

Novel highly active Ag–SiO₂–MgO catalysts used for direct dehydrogenation of methanol to anhydrous formaldehyde

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Direct dehydrogenation of methanol to anhydrous formaldehyde was carried out over a novel Ag–SiO₂–MgO catalyst prepared by the sol–gel method. The catalytic activity was measured over the temperature interval 350–700 °C and the space velocity of $1 \times 10^4 \text{ h}^{-1}$, while the optimum conditions were found to be 20 wt% loading of silver and 650 °C reaction temperature. The catalyst exhibits excellent activity (96% conversion) and selectivity (78%) during the process of dehydrogenation with the yield of formaldehyde up to 75%. X-ray diffraction patterns for the novel Ag(20 wt%)–SiO₂–MgO catalyst correspond to α -cristobalite(100) and Ag(111), (200), (220), (311) and (222). Scanning electron microscopy was used to determine the morphology and particle size. Isolated silver particles with a mean size of about 5 μm were observed on the surface of the catalyst.

KEY WORDS: SiO₂–MgO-supported silver catalyst; direct dehydrogenation; anhydrous formaldehyde; sol–gel.

1. Introduction

In modern industries, anhydrous formaldehyde is used widely, such as in the preparation of many new types of agricultural chemicals and medical intermediates, the production of some traditional chemicals based on anhydrous formaldehyde, the synthesis of polyoxymethylene and solid formaldehyde, and so on. Generally, anhydrous formaldehyde is produced via the dehydration reaction of an aqueous solution of formaldehyde [1–5]. This step is very expensive and determines the final price of anhydrous formaldehyde. Thus, many researchers have devoted themselves to the search for a one-step process to yield anhydrous formaldehyde from methanol directly. The direct dehydrogenation of methanol is a very promising way to produce anhydrous formaldehyde. As is known, methanol can be converted to anhydrous formaldehyde and hydrogen without any catalyst at a very high temperature [6]. The maximum yield of formaldehyde is less than 20% at 900 °C where methanol conversion reaches 45% with only 43% selectivity toward formaldehyde, owing to a complex reaction scheme of 13 elementary reactions [7]. Therefore, a highly active and selective catalyst is needed in this process. Unfortunately, the results for those catalysts reported in the past two decades were not satisfactory due to their low conversion of methanol, low selectivity toward formaldehyde or the high reaction temperature. These included Ag [8], Ag/Cu [8], Ag/Cu–Si [9], supported or unsupported Cu catalysts [10,11], supported or unsupported Zn catalysts [12] and Na⁺ or Li⁺ salts [13–15]. Until now, there has been only one literature

report of a yield of anhydrous formaldehyde at the highest value of 70% over Li_{0.5}Na_{0.5}AlO₂ [16], but a much higher reaction temperature of up to 900 °C was also needed. It is well known that both metallic and supported silver-based catalysts are widely used in the partial oxidation of methanol to formaldehyde [17–19], so that a silver-based catalyst may naturally be chosen as a good one in the dehydrogenation process. Recently, we reported a novel Ag-containing ceramic catalyst [20], which shows reasonable activity in the direct dehydrogenation of methanol to formaldehyde. The yield of formaldehyde reached 70% and the selectivity was as high as 100% under optimum reaction conditions. But the low conversion of methanol and short lifetime restricted its further application. In addition, MgO is normally considered as one of the most convenient supports for a wide variety of catalysts used in redox systems [21–25]. Composite systems formed by silver clusters or ions embedded in a sol–gel network as promising materials for optoelectronic [26] and catalytic [1,2] applications have been intensively investigated.

In this work, we report a series of novel Ag–SiO₂–MgO catalysts prepared by the sol–gel method that exhibit significantly high catalytic activity and selectivity in the direct dehydrogenation of methanol to anhydrous formaldehyde. BET, X-ray diffraction (XRD) and scanning electron microscopy (SEM) have been used for their characterization.

