APPLIED CATALYSIS

A: GENERAL

Oxidative dehydrogenation of methanol to formaldehyde on electrolytic silver catalyst modified with iodides

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Abstract

Iodides, especially CH_3I, were used as modifiers in the oxidative dehydrogenation of methanol to formaldehyde over electrolytic silver catalyst. The yield of formaldehyde was as high as 93% at 98% conversion of CH_3OH for the I-modified catalyst, while it was only 85% at 94% conversion without I-modification. The optimum reaction conditions were determined and the interaction between the silver surface and the iodide additive was investigated by means of XPS and SEM. The chemisorbed iodine atoms on the silver surface caused a decrease of the surface concentration of atomic oxygen species and prevented the complete oxidation of CH_3OH to CO_2. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

The partial oxidation of methanol to formaldehyde over silver-based catalysts is one of the most important commercial processes [1]. As a widely used industrial catalyst, electrolytic silver shows excellent properties in this process. Formaldehyde can be produced from methanol on industrial electrolytic silver at a conversion of 94% and a selectivity of 92% [2]. Because of the great production capacity of formaldehyde ($\sim 3 \times 10^7$ tons per year all over the world in 1997), even a very slight increment of the yield of formaldehyde will bring a lot of economic benefits. So many researchers have devoted themselves in exploring new methods to increase the yield of formaldehyde [3–8]. Most of those methods try to modify the catalyst. Almost every metal element has been tried as the modifier of the silver catalyst. According to the results of those reports [3–8], the increment is not high and the methods are over-elaborate. Very few reports mentioned any non-metal elemental modifiers [9,10]. Our previous work [11] showed that a higher yield of formaldehyde could be obtained over a phosphorous-modified electrolytic silver catalyst. With this P-modified silver catalyst, however, a much higher O_2/CH_3OH ratio was needed in order to get the same conversion of methanol. Similar results were also obtained by Aicher et al. [10]. Fliol [12] reported the promoting effects of halides. He found that HCl and HBr improved silver catalysts, while HI showed no positive effects. Here we report organic halides as a new set of modifiers on the electrolytic silver catalyst. To our surprise, only organic iodides displayed a significant promoting

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effect, which can increase not only the conversion of methanol from 94% to 98%, but also the selectivity toward formaldehyde from 92% to 95%. Such a promoting effect of iodide is discussed on the basis of various characterizations, such as XPS and SEM.

2. Experimental

2.1. Materials

Methanol, methyl iodide and isopropyl iodide are all reagent grade. Compressed air is used without further purification. Electrolytic silver catalyst (purity>99.999%) is purchased from Shanghai Petroleum Chemical Engineering (China).

2.2. Reaction and analysis

The oxidation reaction was carried out on a fixed-bed reactor. The reactor, a quartz tube with an i.d. of 18 mm, was loaded with 3 g of catalyst (40–60 mesh). An aqueous solution of methanol (60 wt%) was pumped into a quartz evaporator through a micro-pump and mixed with air before entering the reactor. The iodide additive was added directly into the aqueous solution of methanol with a volume concentration ranging from 3 to 1000 ppm. The vaporization temperature was kept at $220^{\circ}C$. The temperature of the reactor was controlled by a DWK-702 temperature controller ($\pm 0.5^{\circ}C$). The product mixture was firstly quenched to room temperature and then collected through an absorption tower. The tail gas was analyzed by using a QF-1903 gas analyzer to determine the contents of CO_2, CO and O_2. The contents of H_2 and N_2 were analyzed through a GC method using TDX-101 as the separating column and using a TCD detector. The concentration of formaldehyde was determined by a titration method. The content of

methanol was obtained by 102-GD GC with a FID detector using a 2 m column of 10% SE-30+7% PEG-20M on white Chromosorb 101; tetrahydrofuran was used as the internal standard.

