J Mater Sci (2009) 44:5836–5841
DOI 10.1007/s10853-009-3823-y

Influence of a fiber-network microstructure of paper-structured catalyst on methanol reforming behavior

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Received: 1 June 2009 / Accepted: 18 August 2009 / Published online: 27 August 2009

Abstract A novel microstructured catalyst that consists of Cu/ZnO catalyst powders and ceramic fibers was successfully prepared using pulp fibers as a tentative matrix by a papermaking technique. As-prepared material, called a paper-structured catalyst, possessed porous microstructure with layered ceramic fiber networks (average pore size ca. 20 μm, porosity ca. 50%). In the process of methanol autothermal reforming (ATR) to produce hydrogen, paper-structured catalysts demonstrated both high methanol conversion and low concentration of undesirable carbon monoxide as compared with catalyst powders and pellets. The catalytic performance of paper-structured catalysts depended on the use of pulp fibers, which were added in the paper-forming process and finally removed by thermal treatment before ATR performance tests. Confocal laser scanning microscopy and mercury intrusion analysis suggested that the tentative pulp fiber matrix played a significant role in regulating the fiber-network microstructure inside paper composites. Various metallic filters with different average pore sizes, used as supports for Cu/ZnO catalysts, were subjected to ATR performance tests for elucidating the pore effects. The tests indicated that the pore sizes of catalyst support had critical effects on the catalytic efficiency: the maximum hydrogen production was achieved by metallic filters with an average pore size of 20 μm. These results suggested that the paper-specific microstructures contributed to form a suitable catalytic reaction environment, possibly by promoting efficient diffusion of heat and reactants. The paper-structured catalyst with a regular pore microstructure is expected to be a promising catalytic material to provide both practical utility and high efficiency in the catalytic gas-reforming process.

Introduction

Catalytic reforming of methanol has widely been applied to produce hydrogen for new power generation systems such as polymer electrolyte fuel cells (PEFCs) [1]. In general, methanol reforming has been performed over Cu/ZnO catalysts at a relatively low temperature (below 300 °C) [2]. However, the random packing of catalyst particles into the reactor frequently causes a high-pressure drop and fluid bypassing, resulting in the crucial inefficiency of the catalytic reforming process. Therefore, one area of increasing attention has been the development of microstructured catalysts that have effective diffusion properties of heat and reactants [3].

Honeycomb-type structured catalysts, which consist of regularly arranged parallel channels, have many applications in the energy and environmental area because of their low pressure drop [4, 5]; however, they have some limitations such as the lack of radial mixing of reactant gases [5]. Thus, extensive efforts have been devoted to develop novel structured catalysts with various shapes, such as foam [6], string [7], and egg shells [8]; the structural effect of microstructured catalysts on the catalytic performances has become the focal point for these researches.

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In our previous studies, Cu/ZnO catalyst powders were successfully supported on a layered ceramic fiber network by a papermaking technique [9–13]. As-prepared materials, called paper-structured catalysts, were applied to the autothermal reforming (ATR) of methanol ($4CH_3OH + 3H_2O + 1/2O_2 \rightarrow 11H_2 + 4CO_2$, $\Delta_r H^0_{573} \approx 0$ kJ mol^{-1}) for hydrogen fuel cell applications. Paper-structured catalysts demonstrated high catalytic efficiency and durability as compared with the original catalyst powder, possibly indicating that the porous paper structure improved the practical performance of the Cu/ZnO catalyst [12–14]. However, the detailed correlation between the ATR performance and paper-specific microstructure had not been clarified.

In this study, the effects of fiber-network microstructures of paper-structured catalysts on methanol reforming behavior were investigated in detail by structural analysis and model experiments. The unique fiber-network structure inside paper composites (e.g., pore structure and fiber orientation) was analyzed by confocal laser scanning microscopy (CLSM) and mercury intrusion analysis. The correlation between the pore sizes of catalyst supports and the ATR performance was investigated using metallic filters with definite pore structures.

