

Novel highly active Ag–SiO₂–Al₂O₃–ZnO catalyst for the production of anhydrous HCHO from direct dehydrogenation of CH₃OH

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Abstract

A novel four-component Ag–SiO₂–Al₂O₃–ZnO catalyst prepared by sol–gel method shows an outstanding catalytic activity (99% conversion and 87% selectivity) during the process of the direct dehydrogenation of methanol to anhydrous formaldehyde (HCHO). The optimal preparation conditions were found to be 20 wt.% loading of silver and zinc content of 15%. The catalytic activity was measured in the temperature range 450–700 °C and at the space velocity of $1 \times 10^4 \text{ h}^{-1}$, while the optimum reaction temperature was determined to be 650 °C. The catalyst was characterized by several kinds of methods: BET method of nitrogen adsorption at –196 °C, TG–DTG, SEM, XRD, and NH₃-TPD. The catalysts were white powder-like materials and that the BET surface area was $\sim 0.5 \text{ m}^2 \text{ g}^{-1}$. All silver was present in an ionic state in the framework of the SiO₂–Al₂O₃–ZnO carrier before catalytic reaction and was thermally stable up to 1000 °C. After the reaction, silver was present in the crystalline metal state. The particles were smaller than those found on Ag–SiO₂–Al₂O₃ catalyst.

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1. Introduction

HCHO is a very important commercial chemical material. The annual worldwide production capacity is 2×10^7 to 3×10^7 tons, a vast majority of which is produced from partial oxidation of methanol with air in the presence of a silver catalyst or an iron–molybdenum mixed-oxide catalyst. However, only aqueous solutions of HCHO can be obtained [1,2]. In recent years, anhydrous HCHO has received more attention due to its important applications in many fields, such as the preparation of many new types of agricultural chemicals and medical intermediates, the production of some traditional chemicals based on anhydrous HCHO, and the synthesis of polyoxymethylene and solid HCHO. However, the removal of water is inconvenient and quite expensive due to the negative deviation from ideal solution behavior and the formation of azeotropes in this process [3].

Methanol can be converted to anhydrous HCHO and hydrogen without any catalyst at a temperature as high as 900 °C [4]. Consequently, the direct dehydrogenation of methanol has been considered to be a promising approach to obtain anhydrous HCHO and the development of highly active and selective catalysts is very important. Many materials, including transition metal oxides, sodium carbonate, and zeolites, showed some activity in the title reaction. However, the results were not satisfactory due to their low conversion of methanol, low selectivity toward HCHO and/or the high reaction temperatures, about 800 or 900 °C [5–11]. Silver-based catalysts that are widely applied in the partial oxidation of methanol to HCHO [12–15] may be naturally a good choice for the process of the direct dehydrogenation of methanol, which our previous work has already proved to be possible [16,17]. Although both Ag–SiO₂–Al₂O₃ and Ag–SiO₂–ZnO showed high activity, there were certain amounts of by-products, such as di-methylether (DME) and CO, produced from the acid centers and the basic centers on the surface of the catalysts, respectively [18,19], resulting in lower selectivity toward HCHO. Thus, a novel Ag–SiO₂–Al₂O₃–ZnO catalyst was prepared by combining the above two silver-based cata-

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lysts. It showed an outstanding catalytic performance (99% conversion and 87% selectivity) in the direct dehydrogenation of methanol to anhydrous HCHO. In addition, the composite catalyst showed a much longer lifetime (about 2 h) than the Ag–SiO₂–Al₂O₃ and Ag–SiO₂–ZnO catalyst counterparts (only 1 h) through simple treatment with air at suitable interval times. Compared to Ag–SiO₂–Al₂O₃ catalyst, the peculiar surface morphology and the relative lower acidity on the surface of Ag–SiO₂–Al₂O₃–ZnO contribute to its excellent catalytic performance. BET, TG–DTG, SEM, XRD and NH₃–TPD were used for characterizations.