2.3. Characterization of catalyst

A Perkin-Elmer PHI 5000C ESCA System equipped with a dual Al K_{α} (1486.6 eV) and Mg K_{α} (1253.6 eV) anode X-ray source and spherical capacitor energy analyzer (SCA) was used to carry out the X-ray photoelectron spectroscopy (XPS) experiments. The base pressure of the test chamber was about 1×10^{-9} Torr. Powdered samples were first pressed into a disc (1×13 mm) and fixed on the sample-holder, then introduced into the spectrometer for XPS study. XPS spectra were taken using Mg K_{α} radiation. Scanning electron micrographs (SEM) were obtained on a Hitachi H600 electron micrograph.

3. Results and discussion

3.1. Catalytic activity measurements

The experimental conditions chosen for the catalytic measurement were: reaction temperature: 500–$650^{\circ}C$; O_2/CH_3OH ratio: 0.30–0.45; space velocity (at reaction temperature $\sim 650^{\circ}C$): $\sim 1.2 \times 10^5 \ h^{-1}$. Several iodides, such as CH_3I and CH_3CHICH_3, were chosen as the promoters. In our experiments, we found that the molecular structure of iodides produced no obvious effects on the reaction. So we chose only CH_3I as the promoter in our further research. After a set of experiments, the optimum values of the modifier concentration were found to be in the range 30–100 ppm (see Table 1). If the modifier concentration is very low (about 3 ppm), there are no obvious changes. When it is very high (about 1000 ppm),

Table 1
The effects of the concentration of CH_3I

CH_3I concentration (ppm)	0	3	10	30	100	300	1000
Conversion of CH_3OH (%)	92.5	96.7	96.8	98.0	98.7	96.7	91.6
Selectivity of HCHO (%)	92.2	90.4	92.0	94.7	94.8	89.8	81.3

Reaction conditions: 3 g electrolytic silver, 60% aqueous solution of methanol, space velocity $\sim 1.2 \times 10^5 \ h^{-1}$, reaction temperature $\sim 620^{\circ}C$, O_2/CH_3OH molar ratio ~ 0.40, pre-reaction time ~ 2 h.
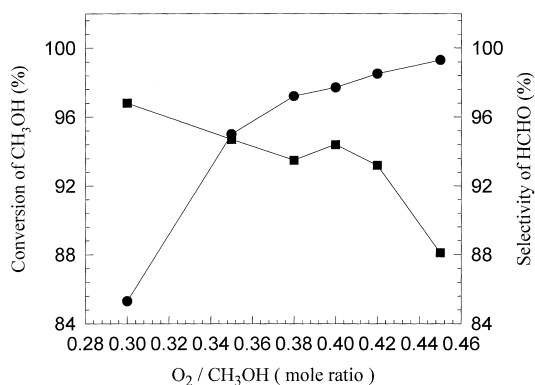
Fig. 1. The effects of the O_2/CH_3OH ratio on the catalytic reaction: (●) conversion, and (■) selectivity. Reaction conditions: 3 g electrolytic silver, 60% aqueous solution of methanol, CH_3I ~100 ppm, space velocity ~1.2×10^5 h^{-1}, and reaction temperature ~620°C.
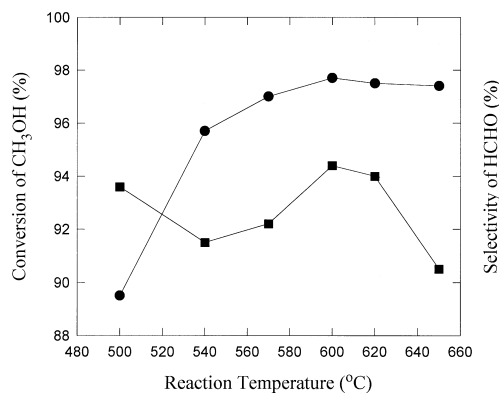

Fig. 2. The effects of reaction temperature on the catalytic reaction: (●) conversion, and (■) selectivity. Reaction conditions: 3 g electrolytic silver, 60% aqueous solution of methanol, CH_3I ~100 ppm, space velocity ~1.2×10^5 h^{-1}, and O_2/CH_3OH ratio ~0.40.

