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A study of the ageing and deactivation phenomena occurring during operation of an iron molybdate catalyst in formaldehyde production

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Abstract

Catalyst from a Perstorp Formox formaldehyde plant, operating with high inlet concentration of methanol (10.2 vol.%), was discharged from single tubes of a multi-tube reactor after half the expected lifetime of the catalyst and again after termination of the load. Each tube was filled with two different layers of catalyst. From the inlet of the reactor the first layer was a catalyst mixed with inert rings, which was followed by a second layer of pure catalyst extending from the middle to the outlet of the reactor. Catalyst fractions from the two layers were characterized with various techniques including BET, Fourier transform Raman (FT-Raman) spectroscopy, X-ray diffraction (XRD), elemental analysis with atomic absorption spectroscopy (AAS) and activity measurements. It was found that the surface area of the catalyst in the mixed layer increases during operation while a small decrease is noticeable for the catalyst below in the pure layer. Elemental analysis, XRD and FT-Raman show that during operation of the catalyst there is migration of Mo species from the upper part of the reactor towards the outlet. Activity measurements reveal severe deactivation of the catalyst in the mixed layer. It is concluded that the deactivation primarily is due to formation of volatile species formed by the MoO_3 surface reacting methanol, causing a decrease of the $MoO_3/Fe_2(MoO_4)_3$ mole ratio in the catalyst. Concerning the catalyst in the pure layer, the condensation of needle-like crystals of MoO_3 mainly occurs on the external surface of the catalyst ring.

Keywords: Methanol oxidation; Formaldehyde; Iron molybdate catalyst; Catalyst deactivation

1. Introduction

All industrial production of formaldehyde uses methanol and air as the raw materials. Two competing technologies are available, which commonly are referred as the silver process and the oxide process, respectively [1]. The silver process operates at methanol rich conditions with silver as catalyst, while the oxide process uses an iron molybdate catalyst under methanol lean conditions. Perstorp Formox is a leading supplier of the latter technology including the catalyst. The lifetime of the oxide catalyst is about 1–2 years depending on the operating conditions. There are several factors that might cause deactivation of the catalyst. Normal ageing of the catalyst shows up with time on stream as decreasing activity, which is compensated for by increasing the temperature of the heat transfer fluid (HTF), decreasing selectivity for formaldehyde and increased pressure drop. Most often it is the decrease in activity and selectivity that determines when the catalyst load has to be replaced. During the years several publications have treated the deactivation of the iron molybdate catalyst [2–5], however, few of them have dealt with deactivation of loads from industrial reactors. In a previous work [3], a load from an industrial plant was characterized. Here it was reported that there is loss of Mo from the hot spot and that the gaseous Mo species condenses in the cold part of the reactor. After that investigation was performed, process intensification efforts have led to the use of a mixed layer with catalyst and inert rings in the first part of the reactor, enabling the methanol concentration in the feed to be increased to about 8.5 vol.%. Currently there is an interest in increasing the plant capacity further by operation with higher methanol inlet, which requires a refined catalyst activity profile (CAP) that allows the heat of reaction to be properly distributed along the length of the reactor tube. In order to improve the lifetime of the catalyst, Perstorp Formox continuously characterizes catalyst loads being used under different operating conditions and for

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different time on stream. This report summarizes some of those findings obtained with high inlet concentration of methanol.

2. Experimental

Catalyst from a selection of tubes in an industrial multi-tube reactor was discharged as five fractions along the tubes using a vacuum cleaner. The tube load was 140 cm long and consisted in the order from the gas inlet of 32 cm (bed position: 0–32 cm) inert ceramic rings, 50 cm (32–82 cm) of 45 vol.% KH44L catalyst mixed with inert rings, 53 cm (82–135 cm) of a pure layer with KH26 catalyst, and finally at the outlet 5 cm (135–140 cm) inert material. Three sample fractions were from the mixed layer and are denoted 32–49 cm mix, 49–65 cm mix and 65–82 cm mix, respectively, after the position in the bed, and two fractions were from the pure layer and are accordingly denoted 82–109 cm and 109–135 cm, respectively. Samples were taken both after half the expected lifetime (denoted HT) and again after termination of the load (denoted FT). The plant was operated under pressure (0.3 bar g) with high inlet concentration of methanol (10.2 vol.%). The oxygen content in the feed gas before mixing with methanol was 10.0 vol.%. All sample fractions as well as the fresh catalyst were characterized regarding surface area, porosity, elemental composition, phase composition and catalytic activity.

