Short communication

Precise recognition of catalyst deactivation during acetylene hydrogenation studied with the advanced TEMKIN reactor

Martin Kuhn, Martin Lucas, Peter Claus *

Technische Universität Darmstadt, Department of Chemistry, Ernst-Berl-Institute, Chemical Technology II, Alarich-Weiss-Straße 8, D-64287 Darmstadt, Germany

ABSTRACT

C_6 hydrocarbons were identified as an important indicator for deactivation behaviour in acetylene hydrogenation on Pd–Ag/Al_2O_3 egg-shell catalysts. Thereby significant differences between highly developed catalysts can be identified, helping to forecast differences in deactivation behaviour over 100 h time-on-stream in a short and cheap catalytic test.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Ethylene is one of the most important petrochemical bulk chemicals. It is mostly used for polymerization to polyethylene with different properties. Ethylene is mainly produced by steam cracking of naphtha at high temperatures above 800 °C; impurities (e.g. acetylene) are formed. The acetylene content has to be reduced to concentrations lower than 1 ppmv to avoid irreversible damage of the catalysts used in downstream processes of the steam cracker. The catalytic removal is carried out by selective hydrogenation of acetylene to ethylene. Pd–Ag/Al_2O_3 eggshell catalysts with low metal loadings are commercially used at front-end and tail-end conditions [1]. Hydrogenation of acetylene under conditions described above leads to ethylene and ethane caused by consecutive hydrogenation (Scheme 1). An essential problem of the industrially used Pd–Ag/Al_2O_3 eggshell catalysts in the selective hydrogenation of acetylene under tail-end conditions is the fast deactivation, induced by formation and deposition of hydrocarbons (green oil) and coke on the catalytic surface (Scheme 1) [2]. Butadiene is proposed to be a precursor of the green oil formation [3–5], mainly consisting of olefins and paraffins as well as aromatics and diolefins [6,7]. Green oil and coke form during hydrogenation of acetylene leading to a decrease of conversion and reduction of time-on-stream (TOS) [2]. A previous study of our working group demonstrates green oil and coke formation as well as the start of deactivation in the first part of the reactor that proceeds along the reactor [8]. However at the beginning of the reaction subsurface carbon is formed, suppresses subsurface hydrogen and palladium hydride, and affect the total hydrogenation of acetylene [9].

Further pore filling of the catalyst by green oil and coke causes a reduction of the effective diffusion coefficient (D_{eff}) followed by an increase of ethane formation [3]. Additionally, a spillover mechanism for ethylene hydrogenation to ethane is discussed in literature.

Activated hydrogen is transferred from palladium to the support over the coke depositions and converted with ethylene to ethane [7]. Addition of Ag to Pd/Al_2O_3 catalysts suppresses the palladium hydride formation and spillover hydrogen and increases selectivity to ethylene [10]. Furthermore the deposited green oil serves as hydrogen reservoir especially for the consecutive hydrogenation to ethane [7]. The target improvements of the Pd–Ag/Al_2O_3 eggshell catalysts are to increase the selectivity to ethylene, raising the amount of ethylene gain and to force up the long-term stability. For the presented study commercial Pd/Al_2O_3 and Pd–Ag/Al_2O_3 eggshell catalysts were used. *Cat B* and *Cat C* are silver containing Pd–Ag/Al_2O_3 eggshell catalysts and *Cat D* is the silver free version of *Cat C*. Characterization of these catalysts by Pachulski et al. [2] is summarized in Table 1.

The objective of this study is to point out the importance of the formed by-products detected via online GC to increase the significance of a catalytic test in relation to deactivation and long-term stability.

2. Material and methods

The standard catalytic tests and the 100 h long-term tests were performed in the Advanced TEMKIN reactor [8] at 10 bar gauge pressure, 45 °C and a GHSV of 4000 h^{-1}. The reaction mixture was based on tail-end conditions and contains 1 vol.% acetylene, 1 vol.% hydrogen, 1 vol.% propane (internal standard) and 30 vol.% ethylene in argon. The catalysts were reduced in situ for 1 h at 100 °C in 100% hydrogen prior to catalytic testing. For more information see our previous work [8].
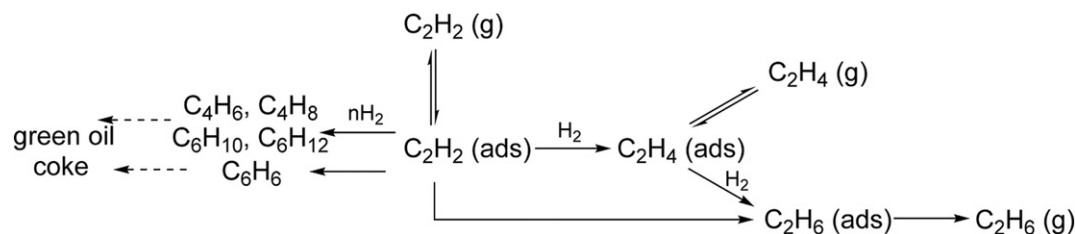
Scheme 1. Reaction network of the selective hydrogenation of acetylene.

Additionally the exhaust gas was analysed with a GC-MS (Shimadzu, GCMS-QP2010SE).

3. Results and discussion

The three catalysts, described above, were tested for selective hydrogenation of acetylene under tail-end conditions. The testing procedure, the used Advanced TEMKIN reactor and detailed results were described elsewhere [8]. The used Advanced TEMKIN reactor is predestined for highly reproducible testing of egg-shell catalysts without transport limitations and effect of reactor design [8,11]. The results of a standard catalytic test at industrial conditions are summarized in Table 2. Depending on the Ag content of the catalysts, the highest conversion was found for *Cat D* with 90.2% followed by *Cat C* (76.9%) and *Cat B* (59.1%). The selectivity to ethylene was determined indirectly via online GC, because changes in the ethylene concentration cannot be detected accurately [12], appropriate the selectivity of the by-products ethane and the C_4 compounds were used (see supplementary information).