2. Experimental

The Ag–SiO₂–MgO sol–gel composites were prepared from the precursors Si(OC₂H₅)₄ (TEOS), Mg(NO₃)₂·6H₂O and AgNO₃. TEOS (32.4 mL) was

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mixed with 2 mL of 0.1 M HNO₃ in 50 mL of ethanol at 70 °C for 1 h to obtain a silica sol solution. The solution was refluxed by agitating with a magnetic stirrer in an oil bath for another 2 h, and to the refluxing solution was added the desired amount of aqueous solution of AgNO₃ and 5.56 g of Mg(NO₃)₂·6H₂O, followed by 50 mL of distilled water. The resulting mixed sol was stirred at 75 °C for an additional 12 h. Finally, the gel was dried at 120 °C overnight followed by calcination at 900 °C in air for 10 h. The brown-colored Ag–SiO₂–MgO catalyst thus obtained was then ground to a grain size of 40–60 mesh for the activity test. The surface characteristics, namely specific surface area (S_{BET}), total pore volume (V_p) and mean pore radius (r), of different catalysts were determined from N₂ adsorption isotherms at –196 °C using a Tristar 3000 apparatus. XRD patterns were recorded using a Bruker D8 advance spectrometer at 2θ range of 10–90° with CuK α radiation. SEM was performed using a Philips XL30 instrument.

The direct dehydrogenation of methanol over the Ag–SiO₂–MgO sol–gel composites was carried out in a flow-type quartz reactor (i.d. = 4.5 mm) at a reaction temperature of 350–700 °C with a space velocity (GHSV) of $1 \times 10^4 \text{ h}^{-1}$. Anhydrous methanol was evaporated and then fed into the reactor in a high-purity argon (>99.999%) flow. The weight ratio of methanol in argon was determined as 19.3%. The products were analyzed using on-line gas chromatography.

3. Results and discussion

3.1. Catalyst characterization

The specific surface area (BET) of the catalyst is very low, which is considered to be very suitable for the

Table 1
Surface characteristics of the pure and silver-loaded catalysts

Ag (wt%)	S_{BET} (m ² g ^{−1})	V_p (cm ³ g ^{−1})	r (nm)
0	79.7	0.33	16
5	3.0	0.021	35
10	0.78	0.0093	71
15	0.65	0.0082	76
20	0.40	0.0067	80
25	0.36	0.0063	82
30	0.21	0.0054	87

manufacture of formaldehyde [27]. Some catalysts with larger BET area were prepared and tested, but showed poor selectivity toward formaldehyde, which might be due to the further decomposition of formaldehyde in the small pores. Therefore, a high-surface-area catalyst is detrimental to this reaction. Table 1 lists the BET surface areas (S_{BET}) of these Ag–SiO₂–MgO catalysts with different silver loadings. It is interesting that S_{BET} and total pore volume (V_p) decrease but the mean pore radius (r) increases with increasing silver content, which might be due to the blockage of the pores of the supports with the active component.

The XRD patterns of the as-prepared SiO₂–MgO mixed oxides and the Ag–SiO₂–MgO catalysts with different silver loadings from 5 to 30 wt% are shown in figure 1. There is no sharp peak of the SiO₂–MgO support, meaning that no detectable crystalline phases corresponding to SiO₂ and/or MgO are formed. However, if silver is introduced into the mixed oxide support of SiO₂–MgO, a set of sharp peaks are observed at 2θ values of 22.0, 38.1, 44.5, 64.6, 77.5 and 81.5°, which can be easily attributed to α -cristobalite(100), Ag(111), Ag(200), Ag(220), Ag(311) and Ag(222), respectively