The specific surface areas of the samples were measured with a Micromeritics Flowsorb 2300 instrument. For determination of the pore volume, a weighed sample of catalyst rings was immersed in ethanol. After 10 min, the liquid was decanted and the external surface of the rings was dried on a piece of absorbing paper. Then, the uptake of ethanol was immediately determined gravimetrically. A few comparisons with results obtained on a mercury porosimeter (Micromeritics AutoPore III) showed no difference within ±0.01 cm^3/g.

X-ray diffraction (XRD) patterns were recorded using a Seifert XRD 3000TT diffractometer. The measurements were made on ground samples in a rotating sample holder.

Elemental analyses of the catalyst samples were performed with atomic absorption spectroscopy (AAS) after dissolution of the samples in acid solution to suitable concentration.

Fourier transform Raman (FT-Raman) spectra were recorded on a Bruker IFS66 FTIR spectrometer equipped with a Bruker FRA106 FT-Raman device, a Nd:YAG-laser and a germanium diode detector. The laser power was 100 mW, the resolution was 4 cm^{-1} and 400 scans were recorded for every spectrum.

Comparative activity measurements on fresh and used samples were made in a stainless-steel micro reactor under adiabatic conditions. The conversion of methanol was calculated comparing the signal from a Bernath Atomic 3006 FID-analyzer before and after the reactor.

3. Results and discussion

The data in Table 1 show that after half the expected lifetime of the catalyst, the surface area of the KH44L catalyst in the mixed layer has increased. The increase is larger at the inlet than in the lower part of the mixed layer. A concurrent decrease in the surface area is noticed for the first part of the pure layer with KH26 catalyst. No change in surface area is observed for the last part of catalyst at the outlet from the reactor. The trends and changes observed at half time become more pronounced with the further use of the catalyst. After termination of the load, only the last part of the pure layer seems to be relatively fresh.

Parallel to the changes in surface area, the pore volume of the catalyst increases with time on stream, more at the inlet than at the outlet of the reactor. Especially the catalyst at the inlet shows a considerable increase in pore volume from 0.27 cm^3/g for the fresh catalyst to 0.44 and 0.49 cm^3/g after half time and full time, respectively.

In a previous characterization of a Fe-Mo-oxide catalyst being used in methanol oxidation as a straight load without inert material, it was observed that the specific surface area of the catalyst in the first 6–7 cm at the inlet remained unchanged while otherwise it had decreased throughout the tube [3]. Similar observations have been made with straight loads in plants belonging to Perstorp AB. The present results for loads with a mixed layer at the inlet, however, clearly evidences that a mixture of catalyst and inert rings reduces the hot spot

Table 1
Specific surface area, pore volume and elemental composition of fresh and used catalysts

Sample	Specific surface area (m^2/g)	Pore volume (cm^3/g)	Mo/Fe (atom ratio)	$MoO_3/Fe_2(MoO_4)_3$ (mole ratio)
KH44L mix, fresh	4.5	0.27	2.43	1.86
KH26, fresh	5.4	0.29	2.29	1.58
HT32-49 cm mix	6.3	0.44	1.55	0.10
HT49-65 cm mix	5.1	0.38	1.60	0.20
HT65-82 cm mix	4.7	0.31	2.10	1.20
HT82-109 cm	4.9	0.28	2.36	1.72
HT109-135 cm	5.3	0.27	2.27	1.54
FT32-49 cm mix	6.6	0.49	1.47	0.00
FT49-65 cm mix	5.7	0.46	1.56	0.13
FT65-82 cm mix	5.2	0.38	1.75	0.50
FT82-109 cm	4.4	0.34	2.26	1.52
FT109-135 cm	5.2	0.26	2.42	1.83

temperature and the associated sintering of the catalyst, admitting operation at higher methanol inlet pressure and higher productivity.

