OXIDATION OF ETHYLENE TO ETHYLENE OXIDE: A TPR STUDY ON FRESH AND AGED CATALYSTS

G. Leofanti, G. R. Tauszik and *M. Padovan*

MONTEDIPE S.P.A., CENTRO RICERCHE DI BOLLATE, VIA SAN PIETRO 50, 20021 BOLLATE MI, ITALY

The deactivation of a silver catalyst was investigated after six years of industrial production of ethylene oxide. Temperature-programmed reduction was used to characterize the chemical nature of the silver and its reactivity towards oxygen. The fresh and some aged catalysts were examined, also after different thermal treatments.

During the industrial run, the surface species were modified and some oxygen diffused into the bulk of the metal. Aging caused permanent changes in the characteristics of the silver, resulting in a different interaction with oxygen. The TPR spectra exhibited a trend along the reactor axis, suggesting a correlation with the degree of deactivation of the catalyst.

In spite of the great number of studies devoted to the oxidation of ethylene to ethylene oxide (EO) [1–3], the aging of silver catalysts under industrial conditions has received little attention in the open literature. In a previous work [4], we examined catalyst samples from an industrial plant, operating with air-based technology, after 6-year run. Micropilot plant tests showed a great deactivation with respect to the fresh catalyst and gave a trend of aging along the reactor axis. In particular, the samples from the top of the reactor (gas inlet) were characteristic of: (i) the lowest values of activity per weight unit, selectivity to EO and apparent activation energies; (ii) the highest activity per metal area unit; (iii) the temperature oscillations occurring in the test reactor. Physico-chemical characterization of the samples revealed poisoning by sulphur, sintering of the silver and some changes in the morphology of the metal particles, all being more marked in the top layers of the catalyst bed. These phenomena were examined as possible explanations of the modified performances of the discharged catalyst; however, on the basis of the previous knowledge on the subject, they did not appear sufficient to account for all the catalytic results [4].

In a contemporary work [5], it was concluded that catalyst aging was caused by the deposition of sodium and potassium salts, decreasing the selectivity for EO. In our samples, the concentrations of Na and K were low and constant along the catalyst bed, except for a maximum of Na in the very top layer. Instead, the above-mentioned loss of selectivity occurred for a larger fraction of the catalytic bed.

Therefore, even assuming that poisoning by sodium could contribute to aging, a fully satisfactory explanation of the behaviour of our aged catalyst is still not available.

With the aim of a deeper understanding of the catalyst aging mechanism, in this work we have investigated how the industrial run modified the chemical nature of the silver, and especially its reactivity towards oxygen. Temperature-programmed reduction (TPR) experiments were therefore carried out on the fresh catalyst and on some aged samples, also after appropriate thermal and oxidizing treatments.

Experimental

The commercial catalyst under study consisted of silver dispersed on a low-area alumina + silica support. The samples examined were:

F, fresh catalyst;

A, catalyst activated and tested in the micropilot plant of [4] (in all, 1 month on stream);

U1, U2, U4 and *U6*, catalyst samples unloaded from the industrial reactor, *U1* being taken from the top (gas inlet) and *U6* from the bottom (gas outlet) of the reactor itself.

The TPR experiments were carried out in a typical gas chromatographic apparatus, using purified H_2 (38 v% in Ar). A cold trap and a tube filled with supported NaOH (Merck) were put between the sample holder and the detector. The temperature was varied between r.t. and 770 K, at a heating rate of 25 deg/min. The consumption of hydrogen during TPR was calibrated by the injection of known amounts of hydrogen in the $Ar + H_2$ flow, as well as by the reduction of known amounts of pure oxides.

The following experiments were carried out:

TPR–1, without pretreatment of the samples;

TPR–2, after heating of the samples in air for 15 h at 550 K;

TPR–3, after heating of the samples in air for 15 h at 770 K;

TPR–1b, after TPR–1 and reoxidation with air for 1 h at 480 K.

In a few cases, some other pretreatments were also adopted (see later).

