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Selectivity enhancement during formaldehyde synthesis from methanol by in situ CH_3I addition

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This paper is dedicated to Prof. F. Trifirò on the occasion of his 65th birthday.

Abstract

The effect of CH_3I on the formaldehyde synthesis from methanol over a polycrystalline silver catalyst was investigated at temperatures up to 993 K. While the conversion of both CH_3OH and O_2 were reduced, the selectivity to HCHO increased and to CO_2 decreased after treating the Ag catalyst with CH_3I. A notable observation drawn from a long-time operation indicates the CH_3I treatment strongly restrained the formation of HCOOH that had gradually increased with time-on-stream (TOS). It must be noted that the formaldehyde yield did not increase, but that the suppression of formic acid may make the treatment interesting nevertheless. Finally, it was found that the iodide-induced change of the reaction performance was reversible. All observations may well be explained with the assumption of an iodide-induced re-population with different oxygen species on the silver surface.

Keywords: Formaldehyde; Methyl iodide; Silver catalyst; Methanol partial oxidation; Oxidative dehydrogenation; Oxygen species

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1. Introduction

Formaldehyde is one of the world's most important chemicals for the production of urea-phenolic, melamine and acetal resins. Most commercial formaldehyde production is based on oxidative conversion of methanol. The route of silver catalyzed process at air-lean conditions, due to its low investment cost, stable production and simple regeneration of Ag, plays an important role in formaldehyde production [1]. After a century of industrial production, and extensive work [2–4] to understand well the reaction mechanism, relatively little comprehensive knowledge is still available. In a notable recent paper, Andreasen et al. have brought forward a kinetic model that is in good agreement with experimental studies [5]. For the sake of simplicity, however, the undesired formation of formic acid had been ignored. While this simplification may be legitimate for fresh catalysts, it may not be after some time-on-stream [2]. Considering the huge market demand of formaldehyde (worldwide production of 2.5–2.7 × 10^7 t/a in 2000), this system is a prime example for the *selectivity issue* in oxidation catalysis, as even small improvements in selectivity will be economically interesting [6].

Although some new silver catalysts supported on SiO_2 or pumice have been reported [7,8], it seems still quite difficult to adapt them in commercial production instead of traditional polycrystalline silver that can be easily recycled. Recently, modifying Ag catalyst with some trace promoters has become an attractive subject and numerous metal elements were screened out as promoter of the reaction [9–11]. However, considering either transitory activity of modified catalyst or too complicate operation, most of the processes show only little industrial significance for economic reasons. Hence, choosing nonmetal promoters was gradually taken into account.

As commonly known, in the commercial ethylene epoxidation, traces of organic chlorides are continuously added to the feed to improve the product selectivity [12,13]. Campbell and Koel proposed that the efficiency-enhancing

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role of Cl on Ag catalysts occurred primarily through a blocking of those surface sites where total oxidation takes place [14].

STM also indicated chlorine adsorption induced dynamic restructuring of the silver surface [15,16]. Since silver undergoes the similar morphological structural changes at high temperatures in the presence of oxygen, it may be reasonable to use halides as promoters in the formaldehyde synthesis. However, the halides effect on the Ag-catalyzed methanol conversion has been a subject of much controversy. Halides have been intuitively assumed to poison Ag catalysts in the formaldehyde production for a long time, just like e.g. iron-containing impurities in the feed [17,18]. However, no direct evidence has been reported so far for catalyst deactivation by halide poisoning. On the contrary, Flid et al. found that an addition of HCl or HBr (but not HI) to silver catalysts improved their activity and selectivity in the Ag-catalyzed methanol conversion [19]. Deng and coworkers studied how the catalytic activity of crystalline silver changed after a treatment with various organic halide compounds (CH_3Cl, CH_3Br and CH_3I). It was found all these halides promoted not only the selectivity to formaldehyde but also the conversion of methanol [20–23]. Using a density functional theory approach, Shen et al. have evaluated the effect of O, Cl, Br and I on the methanol oxidation over Ag (1 1 1) and found that the I atom showed the strongest beneficial effect [20,24].

