1. Introduction

1.1 Recent advances in catalysts

Metal catalysts have played essential roles in a wide range of chemical industrial processes [1-3]. For example, the copper/zinc oxide (Cu/ZnO) catalyst has been especially important for methanol synthesis [4] and alcohol reforming to produce hydrogen for fuel cell applications [5]. Energy, environmental and resource problems have escalated in recent times. Therefore, the development of high-performance catalytic materials that can effectively and selectively promote desired reactions is required for sustainability.

1.1.1 Metal nanocatalysts

Nanosized metal particles have received an increasing amount of attention in various fields, such as in electronic [6], optical [7] and biomedical [8] applications, because of their unique and specific properties. In particular, the extremely large specific surface areas of metal nanoparticles (NPs) are very advantageous for effective catalytic reactions [9]. This has led to the active use of metal NPs as heterogeneous catalysts for a variety of industrial processes [9] including energy conversion, fine chemical synthesis and environmental cleanup. For example, gold (Au) nanocatalysts have received considerable interest for use in various reactions, including the reduction of 4-nitrophenol (4-NP) in the liquid phase [10] and low-temperature carbon monoxide (CO) oxidation [11] in the gas phase, even though bulk Au is typically regarded as an ineffective catalyst. However, the practical implementation of metal NPs is difficult, because they are difficult to handle and they aggregate easily, which minimizes their surface area. The aggregation of metal NPs results in the formation of ordinary bulk metals, and this consequently deteriorates their excellent functionalities. Therefore, catalytic metal NPs are generally attached to various support materials, such as polymers [9,12] and metal oxide powders [9,13]. Since these supported catalysts are fine and are handled with difficulty in practice, they are generally fashioned as beads or pellets. This eventually decreases their catalytic reactivity, because of the poor contact efficiency between the reactants and the catalytically active sites [14]. In addition, filling a reactor with solid catalysts can cause a high pressure drop, local reactant flow and an uneven thermal environment inside the catalyst layer, leading to an inefficient overall process, particularly for flow-type reactions. Therefore, establishing an efficient and practical immobilization technique that enables highly active metal NPs to be attached to and exposed on easy-to-handle porous matrices is a challenge.
1.1.2 Structured catalysts

Recently, structured matrices that contain micrometer-scale open paths for fluids have attracted much attention as promising catalyst supports, since they allow for the effective diffusion of heat and reactants during catalytic reactions [15]. In this context, various types of structured supports, such as foams [16], strings [17] and honeycombs [18,19], have been developed. In particular, honeycomb-structured supports with regularly arranged parallel channels have been popularized, especially in environmental applications including nitrogen oxide (NOx) reduction. However, they have some limitations, such as weight and the lack of radial reactant mixing [19]. Consequently, the structural design of the porous catalytic supports is being intensively investigated for efficient practical applications.

1.2 Paper-like fiber/catalyst composites

Paper is a lightweight and easy-to-handle material, and is used for a wide range of purposes, such as writing, printing, wrapping and packaging. While most paper is made from organic fibers, including wood pulp and cotton, inorganic fibers, such as ceramic and glass fibers, are also used for functional applications. Paper materials possess a highly porous microstructure, which is derived from layered fiber networks. Therefore, paper is expected to be useful as a structured catalyst support.

In our previous studies, various catalyst powders, e.g. zeolite [20], titanium dioxide [21], Cu/ZnO [22-24] and platinum/aluminum oxide (Pt/Al2O3) [25,26], were successfully supported on a microstructured paper matrix composed of ceramic fibers, using a papermaking technique combined with a dual polymer retention (DPR) system. We found that the as-prepared composites, which we referred to as paper-structured catalysts, had paper-like practical utility and a highly porous microstructure that was derived from their ceramic fiber networks (Fig. 1). In addition, the paper-structured catalysts were highly effective in various catalytic processes, such as the photodecomposition of bisphenol A in water [21], methanol reforming for hydrogen production [22-24] and NOx removal for exhaust gas purification [25-27]. Several of our studies suggest that the paper-specific microstructure effectively improves the efficiency of catalytic reactions [28]. Therefore, paper is expected to be a promising structured catalyst support, and this concept has recently gained worldwide interest [29]. Our established papermaking technique allows for the versatile combination of various fibers and catalyst powders. Further functional development of these paper composites is a significant challenge during the establishment of more effective catalytic processes.