2. Experimental

The preparation procedure of the Ag–SiO₂–Al₂O₃–ZnO catalyst was as follows: 32.4 mL of Si(OC₂H₅)₄ (TEOS) was mixed with 50 mL of ethanol. Then, 3 mol dm⁻³ HNO₃ was added until the pH reached 5.0. The solution was refluxed by agitating with a magnetic stirrer oil bath at 70 °C for 1.0 h to obtain a silica sol solution. To the refluxing solution was then added a desired amount of aqueous solution containing AgNO₃, Al(NO₃)₃·9H₂O and Zn(NO₃)₂·6H₂O, followed by 50 mL of distilled water. The resulting mixed sol was stirred at 75 °C until gel was formed (~12 h). Then the gel was dried at 120 °C overnight, followed by calcination at 800 °C in air for 12 h, the material was finally ground to grain size of 40–60 meshes for catalytic activity tests.

BET specific surface areas of different catalysts were measured by using N₂ adsorption isotherms at –196 °C with Micromeritics TriStar 3000 apparatus. TG–DTG curves were recorded on a Perkin Elmer 7-series thermogravimetric analyzer. XRD patterns were recorded on a Bruker D8 advance spectrometer at 2θ range of 10–90° with Cu Kα radiation. SEM was performed on a Philips XL30 electron micrograph. Temperature programmed desorption of ammonia (NH₃–TPD) was performed in a flow-type reactor equipped with a thermal conductivity detector (TCD). After being pre-treated in a purified He flow (25 mL min⁻¹, at 450 °C for 2 h), the sample (150 mg) was cooled to 100 °C in a He flow. Then the 5 vol.% NH₃/He flow was supplied over the samples at 100 °C with a flow rate of 25 mL min⁻¹ for 20 min. After that, the NH₃–TPD experiments were carried out by heating the sample in He flow at a rate of 10 K min⁻¹.

The catalytic test was performed in a fixed-bed flow-type quartz reactor (i.d. = 4.5 mm) in a reaction temperature range 450–700 °C with the space velocity (GHSV) of 1 × 10⁴ h⁻¹. Before methanol was fed into the reactor, the catalyst was treated in situ with high purity argon (>99.999%) flow at 600 °C for 3 h to get rid of any influence of the oxygen adsorbed in the catalyst. Methanol was evaporated and then fed into the reactor by argon flow. The weight ratio of methanol in argon was fixed at 19.3%. The reaction products were analyzed by on line gas chromatography.

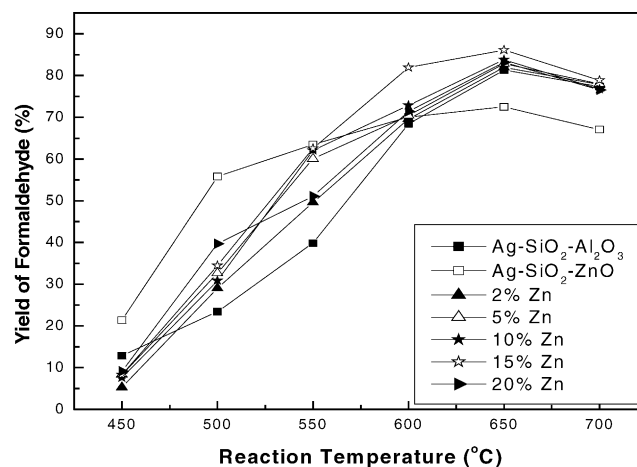


Fig. 1. The influence of reaction temperature on the yield of HCHO for the Ag–SiO₂–Al₂O₃–ZnO catalysts with different zinc contents. Reaction conditions: GHSV = 1 × 10⁴ h⁻¹, height of the catalyst bed = 35 mm.

3. Results and discussion

3.1. Activity test

It was previously reported that Ag–SiO₂–Al₂O₃ catalyst with 20 wt.% silver loading showed excellent activity in the oxidation of methanol to HCHO [20]; a similar phenomenon was found in the direct dehydrogenation process of methanol [21]. Thus, a series of Ag–SiO₂–Al₂O₃–ZnO catalysts with silver loading fixed at 20 wt.% and with different zinc contents were prepared; their catalytic performance was measured through the direct dehydrogenation of methanol. As shown in Fig. 1, the yield of HCHO increases with the increase of the reaction temperature and reaches the highest value at 650 °C over all the Ag–SiO₂–Al₂O₃–ZnO series catalysts. Then the HCHO yield decreases with further increasing of the reaction temperature, due to the increase of the side-products. Compared to the HCHO yield with the Ag–SiO₂–Al₂O₃ catalyst, the HCHO yield increased with the addition of zinc at reaction temperatures above 500 °C. The Ag–SiO₂–Al₂O₃–ZnO catalyst with 15% zinc content showed outstanding performance, with a HCHO yield of up to 86.1%. To the best of our knowledge in this field, this yield is the highest one reported and is at least 5% higher than the value over Ag–SiO₂–Al₂O₃ catalyst measured in our previous work, which was reported as 10% higher than the values in other reports.