It is generally accepted that explaining the reaction mechanism of the silver-catalyzed methanol conversion is based on understanding the interaction of oxygen with silver catalyst. This includes understanding the incorporation and distribution of oxygen species in the silver, as well as the reaction-induced restructuring of silver in the presence of oxygen [25–27]. From the body of literature, three different oxygen species O_α, O_β and O_γ are assumed to form during the reaction. The detailed description of their category is given in [2]. Under reaction conditions, the silver is constantly exposed to oxygen, part of which will penetrate into the crystal lattice of silver and form the oxygen species of O_α, O_β and O_γ species that are depleted by the corresponding reactions, which shows a dynamic equilibrium [28]. In an in situ Raman spectroscopic study, Dai et al. [23] observed that the addition of CH_3I led to a repopulation of different oxygen species on silver. In particular, it inhibited the formation of the surface atom oxygen species O_α corresponding to deep oxidation. The presence of CH_3I also seems to influence the adsorption of methanol, which hardly occurs on an oxygen-free silver surface [29].

The population of oxygen species, which has recently been studied in detail by Waterhouse et al. [30], is a strong function of operating parameters. The three oxygen species have e.g. stability regions at different temperatures. In addition, the population of oxygen species was also affected by the reaction-induced restructuring of silver catalyst, which occurs drastically at high temperature in reaction gas composition [31–34]. Dai et al. observed that Ag tended to form some microstructure and many small ‘‘branches’’ (elongated features) on the surface after it was exposed to a methanol-air mixture with traces of CH_3I at 620 °C for about 2 h [21]. This I-induced morphological restructuring, as well as the above-mentioned reaction-induced restructuring, reinforces the formation of grain boundary defects over the catalyst, which permits more oxygen to penetrate into the silver lattice and, in turn, to intensify the reaction [35].

In the present study, the partial oxidation of methanol to formaldehyde is investigated in a laboratory-scale setup for a long-time operation. In the meantime, the Ag catalyst was treated by 100 ppm CH_3I added to the feed. The effect of CH_3I addition on formaldehyde selectivity and catalyst activation was investigated. Moreover, the selectivity to the byproducts (CO_2, H_2 and HCOOH) was closely monitored with time in order to gauge the long-time behavior of catalytic activity change resulted from the CH_3I treatment.

2. Experimental

2.1. Apparatus

The reaction was carried out in the water ballast mode over an electrolytic silver powder (Bayer AG, 20 mesh) in a tubular fixed-bed reactor. Methanol and water were dosed by pumping the appropriate amounts separately into the respective evaporators that were connected in series. Assisted by N_2 as an inert gas, the composition of the feed mixture was kept outside the explosive regime. Table 1 gives the standard setting of all relevant operating parameters.

The reactor was made of a 50 cm long Al_2O_3 tube and had an inner diameter of 10 mm. The blank activity proved negligible. The 3 cm long Ag catalyst bed was strongly diluted with quartz chips (Ag/quartz: 0.1 g/3 g) in order to weaken the local heating effects and reduce the internal temperature gradient. Heating was provided by an electric heat coil controlled by a temperature controller (Jumo: Dicon SM), which monitored the temperature with the help of a thermocouple, located directly in the middle of the catalyst bed through a capillary Al_2O_3 tube.

Analysis of the products was made by on-line gas chromatography (HP 5890 Series II) with two TCD detectors. Qualitative and quantitative separation of both high and

Table 1
Standard settings of operating parameters in the laboratory-scale setup

	Standard settings
Temperature	823 K
Residence time (at 823 K)	0.085 s
GHSV (at 298 K)	$1.5 \times 10^4\ h^{-1}$
WHSV (at 298 K)	$440\ h^{-1}$
CH_3OH fraction in the feed	17.5 vol.%
O_2 fraction in the feed	7 vol.%
CH_3OH/O_2 molar ratio	2.5
H_2O/CH_3OH molar ratio	0.67