Fig. 1 Optical images of the paper-structured catalysts; (a) circular shape and (b) folded shape, (c) SEM and (d) 3D CLSM images of the paper-structured catalysts.

Fig. 2 Schematic of the on-paper synthesis of the AuNPs.
1.3 Contents

In this review article, we present a facile technique for the in situ synthesis of highly active metal nanocatalysts on an easily handled paper matrix with a porous microstructure. For example, the outline of our strategy for the ‘on-paper’ synthesis of AuNPs is highlighted in Fig. 2. The on-paper synthesis of metal NPs, such as CuNPs, PtNPs and AuNPs, was achieved using an inorganic paper matrix composed of ceramic fibers as the main framework, and ZnO whiskers as a selective scaffold for the synthesis of metal NPs. First, we present metal NPs synthesis on ZnO whiskers. Second, we describe the incorporation of ZnO whiskers into a ceramic paper matrix using a papermaking technique and the direct in situ synthesis of metal NPs on ZnO whisker-containing paper (ZnO paper). The excellent catalytic performance of the as-prepared metal NPs@ZnO paper is also reviewed; CuNPs@ZnO paper for methanol reforming to produce hydrogen, PtNPs@ZnO paper for NOx gas purification and AuNPs@ZnO paper for CO oxidation and 4-NP reduction are also introduced.

2. Experimental

2.1 Papermaking procedure

ZnO paper was prepared using a papermaking technique combined with a DPR system. An outline of the papermaking procedure has been described in our previous reports [30] and can be summarized as follows. A suspension of ceramic fibers and ZnO whiskers/water was mixed with cationic polydiallyldimethylammonium chloride, an alumina sol binder and an anionic polyacrylamide, in that order. The mixture was added to a suspension of pulp fibers and was solidified by dewatering using a 200-mesh wire. The handsheets were dried in an oven at 105°C for 1 h, following pressing at 350 kPa for 3 min. The obtained paper composite (2 × 10^4 mm²) consisted of ZnO whiskers (3.1 g), ceramic fibers (5.0 g), alumina sol (0.50 g) and pulp fibers (0.25 g). The obtained ZnO paper was calcined at 350°C for 12 h to remove the pulp fibers and to improve the physical strength by binder sintering.

2.2 Preparation and characterization of metal NPs@ZnO paper

The in situ synthesis of metal NPs on ZnO paper was carried out as follows. For the on-paper synthesis of CuNPs [30], ZnO paper was cut into circular-shaped disks (8 × 10^3 mm²) and immersed in an aqueous solution of copper nitrate (Cu(NO₃)₂) for 20 min. The disks were then removed from the solution, followed by thorough washing with deionized water, drying at 105°C for 3 h and reduction in hydrogen at 250°C for 1.5 h. To prepare the PtNPs@ZnO paper [31], ZnO paper was immersed in an aqueous solution of chloroplatinic acid (H₂PtCl₆) for 48 h. The treated disks were then washed with deionized water and reduced in an aqueous solution of sodium borohydride (NaBH₄) for 3 min, followed by thorough washing with deionized water and drying at 105°C for 3 h. For AuNPs@ZnO paper [32,33], ZnO paper was soaked in an aqueous solution of tetrachloroauric acid (HAuCl₄) for 6 h. The disks were then removed from the solution, washed with deionized water and dried at 105°C for 3 h. The metal NPs@ZnO whiskers (not a paper shape) were prepared in a similar manner. The characterization of the as-prepared metal NPs@ZnO whiskers and paper was conducted by atomic absorption analysis, scanning electron microscopy (SEM), transmission electron microscopy (TEM), selected-area electron diffractometry (SAED), confocal laser scanning microscopy (CLSM), X-ray diffractometry (XRD), X-ray photoelectron spectroscopy (XPS) and mercury intrusion porosimetry.

2.3 Catalytic performance test

The catalytic performances of the CuNPs@ZnO paper and the PtNPs@ZnO paper were evaluated for the autothermal reforming (ATR) of methanol [30] and NOx removal with propene (C₃H₆) [31], respectively. The AuNPs@ZnO paper was subjected to CO oxidation [32]. These gas-phase catalytic processes were carried out using a fixed-bed flow-type reactor with on-line gas chromatography (GC) [22,24] and a NOx analyzer system [25]. For AuNPs@ZnO paper, a liquid-phase 4-NP reduction process to produce 4-aminophenol (4-AP) was also conducted in batch mode, and the reaction progress was monitored by UV-vis spectrometry [33].

