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Retarding, blocking and activating the cobalt catalyst by carbonaceous deposits formed in hydrogenation of ethylene

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Abstract

Different functions of the carbonaceous deposits have been recognised in ethylene hydrogenation ($150\,^{\circ}C < T < 450\,^{\circ}C$) over the model cobalt foil catalyst: retarding, blocking and activating. The carbonaceous deposits were investigated by TPO, TPR and SEM methods. Their quantitative results were related to the number of metallic active centres measured also by TPO and TPR. It has been shown that retarding the reaction rate by the hydrocarbon deposit takes place below 300 °C; blocking the catalyst by the dehydrogenated deposit occurs between 300 and 400 °C; restoring the catalyst activity above 400 °C. The renewed activity was explained by the diffusion of cobalt atoms to a deposit surface.

Keywords: Carbonaceous deposits; Cobalt catalyst; Ethylene hydrogenation

1. Introduction

Our study has focused on the characterisation of various forms of carbonaceous deposits collected during the hydrogenation of ethylene used here as a test reaction. For this purpose we applied a well-characterised model catalyst obtained from polycrystalline cobalt foil. The material of the active catalyst was described in our previous papers [1–4]. In brief, a sample of the catalyst, having undergone the whole activation procedure [3], exhibits a sandwich-like structure built of four layers: the original foil, the dispersed CoO layer, the dispersed Co layer, and finally, on top, the residual oxygen layer including O^{2-}, OH^{-} and H_2O molecules [4]. The dimension of the Co layer, in which Co active centres are localised, increases with the temperature of activation [3,4].

Deactivation of the cobalt foil by the carbonaceous deposits was studied before in the hydrogenation of CO_2 [1,2,5]. As a result of that study the model of deactivation was put forward and tested on the previous data set [5]. The model assumes the transformation of the active deposit in the form of hydrocarbon condensates into the inactive deposit in the form of graphite ensembles that block active centres of hydrogenation. These forms of deposits set limits within which carbonaceous deposits can be investigated for the related reactions of hydrogenation.

This paper poses a sequence to the study on modelling of the cobalt catalysts deactivation by carbon deposits. Following the conclusions drawn from the previous model it intends to create a new experimental basis for model refining and expansion.

2. Experimental

2.1. Catalyst preparation

The cobalt foil (Aldrich) of >99.99% purity, 0.1 mm thick, was used as an initial material for the catalyst preparation. Typical samples were rectangular pieces (ca. 6 mm × 5 mm) of a mass between 15 and 44 mg. Their activation procedure consisted of three steps: preactivation, activation proper and regeneration. The preactivation involved about 10 subsequent oxidation and reduction cycles which were carried out under the following conditions: reduction in 5% (v/v) H_2 in Ar (Linde) at a flow rate of 8.5 cm^3/min for 30 min, at 550 °C, oxidation in 5% (v/v) O_2 in He (Linde) at a flow rate of 8.5 cm^3/min for 30 min at the same temperature. The activation, used before each catalytic test, involved reducing of a preactivated oxidised sample in pure H_2 (HG Packard) at a temperature of the catalytic test. The sample was regenerated by oxidation in 5% O_2 at 550 °C each time after a catalytic test. The regeneration procedure restored the initial activity of the catalyst [3,4]. Before SEM analyses, the reduced samples were passivated in the gas mixture containing 5% O_2 in He at a flow rate 8.5 cm^3/min for 15 min at 60 °C.

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2.2. Reaction procedures and apparatus

TPO, TPR studies and catalytic tests were carried out in a microreactor unit equipped with two types of products detection: Shimadzu 14A GC equipped with FID and TCD detectors and a packed HayeSep DB column, and VG SX 200 QMS. This system operates in a continuous flow of reactants at atmospheric pressure. The detailed description of the apparatus, the reader can find in [4].

TPR/TPO were performed at a heating rate of 10 °C/min in the temperature range usually from 20 to 550°C. The catalytic tests were performed using a reaction mixture of H_2 (HG Packard) and C_2H_4 (2:1–40:1) (Aldrich 99.9) at temperatures from the range 150–450 °C. Unless otherwise stated, a typical reaction mixture contained H_2:C_2H_4 = 6:1 at a volumetric flow rate 25 ml/min. The catalytic reaction was initiated by switching on the flow of C_2H_4 to the reactor immediately after the activation of the samples in pure H_2 was completed.