the yield of formaldehyde will decrease quickly to a much lower value. The effects of the O_2/CH_3OH ratio and the reaction temperature on the oxidation reaction modified with 30 ppm CH_3I were studied, as shown in Figs. 1 and 2. It is obvious that the optimum reaction condition is: O_2/CH_3OH ratio in the range 0.38–0.42 and the reaction temperature at about 600–620°C; these ranges are almost the same as the ones without modification of promoters. In other words, if such promoters were used in the commercial process, only very little changes would be demanded in the industrial conditions. Table 2 shows the difference of the main products over silver catalysts with or without iodide-modification under the optimum reaction conditions. It is clear that, when modified with 100 ppm CH_3I, the activity and the selectivity of electrolytic silver will increase simultaneously. The conversion of CH_3OH increases from 94% to 98% and the selectivity to HCHO increases from 91% to 95%. The main by-

product – CO_2, which is a product of the deep oxidation of CH_3OH, drops from 8% to 4%, whereas the yield of hydrogen does not change at all.

3.2. SEM morphology and structure

The results of the interaction between the added iodide and the silver surface can be observed by scanning electron microscope (SEM) measurements. Fig. 3(a) is the SEM micrograph of the electrolytic silver catalyst after the catalytic reaction, which shows some of silver branches with smooth surfaces. The SEM micrograph for iodine modified electrolytic silver catalyst (Ag-I) at the CH_3I concentration of 10 ppm is shown in Fig. 3(b). The morphological configuration of this Ag-I catalyst shows some small holes in the branches of the silver catalyst, which can be explained by the corrosion of CH_3I as:
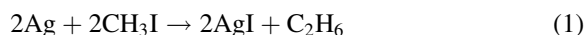
$$2Ag + 2CH_3I \rightarrow 2AgI + C_2H_6 \qquad (1)$$

Table 2
Typical reaction products and results for electrolytic silver catalyst and iodine-modified electrolytic silver catalyst

Sample	O_2/CH_3OH ratio	Conversion of CH_3OH (mol%)	Yield of products (mol%)			Selectivity of HCHO (mol%)
			HCHO	CO_2	H_2	
Electrolytic Ag	0.40	94.2	85.5	7.9	36.4	90.8
I-modified Ag	0.40	98.3	93.2	4.2	35.9	94.8