3. Results and discussion

3.1 Metal NPs synthesis on ZnO whiskers

ZnO is commonly used as an inorganic additive for various products, such as rubbers, paints, pigments, foods and adhesives, since it is inexpensive, relatively-abundant, non-toxic and biocompatible. Recently, ZnO-mediated photocatalysis for optical [34] and photoelectronic [35] applications, such as semiconductors, sensors and solar cells, has increased in importance. In this review, we propose a new method of using ZnO as a scaffold for the synthesis and immobilization of metal NPs.

3.1.1 CuNPs synthesis on ZnO whiskers

CuNPs synthesis on ZnO was accomplished by soaking ZnO whiskers in a Cu(NO₃)₂ solution and a
subsequent reduction treatment, in which the ionic Cu species was adsorbed on a ZnO support by ion exchange, and was subsequently reduced to form CuNPs [30]. The procedure is shown in (Fig. 3).

First, ZnO whiskers were suspended in an aqueous solution of Cu(NO₃)₂, with stirring for 20 min, filtered and thoroughly washed with deionized water. The ZnO whiskers and Cu(NO₃)₂ solution immediately changed from white to blue and from blue to transparent, respectively. XPS and XRD analysis indicated that the Cu²⁺ species (Cu₂(OH)₃NO₃) adsorbed onto the ZnO whiskers (Fig. 4b). In addition, the elution of the Zn species from the ZnO whiskers was confirmed by atomic absorption analysis. When using aqueous solutions of cobalt nitrate (Co(NO₃)₂) and nickel nitrate (Ni(NO₃)₂), only a slight color change was observed for the ZnO whiskers and the nitrate solutions within 20 min (Fig. 3). These results strongly suggest that the rapid adsorption of the Cu²⁺ species onto the ZnO whiskers involves a large difference in ionization tendency between the Cu and Zn species. Subsequently, the Cu(NO₃)₂-treated ZnO whiskers were dried and then completely reduced in a hydrogen flow to a dark red product. TEM images of the original ZnO whiskers and the Cu(NO₃)₂-treated ZnO whiskers before and after reduction are shown in Fig. 5. The ZnO whiskers used in this study had a tetrapod-like nanostructure (Figs. 5a and 5b). For the Cu(NO₃)₂-treated ZnO whiskers before reduction, several needle-like crystals that derived from (Cu₂(OH)₃NO₃) were observed on the surface of the ZnO whiskers (Fig. 5c). After the reduction, many NPs of 20-50 nm in size were formed on

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**Fig. 3** Adsorption of the Cu species from a Cu(NO₃)₂ solution onto the ZnO whiskers and the sequential CuNPs synthesis on the ZnO whiskers.

**Fig. 4** XPS (left) and XRD (right) spectra of (a) the original ZnO whiskers and the ZnO whiskers treated with a Cu(NO₃)₂ solution; (b) as-dried and (c) reduced. ○: Cu₄(OH)₃(NO₃), □: Cu, ■: ZnO.
3.1.2 PtNPs synthesis on ZnO whiskers

The synthesis of PtNPs on ZnO whiskers was accomplished using H$_2$PtCl$_6$ as a PtNPs precursor [31]. The ZnO whiskers were suspended in an aqueous yellow solution of H$_2$PtCl$_6$, removed from the solution and then washed thoroughly with deionized water and heat-dried. The ZnO whiskers changed from white to light yellow. The H$_2$PtCl$_6$-treated ZnO whiskers were then reduced in an aqueous solution of NaBH$_4$ to obtain a grey-colored product (Fig. 6a). A TEM image of the H$_2$PtCl$_6$-treated ZnO whiskers after NaBH$_4$-reduction is shown in Fig. 6b. A large amount of fine NPs were observed on the ZnO whiskers. The SAED pattern confirmed face-centered cubic single crystals of Pt (Fig. 6c), clearly indicating that the as-synthesized NPs shown in Fig. 6b corresponded to PtNPs. In this case, no ion exchange occurred between the Pt and Zn species, since the PtNP precursors exist in the form of Pt$^{4+}$ complex anions ([PtCl$_6$]$^{2-}$) in an acidic solution. On the basis of XPS results [31], we conclude that PtNPs formation on ZnO whiskers proceeds as follows: (1) the coordinated Cl$^-$ ions of [PtCl$_6$]$^{2-}$ are partially replaced by OH$^-$ ions to become [PtCl$_{6-n}$(OH)$_n$]$^{2-}$ complexes; (2) the outer surface of the ZnO whiskers are hydroxylated to form Zn(OH)$_2$ in an aqueous solution of H$_2$PtCl$_6$; (3) anionic [PtCl$_{6-n}$(OH)$_n$]$^{2-}$ and positively charged Zn(OH)$_2$ in the acidic solution [36] attract each other because of electrostatic interactions; (4) the [PtCl$_{6-n}$(OH)$_n$]$^{2-}$ species reacts with Zn(OH)$_2$ to form Zn-O-Pt bonds through a condensation reaction between Pt-OH and Zn-OH; (5) subsequent treatment with NaBH$_4$ leads to the reduction of Pt$^{4+}$ to Pt$^0$ to form metallic PtNPs on the ZnO whiskers. The molar ratios of Pt to Zn estimated from the results of XPS and atomic absorption analyses were ca. 0.1066 and ca. 0.0070, respectively, indicating that many PtNPs were present on the surface of the ZnO whiskers [31].