As for the Ag–SiO₂–Al₂O₃–ZnO catalyst with zinc content of 15%, Fig. 2 shows the relationship between the conversion of methanol and the selectivity to HCHO as a function of reaction temperature. One can find that the conversion of methanol increases rapidly with the reaction temperature and reaches 99% at 650 °C, where the selectivity toward HCHO also gains the highest value (about 87%). The results were repeated three times, and the mean error was below ±3%. With the temperature increasing further,

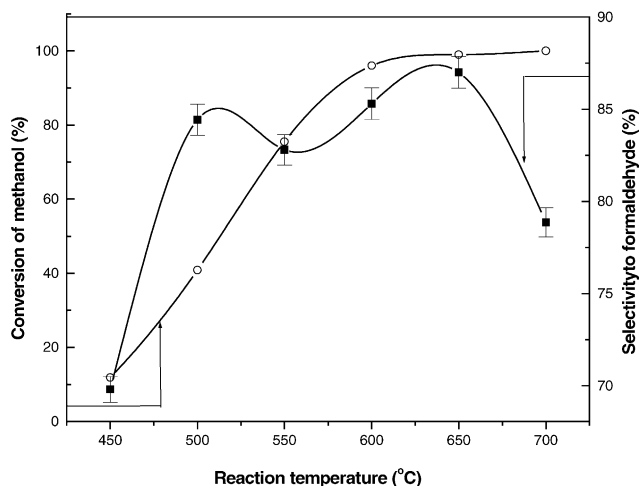


Fig. 2. The relationships among the conversion of methanol, the selectivity toward HCHO and the reaction temperature over the Ag–SiO₂–Al₂O₃–ZnO catalyst with the zinc content of 15%. Reaction conditions: GHSV = $1 \times 10^4 \text{ h}^{-1}$, height of the catalyst bed = 35 mm.

the HCHO yield decreases abruptly. Hence, the optimum reaction temperature is set at 650 °C.

At the optimal reaction temperature (650 °C), the relationship between the yield of HCHO and the selectivity to HCHO as a function of the amount of zinc was investigated; the results are illustrated in Fig. 3. In good agreement with the above results, the highest values of both the HCHO yield and the selectivity to HCHO are obtained over the Ag–SiO₂–Al₂O₃–ZnO catalyst with the zinc amount at 15%. At the optimal reaction temperature, the conversion of methanol is near 100%, while the yield of HCHO exceeds 86%. Therefore, in the direct dehydrogenation of methanol, the optimal zinc content was 15% over the 20 wt.% Ag/SiO₂–Al₂O₃–ZnO catalysts.

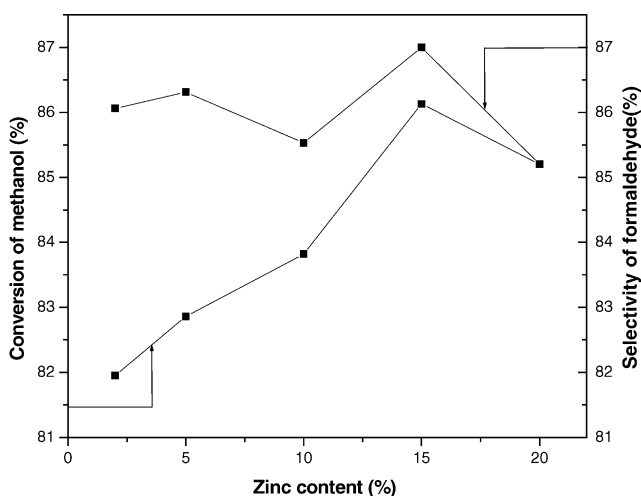


Fig. 3. The relationships among the yield of HCHO, the selectivity to HCHO and the zinc content at 650 °C. Reaction conditions: GHSV = $1 \times 10^4 \text{ h}^{-1}$, height of the catalyst bed = 35 mm.

