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Time on stream behaviour in the (amm)oxidation of propene/propane over iron antimony oxide: cyclic operation

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Abstract

The time on stream behaviour of the selective (amm)oxidation of propene and propane over an active iron antimony oxide catalyst showed that the activity and selectivity of these catalysts decreased significantly with time on stream. Also γ-Bi_2MoO_6 shows a strong time on stream behaviour. It is shown that the selectivity for acrolein increases strongly with time on stream for the bismuth molybdate catalyst. The activity, however, decreases strongly. The catalytic performance of iron antimony oxide catalyst can be improved by operating the partial oxidation/ammoxidation in a cyclic mode, i.e. alternating the feed from reducing (hydrocarbon/air(/ammonia)) to oxidising (air) atmospheres. It is shown that the re-oxidation of the catalyst can be performed at the same temperature as the reaction temperature. The original oxidation state is, however, not fully regained. Elevated temperatures or prolonged oxidation times are required to regain the original oxidation state of the catalyst.

Keywords: Stream behaviour; (amm)Oxidation; Cyclic operation

1. Introduction

Mixed oxides are widely used as catalysts in the selective oxidation of hydrocarbons. In the partial oxidation of propene bismuth molybdate and iron antimony oxide seem to be the preferred catalysts. Iron antimony oxide is also a selective catalyst for the ammoxidation of propane [1]. In a previous work [2], we observed that the activity and selectivity of the partial oxidation of propene over iron antimony oxide catalysts decrease drastically in the first few minutes of reaction. Furthermore, it was observed that the autoreduction of the catalyst led to a lower maximum activity. It was thus concluded that the fully oxidised catalyst was the most active and the most selective catalyst. At steady state, the iron antimony oxide operates at a partially reduced state.

Partial oxidation of hydrocarbons over mixed metal oxides generally proceeds via a redox cycle (Mars–van Krevelen mechanism) [3]. According to this mechanism, the hydrocarbon reduces the catalyst surface under the formation of the selective partial oxidation products and combustion products. The catalyst is subsequently re-oxidised by gaseous oxygen. At steady-state operation the rate of reduction and the rate of re-oxidation are equal. Initially, the rate of re-oxidation is slower than the rate of reduction. The catalyst is partially reduced until a steady-state situation is achieved.

The oxidation and reduction reactions are generally performed simultaneously, but can also be physically

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separated by performing the reaction in two separate reactors as discussed by Callahan et al. [4]. Another alternative might be alternating the feed from reducing to oxidising atmospheres. This would bring the catalyst, on the average, to a higher oxidation state, which in turn would lead, on the average, to a higher activity and selectivity over the iron antimony oxide catalyst. The concept of alternating the feed to enhance activity and/or selectivity has been discussed by Silveston et al. [5]. It has been reported that alternating the feed might enhance the selectivity in the partial oxidation of propene to acrolein over Sb–Sn–O [6] and over Sb–Sn–V–O [7], of benzene to maleic anhydride over V_2O_5–MoO_3/TiO_2 [8], and of butadiene to maleic anhydride over VPO [9]. In these studies the switching time was chosen to be fairly lengthy (up to several hours).

Relatively short switching times are required for the iron antimony oxide, since the decrease in activity with time on stream is quite strong [2]. Here, we present our preliminary results on a study of the feasibility of switching reactors as a method to increase the average activity and selectivity for the (amm)oxidation of C_3-hydrocarbons.

2. Experimental

The iron antimony oxide catalyst was prepared according to the method described by Allen et al. [10]. Briefly, the catalyst was prepared by heating the required mass of $Fe(NO_3)_3{\cdot}9H_2O$ to 60°C. A solution of iron nitrate in the water of crystallisation was formed. The corresponding mass of Sb_2O_3 was added to the solution to obtain a catalyst with a Sb/Fe ratio of 1. The temperature was raised to 80°C and the pH adjusted to 3.0 using an aqueous NH_3-solution. The catalyst was dried at 120°C for 16 h and subsequently calcined at 800°C for 7 h.

The catalyst was characterised by XRD using a Phillips X-ray diffractometer generating Cu K_α radiation operating at 40 kV and 40 mA. The region of 2θ between 20° and 70° was scanned with a step size of 0.1°. The XRD of the iron antimony oxide catalysts showed only the existence of the $FeSbO_4$ phase.