Further characterization of the used catalyst was performed to explain the observed changes in the surface area and the pore volume of the catalyst. The Mo and Fe content of the catalyst fractions were analyzed with AAS and the data are given in Table 1 as the Mo/Fe atomic ratio. The ratios in fresh KH44L and KH26 are 2.4 and 2.3, respectively. Considering the data for used catalysts, these show that the Mo/Fe ratio for KH44L in the mixed layer decreases with time on stream. After termination of the load the Mo/Fe ratio in the mixed layer is around 1.5 or slightly higher. In the pure layer, on the other hand, the Mo/Fe ratio increases with time on stream. The half time analyses show that the ratio, compared to that of the fresh KH26, is higher in the first part of the pure layer and unchanged in the second part. In full time, however, the Mo/Fe ratio is the highest in the last part of the pure layer and, compared with the analysis in half time, it has decreased somewhat in the upper 82–109 cm part of this layer.

To obtain information about the changes in the phase composition being associated with the changes in the elemental composition, XRD patterns were collected. In Fig. 1 the patterns are shown for the fresh KH26 catalyst and the two used catalyst fractions that have the lowest and the highest Mo/Fe ratio, respectively. The diffraction pattern of the fresh catalyst shows reflections from both orthorhombic MoO_3 and monoclinic $Fe_2(MoO_4)_3$ in agreement with the JPDS files no. 35–609 and no. 35–183, respectively [6]. It can be noticed, moreover, that the sample from the inlet (FT32-49 cm mix) shows only reflections from the $Fe_2(MoO_4)_3$ phase while the sample from the outlet (FT109-135 cm) shows considerably more intense reflections from MoO_3 as compared to the fresh catalyst. Support for this result is found in Table 1 where the Mo/Fe atomic ratios have been recalculated as $MoO_3/Fe_2(MoO_4)_3$ mole ratios. Only the upper part of the catalyst (FT32-49 cm mix) is free from MoO_3 and shows a Mo/Fe ratio slightly below 1.5, indicating formation of some iron oxide. For this fraction the ratio 1.47 corresponds to a $Fe_2O_3/Fe_2(MoO_4)_3$ mole ratio of 0.02, or 0.55 wt.% Fe_2O_3. Concerning the appearances of the used FT-catalyst rings, in the upper part of the mixed layer (FT32-49 cm mix) the catalyst was reddish brown in a thin layer at the surface, which is in agreement with the formation of Fe_2O_3 in an amount (0.55 wt.%) that is below the detectability limit in XRD and, compared with freshly prepared catalyst, the rings had become more fragile. In the pure catalyst layer many colourless needle-like MoO_3 crystals were observed. Thus, the results obtained (Table 1 and Fig. 1) show that during operation of the catalyst, with time on stream there is progressing migration of Mo species from the inlet of the reactor towards the outlet. According to earlier reports, the mechanism for the transport is sublimation and subsequent condensation/decomposition of the gaseous Mo species [2,3,7], which can be, e.g. $MoO_2(OH)_2$, $MoO_2(OCH_3)_2$, $MoO_2(OH)(OCH_3)$, $MoO_2(OH)$ and $MoO_2(OCH_3)$ [2]. The XRD results in Fig. 1 suggest that the volatile species are formed on MoO_3 rather than $Fe_2(MoO_4)_3$. Support for this supposition is obtained considering the $MoO_3/Fe_2(MoO_4)_3$ ratios in Table 1 for the first two catalyst fractions in the mixed layer, showing a rapid initial decrease of the Mo-content followed by a much slower decrease after half time. Moreover, Popov et al. [2] have presented evidence for excess MoO_3 in the catalyst accelerates the extent of sublimation. Considering the fact that the partial pressures of methanol and water are the highest at the inlet and outlet of the reactor, respectively, the present data indicate that the main reason for the sublimation of Mo from the catalyst is the interaction of methanol with MoO_3 producing gaseous methoxy species. The interaction of MoO_3 with water to form gaseous hydroxy species plays a minor role. This inference agrees with a previous report [2], where it was experimentally found that the effect of water on the sublimation of Mo is three orders of magnitude lower than that of methanol. Most likely, the formation of MoO_3 needles in the lower part of the reactor is due to the reason that the methoxy species decompose due to either the partial pressure of methanol being reduced or the temperature being high. It should be noted that during operation of the load, the hot spot zone in the reactor successively moves downwards the reactor and that the temperature never is the highest in the very first part of the reactor, which is the first part to loose Mo. The latter observation is opposed to the opinion expressed in a previous work [3] that the sublimation of Mo is related to the high temperature in the hot spot.

