

First observation of highly efficient dehydrogenation of methanol to anhydrous formaldehyde over novel Ag–SiO₂–MgO–Al₂O₃ catalyst†

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Novel Ag–SiO₂–MgO–Al₂O₃ catalyst prepared by sol–gel method showed extremely high activity and selectivity (both equal to 100%) in the direct dehydrogenation of methanol to anhydrous formaldehyde.

Beyond the memory of catalysis, one of the ultimate goals of all the chemists in this field is to find or develop the highly efficient catalyst. That is, the raw material will be converted completely to the product without any by-products. Therefore, the separation of the product from the product mixture can be omitted due to the absence of any unconverted raw materials and/or by-products and the process will be easily industrialized because of its simplicity and low-cost. In recent years, as a widely-used and commodity chemical, anhydrous formaldehyde (HCHO) has been paid more and more attention due to its comprehensive application in many fields, such as the preparation of many new types of agricultural chemicals and medical intermediates, the synthesis of polyoxymethylene and solid HCHO *etc.*¹ Generally, anhydrous HCHO is now obtained by the dehydration of aqueous solution of HCHO, which mainly produced from partial oxidation of methanol by air in the presence of a silver catalyst or an iron-molybdenum catalyst.^{2,3} However, the removal of water and methanol from the aqueous solution of HCHO is very cumbersome and expensive, leading to the high price of anhydrous HCHO. Thus a one-step process to produce water-free HCHO is a desirable route. It is well known that methanol can be converted to anhydrous HCHO and hydrogen without any catalyst at a very high temperature.⁴ So the direct dehydrogenation of methanol is a very promising way to produce anhydrous HCHO and the selection or development of a highly active and selective catalyst is pivotal.

Many materials, such as: transition metal based oxides, sodium carbonate, and zeolites, showed certain activity in the title reaction, however, the results of those catalysts reported were not satisfactory due to their low conversion of methanol, low selectivity toward HCHO and/or the high reaction temperature.⁵ As we know, besides the main reaction (CH₃OH → HCHO + H₂), there are two side-reactions: the decomposition of methanol (CH₃OH → CO + 2H₂) and the dehydration reaction (2CH₃OH → (CH₃)₂O + H₂O), respectively. To the best of our knowledge, there was no any catalysts reported, which showed yield of HCHO exceeding 70%, restricting its industrial application. Our previous results showed that silver-based catalysts were considered to be promising candidates in the above reaction.⁶ The Ag–SiO₂–Al₂O₃ (A) showed much higher selectivity toward HCHO, while Ag–SiO₂–MgO (B) showed higher methanol conversion. Thus, we believe that one silver-based catalyst that possesses the perfect performance in the direct dehydrogenation could be obtained through careful tuning of the surface properties of the catalyst. Herein we report for the first time the preparation and characterization of the novel Ag–SiO₂–MgO–Al₂O₃ (C) catalyst, which shows a highly efficient performance toward the direct dehydrogenation of methanol.

The preparation of the C 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 dropwise until pH = 5.0. The solution was refluxed by agitating with a magnetic stirrer in an 70 °C oil bath for 1.0 h to obtain a silica sol solution. After that, to the refluxing solution was added a desired amount of aqueous solution containing AgNO₃, Al(NO₃)₃·9H₂O and Mg(NO₃)₂·6H₂O, followed by 50 ml of distilled water. The resulting mixed sol was stirred at 75 °C until the gel was formed (~12 h). Then the gel was dried at 120 °C over night followed by calcination at 800 °C in air for 12 h and finally ground to grain size of 40–60 meshes for catalytic test.