Experimental

Materials

Commercial Cu/ZnO catalyst pellets (MDC-3; cylindrical shape 3-mm diameter and 3-mm height; Süd-Chemie, Ltd.) were used, and some were pulverized to fine powders with 100 mesh-pass size. Pulp fibers as a tentative supporting matrix in the papermaking process were obtained by refining commercial bleached hardwood kraft pulp. Ceramic fibers (IBI-WOOL, IBIDEN, Ltd.) were cut into an average length of ca. 0.5 mm using a four-flute end mill. Two types of flocculants were used as retention aids: cationic polydiallyldimethylammonium chloride (PDADMAC; molecular weight ca. 3×10^5; charge density 5.5 meq g^{-1}; Aldrich, Ltd.) and anionic polyacrylamide (A-PAM, HH-351; molecular weight ca. 4×10^6; charge density 0.64 meq g^{-1}; Kurita, Ltd.). Alumina sol (Snowtex 520, Nissan Chemicals, Ltd.) was used as a binder to improve the physical strength after calcination. Metallic filters with different pore sizes (Bekipore ST AL3, average pore sizes 5, 10, 15, 20, 25, 30, 40, 60, 100 μm, porosity ca. 80%, Bekaert Toko Metal Fiber, Ltd.) were used as a model catalyst support. $Cu(NO_3)_2 \cdot 3H_2O$ and $Zn(NO_3)_2 \cdot 6H_2O$ (99.9% purity) were purchased from Wako Pure Chemical Industries, Ltd.

Preparation of paper-structured catalysts by a papermaking technique

The preparation details of paper-structured catalysts have been described in our previous reports [9–13]. The outline of a papermaking procedure is summarized as follows: a ceramic fibers/water suspension (1.0% w/v) containing Cu/ZnO catalyst powders were mixed with PDADMAC (0.5 wt% per solids), alumina sol, and A-PAM (0.5 wt% per total solids) in that order. The mixture was added to a pulp fiber suspension (0.125% w/v), and solidified by dewatering using a 200-mesh wire. The wet-state handsheets were pressed at 350 kPa for 3 min, followed by drying in an oven at 105 °C for 1 h. The resulting paper composite consisted of Cu/ZnO catalyst powders (1.5 g), ceramic fibers (5.0 g), alumina sol (0.50 g), and pulp fibers (0.00 or 0.25 g). The paper-structured catalyst obtained was calcined at 350 °C for 12 h to remove pulp fibers and to improve the physical strength by binder sintering.

Synthesis of Cu/ZnO catalysts on metallic filters by impregnation method

The impregnation method was used to coat the Cu/ZnO catalyst components onto metallic filters according to a previous report [6]. The metallic filters were cut into disk-shaped pieces (8×10^2 mm^2) and immersed in 100 mL of the mixed aqueous solution of $Cu(NO_3)_2$ (9.4×10^{-2} M) and $Zn(NO_3)_2$ (3.1×10^{-2} M) containing alumina sol (0.2 g); then water was completely evaporated to dryness at 100 °C under continuous stirring. The resulting metallic filters were calcined at 350 °C for 4 h before the ATR test.