SEM images of the surface of the samples were taken ex situ in a scanning electron microscope (Philips XL20) equipped with X-ray probe for chemical analyses.

3. Results and discussion

The results of the catalytic tests (150–450 °C) allowed us to distinguish three temperature ranges in which radically different catalyst behaviour was observed, Fig. 1. They have been assigned to retarding, blocking and activating the catalyst by the carbonaceous deposits. Below 300 °C, deactivation was relatively fast and the reaction rate showed the reverse temperature dependence. Between 300 and 400 °C a huge amount of coke, rapidly and completely blocked out the reaction, covering the surface of the catalyst. Above 400 °C, in spite of the presence of a similar amount of the deposit, a noticeable regeneration of the catalyst activity was observed. The overall deactivation rate was very low because the methanation rate increased with time-on-stream.

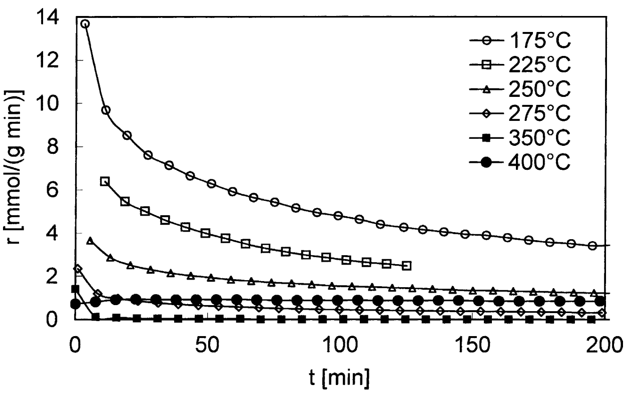

Fig. 1. Temperature influence on ethylene hydrogenation H_2:C_2H_4 = 6:1.

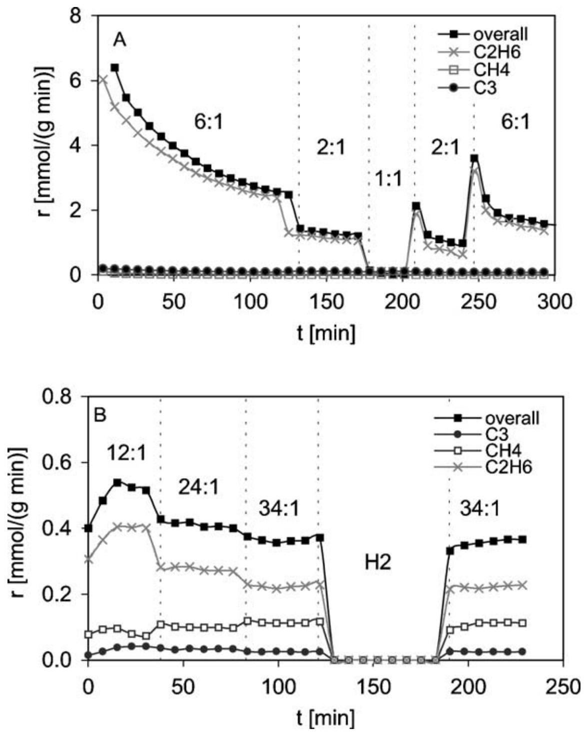

Fig. 2. The dependence of a reactant concentration on the rate of ethylene hydrogenation: (A) at 250 °C, $0 < H_2:C_2H_4 < 6$; (B) at 450 °C, $0 < H_2:C_2H_4 < 35$.

3.1. Retarding

Retarding ethylene hydrogenation takes place at the lower temperature range, below 300 °C. This was observed during catalytic tests at 250 °C when the content of the reaction mixture was varied from 6 to 0 (Fig. 2A). At this temperature there is practically one product: ethane. For comparison, the experiments were repeated at 400 °C (Fig. 2B). At 250 °C, the hydrogenation rate is favoured by the hydrogen content in the reaction mixture: the higher is the content, the higher is the rate (Fig. 2A). However, even at a relatively high hydrogen concentration (H_2:C_2H_4 = 1) the reaction almost ceases, which is reversible. Apparently, ethylene competing with hydrogen for the metallic centres occupies their fraction in the form of a hydrocarbon deposit. This fraction depends on ethylene partial pressure in the reaction mixture (Fig. 2A). Let us also note that whenever the H_2/C_2H_4 ratio was increased (e.g. from 2 to 6) we observed the initial increase and fast drop of the hydrogenation rate (Fig. 2A).