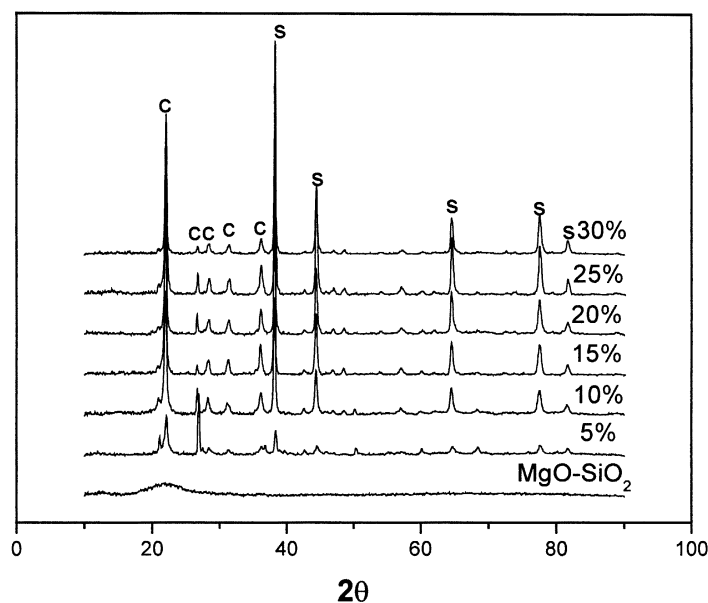


Figure 1. XRD patterns of SiO₂–MgO support and Ag–SiO₂–MgO catalysts with different silver loadings (c, α -cristobalite; s, crystalline silver).

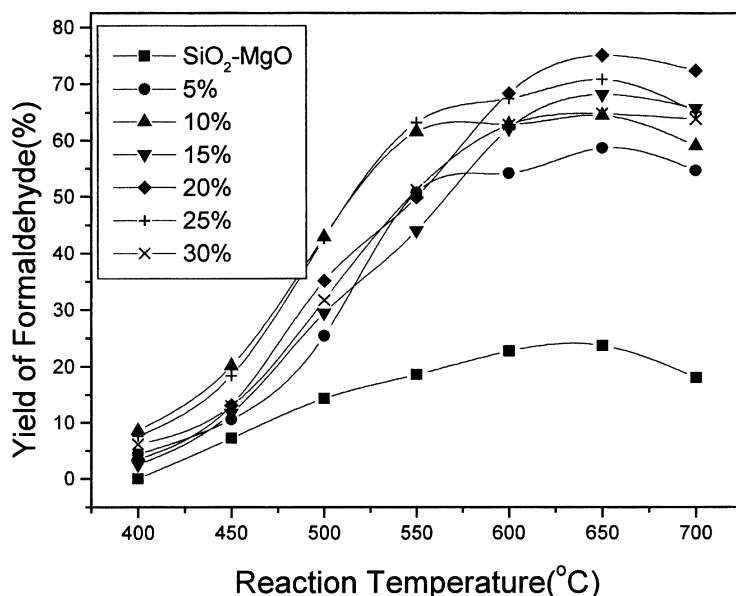


Figure 2. Influence of the reaction temperature on the yield of formaldehyde for the SiO₂–MgO support and Ag–SiO₂–MgO catalysts with different silver loadings. Reaction conditions: GHSV = 1×10^4 h⁻¹; height of the catalyst bed = 35 mm.

[28]. There is no sharp difference between these catalysts except the changes of the intensities of those XRD peaks. After the direct dehydrogenation reaction, there are no new XRD peaks appearing in the XRD patterns, which is in good agreement with the fact that the catalyst maintains nearly its initial high activity after the direct hydrogenation reaction for 1 h.

From the SEM results of the Ag–SiO₂–MgO catalyst before and after the dehydrogenation reactions, it is found that there are many isolated silver particles on the surface and the mean size of the metallic silver particles is estimated to be about 5 μm. There is no obvious increase of the silver particle size after the reaction. Therefore, the SEM result is also in agreement with the XRD result.