Reaction conditions: 3 g electrolytic silver, 60% aqueous solution of methanol, space velocity ~1.2×10^5 h^{-1}, reaction temperature ~620°C, pre-reaction time ~2 h, contents of CH_3I ~100 ppm.
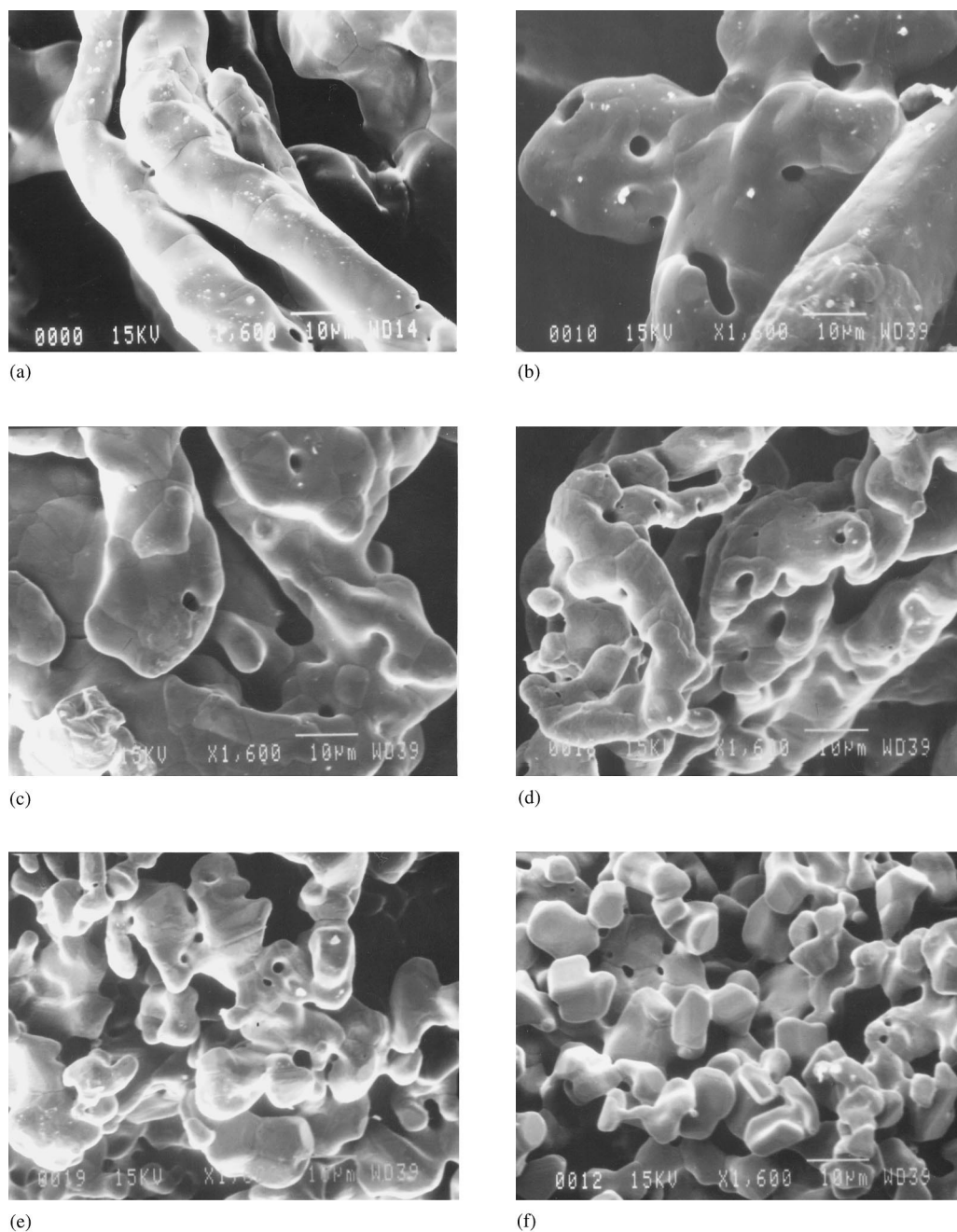
Fig. 3. SEM photographs of the electrolytic silver and Ag–I catalysts with different concentrations of CH_3I additive: (a) electrolytic silver; (b) 10 ppm; (c) 30 ppm; (d) 100 ppm; (e) 300 ppm; (f) 1000 ppm. Reaction conditions: 3 g electrolytic silver, 60% aqueous solution of methanol, space velocity $\sim 1.2 \times 10^5 \ h^{-1}$, reaction temperature $\sim 620°C$, O_2/CH_3OH molar ratio ~ 0.40, pre-reaction time ~ 2 h.

$$2AgI \rightarrow 2Ag + I_2 \qquad (2)$$

A simple experiment was carried out to prove this assumption. A vapor flow of CH_3I was introduced onto the surface of electrolytic silver at 300°C, and C_2H_6 could be detected as the only carbon compound in the product mixtures. On the silver surface, yellow AgI was very obvious. After the surface is heated up to 600°C, I_2 can be detected, and the silver surface turns to grayish white, illustrating the decomposition of AgI.