The above observations made during kinetic experiments lead to postulate hydrogen adsorption as a rate-determining step in ethylene hydrogenation. Hydrogen dissociative adsorption on a clean cobalt surface was reported to proceed without activation energy giving the heat effect: $\Delta H_{ads} = -110$ kJ/mol [6]. The negative value of the apparent activation energy (−110 kJ/mol) originating from the heat of adsorption of H_2 ($E_{app} = E_{ads} + \Delta H_{ads}$and $\Delta H_{ads} < 0$)

may explain the reverse temperature dependence of the hydrogenation rate observed at temperatures below 300 °C (Fig. 1). As we showed further in the next passage, the amount of the carbon deposit that is able to block metallic active centres is negligibly small below 250 °C and thus, it is rather hard to associate this effect with fouling the catalyst surface by the carbon deposit.

Such a value of activation energy implies that hydrogen adsorption is a fast reaction. If the assumption of a rate-determining step is true, other steps in the reaction network should be faster. This could be possible provided that ethylene undergoes hydrogenation without adsorbing on metallic sites but directly from the gas phase on adsorbed H atoms. Indeed, ethylene hydrogenation was also shown to equally proceed without a deposit overlayer on metallic surfaces fully covered with H atoms [7].

According to the results of TPR and TPO (Fig. 3), the retarding deposit is built of hydrocarbons and creates a three-dimensional structure on the catalyst surface (Fig. 3B curve c). The C:H ratio in this deposit measured by QMS during TPO was around 1. The number of active centres appears a convenient reference point to relate the quantitative results of the deposits gasification. In this way, the amounts of deposits collected after 2 h reaction at 250 °C expressed as the number of C atoms on the catalyst initial surface area (N_C mmol Co/g catalyst) were related to a number of the active centres available at the same temperature at the beginning of the reaction (N_0 mmol Co/g catalyst) and measured prior each experiment by TPO of the activated catalyst. The calculated values correspond to the maximum number of deposit monolayers on the catalyst surface, Table 1. Thus, amount of the retarding deposit is around 11 monolayers (the value was obtained by integrating extrapolated curve c in Fig. 3A). This value implies that ethylene can also adsorb on the surface of already formed deposit, which, in fact, is generally accepted in literature [8].

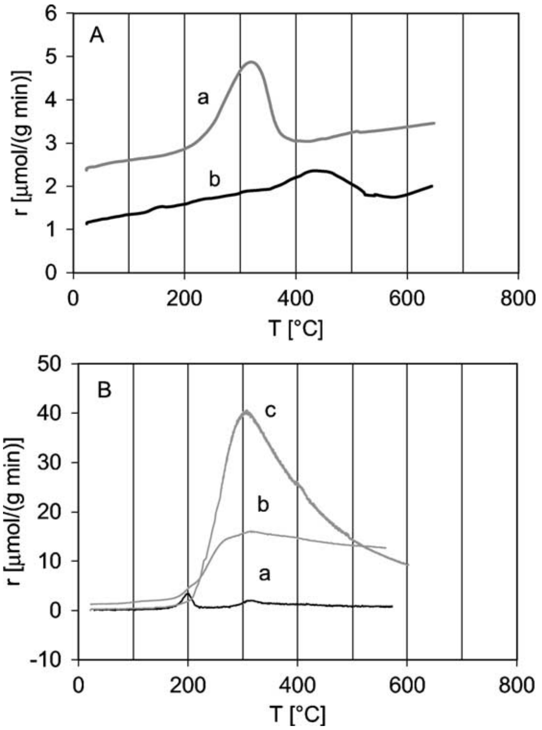

Fig. 3. (A) TPR of the deposits collected at 250 °C; a—after 2 h hydrogenation of ethylene, flushed in He for 12 h at 25 °C, b—after 2 h adsorption of ethylene, flushed in He for 12 h at 25 °C; (B) TPO of the deposits collected at 250 °C during ethylene hydrogenation followed by flushing in He for: a—12 h at 25 °C, b—2 h at 25 °C, c—without flushing.