3.1.3 AuNPs synthesis on ZnO whiskers

AuNPs were also synthesized on ZnO whiskers using HAuCl$_4$ as a AuNPs precursor [32,33]. ZnO whiskers were suspended in an aqueous solution of HAuCl$_4$, followed by stirring for 6 h, filtration, thorough washing with deionized water and drying. An optical image, TEM image and XRD pattern of the HAuCl$_4$-treated ZnO whiskers after drying is shown in Fig. 7. The ZnO whiskers treated with the HAuCl$_4$ solution were pink-purple (a surface plasmon resonance effect) (Fig. 7a). A large number of NPs less than 5 nm then formed on the surface of the ZnO needles (Fig. 7b). The XRD pattern of the HAuCl$_4$-treated ZnO whiskers clearly indicates the formation of Au crystals (Fig. 7c). These results strongly suggest that AuNPs form spontaneously on ZnO whiskers.
after a simple soaking treatment with a HAuCl₄ solution in the absence of reducing agents. A similar phenomenon has been reported by Yokoyama and co-workers: Au³⁺ complex ions that adsorbed on MnO₂ reduced spontaneously to Au⁰ in the absence of reducing agents [37]. They indicated that the rapid reduction of Au³⁺ to Au⁰ was caused by electron transfer from Mn²⁺ in Mn(OH)₂ to the chloro-hydroxy complexes of Au³⁺ ions ([AuCl₄⁻(OH)₃]⁻) through Mn-O-Au bonds, concomitantly with the oxidation of Mn²⁺ to Mn⁴⁺ [38]. In this study, XPS analysis suggests that some Zn²⁺ species on the ZnO surfaces were oxidized to some extent after HAuCl₄ treatment [32]. On the basis of these results and previous reports concerning Au synthesis on metal oxides [37-39], we surmise that the formation of AuNPs on ZnO whiskers progresses as follows: (1) the coordinated Cl⁻ ions in [AuCl₄]⁻ are partially replaced by OH⁻ ions to form [AuCl₄−(OH)₃]⁻ complexes [40]; (2) the outer surface of the ZnO whiskers hydroxylate to become Zn(OH)₂ in the aqueous Au³⁺ complex solution; (3) anionic [AuCl₄−(OH)₃]⁻ ions and positively charged Zn(OH)₂ [36] attract each other because of electrostatic interactions; (4) the [AuCl₄−(OH)₃]⁻ species react with Zn(OH)₂ to form Zn-O-Au bonds through a condensation reaction between Au-OH and Zn-OH; (5) the reduction of Au³⁺ to Au⁰ is caused by the large difference in ionization tendency between Au and Zn: electron transfer from Zn²⁺ on the ZnO surfaces to Au³⁺ proceeds through the Zn-O-Au bonds. The molar ratios of Au to Zn, as estimated from XPS and atomic absorption analyses, were found to be ca. 0.1146 and ca. 0.0041, respectively, suggesting that a large proportion of the AuNPs are present on the surface of the ZnO whiskers. The synthesis of PtNPs and AuNPs, which was achieved using a metal complex precursor, is clearly different from the formation of CuNPs by simple ion exchange. This strongly suggests that the synthesis of metal NPs on the ZnO whiskers can be carried out using various metal precursors.