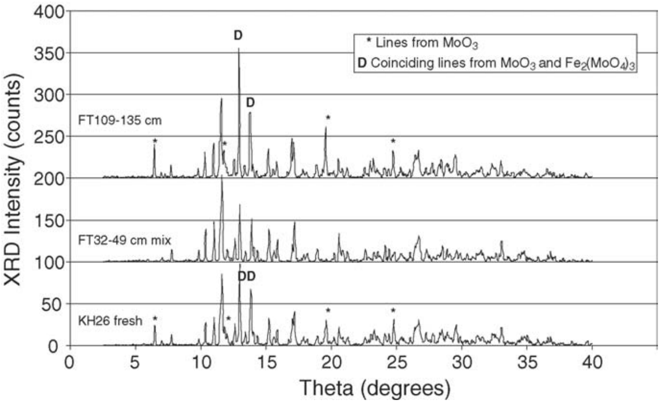

Fig. 1. XRD patterns of fresh KH26 catalyst and used catalyst fractions from the inlet and outlet of the reactor, respectively.

Raman spectra of fresh and used catalyst were recorded to gain information about any possible composition gradients in the catalyst rings. For that purpose spectra were recorded both on catalyst pieces exposing the external surface of the ring and after grinding to a powder. Grinding mainly results in exposure of the inner active surface of the ring. The fact that grinding produces only a negligible amount of new surfaces is evidenced considering that the surface area upon grinding only increased by 0.2–0.3 m^2/g. The Raman spectra recorded showed bands from MoO_3 and $Fe_2(MoO_4)_3$ essentially. Although the FT32-49 cm fraction from the mixed layer was reddish brown on the external surface due to Fe_2O_3, no bands from that phase were visible because it gives only weak bands in Raman. For semi-quantitative purposes, the intensity ratio was calculated between the strongest bands from MoO_3 and $Fe_2(MoO_4)_3$ appearing at 820 cm^{-1} and 784 cm^{-1}, respectively [7–9].

Table 2
Intensity ratio (I_{820}/I_{784}) of the Raman bands at 820 cm^{-1} and 784 cm^{-1} from MoO_3 and $Fe_2(MoO_4)_3$, respectively

Sample	I_{820}/I_{784} for ground catalyst	I_{820}/I_{784} for unground catalyst
KH44L mix, fresh	2.2	2.0
KH26, fresh	1.9	1.9
HT32-49 cm mix	0.21	0.24
HT49-65 cm mix	0.26	0.21
HT65-82 cm mix	0.84	0.23
HT82-109 cm	1.9	3.7
HT109-135 cm	1.8	3.3
FT32-49 cm mix	0.21	0.25
FT49-65 cm mix	0.21	0.21
FT65-82 cm mix	0.28	0.33
FT82-109 cm	0.77	0.21
FT109-135 cm	2.6	6.4