3.2. Activity test

A set of silver contents, 5, 10, 15, 20, 25 and 30 wt%, were firstly chosen to investigate the relationship between the reaction temperature and the yield of formaldehyde, as shown in figure 2. As a comparison, the SiO₂–MgO catalyst without silver is also examined, which shows much lower activity toward this reaction. It is found that the formaldehyde yield increases with increasing reaction temperature before the temperature reaches 650 °C, which is in accordance with the principal law of direct dehydrogenation reactions. Further increase of the reaction temperature does not increase the yield of formaldehyde, but increases the yield of side-products and thus decreases the formaldehyde yield. In addition, the effects of the flow rate on the reaction were also investigated. A higher flow rate leads to lower conversion but higher selectivity, while a

lower flow rate leads to the opposite. However, the maximum yield of formaldehyde still corresponds to 650 °C. Hence, the optimum reaction temperature is set at 650 °C. In addition, the Ag–SiO₂–MgO catalyst maintained its high activity even at temperatures up to 700 °C, which could be ascribed to its excellent thermal stability. An important fact is that for the SiO₂–MgO catalyst without silver, the yield of formaldehyde is much lower than for the other silver-containing catalysts, which indicates that silver might be the active center in this reaction.

Figure 3 shows the relationship between the selectivity of formaldehyde and silver loading. It appears as a typical “volcano” shape. The catalyst with a silver loading of 20 wt% shows the maximum value of formaldehyde selectivity at 78%.

For the 20 wt% Ag–SiO₂–MgO catalyst, figure 4 shows the relationship between the conversion of methanol, selectivity of formaldehyde and reaction temperature. It is found that although the selectivity of formaldehyde is much higher (100%) at lower temperature, the conversion of methanol is rather low. From 500 to 650 °C, the selectivity of formaldehyde remains almost a constant, but the conversion of methanol reaches its highest value (96%) at 650 °C. As the reaction temperature reaches 700 °C, the selectivity toward formaldehyde decreases quickly in spite of the increase of methanol conversion.

In order to illustrate the excellent catalytic properties of the novel as-prepared Ag(20 wt%)–SiO₂–MgO catalyst in the manufacture of anhydrous formaldehyde, detailed experimental results for three typical catalysts, Ag–SiO₂–ZnO [12], Ag ceramics [20], Li–MgO [16] and Cu–SiO₂ [10], from the literatures are listed in table 2

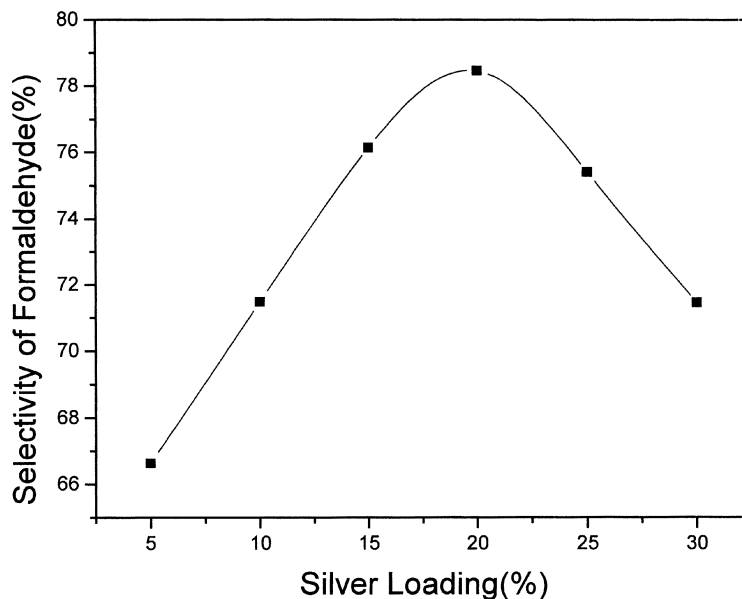


Figure 3. Effects of silver content on the selectivity of formaldehyde. Reaction conditions: GHSV = $1 \times 10^4 \text{ h}^{-1}$; height of the catalyst bed = 35 mm; reaction temperature = 650 °C.

