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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.

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

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 re-population 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

low boiling point compounds was possible in this setup with a mol-sieve (5A, HP) and a polar capillary column (Poraplot-Q, HP). For the temperature variation, a heating rate of 0.16 K/min was selected. More information about the lab-scale apparatus is given in [2]. In this paper, yield and selectivity are expressed with respect to the excess component CH_3OH and not with respect to oxygen.

2.2. On-line treatment with CH_3I

After a short induction time, the catalyzed conversion of methanol showed a steady performance in a long-time phase with basically constant methanol conversion and formaldehyde selectivity (see Section 3.3 in [2]). After 300 days time-on-stream, 100 ppm CH_3I (Merck-Schuchardt, >99%) in methanol was introduced into the reaction system by adjusting this composition in the feed for the methanol evaporator. The silver catalyst underwent this on-line treatment at 823 K with the standard feed composition for 24 h. During this treatment, the product gas composition was monitored while the temperature was varied over a wide range (523–923 K). No formic acid was detected over the entire range.

3. Results

3.1. General observations

The color of the effluent in the washing bottle became brownish yellow during the treatment, which has been not observed before. This color change may be assigned to I_2 which resulted from the decomposition of CH_3I at the high temperature [21]:

$$\begin{array}{c} 2\,Ag + 2\,CH_3I \rightarrow 2\,AgI + C_2H_6 \\ 2\,AgI \rightarrow 2\,Ag + I_2 \\ \hline 2\,CH_3I \rightarrow C_2H_6 + I_2 \end{array}$$

After the above-mentioned treatment, no more CH_3I was added in the following experiments, which ran with the I-free methanol again.

3.2. Effect of CH_3I to the reaction selectivity and catalyst activation

Fig. 1 depicts the exit gas composition at 823 K in the two experiments directly before and after the CH_3I treatment. In comparison with the iodide-free process with about 67% CH_3OH conversion, less CH_3OH (43%) was converted after the silver catalyst was treated with CH_3I. $X(O_2)$ also reduced from 82% to 46%. S(HCHO) jumped from 80 to 86%. Moreover, $S(H_2)$ increased from 19 to 34%, whereas $S(CO_2)$ dropped from 13 to 9%, which implies the total oxidation might be deeply suppressed after the CH_3I treatment. In addition, no formic acid was observed yet in the first test after the treatment, while S(HCOOH) had been about 3% before. Similar results were also found at 773 and 873 K.

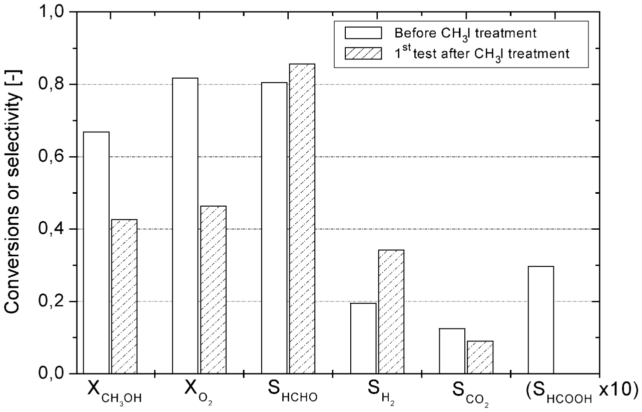

Fig. 1. Comparison of the reaction performance before and after the CH_3I treatment (at 823 K).

3.3. Long time behavior

After the CH_3I treatment, the conversion of methanol was studied further for a long-time operation in order to gauge the behavior of catalytic activity as a function of time after it was changed dramatically as mentioned above.

Fig. 2 shows the S(HCHO) decreased gradually to about the original 80% within about two months, whereas $X(CH_3OH)$ increased again after stopping the CH_3I addition. However, $X(CH_3OH)$ would not reach the previous value (67%, see Fig. 1) even after 2 months. Considering that the silver catalyst had been intensively used in the setup for more than 400 days time-on-stream, the slow deactivation of the silver catalyst accompanied by a loss of conversion may have to be taken into account.