Table 1
Dependence of the flushing time on deposit amounts

	Flushing time (h)	N_C (mmol Co/g catalyst)	N_C/N_0
a	0.2	0.05	0.2
b	2	>0.48	>2
c	12	1.42	11

This deposit is, however, not firmly attached to the surface and can be removed by flushing the catalyst in He at room temperature. For example, 2 h flushing removes around 30% of the deposit (Fig. 3B curve b, Table 1); 12 h flushing removes practically all hydrocarbon deposit (80%) leaving a stable deposit composed mainly of carbon (Fig. 3B curve c, Table 1). The TPR experiments (Fig. 3A), performed in a similar way to the TPO experiments, were not able to distinguish between these fractions.

Accordingly, the hydrocarbon deposit found on the working catalyst appears more a reaction bystander than a reactive intermediate. Jacobs et al. [9] using SF IR spectroscopy proved that some forms of adsorbed ethylene (ethylidine and di-σ ethylene), are non-reactive in ethylene hydrogenation over Pt catalysts at room temperature, although they occupy a majority of the metallic surface. A fraction of this bystander deposit presumably undergoes dehydrogenation into the stable carbon deposit that blocks active centres.

3.2. Blocking

More firmly bonded dehydrogenated species were found on the catalyst surface even at the temperature as low as 250 °C (Fig. 3B curve a). For the related Fe catalyst these species have been recognised as ethyne (=HC–CH=), ethynyl (≡C–CH=) [10]. These may also constitute the stable deposit found on the catalyst at higher temperatures. Other products of ethylene decomposition on the catalyst surface can be cobalt carbides, but they are said to be active intermediates in hydrogenation of CO [11]. In fact, cobalt carbides in low amounts were observed by AES on the deactivated surface of the same catalyst after CO_2 hydrogenation [1,2].

The question arises whether the stable carbon deposit (20%) is the only reason for deactivation at temperatures below 300 °C. As it was measured, at the moment the 20% fraction of the metallic active centres is occupied by the stable carbon deposit, the overall reaction rate dropped by 70 ± 8% of its initial value (Figs. 1 and 3C). Assuming hydrogen adsorption a rate determining step, rate of ethylene hydrogenation could be expressed by a simple kinetic equation: $r = k_{app}\, p_{H2}[*]^2$, where $[*]$ is an instantaneous surface concentration of the Co active centres. Simple recalculation shows that for 20% deposit coverage of the active centres, the rate would drop only by 36% and conversely, the amount of the deposit should have been about 45% if it were the only reason for the observed deactivation.

Thus, apart from carbon deposit there should be another deactivation pathway which sums up to the observed decay of the activity during ethylene hydrogenation. The TPO results (Fig. 3B curve b and c) give some hints to find it. It is noteworthy that a broad TPO maximum with a slow linear decay observed for the deposits collected at 250 °C is characteristic of a diffusion-inhibited process. According to the SEM, TPR, XPS and TG results, the deactivation can be assigned to the surface reconstruction of the catalyst, which, during the catalytic reaction in hydrogen-rich atmosphere, loses its dispersion and the number of active centres. The detailed discussion on this deactivation mode observed on cobalt catalyst can be found in [4]. It is understandable that with the temperature increase the reconstruction proceeds faster until 450 °C above which sintering begins to dominate the deactivation of cobalt catalyst [12].

A huge amount of the stable carbon deposit was found on the catalyst surface at temperatures above 300 °C. This is represented by the line 44 of CO_2 (Fig. 4A). The amounts of other oxidation products were negligibly small. The general trend was a decrease of the deposit reactivity with the catalytic reaction temperature below 400 °C (Fig. 4A curves a–c). This is exhibited by the shift of the TPO profiles towards higher temperatures. The quantitative results of TPO experiments are presented in Fig. 4B. The fact that the number of monolayers (N_C/N_0) grows faster with temperature than the amount of the deposit is due to the increase of the number of active centres with temperature, which expressed in mmol/g catalyst has values <1. Apparently temperature facilitates both the polycondensation and dehydrogenation of hydrocarbon species [10]. As shown by the XPS results of Lahtinen et al. [13] and Nakamura et al. [14] the temperature of 300 °C appears boundary for carbon graphitization. This shed some light on the observed breakdown of the reaction rate observed at 350 °C (Fig. 1).