Table 1
S_{BET} of the Ag–SiO₂–Al₂O₃–ZnO catalysts with different zinc contents

Zinc (wt.%)	S _{BET} (m ² g ⁻¹)
0	0.53
2	0.48
5	0.50
10	0.45
15	0.52
20	0.55

3.2. Catalyst characterizations

The specific surface area (BET) of all the catalysts is very low (about 0.5 m² g⁻¹, see Table 1). The addition of zinc to the Ag–SiO₂–Al₂O₃ catalyst does not change the BET area, which is considered to be very suitable for the manufacture of HCHO [22]. Catalysts with larger BET area show poor selectivity toward HCHO because of the further decomposition of HCHO to CO and H₂ in the small pores located in the catalysts; this is one of the reasons why the high BET surface area will do harm to this reaction.

XRD patterns of the fresh 20 wt.% Ag–SiO₂–Al₂O₃–ZnO catalysts with different zinc contents are shown in Fig. 4. There were no obvious diffraction peaks observed and all the samples showed an amorphous structure with the zinc content ranging from 2 to 20%. This result was similar to the XRD patterns of 20 wt.% Ag–SiO₂–Al₂O₃ catalyst, but rather different from that of fresh Ag–SiO₂–ZnO catalyst, which showed sharp diffraction peaks due to metallic silver (Fig. 5). In other words, the addition of zinc does not change either the structure of the Ag–SiO₂–Al₂O₃ catalyst or the chemical state of silver. The absence of crystalline peaks associated with metallic silver also indicates that the silver

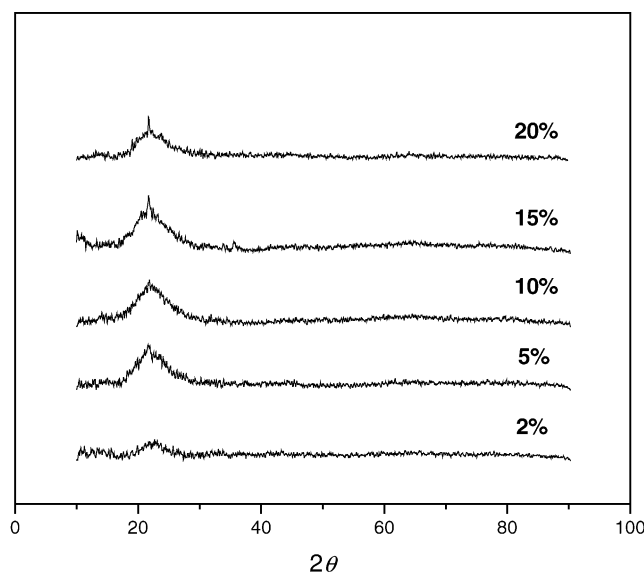


Fig. 4. XRD patterns of the Ag–SiO₂–Al₂O₃–ZnO catalysts with different zinc contents.

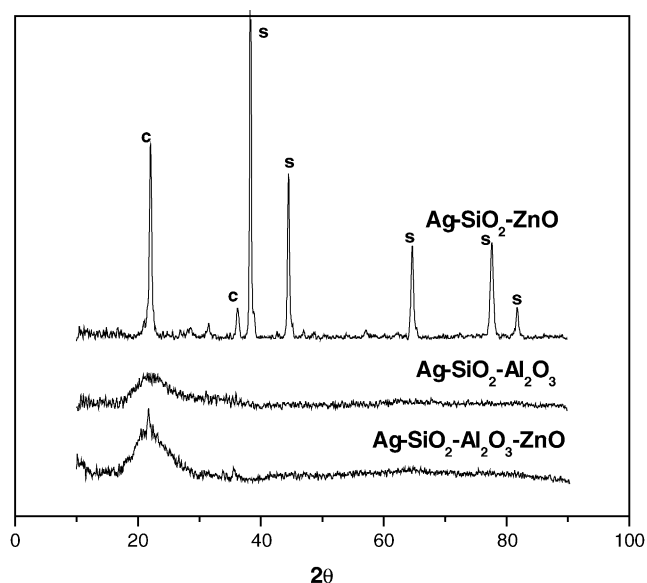


Fig. 5. XRD patterns of the different supported-silver catalysts with a 20 wt.% silver loading (c: α -cristobalite, s: crystalline silver).

species are either highly dispersed or present in an ionic state in the supports.