3.2 In situ synthesis of metal NPs on a paper-structured matrix

As described above, very small metal NPs were successfully immobilized onto the ZnO whiskers. However, the as-prepared metal NPs@ZnO whiskers were still difficult to handle, since the ZnO whiskers are fine fibers. To solve this problem, we investigated the on-paper synthesis of metal NPs; ZnO whiskers were initially incorporated into a ceramic paper matrix and then the metal NPs were synthesized in an in situ manner onto the embedded ZnO whiskers.

3.2.1 Preparation of ZnO paper using a papermaking technique

Before the on-paper synthesis of metal NPs, ZnO whiskers were embedded into a ceramic paper matrix using a high-speed and low-cost papermaking technique [30]. The DPR system, which involves the sequential addition of cationic and anionic polyelectrolytes, enabled ca. 100% retention of the inorganic materials, including the fine ZnO whiskers. The physical strength of the as-prepared ZnO paper composites was significantly improved by alumina binder sintering. Optical and SEM

![Fig. 7](image_url) (a) Optical and (b) TEM images of the HAuCl₄-treated ZnO whiskers after drying and (c) the XRD pattern of the whisker; (i) the original ZnO whiskers and (ii) the HAuCl₄-treated ZnO whiskers after drying.

□: Au, ■: ZnO. Au content: ca. 4.1 mmol mol⁻¹ ZnO⁻¹.

![Fig. 8](image_url) Optical and SEM images of the ZnO paper.
images of the ZnO paper are shown in Fig. 8. The ZnO paper composites look like cardboard and are lightweight (ca. 275-430 kg m\(^{-3}\)), flexible, sufficiently strong and easy-to-handle during practical use. In addition, ZnO paper has a characteristic porous microstructure that derives from their ceramic fiber networks, over which the ZnO whiskers are well scattered.

3.2.2 On-paper synthesis of metal NPs

The in situ synthesis of metal NPs on ZnO paper was carried out using ZnO whiskers as a selective support for the metal NPs, in a similar manner to the synthesis of the metal NPs@ZnO whiskers. The on-paper synthesis of the AuNPs was performed as highlighted in Fig. 2. The ZnO paper was soaked in an aqueous solution of HAuCl\(_4\), followed by its removal from solution, washing with deionized water and drying. Consequently, AuNPs were synthesized selectively on ZnO whiskers, which were pre-incorporated into a ceramic paper matrix. As shown in Fig. 9, the unique porous microstructure that derived from the layered ceramic fiber networks remained almost unchanged after the AuNPs synthesis; the peak pore size was ca. 15 \(\mu\)m and the porosity reached ca. 80%. CuNPs @ZnO paper and PtNPs@ZnO paper were also successfully prepared in a similar manner (Fig. 10) and these paper composites had a high degree of practical use.

The preparation of structured supports with narrow microchannels normally requires complicated, multistep processes, e.g., laser machining [41] or ice templating [42]. Moreover, a subsequent wash-coating process to immobilize the catalyst components onto the as-prepared microstructured supports frequently fills up the pores. On the other hand, our technique described here enables the facile and efficient preparation of microstructured metal NPs/inorganic fiber composites: the on-paper synthesis of metal NPs was easily achieved by initially embedding ZnO whiskers into a microstructured ceramic paper matrix through a simple papermaking technique, and then using the embedded whiskers as a scaffold for the metal NPs synthesis. The on-paper synthesis of metal NPs can be performed using various metal precursors; silver (Ag) NPs@ZnO paper with antibacterial properties was also prepared using AgNO\(_3\) as a precursor [43,44]. Therefore, this facile technique has great potential applicability for a diverse array of metal species.

3.3 Catalytic performance of the metal NPs@ZnO paper

The metal NPs@ZnO paper has both metal nanocatalysts and a porous microstructure, which are regarded to be especially important for high performance catalytic materials. Furthermore, inorganic and porous paper composites have advantages under high temperature and high flow conditions. In this section we discuss the excellent catalytic performance of the metal NPs@ZnO paper.

