
| 60              | 0.255            | 0.180              | 0.270                    | 0.295            | 0.300                    |

**Ether production (catalytic activity) of the rejuvenated catalyst resin at any of the times was observed to be at least as high as that of the new catalyst resin, and significantly superior to that of the spent catalyst resin.**



**We claim:**

- 1. A process for rejuvenating spent acid catalyst resin which comprises treating a spent acid catalyst resin with an effective amount of a sulfonating reagent under sulfonating conditions, and subsequently separating the catalyst resin from the sulfonating reagent.**
- 2. The process of claim 1 wherein the spent acid catalyst resin is a sulfonic-acid-functionalized cation exchange resin.**
- 3. The process of claim 2 wherein the sulfonating reagent is sulfuric acid having a concentration of at least 85 weight percent.**
- 4. The process of claim 2 wherein the sulfonating reagent is oleum having a sulfur trioxide content of from 10 to 40 weight percent.**
- 5. The process of claim 2 wherein the catalyst resin has been used as an etherification catalyst, the elevated temperature is from 60°C to 140°C, and the time sufficient to restore catalytic activity to the catalyst is from one-half hour to six hours.**
- 6. A rejuvenated spent etherification catalyst resin which has been used as an etherification catalyst until its activity was such that it was no longer useful to catalyze the etherification reaction, and which has been rejuvenated by treating the spent catalyst with a sulfonating reagent.**
- 7. The rejuvenated spent etherification catalyst resin of claim 6 wherein the sulfonating reagent is sulfuric acid having a concentration of at least 85 weight percent and the rejuvenated catalyst resin is a monosulfonated catalyst resin.**
- 8. The rejuvenated spent etherification catalyst resin of claim 6 wherein the sulfonating reagent is oleum having a sulfur trioxide concentration of from 10 to 40 weight percent, and the rejuvenated catalyst resin is a polysulfonated catalyst resin.**
- 9. The steps or features disclosed herein or any combination thereof.**