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Enhancement of the catalytic performance of supported-metal catalysts by pretreatment of the support

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Abstract

We report an interesting finding that the catalytic performance of supported Ag/SiO_2 catalysts toward selective catalytic oxidation of CO in hydrogen at low temperatures can be greatly enhanced by pretreatment of the SiO_2 support before catalyst preparation. Calcination of SiO_2 at appropriate temperatures preferentially removes the H-bonded SiOH, which results in the highly dispersive Ag/SiO_2 catalyst and thus improves the catalytic performance.

Keywords: CO selective oxidation; Ag/SiO_2 catalyst; Surface hydroxyls; Calcination

Supported-metal catalysts are widely used in the chemical industry and environmental protection. It is well known that the support has a great influence on the catalytic performance of catalysts, for example, by changing the charge and size of metal particles [1,2], by varying the particle shape and crystallographic structure [3], and by forming the specific active sites at the metal–support boundary [4]. And a great deal of work has been reported on elucidating the effect of supports on the structure and, subsequently, the catalytic performance of supported-metal catalysts [5–7]. Accordingly, the search for an appropriate support is a crucial step in the course of preparing the supported-metal catalyst. The general method is to test various supports and find the best one. In this communication, we report an interesting finding that the catalytic performance of the supported-metal catalyst can be further enhanced via pretreatment of the support before the catalyst preparation.

The probe reaction is selective catalytic oxidation of CO in hydrogen at low temperatures over supported Ag/SiO_2 catalysts, which has a practical application in polymer electrolyte membrane fuel cells (PEMFCs) [8]. Silica with a BET area of 495 m^2/g [denoted as SiO_2 (P), supplied by Qingdao Haiyang Chemicals Co.] was used as the parent support. SiO_2 supports calcined at 550, 700, 900, and 950 °C were denoted as SiO_2 (CA 1), SiO_2 (CA 2), SiO_2 (CA 3), SiO_2 (CA 4), respectively. The supported Ag/SiO_2 catalysts were prepared by incipient wetness impregnation of silica (P) and silica (CA n) with an aqueous solution of $AgNO_3$. X-Ray power diffraction (XRD) analysis of catalyst samples was performed on a Rigak D/max-rb X-ray diffractometer with a monochromatic detector. BET surface areas were determined by nitrogen adsorption on a Micromeritics ASAP2000 instrument with an automated gas sorption system. NMR spectra were measured at room temperature on a Bruker DRX-400 spectrometer with a BBO MAS probe head. ^1H MAS NMR spectra were obtained at 400.1 MHz in single-pulse experiments with a 3-s pulse and a 4-s repetition time and 100 scans, and recorded with samples spun

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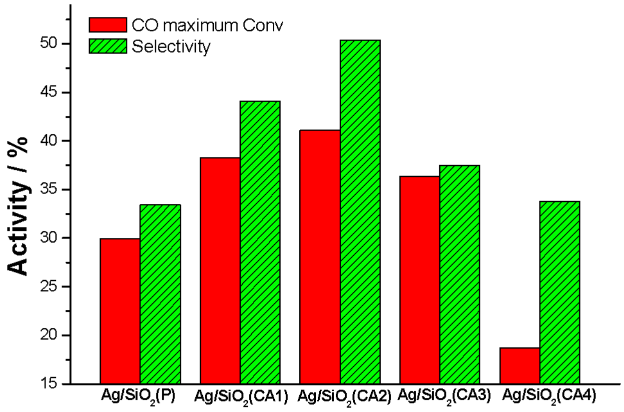

Fig. 1. The highest CO conversion and the corresponding selectivity towards CO_2 over various 8% Ag/SiO_2 catalysts.

at 8 kHz. The chemical shifts were referenced to a saturated aqueous solution of DSS. Catalytic activity tests were performed in a conventional flow reactor. In each experiment 0.25 g of catalyst was used. The catalyst was pretreated in situ under He flowing at 500 °C for 2 h before the measurement. The reactant consisted of a mixture of 1% CO, 0.5% O_2 and 98.5% H_2. A total gas flow of 50 ml/min was applied. On-line gas analysis was performed with a GC-14B gas chromatograph equipped with a Molsieve 5A column to detect CO, O_2, and H_2 and a PQ column for CO_2. The CO conversion was calculated from the change in the CO concentration. Because of the large error in the quantification of H_2O, the oxygen selectivity was calculated from the oxygen mass balance: $S = \{0.5 \times [CO_2]/([O_2]_{in} - [O_2]_{out})\} \times 100\%$.