The selectivity to byproducts also shows a reversibility, as within 2 months $S(CO_2)$ and $S(H_2)$ returned to 13.5 and 24%, respectively (see Fig. 3).

S(HCOOH) as a function of temperature for various times-on-stream is plotted in Fig. 4. It is shown that HCOOH appeared from time-on-stream of about 100 days, but only in a limited temperature region of 600–690 K with $S(HCOOH) < 0.05$. This region grew with time, such that after eight months (240 days), HCOOH could be observed over a wide range of temperatures (580–870 K). However, the growth of this region was suddenly interrupted by treating the silver catalyst with CH_3I, e.g. 1 week after the CH_3I treatment (308 days), the formation of HCOOH was suppressed strongly in a limited region again (565–720 K). After stopping the CH_3I addition, however, HCOOH appeared again with time in a broader region.

An upper (T_{upper}) and a lower (T_{lower}) temperature limit were defined as a function of TOS to visualize the slow extension of HCOOH formation into the high temperature

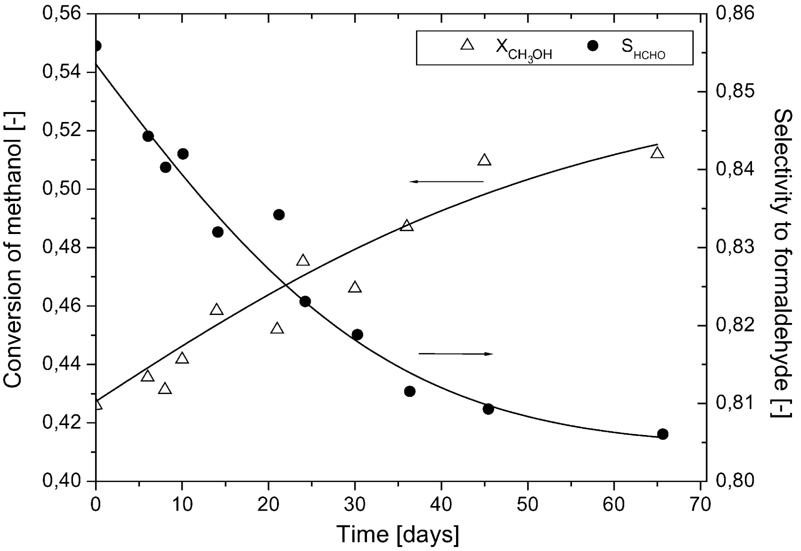

Fig. 2. CH_3OH conversion and HCHO selectivity with time after the CH_3I treatment (at 823 K).

region [2]. A noteworthy observation in a long-time operation is that the upper temperature increased to 870 K linearly during the first 8 months. After this time, the shift into the higher temperature region stopped, and the upper temperature stayed constant with time. However, the upper temperature shift underwent a dramatic reverse to 720 K again by adding CH_3I (see Fig. 5). Since then, it slowly shifted back to the higher temperature region, even in a similar linear manner as during the first 8 months. The lower temperature limit decreased continuously with TOS. After about 12 months, the shift stopped at 530 K, which was also the light-off temperature of the reaction. No pronounced discontinuity was observed even with the CH_3I treatment.

3.4. Establishing S(X) diagrams

In addition to the change of methanol conversion X and formaldehyde selectivity S by the CH_3I treatment (open circles), two other experiments are shown in Fig. 6. The grey triangles indicate the state when changing the concentration ratio $p(O_2)/p(MeOH)$, the black squares reflect a variation of the residence time. It can be seen that the latter has a marked effect on the selectivity even at moderate variations of the conversion. For the CH_3I-treatment, as for the variation of the ratio oxygen to methanol, the selectivity increase is overcompensated by a marked decrease in conversion, leading to a lower overall yield.