For comparison the reaction was also performed using a commercial γ-Bi_2MoO_6-sample (Johnson Matthey, Karlsruhe).

The (amm)oxidation reactions were carried out in a tubular plug flow reactor (l=20 cm with $l_{isothermal}$=4 cm and i.d. 10 mm). The residence time of the empty reactor was 8.4 s and the reactor behaved as an ideal plug flow reactor. The reactor was loaded with 0.5 g catalyst, diluted with 4.0 g of washed sand, in the isothermal zone. The catalyst was heated up to reaction temperature in air. The reaction temperature was 375°C for the partial oxidation of propene, 380°C for the ammoxidation of propene and 470°C for the ammoxidation of propane. All reactions were carried out at WHSV=2 $g_{hydrocarbon}/g_{catalyst}$ h and a total pressure of 1.2 bar. The feed gas consisted of 20% oxygen and 10% propene or propane. For the ammoxidation, the feed contained 10% ammonia. The balance of the feed was nitrogen. A 5% methane in nitrogen gas mixture was added to the effluent of the reactor before the sampling point to serve as an internal standard for the evaluation of the carbon mass balance and the calculation of conversion, yield and selectivity. Mass flow controllers were used to control all flows.

Samples are collected using the ampoule sampling technique [11] and these are analysed in a gas chromatograph using a flame ionisation detector (FID). This technique allows rapid sampling independent of the time of analysis. The total oxidation products, CO_2 and CO were continuously monitored by an on-line CO/CO_2 IR-analyser. The results are reported as a function of time on stream.

In order to test whether the reaction can be performed with a forced feed modulation the (amm)oxidation reactions were performed for 30 min, after which the propene/propane flow were interrupted, so that the catalyst could be re-oxidised for the next 30 min at reaction temperature. After this re-oxidation phase the (amm)oxidation was performed under the same conditions as during the first phase. The switching time was chosen to be rather long in order to study variations in the catalytic behaviour after the re-oxidation phase.

3. Results and discussion

Fig. 1 shows the time on stream behaviour of the partial oxidation of propene over $FeSbO_4$. The variation in the yields with time on stream are not distorted by any residence time effects since the first data point is taken after ca. 25 s. High yields of acrolein are

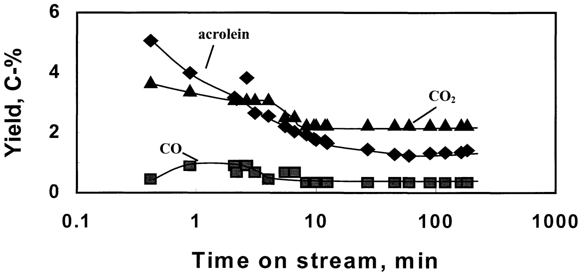

Fig. 1. Yield of products in the partial oxidation of propene at 375°C over iron antimony oxide catalyst as a function of time on stream (Fe/Sb=1; p_{total}=1.2 bar; WHSV=2 $g_{propene}/g_{catalyst}$ h, feed: C_3H_6:O_2:N_2=2:4:17).

initially observed and a decrease in the yield is observed with time on stream until steady state is reached. At steady state, the catalyst is more selective for total oxidation than for selective partial oxidation. The trend is similar to that observed previously in the partial oxidation of propene [2] and the ammoxidation of propene [12] over iron antimony oxide catalysts. This has been explained in terms of an increase in the degree of reduction of the surface layer in the catalyst with continued exposure to propene. Lattice oxygen is used up and gaseous oxygen is required to replenish the vacant sites. Before a steady-state situation is achieved, the rate of reduction of the catalyst is higher than the rate of re-oxidation of the catalyst.

A variation in the activity and selectivity with time on stream behaviour in the partial oxidation of propene is not unique to the iron antimony oxide system, but is also observed over a bismuth molybdenum oxide catalyst (see Fig. 2). The conversion of propene is lower over γ-Bi_2MoO_6 than over $FeSbO_4$. It is interesting to note that, with the iron antimony oxide catalyst, the selectivity for the partial oxidation products is high during the initial phase and decreases with time on stream.