Fig. 6 shows the XRD patterns of the $\text{Ag-SiO}_2\text{-Al}_2\text{O}_3\text{-ZnO}$ catalyst with the zinc content at 15% before and after the direct dehydrogenation. One can find that, after the reaction, the XRD patterns change greatly and several sharp diffraction peaks appear, which can be easily ascribed to the crystalline $\text{Ag}(1\ 1\ 1)$ (38.1°), $\text{Ag}(2\ 0\ 0)$ (44.3°), $\text{Ag}(2\ 2\ 0)$ (64.4°) and $\text{Ag}(3\ 1\ 1)$ (77.5°) [12], respectively, suggesting that the silver ions in the current composite material can be reduced to the metallic state by the reaction gas mixture. In addition, two crystalline peaks (21.9° and 36.1°) ascribed

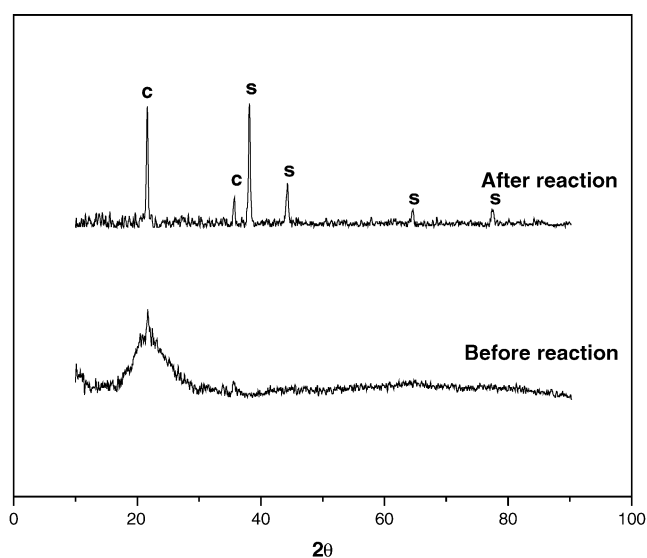


Fig. 6. XRD patterns of the $\text{Ag-SiO}_2\text{-Al}_2\text{O}_3\text{-ZnO}$ catalysts with the zinc content at 15 wt.% before and after reaction (c: α -cristobalite, s: crystalline silver).

to ceramic cristobalite (low syn) were also observed [23], suggesting that crystallization of the amorphous material occurred at a temperature much lower than that required in the present reaction conditions.

The white color of the fresh $\text{Ag-SiO}_2\text{-Al}_2\text{O}_3\text{-ZnO}$ catalyst indicates that there is no reduction of silver ions during the calcination process of the catalyst in air atmosphere. This observation is surprising since previous studies have shown that the decomposition of common silver compounds occurs at about 500°C in air [24]. Our previous studies [12,14] of the sol-gel-derived silver- SiO_2 binary composites also showed that silver was reduced upon calcination at 600°C in air. TG-DTG results (Fig. 7) reveal that the silver ions dispersed in the matrix are extremely stable even at 1000°C in air, which accords well with the results from the $\text{Ag-SiO}_2\text{-Al}_2\text{O}_3$ catalyst.

SEM micrographs of the $\text{Ag-SiO}_2\text{-Al}_2\text{O}_3\text{-ZnO}$ catalyst before (a) and after (b) the dehydrogenation reaction are shown in Fig. 8. The structure of $\text{Ag-SiO}_2\text{-Al}_2\text{O}_3\text{-ZnO}$ observed before reaction is rather different from that of our previous $\text{Ag-SiO}_2\text{-Al}_2\text{O}_3$ catalyst (c), the reason for the difference may be the addition of zinc. However, after the reaction, similar to the case for the $\text{Ag-SiO}_2\text{-Al}_2\text{O}_3$ catalyst (d), there are many isolated silver particles displayed on the surface. The mean size of the metallic silver particles was estimated to be about 50–300 nm; such particles are much smaller than those on the $\text{Ag-SiO}_2\text{-Al}_2\text{O}_3$ (d) catalyst. The SEM result is also in good agreement with that of the XRD. The average particle size of (b) and (d) calculated by the line broadening XRD method is about 112 and 205 nm, respectively. It is obvious that the particle size observed with SEM is the size of congregative particles formed from the smaller particles and that all the particles cannot be very even on the surface. However, XRD results presented the statistic information about all the silver particles presented on the catalyst. The fact that the particle size estimated from XRD method is smaller than that of SEM indicated the presence