ATR performance test

The details of the reactor setup and ATR performance testing are described in our previous reports [12–14]. Ten disk-shaped paper-structured catalysts were stacked vertically (8×10^3 mm^3) and placed inside a stainless steel cylindrical reactor. Cu/ZnO catalyst powders or pellets were loaded inside the reactor, whereas ceramic powders were mixed to adjust the occupied volume to 8×10^3 mm^3. In each case, the catalyst content was set at 0.6 g. In the case of metallic filters, they were stacked in a similar way; the catalyst content and the occupied volume in the reactor were adjusted to 0.5 g (Cu 0.4 g, ZnO 0.1 g) and 4×10^3 mm^3, respectively, regardless of their average pore sizes. A mixed gas with methanol/water/oxygen (molar ratio 1.00:1.50:0.125) vaporized at 200 °C was fed into the reactor at 250 °C at a constant gas-space velocity of 1130 h^{-1}. The gas generated in the ATR reaction was passed through a cold trap in an ice bath; then the unreacted methanol separated from the gaseous components was quantified by a gas chromatograph (GC; GC-17A, Shimadzu, Ltd.) fitted with a Supel-Q Plot column (0.53 μm × 30 m, Shimadzu, Ltd.). The major gaseous products—hydrogen and carbon dioxide—were analyzed online using a GC-thermoconductivity detector equipped with a Porapak-Q column (3 mm × 2 m, Shinwa Chemical Industries, Ltd.). Carbon monoxide as a minor by-product was measured using a GC-flame ionization detector equipped with a Porapak-Q column after the complete conversion of carbon monoxide to methane by an online methanizer (MTN-1, Shimadzu, Ltd.).

Analyses

The catalyst content of the samples was determined by atomic absorption analysis using a Shimadzu AA-6600F apparatus [9–14]. The fiber-network microstructure of a paper-structured catalyst was visualized using a CLSM apparatus (ECLIPSE TE2000-U, Nikon, Ltd.) with a solid-state laser at 488 nm. The obtained CLSM images were analyzed by FiberOri8Single03 software to determine ceramic fiber orientation according to a previous report [15]. Mercury intrusion analysis was carried out using a Poremaster 33P (Yuasa Ionics, Ltd.) to evaluate the pore diameter and porosity of paper composites. The pore size distribution was obtained from the pressure-cumulative mercury intrusion volume curve normalized by the catalyst weight.

Results and discussion

Paper-structured catalyst prepared by a papermaking technique

Figure 1 shows the optical images of paper-structured catalysts, which were just like a cardboard material, lightweight (350 kg m^{-3}), bendable, and easy to handle. The retention of inorganic materials including Cu/ZnO powders reached over 90% by our established papermaking technique [9–13].

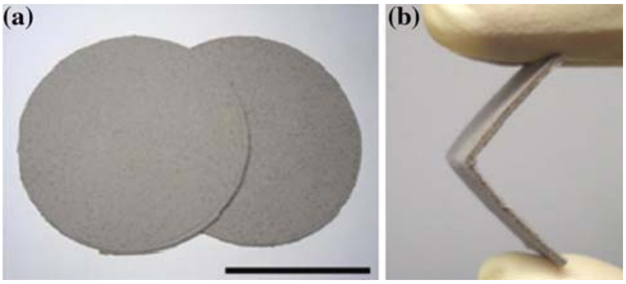

Fig. 1 Optical images of paper-structured catalysts: *circular shape* (**a**) and *folded shape* (**b**). Scale bar indicates 100 mm

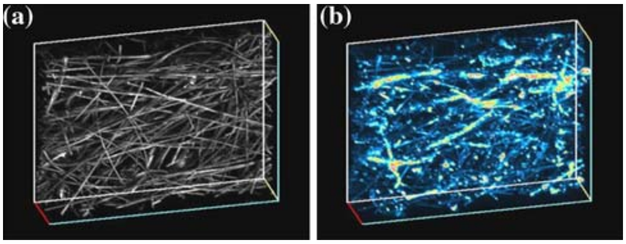

Fig. 2 3D CLSM images of a paper-structured catalyst (400 μm W × 400 μm D × 100 μm H): reflected image (**a**) and fluorescent image (**b**)

Figure 2 displays the 3D CLSM images of a paper-structured catalyst. The image capturing system whereby the focal plane was successively staggered every 0.5 μm in a vertical (height) direction was allowed to build the 3D image of the layered fiber-network structure of a paper-structured catalyst (400 μm W × 400 μm D × 100 μm H). As shown in Fig. 2a, a clear fiber-network structure was observed in the reflected image. Besides, fluorescent imagery could distinguish ceramic fibers and Cu/ZnO catalyst by detecting the difference in inherent self-fluorescence of inorganic components, as shown in Fig. 2b. It was visualized that fine catalyst powders were well scattered on the fiber network, and paper-structured catalyst possessed the unique porous microstructure derived from layered ceramic fiber networks.