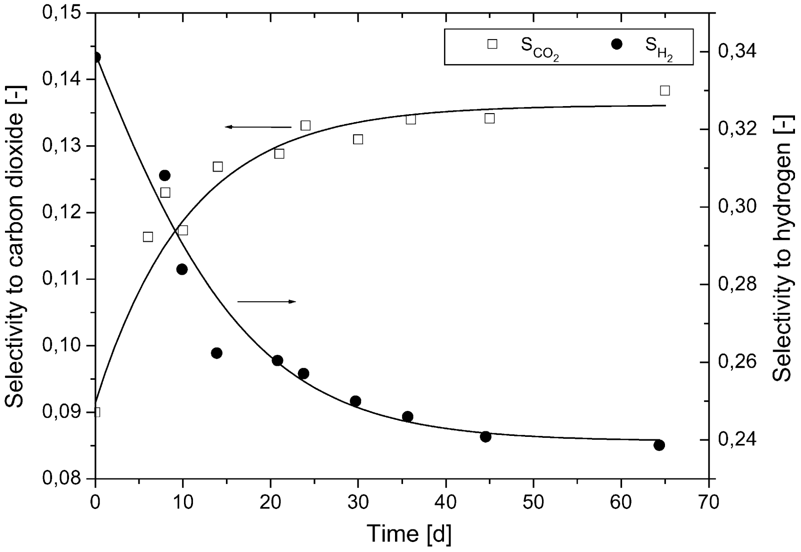

Fig. 3. Selectivity to carbon dioxide and hydrogen vs. time after the CH_3I treatment (at 823 K).

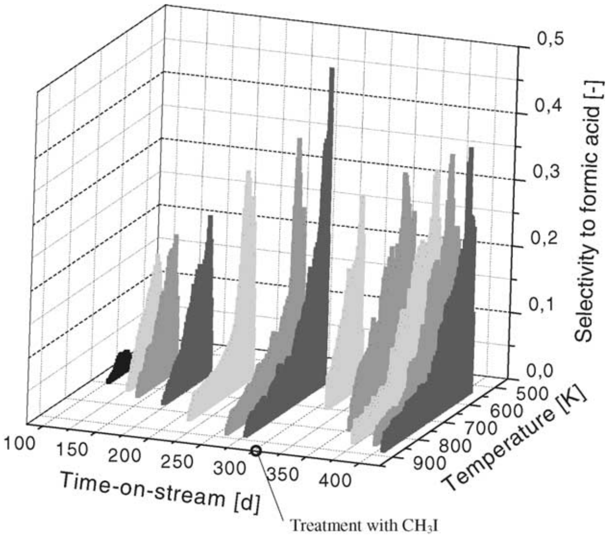

Fig. 4. Selectivity to HCOOH vs. time-on-stream and temperature.

4. Discussion

Because of the aim to perform long-time studies, no catalyst was taken from the reactor to perform ex situ characterization. Also, no in situ spectroscopy was installed at this time. Therefore, it is not possible to draw reliable conclusions on the different types of oxygen. However, since these are the categories in which the reaction system is typically discussed, we will assess the experimental results in this framework and study whether the findings are in agreement with current literature. Obviously, in situ spectroscopic studies are required to validate the conclusions drawn here.

In comparison with the CH_3I-free process, the reaction performance was changed by adding CH_3I. A higher *S*(HCHO) accompanied with an inhibition of CO_2 and HCOOH was observed over an iodide-modified catalyst. Considering that O_α is mainly responsible for the formation of HCOOH and the total oxidation, it is therefore well assumed, after the silver catalyst was treated by CH_3I, the active sites where O_α is formed were deeply blocked by I^- ions. This supposition of a re-population of oxygen species over silver catalyst is not only in agreement with the Raman study of Dai et al. [23], it was also supported by the observation of Waterhouse et al. [30]. By studying the reaction at different temperatures and CH_3OH/O_2 ratio, he found that that the selectivity to formaldehyde was closely related to the relative populations of the O_α and O_γ states, and the increase of formaldehyde selectivity reflected the corresponding increase in the O_γ/O_α ratio during the reaction.