The Raman intensity ratios displayed in Table 2, although being more surface sensitive, are consistent with the data from AAS and XRD in Table 1 and Fig. 1, respectively. A comparison of the data in Table 2 for the unground and ground HT65-82 cm mix sample evidences that the MoO_3 content is lower at the external surface than at the inner surface. The same is true for the FT82-109 cm sample fraction. This finding gives additional support for the migration of Mo being caused predominantly by interaction of MoO_3 with methanol and not with water since the partial pressure of methanol being higher at the outer surface than at the inner part, while the opposite is valid for the product water. Moreover, comparing the Raman intensity ratios for unground HT82-109 cm, HT109-135 cm and FT109-135 cm samples with the corresponding data after grinding, it is seen that the condensation of Mo species is confined to the external part of the catalyst ring.

In Fig. 2 are activity data for the fresh catalysts compared with the corresponding data for the used catalyst fractions. The half time measurements show that the activity of the catalyst in the mixed layer has decreased in spite of the increase in surface area (Table 1). The surface area normalized data confirm that the decrease in activity is a result of the observed loss of Mo from the catalyst and the decreased $MoO_3/Fe_2(MoO_4)_3$ ratio (Tables 1 and 2). No activity measurement on the HT32-49 cm fraction was performed since the sample collected did not contain enough unbroken rings. A simultaneous minor decrease in the activity of the first part of the pure layer (HT82-109 cm) is observed, which can be explained by the decrease of surface area (Table 1). The last part of the pure layer is still relatively fresh.

After full time, the trends observed in half time are reinforced and considerable deactivation of all catalyst fractions is noticeable in Fig. 2. The deactivation of the fractions in the mixed layer can be explained mainly by their loss of Mo-oxide (see Tables 1 and 2). Deactivation causes for the FT82-109 cm fraction are the loss of surface area (Table 1) and the shortage of MoO_3 at the surface of the catalyst (Table 2), although the MoO_3 content is still high in the bulk of the catalyst (Table 1). The most active catalyst is the lower part of the pure layer (FT109-135 cm). However, also this part clearly shows deactivation in spite of its surface area being almost unchanged and, as opposed to the other fractions, the Mo content of this fraction has increased (Tables 1 and 2). The deactivation of this fraction, as expressed per surface area unit, is because the contribution from MoO_3 to the surface area has increased. It is well known that MoO_3 has low specific activity for methanol oxidation [10]. However, it should be noted that the condensation of MoO_3 should not give rise to any deactivation when the performance is compared per bed volume unit, which is relevant for industrial conditions. The latter statement, of course, is valid only as long as the surface area of the original catalyst ring remains unchanged.

Thus, the results clearly implicate that for the fresh catalyst, there is an optimal $MoO_3/Fe_2(MoO_4)_3$ ratio giving good performance. A too high $MoO_3/Fe_2(MoO_4)_3$ ratio gives low activity to the catalyst and requires higher operation