Fiber-network microstructure affecting ATR behavior

Pulp fibers used in the preparation of paper-structured catalyst act as a tentative matrix of the wet-state paper web, and contribute to maintaining the physical strength of paper composites before binder sintering. After calcination, the organic pulp fibers were completely removed; and simultaneously the unique porous microstructure—the inorganic fiber networks—was formed inside a paper-structured catalyst [9–14]. In this study, a pulp-free paper-structured catalyst was prepared without adding pulp fibers to elucidate the influences of pulp fibers on the formation of ceramic fiber-network microstructure and on methanol reforming behavior. Table 1 compares the methanol

Table 1 Methanol reforming behavior at a gas-space velocity of 1130 h^{-1}

Catalyst sample	Methanol conversion (%)	CO concentration (ppm)
Pulp-free paper	85.7 ± 0.8	5500 ± 300
Pulp-added paper	88.9 ± 0.8	3100 ± 300
Catalyst powder	88.7 ± 4.8	6700 ± 800
Catalyst pellet	46.3 ± 2.0	4500 ± 200

reforming behavior of paper-structured catalyst, catalyst powder, and pellets. The methanol conversion of paper-structured catalysts was comparable with that of the original catalyst powder, far higher than that of the commercial pellet-type catalyst. By-product carbon monoxide acts as a catalytic poison for the Pt anode electrocatalysis of PEFCs, and the paper-structured catalysts emitted significantly low carbon monoxide concentrations as compared to the catalyst powder. Especially, pulp-added paper exhibited higher methanol conversion and lower carbon monoxide concentration than pulp-free paper; although, both pulp-added and pulp-free catalyst papers were calcined before the catalytic performance test, resulting in the same composition. Previously, we reported that the calcination treatment in the presence of pulp fibers caused severe Cu sintering due to the combustion heat of pulp fibers, leading to the deterioration of Cu/ZnO catalysts [13]. In fact, when pulp-free paper-structured catalysts were prepared using sintered Cu/ZnO catalyst powders, which were beforehand calcined with pulp at 350 °C for 12 h in a similar manner to the preparation of pulp-added paper-structured catalyst, an obvious decrease in the methanol conversion was found: 80.9 ± 0.6%. These results indicated that ceramic fiber-network microstructure formed by the removal of the pulp-fiber template from paper composites possibly contributed to the certain enhancement of apparent catalytic efficiency.

Figure 3 profiles the pore-size distribution of paper-structured catalysts with and without pulp dosage. In both the cases, the peak pore size was ca. 20 μm in diameter, and the total porosity was ca. 50%. However, a clear peak around 20 μm of the pulp-added catalyst paper was found sharp and narrow as compared to that of pulp-free catalyst paper, indicating more regular pore-size distribution. Figure 4 shows the reflected 2D CLSM images of the paper composites (400 μm W × 400 μm D × 250 μm H). In the case of the pulp-free catalyst paper, some bundles of ceramic fibers were observed (fiber orientation index 1.12). Enomae et al. [15] have determined the degree of fiber orientation by Fourier analysis of digital images of fiber network, and the resulting index of 1.12 indicates clear and intense fiber orientation. Such fiber orientation was possibly caused by bundle-like aggregations of parallel ceramic fibers, resulting in the formation of the sparse-dense matrix inside the paper composites. This result suggested that ceramic fibers possibly coalesced due to some attractive interaction in an aqueous papermaking process. In the case of the pulp-added catalyst paper; however, ceramic fibers were well scattered in every direction (fiber orientation index 1.02, isotropic dispersion). Eventually, pulp fibers acted as a dispersing agent in an inorganic matters/water suspension, leading to the random distribution of the ceramic fibers. Thus, pulp fibers must play a significant role in providing the controlled microstructure inside the paper composites for improving methanol reforming performance. In our previous studies for nitrogen oxides reduction, paper-structured Pt catalysts demonstrated higher catalytic performances than commercial honeycomb-structured Pt catalysts, indicating that fiber-network microstructures of paper-structured catalysts are more effective than conventional honeycomb structures [16, 17]. Furthermore, Patcas and Krysmann [8] have reported that the uniform accessibility of reactants to catalytic sites is of great importance to obtain both a high reactivity and selectivity in various catalytic processes. Therefore, the excellent performance of the pulp-added paper-structured catalysts implies that an adequate fiber-network microstructure would promote a degree of desirable gas accessibility to the catalyst surfaces.