Results

All the TPR profiles were complex, due to the presence of several reducible compounds, and probably also to the overlapping of H_2-desorption signals. The discussion is therefore restricted to the main features of the profiles.
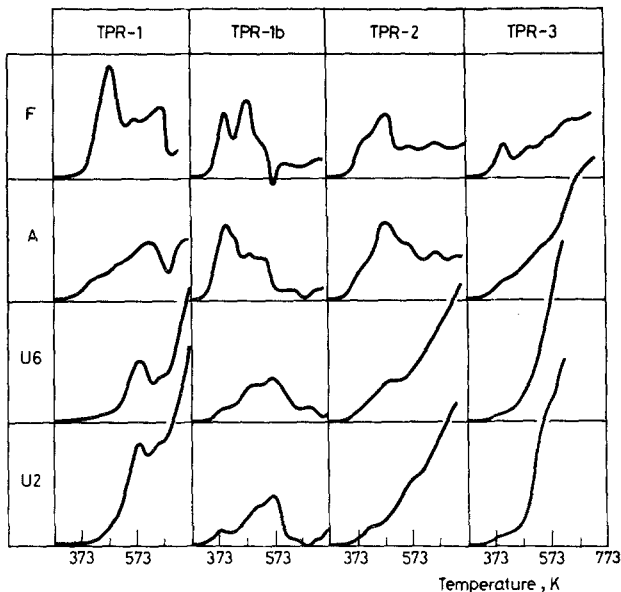
Fig. 1 TPR profiles after different pretreatment conditions

Fig. 2 Trend of the TPR-1 profiles along the catalytic bed U_1—; U_2 ......; U_4 ---; U_6 —.—.—;

TPR-1 revealed great differences between the catalysts (Fig. 1). *F* was characterized by a peak at ca. 460 K (II), followed by signals of lower intensity. Aging caused a gradual decrease of the easier-to-reduce species, resulting, for the samples taken from the industrial reactor, in a signal at ca. 570 K (III), followed by a very strong consumption of H_2 (IV). On going from *U6* to *U1*, i.e. from the least to the most deactivated sample, the intensity of (IV) increased and (III) became less evident (Fig. 2). The intensity of the TPR-1 signals is consistent with phenomena

involving at the most a few monolayers of Ag; only (IV) may be related to the bulk of the catalyst. An even stronger TPR signal, starting above 470 K, was achieved when F was previously heated in air (15 h) at 920 K; this was not the case if heating was carried out in N_2 (Fig. 3). Therefore, it is quite reasonable to attribute (IV) to the reduction of O_2 dissolved in the Ag lattice. Earlier studies on the metal confirm that dissolved O_2 can be eliminated by heating in hydrogen at above 670 K [6].
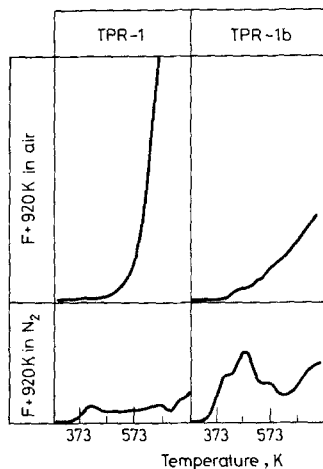

Fig. 3 TPR–1 and TPR–1b profiles of F heated at 920 K (15 h)

TPR–1b indicated that some of the original species could be restored by reoxidation at 480 K, namely (II) for F and (III) for $U2$ and $U6$. They were accompanied by lower-temperature signals; in particular, a well-defined peak at ca. 390 K (I) was evident for F and A. Clearly, (I), (II) and (III) can be definitely attributed to oxygenated Ag compounds. A comparison with the TPR of the unsupported oxides suggests that (I) and (II) correspond to surface species similar to AgO and Ag_2O, respectively (AgO, 410 K; Ag_2O, 450 K). It cannot be excluded that (II) is also partly due to Ag_2CO_3; in fact, the unsupported carbonate was reduced at ca. 470 K. No Ag compound corresponding to (III) was found.