The direct dehydrogenation of methanol was carried out in a fixed-bed flow-type quartz reactor (i.d. = 4.5 mm) at a temperature range of 350–700 °C with the space velocity (GHSV) at 1 × 10⁴ h⁻¹. Before feeding methanol into the reactor, the catalyst was treated *in situ* with high purity Ar (>99.999%) flowing at 600 °C for 3 h to get rid of any influence of the adsorbed oxygen in the catalyst. Methanol was evaporated and then fed into the reactor by Ar flow. The weight ratio of methanol in Ar was determined as 19.3%. The products were analyzed by on line gas chromatography-mass spectroscopy (GC-MS). CH₃OH, HCHO, di-methyl ether (DME) and water were determined by TCD with a Propak-N column, while H₂, CO, CO₂ were analysed also by TCD with a TDX column. Carbon balance was tested as 0.98 ~ 1.02.

From Table 1, it is very interesting to find that, besides Ag and SiO₂, the catalyst with Al₂O₃ leads to higher selectivity while the other with MgO shows much higher methanol conversion under similar reaction conditions. Thus, one can naturally get an idea to try for the composite catalyst consisting of both Al₂O₃ and MgO. To our great surprise, C with a relative mass ratio of Ag : SiO₂ : MgO : Al₂O₃ at 20 : 55.2 : 8.3 : 16.5 shows a highly efficient catalytic performance, that is, 100% conversion and 100% selectivity. Under the optimal conditions, H₂ and HCHO were almost in equal amount as detected by GC and the consumed methanol was also equal to the produced HCHO, while CO and CO₂ were undetectable. In addition, no deposited carbon was observed on the surface of the catalyst, indicating that there were no other carbon-containing products formed under the reaction conditions and methanol was all converted to HCHO and H₂. However, the performance of the novel catalyst will declined to 10% CH₃OH conversion after a 10 h reaction due to the accumulation of silver on the surface as described below. But the selectivity toward HCHO still kept at 100%, indication that there were no any other impurities present in the product except for the unconverted CH₃OH for a long reaction time.

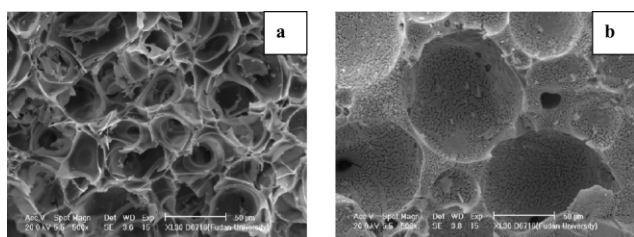
In addition, the content of silver influenced little on its activity when the silver content exceeded 20%. However, much higher silver content (>50%) will do harm to its catalytic performance. Lower silver content only leads to lower conversion of methanol, the selectivity still keeps at 100%. The relative composition of the novel C catalyst shows big influence on its catalytic performance. As can be seen from Table 1, there is an optimal composition among the composite oxides. The optimal content of MgO was first determined as 15 wt% as compared to SiO₂ according to a series of "trial and error"

† Electronic supplementary information (ESI) available: XRD and SEM. See <http://www.rsc.org/suppdata/cc/b3/b310316a/>

Table 1 Effects of different catalysts on catalytic performance in the direct dehydrogenation of methanol to HCHO

Entry	Catalyst	Silver loading (%)	MgO content (%)	Al ₂ O ₃ content (%)	CH ₃ OH conversion (%)	HCHO formation rate(mg/g _{cat} ·h)	BET area* (m ² /g)	Selectivity(%)		
								HCHO	DME	CO
1	A	20	0	8.0	70.0	522	0.40	97.5	2.5	0
2	B	20	13.0	0	95.7	575	0.78	78.5	0	21.5
3	C¹	15	8.8	17.6	84.6	647	0.45	100	0	0
4	C²	20	8.3	16.5	100	765	0.52	100	0	0
5	C³	30	7.2	14.5	100	765	0.65	100	0	0
6	C⁴	20	8.3	18.5	85.0	608	0.49	93.5	6.5	0
7	C⁵	20	8.3	13.0	100	704	0.57	92.0	8.0	0
8	C⁶	20	10.0	16.5	100	689	0.62	90.0	0	10.0
9	C⁷	20	5.0	16.5	90.5	592	0.46	85.5	0	14.5
10	C^{**}	20	8.3	16.5	100	765	0.50	100	0	0

Reaction temperature, 650 °C; GHSV $1 \times 10^4 \text{ h}^{-1}$; height of the catalyst bed 30 mm. **A**—Ag–SiO₂–Al₂O₃; **B**—Ag–SiO₂–MgO; **C**—Ag–SiO₂–MgO–Al₂O₃. *Tested with the fresh samples. **Deactivated catalyst C² after regenerated in oxygen for 2 hours.