In our previous publications, we reported on exploiting the Ag/SiO_2 catalyst that shows rather high activity toward this reaction at low temperature [9–11]. Interestingly, we found that calcination of SiO_2 at appropriate temperatures before catalyst preparation can greatly improve the catalytic activity of the Ag/SiO_2 catalyst. Fig. 1 presents the highest CO conversion and the corresponding oxygen selectivity over various 8% Ag/SiO_2 catalysts. Ag/SiO_2 (CA 1) and Ag/SiO_2 (CA 2) show better catalytic performance than Ag/SiO_2 (P); however, calcination of SiO_2 at higher temperatures results in the inverse effect. Furthermore, the reaction temperature corresponding to the highest CO conversion decreases from 50 °C for Ag/SiO_2 (P) to 35 °C for Ag/SiO_2 (CA 2). The influence of SiO_2 calcination on the catalytic activity is more evident for Ag/SiO_2 catalysts with lower Ag loadings. For 4% Ag/SiO_2 catalysts, the CO conversion over Ag/SiO_2 (CA 2) (36.22%) is more than 2 times that over Ag/SiO_2 (P) (16.13%).

Silica is an inert support and does not take part in the catalytic reaction. Thus above observed changes in the catalytic performance can only be attributed to the change in the structure and size of silver particles induced by the calcination of SiO_2 at different temperatures. Both the surface area and pore volume of SiO_2 decrease only slightly after calcination at 550 and 700 °C, whereas calcining SiO_2 at higher temperatures dramatically decreases the surface area and volume. Fig. 2 gives the XRD patterns of the various 8% Ag/SiO_2 catalysts. Obvious silver diffraction peaks appear for the Ag/SiO_2 (P) catalyst. On the basis of Scherrer's method [12], the average Ag particle size is estimated to be 13 nm from the half-width of the main peak at $2\theta = 38°$. These peaks disappear for the Ag/SiO_2 (CA 1) and Ag/SiO_2 (CA 2) catalysts; however, they reappear for Ag/SiO_2 (CA 3) and Ag/SiO_2 (CA 4). These results clearly show that calcination of SiO_2 at appropriate temperatures (550 and 700 °C) can improve the dispersion of silver particles. Comparing the catalytic activity measurement and the XRD results, we readily draw the conclusion that smaller silver particles dispersed on the support show a higher catalytic activity toward selective catalytic oxidation of CO in hydrogen.

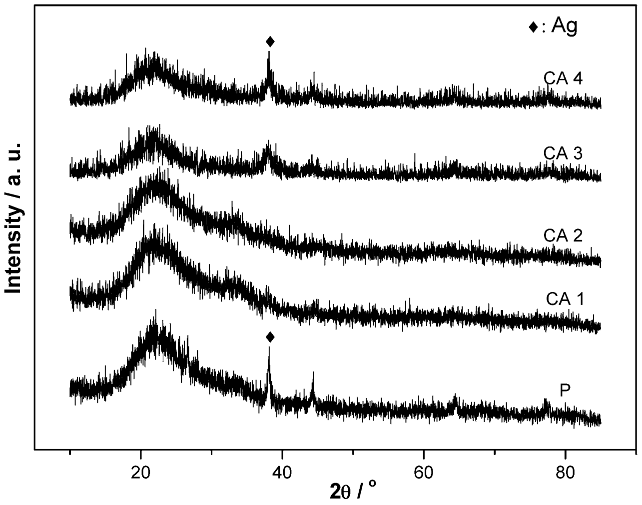

Fig. 2. XRD patterns of silver catalysts supported on SiO_2 calcined at different temperatures.

The aggregation of silver particles on SiO_2 (CA 3 and CA 4) can be reasonably associated with the dramatic decrease in the surface area and pore volume of SiO_2 after calcination at 900 and 950 °C. But compared with SiO_2 (P), calcination of SiO_2 at 550 and 700 °C improves the dispersion of silver particles, although the surface area and pore volume decrease slightly.