With γ-Bi_2MoO_6 the selectivity for the total oxidation products is initially higher. The selectivity for the partial oxidation product acrolein was initially 0% and increased to 100% after ca. 3 min. The change in the selectivity of the partial oxidation reaction can be explained in terms of a change in the composition of the pool of surface oxygen species [2], which contains electrophilic oxygen species and nucleophilic oxygen species [13]. An attack by electrophilic oxygen on the hydrocarbon moiety leads to the formation of the combustion products. A higher selectivity for total oxidation products might then indicate a relatively higher content of electrophilic oxygen species than nucleophilic oxygen species in this pool of surface oxygen species. This would then mean that the γ-Bi_2MoO_6 surface, after heating up in air to reaction temperature, contains relatively more electrophilic oxygen species than $FeSbO_4$. For antimony oxide catalysts, only surface layer reduction occurs, however, deeper layers are reduced for the bismuth molybdate catalyst [14]. This means that, in the bismuth molybdate catalyst, oxygen from the bulk of the lattice is transported to the surface, whereas with iron antimonate only surface lattice oxygen is involved in the partial oxidation reaction. The higher degree of reduction also indicates that the rate of re-oxidation is lower for γ-Bi_2MoO_6 than for $FeSbO_4$. Re-oxidation of the

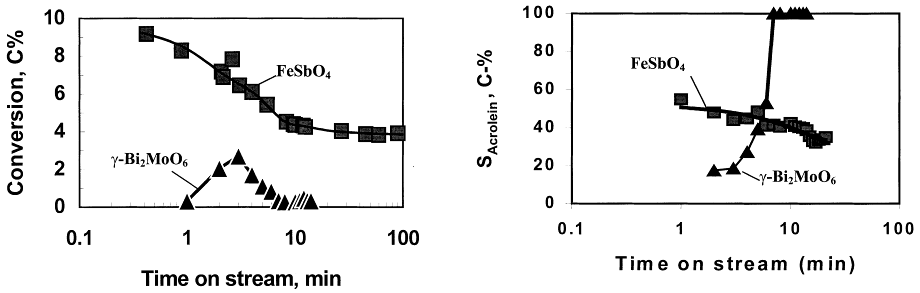

Fig. 2. Comparison of the time on stream behaviour of $FeSbO_4$ and γ-Bi_2MoO_6 in the partial oxidation of propene at 375°C (p_{total}=1.2 bar; WHSV=1.2 bar, feed: C_3H_6:O_2:N_2=2:4:17). Left: conversion of propene as a function of time on stream; right: acrolein selectivity as a function of time on stream.

catalyst generates electrophilic oxygen species. The mobility of bulk lattice oxygen to the surface (nucleophilic oxygen) and the lower rate of re-oxidation imply that under steady-state conditions the relative content of electrophilic oxygen species in the pool of surface oxygen species seems thus to be lower with the bismuth molybdate catalyst than with the iron antimony oxide catalyst.

It is advantageous to operate the bismuth molybdate catalyst at steady-state conditions, since the selective partial oxidation reaction seems to be favoured at a higher degree of reduction. Compared to iron antimony oxide, the activity of γ-Bi_2MoO_6 in the partial oxidation of propene is poor. The iron antimony oxide catalyst, on the other hand, needs to be maintained at a high oxidation state to favour the formation of the partial oxidation products.

In order to maintain this high oxidation state, it has been proposed to re-oxidise the catalyst after a certain reaction time to bring it back in its high oxidation state. This can be achieved in two reactors with alternating feed streams. Such a set-up requires that the reaction time is as long as the re-oxidation time.

The effect of regenerating the catalyst under oxygen flow has been investigated using feed modulation. The partial oxidation was performed for 30 min, after which the propene flow was switched off for the following 30 min. This cycle was repeated three times (see Fig. 3). In the first cycle a strong decrease in the yield of acrolein is observed. The steady-state yield is approximately three times lower than the maximum yield obtained in the initial phase. Also, the selectivity decreases in the first cycle. After 30 min the propene stream was switched off and the catalyst was re-oxidised. Both activity and selectivity of the partial oxidation reaction decrease with time on stream. During the re-oxidation of the catalyst only total oxidation products (mainly CO_2) were observed. Even after 30 min in the re-oxidation phase (i.e. after 60 min of experiment) CO_2 was still present in the reactor effluent indicating combustion of organic residues from the catalyst surface after this period of time. After 60 min propene was switched on again. The yield of acrolein obtained in the first minutes, was ca. two times more than at the end of the first cycle. This indicates that the catalyst was re-oxidised by switching off the propene stream. The yield was, however, not as high in the first few minutes of the first cycle. This indicates that the oxidation was not complete and that longer times and/or higher temperatures are required for complete oxidation of the catalyst. After 90 min (the end of the second cycle) the catalyst was re-oxidised again for 30 min by switching off the propene feed stream. The third cycle essentially mimics the second cycle. This might indicate that the catalyst regained the same oxidation state after the second re-oxidation phase as after the first.