The trend of $S(CO_2)$ depicted in Fig. 3 implies a reversible procedure of population of oxygen species. It may be assumed that I^- adsorbates could gradually desorb from the blocking-sites and a replenishment of the Ag surface with O_α was hence available after stopping the CH_3I addition. This hypothesis is also supported by the performance of *S*(HCOOH) in Figs. 4 and 5, where the formation of HCOOH shifted again in a broader temperature region after it was broken by CH_3I treatment. Thus, it is proposed that, unlike some other impurities (e.g. iron carbonate) that bond strongly with the silver substrate (e.g. in the form of Fe_2O_3) and poison the silver catalyst permanently [36], the effect of I^- ion is reversible.

As chlorine could roughen the silver surface in the ethylene epoxidation, leading to an enhanced subsurface oxygen concentration and thereby to increased selectivity [37,38], it may be assumed that I^- can also intensify the restructuring of silver surface and benefit the oxygen diffusion to form more bulk species O_β and O_γ. In fact, this I^--induced restructuring has indeed been observed experimentally with SEM studies [15,16]. Despite a great diversity

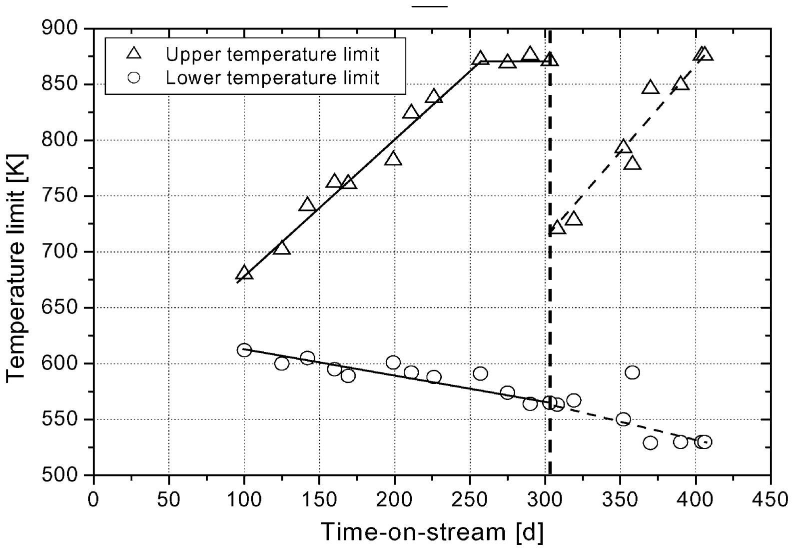

Fig. 5. Upper and lower detection temperature of HCOOH vs. time-on-stream (the time of the CH_3I treatment is indicated by the vertical dashed line).