In addition to the surface area and pore volume, the concentration, distribution, and nature of hydroxyl groups (silanols) on the SiO_2 surface also play important role in the dispersion of metal particles on the SiO_2 [13–15]. Thus we used NMR to study the influence of calcination on the silanols on SiO_2. Fig. 3 presents the ^1H MAS NMR spectra of SiO_2 calcined at different temperatures. The amount of the total OH group decreases with the increase in the temperature of silica calcination, indicating the condensation of hydroxyl groups upon calcination. Compared with SiO_2 (P), only 53 and 20% hydroxyl groups remain on the surface after calcination at 700 °C (SiO_2 (CA 2)) and 900 °C (SiO_2 (CA 3)), respectively. The dramatic decrease in the amount of hydroxyl groups may also account for the aggregation of silver particles on SiO_2 (CA 3) and SiO_2 (CA 4). Careful examination reveals that the ^1H MAS NMR spectra can be

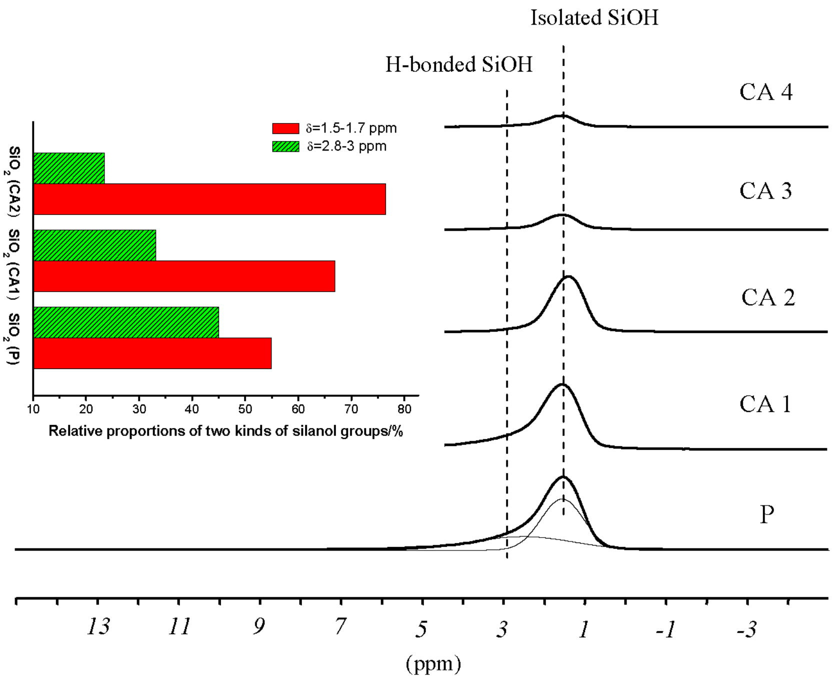

Fig. 3. ^{1}H MAS NMR spectra of SiO_2 calcined at different temperatures.

deconvoluted into two components centered at 1.5–1.7 and 2.8–3.0 ppm, respectively. The peak at about 1.7 ppm has previously been assigned to SiOH moieties of silica or silica-like regions of silica–alumina samples [16]. It is well known that hydrogen bonding produces a proton shift to a lower shielding and that the magnitude of the low-shielding shift increases with stronger hydrogen bonding [17,18]. Thus the peak at 3.0 ppm is assigned to hydrogen-bonded silanols (multi-OH group), and the sharp peak at 1.7 ppm is assigned to isolated (non-H-bonded) silanol. By integrating the corresponding peak, we calculated the relative proportions of these two kinds of silanol groups on different silica surfaces (inset in Fig. 3). It is found that the proportion of isolated SiOH compared with H-bonded silanols increases with the calcination temperature, indicating that the H-bonded silanol groups more readily undergo the condensation of hydroxyl groups than "isolated" (non-H-bonded) silanol during the calcination of SiO_2.