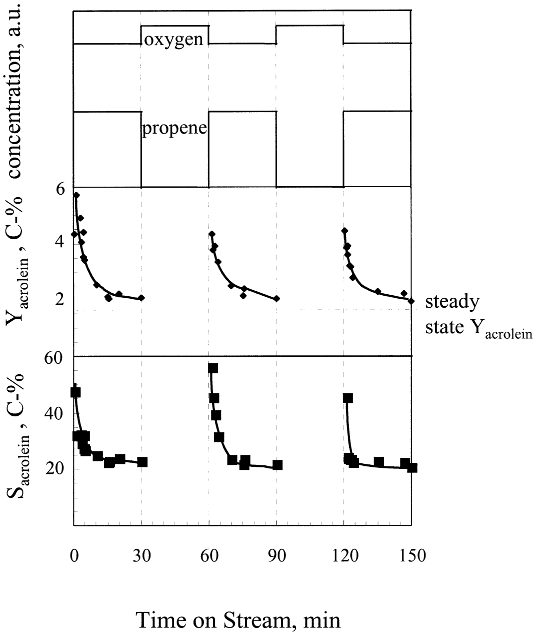

Fig. 3. Partial oxidation of propene over iron antimony oxide catalyst at 375°C with alternating feed (Fe/Sb=1; p_{total}=1.2 bar; m_{cat}=0.5 g; during partial oxidation: C_3H_6:O_2:N_2=2:4:17, V_{total}= 115 ml(STP)/min; during re-oxidation O_2:N_2=4:17, V_{total}= 105 ml(STP)/min).

Propene ammoxidation was performed at 380°C (see Fig. 4). During the ammoxidation of propene only acrylonitrile, CO and CO_2 were observed as products of the reaction. In the first phase the acrylonitrile yield and the selectivity for acrylonitrile increased with increasing reaction time. During the re-oxidation phase only the propene stream was switched off and ammonia, oxygen and nitrogen were flowing through the catalyst bed. After this phase propene was added to the feed stream again. It was observed that the acrylonitrile yield and selectivity then decreased with time on stream. During the second

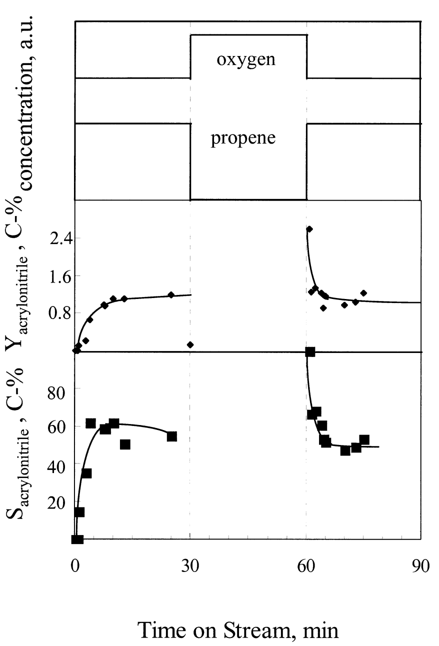

Fig. 4. Ammoxidation of propene over iron antimony oxide catalyst at 380°C with alternating feed (Fe/Sb=1; p_{total}=1.2 bar; m_{cat}=0.5 g; during partial oxidation: C_3H_6:NH_3:O_2:N_2=2:2:4:17, V_{total}=125 ml(STP)/min; during re-oxidation NH_3:O_2:N_2=2:4:17, V_{total}=105 ml(STP)/min).