3.3.1 Methanol reforming for hydrogen production using CuNPs@ZnO paper

The catalytic reforming of methanol using Cu/ZnO catalysts has been energetically investigated as a promising process for the production of hydrogen in new power generation systems, such as polymer electrolyte fuel cells (PEFCs) [45,46]. In particular, autothermal reforming (ATR), which is a combined process consisting of endothermic steam reforming and exothermic partial oxidation, has recently attracted much attention, because of high energy conversion efficiency. The methanol ATR reaction can be represented as follows [47]:

$$\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{3H}_2 \Delta H = -494 \text{ kJ mol}^{-1}$$
The ATR performance of Cu/ZnO powders, CuNPs@ZnO whiskers and CuNPs@ZnO paper is shown in Fig. 11. The ATR processes of methanol were carried out using a fixed-bed flow-type reactor with an on-line gas chromatography system [22, 24]. Briefly, ten disk-shaped CuNPs@ZnO papers (8 × 10^2 mm^2) with a thickness of 1 mm were stacked on top of each other (volume = 8 × 10^3 mm^3) and placed inside a stainless steel cylindrical reactor. For the Cu/ZnO powders or the CuNPs@ZnO whiskers, 100-mesh pass ceramic powders were added to adjust the occupied volume to 8 × 10^3 mm^3. Subsequently, a gas mixture, methanol/water/oxygen (molar ratio: 1.00/1.50/0.125) was fed into the reactor at a constant space velocity of 1130 h^-1 (150 mL min^-1) at atmospheric pressure. At a reaction temperature of 250°C, the CuNPs@ZnO whiskers gave high methanol conversion and hydrogen production compared with the conventional Cu/ZnO powder catalyst. In addition, undesirable CO by-production, which acts as a catalytic poison toward Pt anode electrocatalysts in PEFCs [48], was remarkably suppressed. Under these reaction conditions, CuNPs-free ZnO whiskers had no catalytic activity, indicating that the CuNPs prepared by our simple method gave better catalytic activity than the Cu catalysts prepared by the conventional co-precipitation method. For the conventional Cu/ZnO powders, the Cu components are present on the ZnO surfaces and also inside the ZnO crystals, suggesting that the exposed Cu on the surface is essential for an active catalyst [49]. In addition, the Cu/ZnO precipitates form larger flocs by secondary aggregation. On the other hand, for the CuNPs@ZnO whiskers, most of the CuNPs are well scattered on the ZnO surfaces, as shown in Fig. 5d, and this is supported by XPS data (Fig. 4c). Such a unique morphology possibly contributes to an increase in the active surface area, and results in the good catalytic performance of the CuNPs@ZnO whiskers. Moreover, the CuNPs@ZnO paper containing CuNPs in a microstructured paper matrix gave a higher methanol conversion and better hydrogen production than the CuNPs@ZnO whiskers, while the CO concentration was almost the same. This interesting phenomenon is attributed to the paper-specific structural effects: the porous fiber-network microstructure of the paper composites possibly allow for the effective transfer of heat and reactants to the active sites of the catalysts [28]. For the Cu/ZnO powders, it took a reaction temperature of 310°C to achieve the same methanol conversion (ca. 80%) as the CuNPs@ZnO paper at a reaction temperature of 250°C, and the CO concentration increased to more than 9000 ppm. Therefore, the CuNPs@ZnO paper gave an energy saving of 60 K and resulted in the suppression of undesirable CO by-production to ca. 14% compared to the conventional Cu/ZnO powders. Therefore, CuNPs@ZnO paper is a promising catalytic material for effective hydrogen production.

### 3.3.2 NO\textsubscript{x} removal for exhaust gas purification using PtNPs@ZnO paper

Exhaust gases from plant boilers and vehicles cause serious air pollution problems, and thus efficient purification systems for these pollutant gases are essential for environmental cleanup and protection [50, 51]. The major pollutants in exhaust gases are NO\textsubscript{x}, hydrocarbons and CO. All of these have been historically removed by catalytic converters, which are conventional honeycomb-structured catalysts containing noble metal catalysts, such as Pt, palladium (Pd) and rhodium [52, 53]. However, the limited availability and high cost of these rare metals demands further improvements in their catalytic efficiencies.