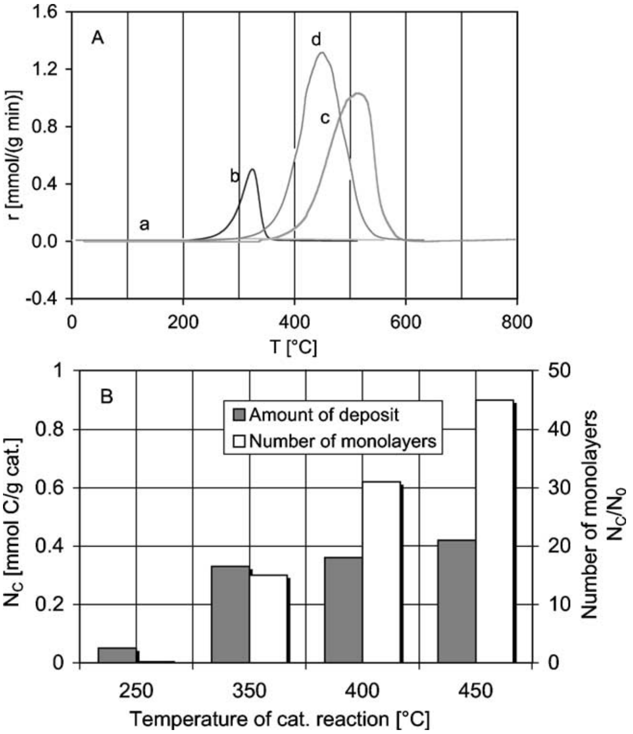

Fig. 4. (A) TPO of the deposits collected at: a—250 °C; b—350 °C, c—400 °C; d—450 °C, 6% mixture of H_2:C_2H_4 = 6:1 in He. The catalyst flushed in He, 12 h, 25 °C; (B) dependence of deposits amounts calculated from A on the reaction temperature; N_C—the amounts of deposit in mmol Co/g catalyst, N_C/N_0—the number of deposit monolayers (N_0 is a number of active centres mmol Co/g catalyst).

3.3. Activating

An interesting issue is why the higher temperature deposit ($T > 400$ °C) is more reactive both in the catalytic reaction (Fig. 1) and in the oxidation observed during TPO (Fig. 4); the maximum of the deposit from 450 °C emerges at temperature by 60 °C lower than the maximum of the one from 400 °C (compare curves d and c Fig. 4A). The explanation may come from the SEM experiments performed on the catalyst exposed to the reaction mixture at various temperatures. All deposits collected at and above 350 °C included metallic cobalt crystallites on their surface, but when perceived with an unarmed eye the lower temperature deposit appeared much thicker than the higher temperature one. As an example, the deposit grown at 450 °C is envisaged in Fig. 5A and B, where cobalt crystallites can be spotted as white dots in picture B. The results of X-ray analyses taken at 100 points of the sample revealed that the higher amount of cobalt on the deposit produced at 450 °C.

The deposits grown at elevated temperatures most probably have a filamentous structure with metallic cobalt clusters built in on top of carbon fibers. Such filamentous deposits have been reported mainly for nickel reforming catalyst and also for Fe–Ni and Co–Cu catalyst [15,16]. It must also be pointed out that 450 °C is the temperature of phase transition between cubic fcc and hexagonal hcp cobalt [17]. As this transition is based on the distortion of every third atomic layer, this must result in the increased mobility of cobalt atoms at this temperature region. Metal particles migrating inside the deposit fibers were observed by TEM for Fe–Ni catalyst [15]. As a consequence, the increased activity of the catalyst at above 400 °C can be accounted for by the increased ability of metallic atoms to migrate throughout the deposit to its surface in order to form metallic centres for hydrogenation.

Alternatively, a whisker growth mechanism could be considered to explain the restoration of the cobalt