When the silver catalyst was modified with a concentration of 30 ppm CH_3I, some changes can be seen on the surface morphology of Ag–I, as shown in Fig. 3(c). The big branches of the pure silver catalyst turn into several small branches on which are deposited small particles, which are suggested to be the AgI micro-crystals. When the concentration of the iodide modifier is increased to 100 ppm, much more micro-structure and smaller branches can be easily found (see Fig. 3(d)). These results confirm that CH_3I reacts with the silver surface intensively and caused more defects and higher surface area as the concentration of CH_3I increased, which coincided well with the activity data (Table 1). But if the concentration was increased over 100 ppm, the particular surface structure of the silver catalyst begins to collapse (see Fig. 3(e) and (f)). The long branches disappeared and broken pieces of silver formed; this led to a decrease in its catalytic activity.

3.3. XPS results

The difference of the I $3d_{5/2}$ XPS spectra of the electrolytic silver sample treated with different concentrations of iodide is shown in Fig. 4. It is very clear that the higher the concentration of iodide in the methanol solution, the higher the concentration of iodine observed on the surface of the catalyst. The binding energy of iodine (I $3d_{5/2}$=619.4 eV) indicates that AgI is present on the surface of the catalyst [13]. Under the reaction conditions, a much stronger interaction between iodide and silver was found. Though the concentration of iodide in the vapor of the reaction mixture was very low (<1 ppm), the iodine concentration on the catalyst surface was relatively very high (about 50 000 ppm). That is to say, iodine will accumulate on the surface of the catalyst. At the same time, iodine can be washed away by the reaction mixture. So
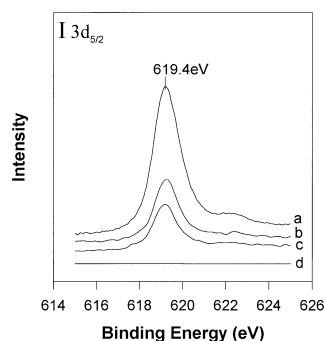

Fig. 4. XPS spectra of I $3d_{5/2}$ on the surface of electrolytic silver catalyst: using different concentrations of CH_3I to treat it: (a) 1000 ppm; (b) 100 ppm; (c) 10 ppm; (d) none. Reaction conditions: 3 g electrolytic silver, 60% aqueous solution of methanol, space velocity $\sim 1.2 \times 10^5$ h^{-1}, reaction temperature ~ 620°C, O_2/CH_3OH molar ratio ~ 0.40, pre-reaction time ~ 2 h.

there is equilibrium between iodine and silver. That is the reason why we have to add the additive continuously in the feed flow.

Table 3 shows the changes of atom densities on the surface of the catalyst when using different concentrations of iodide modifier. We can find that the atom density of oxygen on the silver surface decreases obviously as the atom density of iodine increases. In other words, the adsorption ability of oxygen to silver catalyst decreased when iodine was present on the silver surface. Some iodine atoms may have replaced some adsorbed oxygen atoms just like the effect of chlorine atom in the selective oxidation of ethylene [14]. Combining the activity data and XPS results, we suggest, when the concentration of CH_3I is below 100 ppm, only the oxygen species which lead to

Table 3
The difference of atom densities on the surface of electrolytic silver catalysts

CH_3I concentration (ppm)	Atom density (%)			
	Ag	O	C	I
0	45.0	17.2	37.8	0
10	47.4	15.9	34.4	2.35
100	53.5	10.4	31.2	4.96
1000	56.2	4.5	26.8	12.5

Reaction conditions: 3 g electrolytic silver, 60% aqueous solution of methanol, space velocity $\sim 1.2 \times 10^5$ h^{-1}, reaction temperature ~ 620°C, reaction time ~ 2 h.

total oxidation are replaced; when the concentration of CH$_3$I is much higher (300–1000 ppm), not only the total oxidation oxygen species but also the selective oxidation oxygen species which lead to the formation of formaldehyde are replaced. So the selectivity increases over the range 3–100 ppm CH$_3$I and not only the catalytic activity but also the selectivity toward formaldehyde decreases over the range 300–1000 ppm CH$_3$I. The detailed mechanism will be discussed in our next paper.

Acknowledgements

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