

structure is completely immersed in this solution, and the solution and support are heated to 95° C. After about five minutes of heating, the support becomes black in appearance due to the deposition of a finely-divided metallic platinum coating thereon. After a 20-minute immersion the support is removed from solution, dried, and heated for one hour at 500° C. in a hot air oven. It is then tested for catalytic activity and found to be very active for the oxidation of carbon monoxide and short chain hydrocarbons.

The presence of urea in the solution as shown in the above example accelerates the deposition of platinum, particularly on supports composed of materials such as beta-spodumene and cordierite which have not been coated with alumina or tin oxide. Urea does not, however, appear to have a major accelerating effect on the deposition of palladium on these oxide supports. If desired, the deposition of platinum from the above-described solution may be carried out at room temperature instead of a 95° C., with substantial deposition of platinum occurring within a period of about 48 hours.

EXAMPLE III

A small alumina-silica coated monolithic ceramic support structure essentially identical to the structures treated in Examples I and II above is provided. This structure is first treated according to a tin-sensitization procedure comprising immersion in an acidified stannous chloride solution consisting of 10 weight percent $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in 1 normal HCl for 10 minutes at room temperature, removal and subsequent immersion in distilled water at 95° C. for 10 minutes to hydrolyze the stannous chloride solution to a hydrous tin oxide, and finally removal and slow drying of the hydrous tin oxide coating at room temperature in air.

The structure sensitized as described is then placed in a warm (85° C.) catalyst solution consisting of 1.67 ml. of a platinum chloride solution (containing 3.6 percent platinum by weight) 27 ml. of distilled water, and 0.25 ml. of formic acid, further heated to 95° C. for 5 minutes, and then removed from the solution, dried, and heated for 1 hour at 500° C. in air. The structure is black in appearance after treatment due to the presence of a finely-divided metallic platinum coating thereon.

The catalyst-bearing structure prepared as described is tested for catalytic activity together with another catalyst-bearing structure which has been treated in the identical catalyst solution according to the identical catalyst deposition procedure but which has not been tin-sensitized. While both support structures are quite active for the oxidation of carbon monoxide and short chain hydrocarbons, the tin-sensitized support demonstrates a higher degree of oxidation activity as well as better retention of this activity after exposure to accelerated thermal aging at 800° C. for 24 hours in air. It is also noted that deposition of the catalyst on the support structure proceeds more rapidly on the tin-sensitized support.

EXAMPLE IV

Two cordierite ceramic monolithic structures, similar in size and configuration to the structures treated in Example I but not having silica-alumina coatings, are provided. One structure is subjected to the tin-sensitization procedure described in Example III, except that excess stannous chloride solution is removed from the structure with compressed air prior to hydrolysis and drying. The other cordierite structure is not tin-sensitized.

Both structures are completely immersed in catalyst solutions of the composition described in Example III and heated to 95° C. The black coloration evidencing a metallic platinum coating is observed on the tin-sensitized support within two minutes of immersion in the catalyst solution. However, the addition of some urea (about 1 gram) to the catalyst solution is required in the case of

the unsensitized support to obtain rapid deposition of the catalyst.

Following immersion in the catalyst solution at 95° C. for 20 minutes the catalyst-bearing structures are removed from solution, dried, heated at 500° C. for one hour to remove volatile residues, and finally tested for catalytic activity. Both support structures are quite active for the oxidation of carbon monoxide and hydrocarbons; however, the tin-sensitized support demonstrates a higher degree of oxidation activity as well as better retention of this activity after accelerated thermal aging as described in Example III.

An alternative procedure for tin-sensitizing a support material comprises contacting the support with a stannous chloride solution followed by heating at moderately elevated temperatures to hydrolyze the salt to a hydrous tin oxide. In using this procedure, however, much less concentrated solutions of stannous chloride should preferably be employed; otherwise, excessively heavy coatings of hydrous tin oxide are formed which typically do not adhere strongly to the support. Immersion in aqueous solutions containing 0.25–0.5% $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ by weight followed by heating at temperatures up to about 200° C. comprises a suitable procedure. With very low concentrations of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, e.g., about 0.25 weight percent, the use of HCl to stabilize the salt against hydrolysis in solution is not required.

The described tin-sensitization procedures are particularly useful for depositing noble metals from formic acid containing solutions where alumina or tin oxide are not present in or on the support. Examples of catalyst support oxides, glasses, etc. which have been usefully tin-sensitized for the purpose of coating with noble metal catalysts include porous 96% silica glass, porous glass-alumina mixtures, colloidal silica-alumina mixtures, zirconia-titania mixtures, chromium oxide-alumina mixtures, chromium oxide, cerium oxide, thorium oxide and niobium oxide.

From the foregoing description and examples, it is apparent that the process of the present invention constitutes a useful advance in the art of manufacturing noble metal catalyst-bearing devices.

We claim:

1. In a process for depositing a noble metal catalyst on a refractory metal oxide carrier which comprises the step of contacting the refractory metal oxide carrier with a solution containing a formic acid reductant and noble metal ions selected from the group consisting of platinum, palladium, rhodium, gold, silver and mixtures thereof, the improvement which comprises the addition of urea to the solution in an amount ranging about 1–10% by weight thereof.

2. A process according to claim 1 wherein, prior to contacting the refractory metal oxide carrier with the urea-containing solution, the carrier is contacted with an acidified stannous chloride solution to form a coating of said solution thereon, and thereafter contacted with water to hydrolyze the stannous chloride to hydrous tin oxide and to remove chloride ions from the carrier.

3. A process for depositing a noble metal catalyst on the interior channel walls of a metal oxide carrier consisting of a monolithic honeycomb catalyst support structure which comprises the steps of:

- (a) contacting the honeycomb support structure with an acidified stannous chloride solution to form a coating of said solution on the interior channel walls of said structure;
- (b) contacting the solution-coated structure with water to hydrolyze the stannous chloride to a hydrous tin oxide and to remove chloride ions therefrom; and
- (c) contacting the support structure with a solution containing a formic acid reductant and noble metal ions selected from the group consisting of platinum, palladium, rhodium, gold, silver and mixtures thereof