Heating before TPR–2 and TPR–3 obviously affected the nature and distribution of the Ag species. On elevation of the pretreatment temperature, the TPR evolved towards a profile consisting essentially of a very strong type (IV) signal, while the low-temperature signals were no longer distinguishable. This shows that calcination brought all the samples to a qualitatively similar oxidation state, characterized by a large amount of O_2 dissolved in the metal. However, the temperature required to reach this state depended on the aging: for $U2$, and to a

minor extent also for $U6$, the evolution of the TPR profile was already marked in TPR–2, but for A only in TPR–3, while for F it occured at above 800 K. In this respect, it is of interest that, once F had been heated at 920 K in air and a first TPR carried out, a type (IV) signal could be restored by reoxidation even at 480 K (Fig. 3). In other words, after calcination, the behaviour of F becomes more similar to that of the aged catalysts. This further confirms that, during the years-long operation in the industrial plant, the catalyst approaches a state which can be rapidly achieved by high-temperature treatment. The presence of oxygen is necessary for this transformation; in fact, when F was submitted to the experimental sequence heating at 920 K in nitrogen—TPR—reoxidation at 480 K—TPR, the latter TPR profile was quite similar to the TPR–1b of F (cf. Figs 1 and 3), which was instead achieved without the 920 K treatment. Thus, heating in the absence of oxygen is not sufficient to modify the behaviour of the metal with respect to oxidizing treatment.

Conclusion

TPR–1 revealed the presence of significant amounts of oxygenated Ag compounds, the nature of which changed when the catalyst went into operation and, further, when it was aged in a long industrial run. Of course, this does not exclude that other surface species too, not detected by TPR, could have been modified by operation and/or aging. TPR–1b, TPR–2 and TPR–3 showed that the samples remained significantly different even after reduction + reoxidation or calcination. This confirms that the variation of the TPR–1 spectra was not due simply to contingent factors (e.g. conditions of drawing and storing of the samples from the industrial plant): aging really caused permanent modifications of the characteristics of the Ag, which resulted in a different interaction with O_2, both in the bulk (cf. TPR–2 and TPR–3) and at the surface (cf. TPR–1b). These changes in the behaviour of the metal could be involved in the deactivation of the catalyst, as is suggested by the trend observed in the TPR–1 spectra on moving from the top to the bottom of the industrial reactor; this trend parallels that found for the deactivation of the catalyst.

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References

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Zusammenfassung — Die Desaktivierung eines Silberkatalysators wurde nach 6-jährigem Einsatz zur industriellen Produktion untersucht. Temperaturprogrammierte Reduktion wurde angewandt, um die chemische Natur des Silbers und dessen Reaktivität gegenüber Sauerstoff zu charakterisieren. Frische und einige gealterte Katalysatoren wurden nach verschiedenen thermischen Vorbehandlungen untersucht. Die Alterung verursachte bleibende Veränderungen in charakteristischen Eigenschaften des Silbers, was in der unterschiedlichen Wechselwirkung mit Sauerstoff zum Ausdruck kommt. Die TPR-Resultate zeigen einen Trend entlang der Reaktorachse, was auf eine Korrelation mit dem Grad der Desaktivierung des Katalysators hindeutet.

Резюме — Исследована дезактивация серебрянного катализатора после его шестилетнего использования для промышленного полуния окиси этилена. Метод температурно-программированного восстановления (ТПВ) использован для характеристики химической природы серебра и его реакционной способности по отношению к кислороду. Исследованы свежеприготовленный и состарившийся катализаторы, а также эти же катализаторы, подвергнутые различной термической обработке. В течении промышленного цикла разновидность поверхностей видоизменялась и некоторое количество кислорода диффундировало в глубину металла. Старение катализатора, вызываемое непрерывными изменениями характеристик серебра, является результатом различного взаимодействия его с кислородом. Спектры ТПВ проявляют тенденцию к оси реактора, предполагая корреляцию со степенью дезактивации катализатора.