NO reduction with C\textsubscript{3}H\textsubscript{6} as a combined C\textsubscript{3}H\textsubscript{6} oxidation (C\textsubscript{3}H\textsubscript{6}+9/2O\textsubscript{2}→3CO\textsubscript{2}+3H\textsubscript{2}O) and NO reduction (9NO+C\textsubscript{3}H\textsubscript{6}→9/2N\textsubscript{2}+3CO\textsubscript{2}+3H\textsubscript{2}O) [54] process has been widely investigated as a model reaction for catalytic NO\textsubscript{x} gas purification [55]. Therefore, the catalytic performance of PtNPs@ZnO paper has been evaluated for NO reduction with C\textsubscript{3}H\textsubscript{6} [31]. In a similar manner as for the ATR performance test, seven disk-shaped PtNPs@ZnO papers (8 × 10\textsuperscript{2} mm\textsuperscript{2}) with a thickness of 1 mm were stacked on top of each other (to give a total volume of 5.6
and placed inside a stainless steel cylindrical reactor. Commercial Pt/Al₂O₃ powder or the PtNPs@ZnO whiskers were mixed with ceramic powder to adjust the total occupied volume to 5.6 × 10⁻³ mm³, and then packed into the cylinder. A monolithic honeycomb-structured catalyst (400 channels per square inch, base area 8.0 × 10⁻² mm², longitudinal column height 7.0 mm, Pt content 750 g m⁻³) was placed as is inside the reactor. Subsequently, a gas mixture (NO (400 ppm), C₃H₆ (892 ppm), O₂ (0.5%) and He (balance)) was continuously passed through the packed catalyst samples at a constant gas space velocity of 5357 h⁻¹ (500 mL min⁻¹) at atmospheric pressure. The NOx conversion behavior at elevated temperatures using PtNPs@ZnO paper, PtNPs@ZnO whiskers, commercial Pt/Al₂O₃ powders and a commercial Pt-loaded honeycomb monolith is shown in Fig. 12. In each case, the Pt content (4.2 mg) and the occupied volume (5.6 × 10⁻³ mm³) in the reactor were adjusted to be identical. The PtNPs@ZnO whiskers gave higher NOx conversions than the Pt/Al₂O₃ powders indicating that the PtNPs synthesized in this study have a higher catalytic efficiency than the commercial Pt catalysts, because of the well-dispersed smaller PtNPs that are present on the support surfaces (Fig. 6b). PtNPs@ZnO paper gave the highest NOx conversion response at elevated temperatures. This is very advantageous for a rapid start-up and a rapid response to temperature changes in practical applications. Efficient C₃H₆ conversion has also been achieved [31], suggesting that the PtNPs@ZnO paper is effective for the simultaneous removal of NOx and C₃H₆. Both the Pt-free ZnO paper and the H₂PtCl₆-treated ZnO-free paper gave extremely poor catalytic performance [31], proving that the ZnO whiskers play an important role in the on-paper synthesis of the highly effective PtNPs. It should be noted that the PtNPs@ZnO paper gave much better catalytic performance than the conventional Pt-loaded honeycomb catalyst (400 channels per square inch) (Fig. 12). In general, the honeycomb-structured supports with parallel channels suffer from poor sideways gas diffusion across the channels [19]. On the other hand, the paper-structured supports enable homogeneous gas diffusion in the three-dimensional fiber networks with interconnected pore spaces (Fig. 9) leading to favorable gas accessibility to the surfaces of the highly effective PtNPs. In addition, the PtNPs@ZnO paper gave acceptable catalytic durability upon repeated use and thermal treatment [31]. The excellent performance of the PtNPs@ZnO paper leads to a reduction in the required reaction temperature and the amount of precious Pt catalyst required. As shown in Fig. 13, the PtNPs@ZnO paper clearly gave better catalytic efficiency, while using only one third of the Pt present in a conventional Pt-loaded honeycomb. Additionally, an ca. 30-K energy saving (250°C for paper; 280°C for honeycomb) was achieved for a 70% conversion of NOx at elevated temperatures. The PtNPs@ZnO paper containing both a highly effective Pt nanocatalyst and a porous paper structure is an innovative catalytic material, which makes effective use of the limited-availability of noble metals in gas purification processes.
3.3.3 CO oxidation and 4-nitrophenol reduction using AuNPs@ZnO paper

Recently, extensive effort has been devoted toward Au nanocatalysis, because of high nanocatalyst activity and a wide range of applicable reactions. In particular, the gas-phase CO oxidation \( (CO + \frac{1}{2}O_2 \rightarrow CO_2) \) [11] and the liquid-phase 4-NP reduction [10,56] have been investigated energetically. Therefore, in this study the catalytic performance of AuNPs@ZnO paper was evaluated for CO oxidation [32] and 4-NP reduction [33].