The catalytic results show the highest selectivity to ethylene for *Cat B* and *Cat C*, but no significant differences in selectivity to ethane, C_4 and ethylene between these two catalysts can be determined. However, for the silver free palladium catalyst *Cat D* the amounts of formed ethane and C_4 are much higher, resulting in a decreased selectivity to ethylene by 7% in comparison with the other two catalysts. Based on these catalytic results and the literature, assuming C_4 or rather 1,3-butadiene as precursor for green oil formation [3–5], the long-term stability can be estimated. Therefore for *Cat B* and *Cat C* nearly the same deactivation behaviour can be expected but *Cat D* will be deactivate much faster. Long-term measurements were performed under industrial tail-end conditions over 100 h, using the three catalysts described above. The observed changes in conversion after a standard catalytic test, including run-in period and variation of the modified residence time [8], are shown in Fig. 1. The fastest decrease in activity was detected for the silver free palladium catalyst *Cat D* with a loss of conversion of about 28% over 75 h TOS, as expected out of the catalytic results in Table 2. The forecast for long-term stability of *Cat B* and *Cat C* cannot be confirmed. The conversion of *Cat B* decreases with 10% much faster than *Cat C* with 5% over 75 h TOS. Deactivation of palladium containing catalysts in the selective hydrogenation of acetylene is caused by deposition of higher hydrocarbons and coke [2]. Therefore the deposited amount of these by-products after 100 h long-term test was determined by weighing the three catalysts before and after each test. This method was verified by thermogravimetric analysis. For *Cat D* the highest increase of mass was determined with 14.3 wt.%, followed by *Cat B* with 5.1 wt.% and *Cat C* with 2.3 wt.%. This observation reflects the

determined loss in conversion over 75 h TOS. Additionally the selectivity to ethane increases for *Cat D* from 7% to 41% as shown in Fig. 2. For *Cat B* the selectivity to ethane increases by 10% to 14%. Only for *Cat C* the ethane selectivity slightly increases to 6%. Accordingly, the deactivation (Fig. 1) and the increased consecutive hydrogenation of ethylene to ethane (Fig. 2) can be correlated with the progress of hydrocarbon and coke deposition. Hg-porosimetry of fresh and used catalysts implicates a reduction of the pore volume from 0.44 ml g^{-1} to 0.42 ml g^{-1} for *Cat D* caused by deposits, while the pore volume for *Cat C* is constant (see supplementary information). The pore size distribution shifts to smaller pore sizes. Pore filling and blocking of the catalyst by green oil and coke causes a reduction of the effective diffusion coefficient (D_{eff}). Asplund [3] estimates a reduction of D_{eff} by 1/10. The rising mass transfer resistance leads to an increased consecutive hydrogenation of ethylene to ethane. This phenomenon is especially pronounced for *Cat D* and *Cat B* because of the increased green oil and coke formation, indicated by the C_6 selectivity. Furthermore this can be explained by an increasing Thiele module φ: the degree of efficiency η is decreased and the conversion is decreased as well, by reduction of the D_{eff}. Thermal gravimetric analysis (TGA) confirms the amount of deposited hydrocarbons on the catalyst surface, determined by weighing the catalysts before and after each test. The derived thermogravimetric signals (DTG) (see supplementary information) reflect the results of Pachulski et al. [2] and four ranges of mass loss can be observed: loss of humidity (up to 110 °C), a mobilization of light hydrocarbons (120 °C to 250 °C), burning off heavy hydrocarbons (280 °C to 350 °C) and burning off fixed coke (400 °C to 510 °C). The first two ranges were detected as endothermal processes and the last two peaks were detected as exothermal processes via differential scanning calorimetry (DSC), affirming the published characterizations. Further characterization of the deactivated catalysts is reported by Pachulski et al. [2]. They clearly show that the deactivation of the used Pd–Ag/Al$_2$O$_3$ eggshell catalysts is caused by deposition of green oil and coke on the catalytic surface. Regeneration in a steam–air-mixture and reduction in hydrogen offers the possibility to regenerate the catalysts without an observable effect on catalytic performance. For further qualitative analysis of the type of deposited hydrocarbons, the used catalysts were washed with n-pentane and the yellow solution was analysed via GC-MS. Hydrocarbons from C_6 to C_{26} were found, but no significant differences between the used catalysts can be determined. These findings are close to the observations of LeViness [13]. The observations show, that the type of formed and deposited by-products on the palladium containing catalysts are equal, but the amount of depositions is important for deactivation and long-term stability.

Nevertheless the differences between *Cat B* and *Cat C* in long-term behaviour cannot be estimated by results of a standard catalytic test

Table 1
Characteristics of industrial catalysts for selective hydrogenation of acetylene.
Source: [2].

	Cat B	*Cat C*	*Cat D*
Pd [wt.%]	0.035	0.036	0.036
Ag [wt.%]	0.079	0.015	0
n_{CO} [$\mu mol_{CO}/g_{Cat}$]	0.45	0.09	0.65
Catalytic zone	400	300	300

Table 2
Catalytic result of industrial acetylene hydrogenation eggshell catalysts ($T = 45$ °C, $p = 10$ bar, $GHSV = 4000$ h^{-1}).

Catalyst	$X_{acetylene}$ [%]	$S_{ethylene}$ [%]	S_{ethane} [%]	$S_{\Sigma C4}$ [%]
Cat B	59.1	82.6	4.1	13.3
Cat C	76.9	83.0	4.8	12.2
Cat D	90.2	76.1	6.5	17.3