NMR was further used to study the interaction of Ag particles with SiO_2 in the Ag/SiO_2 catalysts. Fig. 4 shows the ^{1}H MAS NMR spectra of SiO_2 and supported silver catalysts with different silver loadings. The amount of OH group decreases with the increase in silver loading, showing that some hydrogen of the hydroxyl group is removed during the preparation of Ag/SiO_2 catalyst. Interestingly, by deconvoluting the spectra, we find that the silver species tend to interact with the H-bonded SiOH first during the course of catalyst preparation. The inset in Fig. 4 summarizes the relative proportions of the two kinds of silanol groups for SiO_2 (P) and Ag/SiO_2 (P) with various silver loadings. Loading silver results in a decrease in the percentage of H-bonded SiOH from 45% on SiO_2 (P) to 30% on 4% Ag/SiO_2 (P) and further to 20% on 8% Ag/SiO_2 (P). Increasing the silver loading to 16% does not change the distributions of silanol groups on SiO_2 any further. Thus during the course of catalyst preparation and pretreatment, the impregnated silver species react with the hydroxyl group on the silica surface and are more prone to react with the H-bonded SiOH. In other words, the dispersion of the silver species on the surface of silica is due to its interaction with surface silanol groups. The silver precursor used in our case is $AgNO_3$; thus we assume that the removal of H in the hydroxyl group is through the reaction with NO_3^- to form H_2O, NO_2, and O_2, resulting in quite strong interactions between Ag and SiO groups.

On basis of the above XRD, NMR, and catalytic test results, we propose the following model accounting for the enhancement of the catalytic performance of Ag/SiO_2 via calcination of the SiO_2 support at appropriation temperatures. Silver species interact with the H-bonded SiOH, which will eventually result in the formation of silver particles with large size, resulting in poor catalytic performance; however, interaction with isolated SiOH leads to the formation of relatively smaller silver particles, giving better catalytic performance. Calcination of SiO_2 at appropriate temperatures preferentially removes the H-bonded SiOH, which results in the highly dispersive Ag/SiO_2 catalyst and thus improves the catalytic performance.

In summary, we report that calcination of SiO_2 at appropriate temperatures before catalyst preparation can markedly enhance the catalytic activity of Ag/SiO_2 catalyst toward selective catalytic oxidation of CO in hydrogen at low tem-

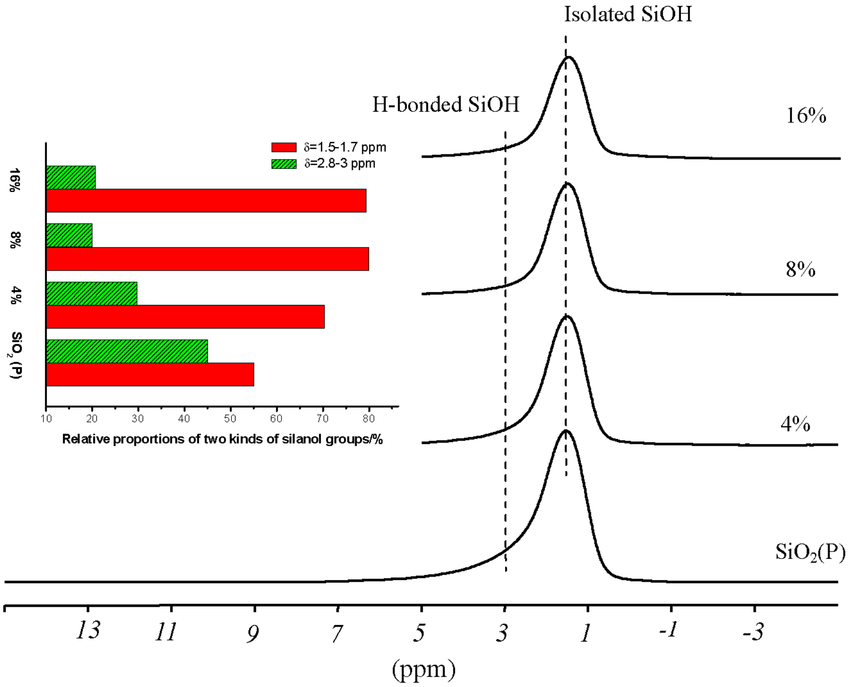

Fig. 4. ^{1}H MAS NMR spectra of SiO_2 (P) and supported silver catalysts with different silver loadings.

peratures. This finding provides an alternative method for improving the catalytic performance of supported-metal catalysts.

Acknowledgments

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