for comparison. Although the selectivity toward formaldehyde over Ag–SiO₂–ZnO, Ag ceramic and Cu–SiO₂ catalysts is higher than that of the Ag–SiO₂–MgO catalyst, the values of the methanol conversion are much lower, only 48, 70 and 21%, respectively. As for the Li–MgO catalyst, the methanol conversion and the formaldehyde selectivity is lower than for the novel Ag(20 wt%)–SiO₂–MgO catalyst. Our novel catalyst reaches the highest conversion of methanol (96%) at 78% selectivity of formaldehyde, resulting in the much

higher yield of formaldehyde (75%). To the best of our knowledge of the direct dehydrogenation of methanol to formaldehyde, this value is the highest one as compared to those reported in the literature. However, the reason why this catalyst shows such exciting activity results for the direct dehydrogenation of methanol to anhydrous formaldehyde is not clear yet. A detailed mechanism study with this novel catalyst is under way, and we will report the structural factors affecting its activity in a future paper.

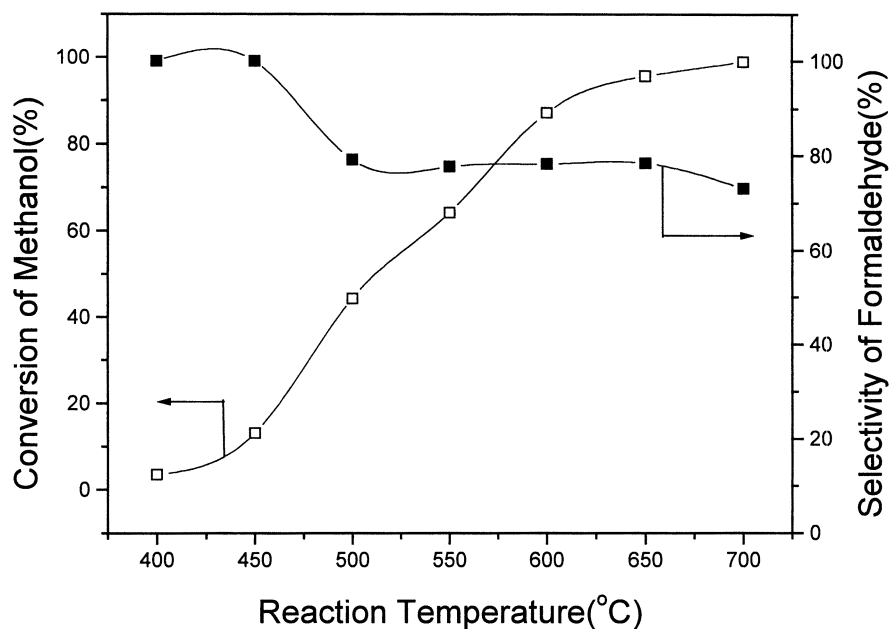


Figure 4. Relationship between the conversion of methanol, selectivity towards formaldehyde and reaction temperature over 20 wt% Ag–SiO₂–MgO catalyst. Reaction conditions: GHSV = $1 \times 10^4 \text{ h}^{-1}$; height of the catalyst bed = 35 mm; reaction temperature = 650 °C.

Table 2
Activities of various catalysts in the dehydrogenation of methanol^a

Catalyst	Reaction temperature (°C)	Yield of HCHO (%)	Conversion of CH ₃ OH (%)	Selectivity of HCHO (%)
Ag–SiO ₂ –ZnO [12]	600	39	48	81
Ag ceramics [20]	600	70	70	100
Li–MgO [16]	690	12	20	60
SiO ₂ –MgO	650	20	36	56
CuO–SiO ₂ [10]	500	17	21	80
Ag(20 wt%)–SiO ₂ –MgO	650	75	96	78

^a Reaction conditions: GHSV, $1 \times 10^4 \text{ h}^{-1}$; height of the catalyst bed, 35 mm.

4. Conclusions

A novel Ag–SiO₂–MgO catalyst prepared by the sol–gel method is reported, which shows rather high activity (conversion, 96%; selectivity, 78%) in the direct dehydrogenation of methanol to anhydrous formaldehyde. The optimum silver content is 20 wt% and the optimum reaction temperature is 650 °C. The excellent thermal stability also makes it potentially very useful.

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