**Fig. 1** SEM morphology of fresh(a) and used(b) catalyst C²

experiments. After that, the Al₂O₃ content was set based on the results both from the catalytic performance and the determination of the acid centers. The Al₂O₃ content was finally ascertained as 30 wt% relative to SiO₂. Lower or higher content of Al₂O₃ all lead to the decrease of the selectivity toward HCHO. The catalytic performances over three different types of silver-based catalysts are summarized in Table 1. For **A**, the main by-product is DME, which was commonly considered as the dehydration of methanol over acid centers on SiO₂–Al₂O₃ support. Owing to the basic centers of MgO, **B** mainly produces CO as the by-product. But for **C** at its optimal composition, there is no any outgrowth to be produced. The selectivity to HCHO keeps 100% with the silver loading changing, suggesting that there were no active sites both from acid and base. Results from NH₃-TPD and CO₂-TPD all supported the conclusions as: **B** has many basic sites, while **A** has many acidic sites, however, **C²** has neither strong acid sites nor strong basic sites. Although **B** shows a high conversion (95.7%) for methanol, the selectivity to HCHO is relatively low (78.5%) due to its basic centers on the catalyst surface which led to the production of CO. It is well known that SiO₂–Al₂O₃ mixed oxides⁷ has many strong acid centers and our present study show that the main by-product over **A** is DME, which can be unreasonably ascribed to the contribution from the acid centers. Owing to the simple principal of acid–alkali neutralization, **C²** has neither strong acid centers, nor strong basic centers and shows perfect catalytic performance in the direct dehydrogenation of methanol to HCHO without any side-reactions.

Great differences can be found in the crystalline phase between the fresh and the used **C²** as observed from its XRD patterns. That is, there is no any silver crystal in the fresh catalyst, while the used catalyst shows sharp peaks corresponding to crystalline silver. This phenomenon seems just the same as that from **A**, but totally different with that from **B**, which shows little difference between the fresh and the used catalyst in its XRD pattern. The interesting phenomenon can be directly observed from the SEM photos as shown in Fig. 1. On the surface of the fresh **C²**, a periodic beautiful flower-like framework of the carrier can be observed, and no silver particles

can be seen as determined by EDS method accompanied with SEM. However, as to the used catalyst, many isolated silver particles with a mean particle size as 400 ~ 600 nm displayed on the surface and covered the fine structure of the framework.

More interestingly, this difference between the fresh and the used catalyst can be repeated by easy treatment with pure oxygen or air and the feed gas alternately. The initial peculiar flower-like morphology will be totally recovered after treating the used catalyst in oxygen at 700 °C for 2 hours, inclining the reverse process (Ag⁰ → Ag⁺) takes place. The peculiar process can be repeated for more than 10 times and no obvious changes could be observed. It should be noted that the peculiar flower-like appearance could not be seen in other silver-based catalysts, such as **A** and **B**, which show a smooth surface and a rough surface with isolated silver particles, respectively. Even the **C** catalysts with different compositions do not show such morphology. Although we don't know how this peculiar surface structure affects the catalytic performance, it is evident that this flower-like structure is necessary for its excellent performance.

In conclusion, the novel **C** catalyst is very active and selective in the direct dehydrogenation of methanol to anhydrous HCHO. Thanks to its special surface structure, the catalyst shows an outstanding performance. Considering the simplicity of preparation procedure and easiness of regeneration, the novel catalyst shows much promising potential for anhydrous HCHO production. Further investigation on its detailed mechanism is being underway in our group.

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