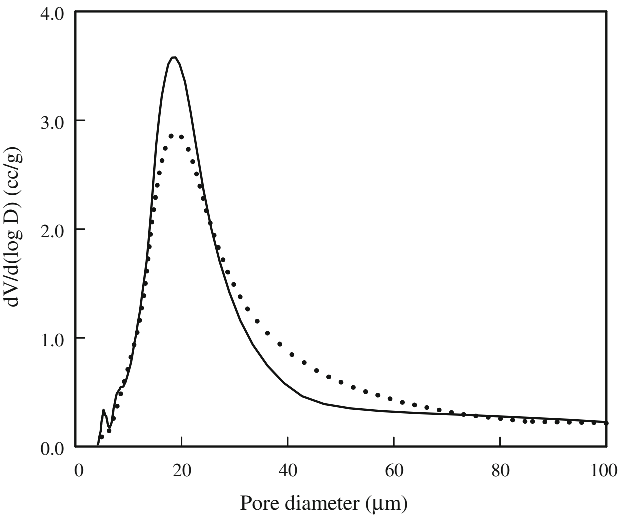

Fig. 3 Pore-size distribution curves of paper-structured catalysts: pulp free (*dotted line*) and pulp addition (*solid line*). Pulp-free and pulp-added catalyst paper showed the peak pore sizes of ca. 20.5 and ca. 19.7 μm, respectively

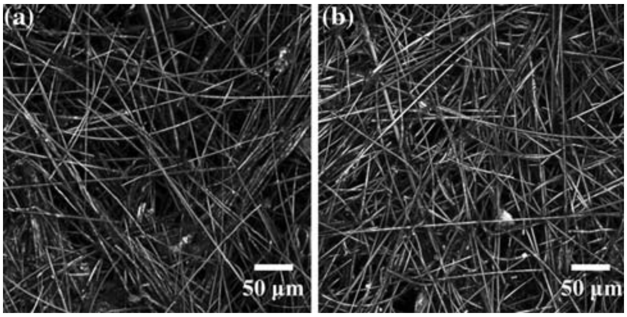

Fig. 4 Reflected 2D CLSM images of paper-structured catalysts (400 μm W × 400 μm D × 250 μm H): pulp free (**a**) and pulp addition (**b**)