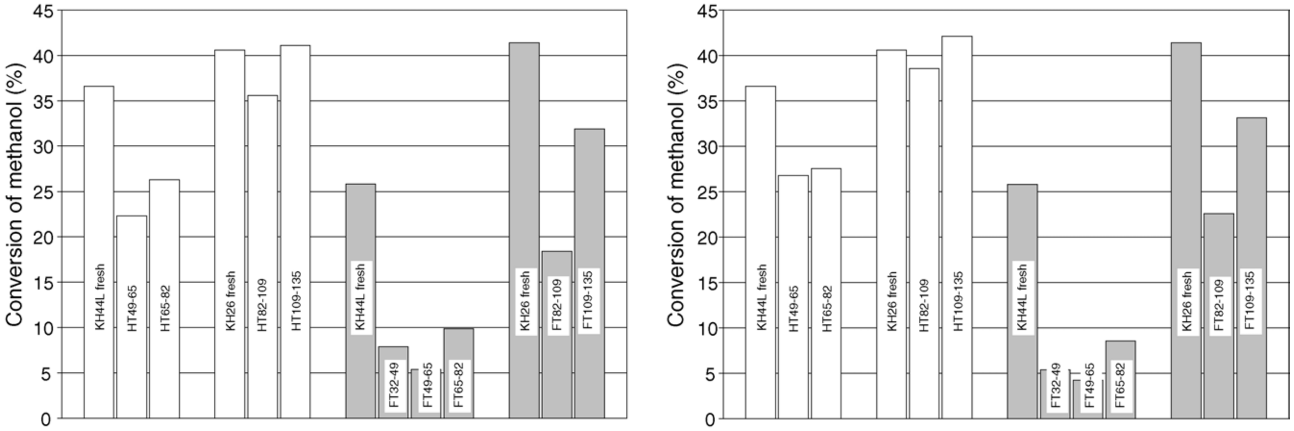

Fig. 2. Conversion of methanol as measured in an adiabatic micro reactor (21 mm in diameter) over freshly prepared KH44L and KH26 Perstorp catalysts and the corresponding samples after use in an industrial multi-tube reactor. Reaction conditions: 1.75 vol.% methanol in dry 25 N L/min air with an inlet temperature of 260 °C. Left figure: The amount of catalyst in the micro reactor was either 75 mm of unbroken catalyst rings (HT-samples, unfilled columns) or 13 g of 1 mm catalyst particles of crushed and sieved catalyst (FT-samples, shaded columns). Right figure: The same data are compared on equal surface area basis after normalization of the data for the used samples accounting for the changes in catalyst particle weight and specific surface area using data from Table 1.

temperature. Moreover, the rates of sublimation and needle formation are increased, leading to faster increase of the pressure drop over the reactor. On the other hand, a too low $MoO_3/Fe_2(MoO_4)_3$ ratio leads to rapid deactivation of the active $Fe_2(MoO_4)_3$ phase. To maintain the active phase, an excess of MoO_3 is needed according to the redox process as follows:

Main reaction: $CH_3OH + Fe_2(MoO_4)_3 \rightarrow CH_2O + H_2O + 2FeMoO_4 + MoO_3$.
Reoxidation in excess of MoO_3: $2FeMoO_4 + MoO_3 + \frac{1}{2}O_2 \rightarrow Fe_2(MoO_4)_3$.
Reoxidation in shortage of MoO_3: $3FeMoO_4 + \frac{3}{4}O_2 \rightarrow Fe_2(MoO_4)_3 + \frac{1}{2}Fe_2O_3$.

Thus, when the content of MoO_3 is too low in the catalyst, the activity decreases and unselective Fe_2O_3 is formed.

Previous reports claimed that a Mo/Fe ratio of 1.7, corresponding to a $MoO_3/Fe_2(MoO_4)_3$ ratio of 0.40, gives the highest activity [10,11]. However, the present results demonstrate that the optimal ratio is higher. Here it is appropriate to point out that performance not only depends on the ratio but also on the mixing, crystal size and crystal shape of the constituent phases.

4. Conclusions

During operation of the Perstorp Formox methanol oxidation catalyst with high inlet concentration of methanol, sublimation of Mo species occurs from the mixed layer with catalyst and inert rings. The formed Mo species subsequently condenses/decomposes to form needle-like MoO_3 crystals in the pure layer. The sublimation of Mo from the mixed layer causes increased specific surface area, increased pore volume and decreased activity. In the pure layer, the formation of MoO_3 needles predominantly occurs on the external surface of the catalyst rings. According to the results, formation of volatile methoxy species through the interaction of methanol with the MoO_3 surface is the main cause for the redistribution of Mo that occurs during use of the catalyst. The decomposition leading to the formation of needle-like MoO_3 crystals seems to be an effect of temperature and/or methanol pressure.

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