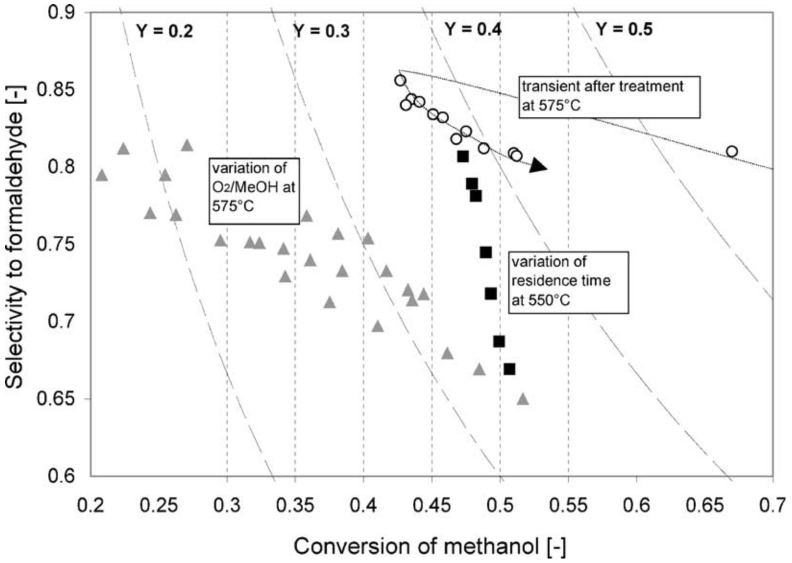

Fig. 6. The variation of formaldehyde selectivity with methanol conversion in different experiments.

about how the subsurface species O_γ participates in the reaction [30], it is generally accepted that O_γ benefits the generation of hydrogen. In the present study, $S(H_2)$ jumped after the CH_3I treatment (see Fig. 1), which supports well the above assumption. It is shown in Fig. 3 that the increase of $S(H_2)$ also is reversible, as that selectivity slowly decreased towards the original value after the addition of CH_3I was stopped. Considering the surface of silver undergoes a dynamic mobility at higher temperature, it is proposed that the I^--induced roughening of the Ag surface tended to be healed with time in a ‘‘clean’’ condition, and that hence the formation of O_γ was gradually reduced. However, it should be noted, due to the absence of spectroscopic studies, that such re-population of oxygen species can only be approached here from the experimental reaction in an indirect manner. As a matter of fact, an in situ fiber-optic observation with Raman spectroscopic technology has been taken into account.

Dai et al. have found the silver restructuring was dependent on the CH_3I concentration [21]. Too high I^- concentrations made the silver crystalline collapse and even reduced the conversion of methanol. Hence, the reason that a relatively low conversion of methanol was found in the present study may be that 100 ppm CH_3I was not such an optimal concentration under the actual operation conditions. Different ideal amounts of additive may be eventually found, depending on the operation conditions. On the other hand, the I^--promoted CH_3OH adsorption (even on a clean silver surface) led to a competitive inhibition of oxygen adsorption, which may also reduce the general amount of oxygen species and therefore depress the reaction conversion. The observation in the present study is in good agreement with the effect of Cl^- addition in the ethylene epoxidation where the selectivity to ethylene oxide is enhanced at the cost of a lower overall reaction rate [12,39]. In the present case, the main effect of the CH_3I addition is the suppression of HCOOH formation over a wide temperature range for various weeks. In a given production, this might postpone the exchange of the aged catalyst and thus save expenses in spite of decreased formaldehyde yield. Detailed spectroscopy-supported mechanistic studies and a thorough parameter screening for an optimal regeneration protocol both are crucial next steps towards an economically and ecologically improved production, pushing the *selectivity issue*.

5. Conclusions

The effect of CH_3I (100 ppm) on the silver-catalyzed formaldehyde synthesis from methanol was investigated in a long-time operation.

In comparison with the I^--free process, S(HCHO) was enhanced after the CH_3I treatment, whereas less methanol was converted over an I^--modified catalyst. The overall formaldehyde yield decreased. The crucial observation is that the formation of formic acid was stopped altogether. This technically detrimental side product had been increasingly formed over time-on-stream. That development could be pushed back to a certain extent by the addition of methyl iodide.

The experimentally observed effects are in agreement with the hypothesis that the addition of CH_3I leads to a re-population of different oxygen species on the catalyst surface. The inhibition of S(HCOOH) and $S(CO_2)$ implies that the active sites where the oxygen species O_α is formed were blocked by the I^- ion.

Moreover, it is found that I^- adsorbates were gradually desorbed from the blocking-sites after stopping the CH_3I-addition. The effect of I^- ion on the methanol conversion seems to be reversible with time.

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