Effects of pore sizes of catalyst support on ATR behavior

To elucidate the effects of the pore sizes of catalyst support on methanol reforming behavior, Cu/ZnO catalysts were synthesized on various metallic filters having different average pore sizes (average pore size 5–100 μm, porosity ca. 80%) by the impregnation method. Regardless of an average pore size, the same amount of Cu/ZnO catalyst (0.5 g) was successfully mounted on the same volume of metallic filters (4×10^3 mm^3). Figure 5 shows the ATR performances of metallic filters at a gas-space velocity of 1130 h^{-1}. Among all the samples, methanol conversion reached over 90% (data not shown); there was a little difference in methanol conversion. However, the maximum hydrogen production was recorded by the metallic filter with an average pore size of 20 μm, and carbon monoxide concentration decreased with increasing average pore size. To produce pure hydrogen in the ATR process, it is critical to suppress side reactions, typically a reverse water-gas shift (rWGS) reaction ($H_2 + CO_2 \rightarrow CO + H_2O$, $\Delta_r H^0_{298} \approx +41\,\mathrm{kJ\,mol^{-1}}$), in addition to the promotion of the principal ATR reaction. In our previous report, computational fluid dynamics analysis suggested that the localization of heat and major products, hydrogen and carbon dioxide, inside the catalyst layer leads to an undesirable rWGS reaction [11]. Therefore, micrometer-scale pores of a fiber-network catalyst support must influence the diffusion of heat and reactants inside the catalyst layer, and dominate the overall methanol reforming performance. As shown in Fig. 5, larger pores in the catalyst layer inhibited carbon monoxide formation, possibly by avoiding the long residence of generated gases, hydrogen and carbon dioxide, in the catalyst layer; but at the same time decreased the hydrogen production efficiency due to the lower gas accessibility to the catalytic sites. Therefore, it has been suggested that the well-controlled fiber-network microstructure with a uniform pore size of ca. 20 μm provided a favorable reaction environment for the autothermal hydrogen production at the given gas-space velocity; such a phenomenon would be closely involved in the practical performance of a paper-structured catalyst.

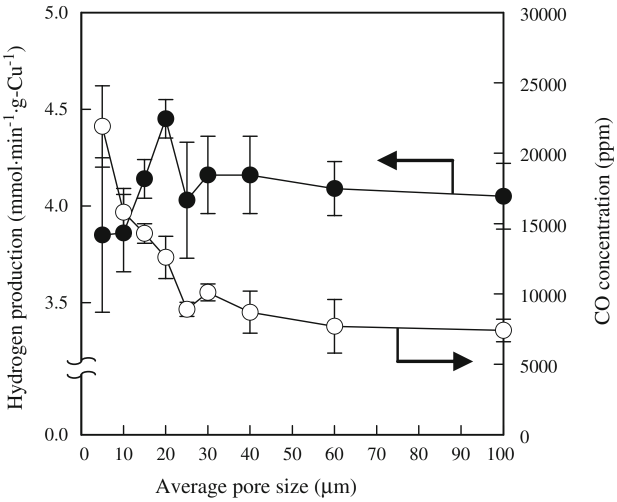

Fig. 5 Correlation between the average pore sizes of metallic filters impregnated with Cu/ZnO catalyst and methanol reforming behavior at a gas-space velocity of 1130 h^{-1}: hydrogen production (*closed circles*) and CO concentration (*open circles*). Catalyst content: 0.5 g/ 4×10^3 mm^3

Conclusions

Paper-structured catalysts with ceramic fiber-network microstructure were successfully prepared by a high-speed and low-cost papermaking technique. The pulp fiber addition as a tentative matrix in the paper-forming process improved the ATR performance of the paper-structured catalyst: high methanol conversion and low carbon monoxide concentration. The pulp fibers acted as a dispersing agent of inorganic components, leading to the uniform arrangement of fiber networks and the formation of regularly sized pore spaces (ca. 20 μm). It was suggested that the pore size of the catalyst support was a critical factor in determining the catalytic performance: high hydrogen production and relatively low carbon monoxide concentration was confirmed by using a metallic filter with a uniform pore size of 20 μm. Thus, the well-controlled fiber-network microstructure with connected pore spaces formed by fiber components inside a paper-structured catalyst must provide a suitable catalytic reaction environment by promoting the degree of desirable gas accessibility to the catalyst surfaces.

Acknowledgements The authors wish to thank Dr. T. Enomae for providing FiberOri8Single03 software. This research was supported by a Research Fellowship of the Japan Society for the Promotion of Science for Young Scientists (H. Koga) and by an Industrial Technology Research Grant Program from the New Energy and Industrial Technology Development Organization (NEDO) of Japan (T. Kitaoka).

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