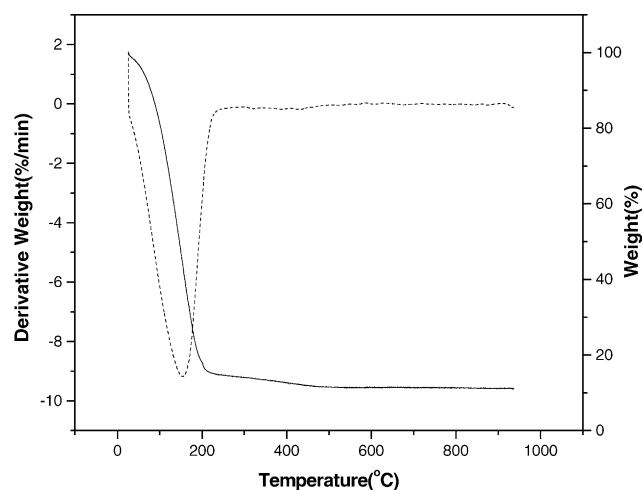


Fig. 7. TG(—)–DTG(---) of the as-prepared $\text{Ag/SiO}_2\text{-Al}_2\text{O}_3\text{-ZnO}$ catalyst.

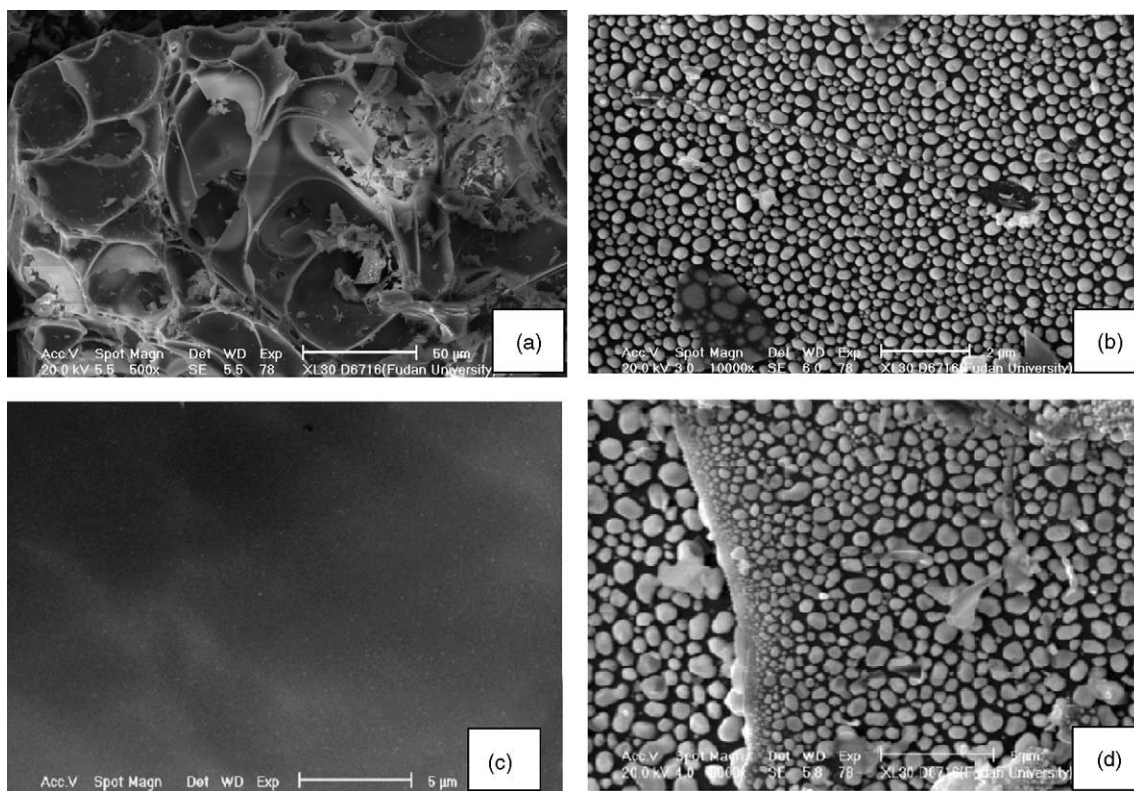


Fig. 8. SEM micrographs of the Ag-SiO₂-Al₂O₃-ZnO catalyst before (a), and after (b) the reaction and of the Ag-SiO₂-Al₂O₃ catalyst before (c) and after (d) the reaction.

of many smaller particles which cannot be easily observed and distinguished with SEM. Therefore, the high catalytic activity of our novel Ag-SiO₂-Al₂O₃-ZnO catalyst might be attributed to the change of the carrier structure by the addition of zinc as the fourth component.