The oxidation processes of CO were carried out in a similar manner as for the ATR performance test. Briefly, ten disks of the AuNPs@ZnO paper were vertically stacked (8 × 10^3 mm^3) and placed inside a stainless steel cylindrical reactor. In a similar way, the Au/ZnO powders or the AuNPs@ZnO whiskers were loaded inside the reactor, while ceramic powders were mixed to adjust the occupied volume to 8 × 10^3 mm^3. Then, a reactant gas consisting of 1 vol% CO balanced with air was fed into the reactor at a constant gas space velocity 1.2 × 10^5 h^{-1} mL per g-Au catalyst (20 mL min^{-1}) at atmospheric pressure. A comparison of the CO oxidation performance for the AuNPs@ZnO paper, the AuNPs@ZnO whiskers and the Au/ZnO powder is given in Fig. 14. The AuNPs@ZnO whiskers gave much higher CO conversion compared to the Au/ZnO powder prepared by a conventional co-precipitation method [57,58]. This indicated that the AuNPs that were synthesized on the surfaces of the ZnO whiskers are highly effective for CO oxidation. The AuNPs@ZnO paper gave excellent catalytic performance compared to the AuNPs@ZnO whiskers; complete CO conversion was achieved at room temperature. Therefore, a paper-specific structural effect was confirmed even for the CO oxidation reaction. As shown in Fig. 14, the AuNPs@ZnO paper accomplished an energy saving equivalent to 140 K compared with the conventional Au/ZnO powder. In addition, the excellent catalytic performance of the AuNPs@ZnO paper remained unchanged over at least 24 h [32]. In previous reports by Haruta and co-workers, they suggested that Au nanocatalysts have much higher catalytic activity for low-temperature CO oxidation than other noble metal nanocatalysts, including Pd and Pt [58,59]. In this study, these highly active AuNPs were incorporated into a microstructured paper matrix that acts as a favorable reaction environment in the catalyst layer, leading to a further improvement in the CO oxidation efficiency.

Subsequently, AuNPs@ZnO paper was used in the 4-NP reduction to 4-AP aqueous process to investigate a possible application in liquid-phase catalytic reactions [33]. The 4-NP reduction efficiencies in batch mode of the AuNPs@ZnO paper, the AuNPs@ZnO whiskers and the Au/ZnO powders are shown in Fig. 15. The characteristic peaks at 300 nm and 400 nm are due to 4-AP and 4-NP [10,56], respectively. The AuNPs@ZnO paper gave a much higher catalytic efficiency than the AuNPs@ZnO whiskers and the Au/ZnO powder; complete conversion of 4-NP to 4-AP was achieved within 10 min. As shown in Fig. 2, the AuNPs@ZnO...
paper had a highly porous microstructure in which the ZnO whiskers were supported and the AuNPs were exposed on the surface of the ZnO whiskers. Therefore, we suggest that the combination of a unique paper structure with an open porous network throughout and the exposure of the AuNPs to the reactants contributes to the effective transport of 4-NP to the Au surfaces, leading to excellent catalytic performance for the AuNPs@ZnO paper. Furthermore, the AuNPs@ZnO paper is reusable, because of its paper configuration [33]. These results indicate the high potential availability of AuNPs@ZnO paper for liquid-phase catalytic processes, as well as for gas-phase processes. Catalytic metal NPs@ZnO paper composites with paper-like flexibility can fit various reactor configurations, and are thus expected to be used as advanced catalytic materials to improve the practical use and catalytic performance of these systems in a wide range of industrial chemical processes.

4. Conclusions

This review article presents the facile and effective immobilization of metal NPs on a microstructured paper support, through the direct in situ synthesis of highly active metal NPs on ZnO whiskers embedded in a porous ceramic paper matrix. Inorganic metal NPs@ZnO paper with paper-like utility and a porous structure is very convenient for practical use, and it possesses high thermal stability and gas permeability. In addition, the metal NPs@ZnO paper gives excellent catalytic performance in a wide range of catalytic processes, suggesting that the combination of metal NPs with high catalytic activity and paper-structured support with a fiber-network microstructure contributes to the dramatic improvement in catalytic efficiencies for various reactions. This concept for effective catalytic processes breaks new ground in sustainable development, and metal NPs@ZnO paper composites that handle conveniently are promising materials for a wide range of future applications.

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