Micro Tubular Reactors with Thin Catalytic Inner Layer; Fabrication and Application to Rapid and Efficient Reaction Processes

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論　文　内　容　要　旨

Micro channel devises have realized highly efficient reactions owing to the excellent mass and heat transfer properties and large surface to volume ratio. Micro tubular reactors have been applied to various organic reactions and continuous material processing, particularly by the combination with heterogeneous catalysts. The objective of this study is to fabricate micro tubular reactors with thin catalytic inner layer and their application to rapid and efficient reaction processes.

In chapter 1, general aspects and histories of the micro reactor processes are overviewed and then the

objective of the thesis is described.

In chapter 2, coating of thin catalytic layer (Pd, Pt) over the inner wall of silica capillary by electroless plating was described. Uniform coating of the catalytic metal layer was confirmed by the SEM observation that agreed with the calculated thickness. I applied Pd and Pt coated silica glass micro reactors to the continuous decomposition of H_2O_2. The capillary provides a remarkably high surface area and volume ratio ($1.25 \times 10^4\ m^2\ m^{-3}$). As the result, efficient decomposition of H_2O_2 ($15\ g\ L^{-1}$) was achieved simply by passing the solution into the reactor. I found, Pd(II)oxide and Pt(0) were responsible for catalytic decomposition. Complete decomposition of H_2O_2 was achieved by Pt coated micro reactor at 20°C within 10 s residence time.

In chapter 3, I attempted to fabricate the metallic reactors with thin catalytic layer of Pd, Pt, Rh, Au and Pd-Cu alloy in order to gain mechanical, thermal and chemical stability. The tubular reactor (i.d.:0.5 mm, length: 100 cm) composed of Ni base alloy (Inconel 625) tube as the support, TiO_2/Ti intermediate layer and thin catalytic film layer was obtained. TiO_2 layer acts as a barrier that prevents inter-metallic diffusion between Ti and metal catalyst. By sequential electroless plating of Pd and Cu followed by thermal treatment, Pd-Cu alloy layer was coated. These metallic reactors with catalytic layer could withstand high pressure and high temperature water in basic and acidic media without significant loss of metals.

In chapter 4, the metallic reactors were applied to the continuous decomposition of Orange II (azo-dye). Steady decomposition of the azo-dye was observed by continuous feed of the solution with H_2O_2. Presence of Pd layer enhanced the dye decomposition greatly. By use of Pd-coated reactor, COD was completely diminished at 300°C, which is in accord with disappearance of UV/Vis peaks of dye within 4 s residence. In contrast, in the absence of Pd layer, orange color and the peaks of UV/Vis absorption still remained to a great degree. Catalytic wet oxidation is very efficient due to the generation of ·OH and ·OOH radicals acting as strong oxidants.

There has been significant interest for use of water as a replacement for organic solvents particularly at high pressure and high temperature conditions. In chapter 5, I applied Pd, Pd−Cu alloy reactors to Sonogashira (C−C) coupling with ethynylbenzene and iodobenzene under flow process in an aqueous medium. Rapid mixing and high pressure and high temperature condition generated the micro emulsion that enabled rapid organic reaction in water media. Most of the cases, single C−C coupling product was selectively yielded at 250°C and 16 MPa (optimized conditions) but a number of by-products were found in supercritical water conditions (above 374 °C, 22 Mpa), due to oxidative nature of supercritical water. It should be emphasized, that the reaction conversion was remarkably enhanced by alloying with Cu. In Pd−Cu alloy reactor, Cu may work coupled with Pd as a co-catalyst. These micro reactors with catalytic layer did not cause contamination of product with metal catalysts.

In chapter 6, I summarized the content of my thesis. Thin catalytic layers (1−3 μm) of various metals alloys were uniformly coated over the inner surface of tubular reactor by electroless plating. Mechanically, thermally and chemically stable metallic reactors were developed that withstood at high pressure and temperature, including supercritical water conditions. The high performance of these catalytic reactors was demonstrated by the reactions in water, i.e., decomposition of H_2O_2 and wet oxidation of azo-dye. The active oxi dants ·OH and ·OOH generated as reaction intermediates effectively decomposed the stable aromatic rings of azo-dye compound. In addition, catalytic micro tubular reactors were applied to Sonogashira (C−C) coupling as an example for organic synthesis in water.

Because of their high tolerance to high pressure and high temperature and the wide choice of metal catalysts, these metallic reactors are applicable to a broad scope of catalytic reactions in continuous flow processes.

論文審査の結果の要旨

マイクロリアクタは、熱や物質移動が速やかで表面積/体積の比率が大きいため、迅速で高効率の反応プロセスを実現すると期待されている。Rahat Javaid提出の博士論文は、内壁に触媒金属の薄膜を被覆したマイクロチューブリアクタの開発と、水中での連続触媒反応プロセスへの応用に関するものである。

チューブリアクタの内壁に触媒機能を付与する事で、触媒反応を連続通液で行うことができる。チューブ内壁に金属粒子や金属錯体を固定することは既に試みられていたが、耐熱、耐圧の限界や、腐食、触媒金属の流失などの課題があった。Rahat Javaidは、触媒金属（Pd, Pt, Rh, Auなど）薄膜を均一に全面被覆することで、触媒面積を増大させ、溶出による触媒活性の損失を最小化しようと試みた。厚さ１－２μmの金属薄膜を被覆する手法として、無電解メッキを適用した。支持体細管（内径0.3-0.5mm）内に無電解メッキ液を通液し、種々の金属の薄膜を被覆した。また、耐腐食性を持つ合金二重管への触媒金属薄膜の均一被覆に成功し、常温・常圧から高温・高圧までの反応条件に耐久性を有する多層合金リアクタの開発に成功した。金属製細管を用いることで、二種金属のメッキと熱処理による合金化が可能となった。これによりPd, Pt, Rh, Auのみならず Pd-Cu合金, Pd-Ag合金など多岐にわたる触媒金属薄膜を、内壁に均一に被覆したチューブリアクタが得られた。

これらのチューブリアクタを用い、１）過酸化水素の連続分解、２）難分解芳香族色素の連続分解、３）水中での有機反応（C-Cカップリング反応）などの流通反応に適用した。過酸化水素の分解では、パラジウム酸化物（Pd－O）表面が、PtではPt金属が触媒活性で、いずれも中間体として・OH, ・OOHラジカルを生成する。触媒表面で生成した上記ラジカルにより、過酸化水素による難分解芳香環の完全分解が迅速に達成された。また、有機分子と高温高圧水とを金属細管中で高速混合してエマルジョンとすることで、水中での有機反応（C-Cカップリング）が速やかに進行することを確かめ、触媒チューブリアクタによる水中における迅速な有機合成に道を拓いた。とりわけ機械強度に優れ、超臨界水などの高温高圧状態においても熱的、化学的に安定な金属製リアクタは、幅広い温度・圧力条件において適用でき、実用の観点でも特筆に値する。

以上、本論文で述べられた触媒被覆マイクロチューブリアクタは、連続反応プロセスの新しい展開に大きく貢献すると評価される。また論文提出者が自立して研究活動を行うのに必要な研究能力と学識を有していることを示している。従って提出者、Rahat Javaidの博士論文は博士（理学）の学位論文として合格と認める。