reaction phase, the acrylonitrile selectivity was initially 100% and dropped quickly to the steady-state value of ca. 55–60 C%. The opposite behaviour, during the first and second reaction cycle, might be attributed to the difference in the initial concentration of NH-surface species. On the fully oxidised iron antimony oxide catalysts ammonia does not yield enough NH-surface species and the acrylonitrile yield is low. If the surface becomes partially reduced, the concentration of NH-surface species increases and acrylonitrile can be formed. Hence, the yield and selectivity of acrylonitrile increased with time on stream. During the re-oxidation phase ammonia was still present in the feed. On switching on the propene stream, enough surface NH-species are present to convert propene into acrylonitrile. Propene and ammonia compete for the same site and thus the acrylonitrile yield decreases. Due to the lower availability of NH-surface species the probability for total oxidation increases and thus the selectivity for acrylonitrile decreases.

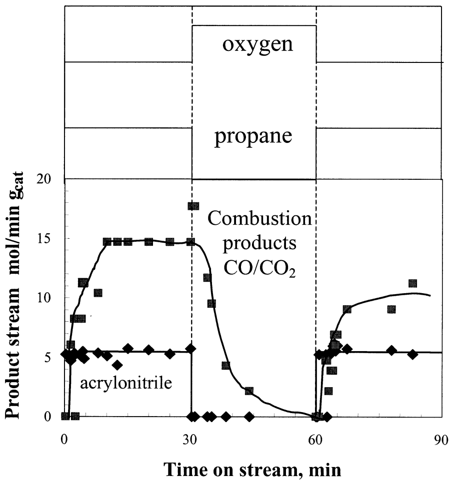

Fig. 5. Ammoxidation of propane over iron antimony oxide catalyst at 470°C with alternating feed (Fe/Sb=1; p_{total}=1.2 bar; m_{cat}=0.5 g; during partial oxidation: C_3H_8:NH_3:O_2:N_2=2:2:4:17, V_{total}=125 ml(STP)/min; during re-oxidation NH_3:O_2:N_2=2:4:17, V_{total}=115 ml(STP)/min).

Propane ammoxidation was performed at 470°C. Fig. 5 shows the rate of formation of acrylonitrile and the total combustion products as a function of time on stream. During the first reaction phase the rate of formation of acrylonitrile remains almost constant. With increasing time on stream the rate of formation of the total combustion products increases. The selectivity for partial oxidation products in the propane ammoxidation over iron antimony oxide is thus also initially higher as observed in the partial oxidation of propene. The difference between propene and propane ammoxidation might be attributed to the difference in the strength of adsorption of propene and propane. Ammonia will adsorb more strongly than propane on iron antimony oxide and thus the formation of NH-surface species is thus favoured. This will lead to the formation of acrylonitrile. With time on stream the concentration of hydrocarbon species slowly increases and the concentration of NH-species decreases. Due to the decrease of the NH-surface species, the probability of total combustion increases. After the re-oxidation phase in which the propane flow was switched off, the observed time on stream behaviour is essentially the same. The increase in the rate of formation of total combustion products is however less than during the first reaction phase. This might be attributed to the larger amount of NH-surface species which are initially on the catalyst surface.

4. Conclusions

The performance of the partial oxidation of propene over iron antimony oxide catalysts can be improved by operating at short times on stream, since the yield and the selectivity of acrolein decreases with time on stream. γ-Bi_2MoO_6 behaves differently. Although the conversion of propene also decreases with time on stream over this catalyst, the selectivity of acrolein increases. Its performance cannot be thus improved by operating in switching reactors.

With the introduction of a re-oxidation phase the average performance of an iron antimony oxide catalysts can be drastically improved. During the 30 min of reaction, a drastic decrease in activity and selectivity was observed in the partial oxidation of propene. During the re-oxidation phase some of the activity and selectivity was regained. Longer re-oxidation times, higher re-oxidation temperatures, and/or the addition of an oxidation promoter to the catalyst formulation are however necessary to obtain the original oxidation state of the catalyst.

The performance of iron antimony oxide as a catalyst for the (amm)oxidation of propene and propane can also be improved by operating in the switching mode, i.e. switching on and off the hydrocarbon feed stream. The differences in behaviour in the first reaction phase and the second reaction phase could be explained in terms of the concentration of NH-surface species.

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