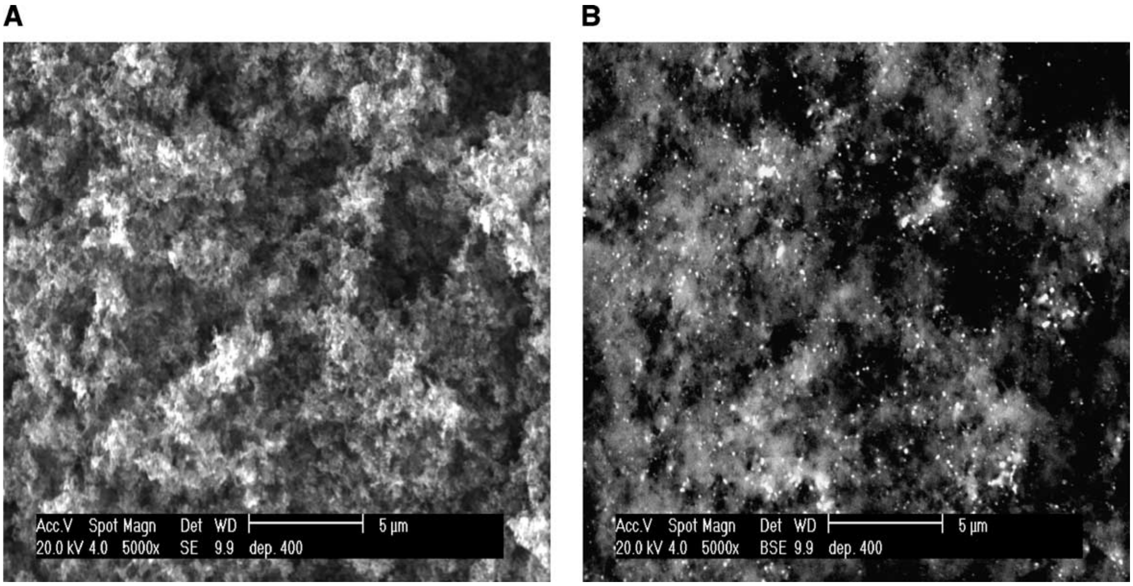

Fig. 5. SEM of the surface of the cobalt catalyst after ethylene hydrogenation, H_2:C_2H_4 = 6:1 for 2 h, at 450 °C; (A) deposit in the light of secondary electrons (5000×), (B) the same deposit in the light of back scattered electrons (5000×).

catalyst activity. However, it does not explain why, in the temperature range 300–400 °C, we observed the collapse of the hydrogenation rate though there were cobalt atoms present on the deposit surface.

3.4. *On the mechanism of ethylene hydrogenation and deposit growth*

Formation of the new metallic centres does not account for the change in the mechanism of ethylene hydrogenation observed at higher temperatures (Fig. 2B); to remind, at the lower temperature range hydrogenation rate is controlled by hydrogen adsorption. Moreover, as was mentioned above, they appear not to be the only active centres for this reaction in the higher temperature range [8,10].

The deficit in the metallic centres at higher temperatures can force mobile hydrogen atoms to leave them immediately after adsorbing and dissociating, and to diffuse over the deposit until they meet an ethylene molecule to hydrogenate it into ethane. In this way, the deposit becomes some sort of hydrogen reservoir for the ethane formation. The new hydrogenation route towards ethane occurring on the deposit sites can elucidate the initial increase in the reaction rate during a typical catalytic test above 400 °C (Fig. 1). The opposite impact of ethylene pressure on the methane formation (Fig. 2B) indicates that the methanation route proceeds through dissociative adsorption of ethylene on the metallic centres or, which is also possible, through hydrogenolysis of the hydrocarbon agglomerates. The observations made during ethylene hydrogenation on the deactivated catalyst without a deposit (Fig. 6) imply methane precursors being the intermediates both for methanation and the deposit growth. During such an experiment the deactivated catalyst was gradually regaining its activity with time-on-stream. Methane, however, was the only product during first hour of the reaction, after which a slow regeneration towards C_3 hydrocarbons was also observed, but no ethane was formed over the reaction time.

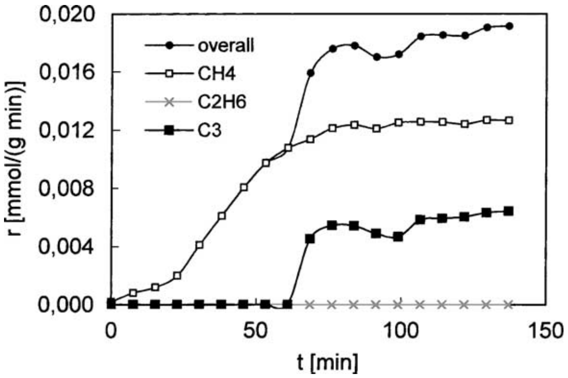

Fig. 6. Ethylene hydrogenation at 350 °C carried out on the deactivated catalyst from which the deposit was removed prior the reaction.

Acknowledgements

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