The surface acid properties of the catalysts have been investigated by the NH₃-TPD method. As shown in

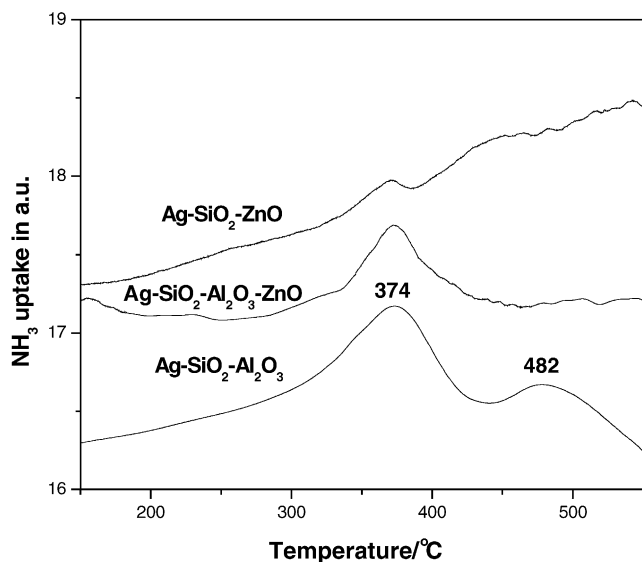


Fig. 9. NH₃-TPD curves of differently supported silver catalyst.

Fig. 9, there are two acidic centers on the surface of the Ag-SiO₂-Al₂O₃ catalyst; these are located at 374 and 482 °C. And no obvious acidic centers could be found on the Ag-SiO₂-ZnO surface, indicating that there is no DME produced during methanol dehydrogenation process with Ag-SiO₂-ZnO as the catalyst, this result was confirmed by the previous report [19] and by the present work (see Table 2). As for the Ag-SiO₂-Al₂O₃-ZnO catalyst, there is one acidic center at the lower temperature of 374 °C. From Table 2, one can see that there were no DME by-products over Ag-SiO₂-ZnO catalyst, and that the DME yield over Ag-SiO₂-Al₂O₃-ZnO was much lower than that over Ag-SiO₂-Al₂O₃ catalyst. Therefore, a conclusion can be drawn from the above results. Compared with the Ag-SiO₂-Al₂O₃ catalyst, the increment of the selectivity to

Table 2
Catalytic performance of the differently supported silver catalysts under the optimal reaction conditions

Catalyst	Conversion (%)		Yield (%)	
	MeOH	HCHO	DME	CO
Ag-SiO ₂ -Al ₂ O ₃	94.9	81.2	10.1	3.6
Ag-SiO ₂ -ZnO	82.3	72.2	0	10.1
Ag-SiO ₂ -Al ₂ O ₃ -ZnO	99.1	86.1	3.2	9.7

Reaction conditions: GHSV = 1 × 10⁴ h⁻¹ and height of the catalyst bed = 35 mm.

HCHO on the Ag–SiO₂–Al₂O₃–ZnO catalyst was owing to the decrease of the acidic centers after the addition of zinc. There were no obvious changes of the basic centers for the ZnO-containing catalysts, as proved by the CO₂-TPD method, and the yield of the CO by-product changed little. However, the CO yield over the Ag–SiO₂–Al₂O₃ catalyst was much lower than that over the other two catalysts, although the mechanism is not clear yet. Further studies on the adjustments for basic centers on the surface of the silver-based catalysts are under way.

4. Conclusions

In this work, a novel four-component Ag–SiO₂–Al₂O₃–ZnO composite catalyst prepared by the sol–gel method is reported, which shows an outstanding catalytic performance (conversion 99% and selectivity 87%) in the direct dehydrogenation of methanol to anhydrous HCHO. The optimal zinc content is 15% and the optimum reaction temperature is 650 °C. Silver still exists as an ionic state, similar as that in the Ag–SiO₂–Al₂O₃ catalyst. The addition of zinc changes the carrier structure and reduces the surface acidity greatly. The special thermal stability also makes it quite convenient for future applications.

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