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On deactivation of $CrO_x/La_2O_3/ZrO_2$ catalyst during n-octane dehydrocyclisation. I. Investigation of dehydrogenation capability by the homomolecular H–D exchange of molecular hydrogen

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Based on the time on stream dependence of product distribution during deactivation and on additional investigations of fresh and deactivated samples by the homomolecular H–D exchange of molecular hydrogen, it is concluded, that the deactivation during n-octane dehydrocyclisation on $CrO_x/La_2O_3/ZrO_2$ catalysts is caused by a decreasing dehydrogenation capability of the active surface and not by increasing mass transport resistance.

Keywords: deactivation, dehydrocyclisation, dehydrogenation, isotope exchange

1. Introduction

In C_{6+} paraffin dehydrocyclisation (DHC), chromium(III) oxide on lanthana-doped zirconia exhibits promising alkyl aromatics productivities [1]. Sufficiently low deactivation rate of the catalyst would be a precondition of industrial use. Therefore, knowledge on reasons and mechanism of catalyst deactivation is desirable. In case of metal-containing bifunctional naphtha reforming catalysts it has clearly been shown [2] that deactivation is predominantly caused by coking. With high probability, this also applies to the $CrO_x/La_2O_3/ZrO_2$ catalyst [3]. Coke deposits can influence the reaction in various manner. They can change the number and/or nature of active sites by simple coverage or by chemical interaction, as well as limit mass transport rates within the catalyst grains [4]. The aim of the present investigation is to decide between these two possibilities.

For metal-containing catalysts it has recently been demonstrated [5] that the initial step of the DHC reaction sequence, the dissociative adsorption of paraffin molecules, is rate limiting, followed by stepwise further dehydrogenation and cyclisation. We assume that this is also true for our catalyst system.

If, as a result of deactivation, an additional limitation would appear at later reaction stages (olefins to diolefins, diolefins to triolefins or cyclic olefins, e.g.), we would have to observe a distinct increase of the intermediates share (olefins, diolefins, e.g.) in the product spectrum, while the reaction rate would decrease only moderately.

No significant changes in selectivities with progressing deactivation would mean that the dissociative paraffin adsorption itself was affected or that the educt transport became rate limiting.

In the latter case one would have to look for an additional criterion, which allows one to distinguish between decreasing mass transport rates and decreasing activity in dehydrogenation. Such a criterion is the influence of the molecule size on dehydrogenation activity.

The dehydrogenation (dissociative adsorption) of the small dihydrogen molecule should be less sensitive to mass transport limitations than the dehydrogenation of the large n-octane molecule. Therefore, the H_2 dissociation rate should be almost independent of the catalyst state (fresh or used), if the observed deactivation in n-octane DHC was the result of educt transport limitations. On the other hand, the n-octane DHC rate and the H_2 dissociation rate are expected to change simultaneously, if coke influenced the number or the state of active sites.

The H_2 dissociation can be characterised [6] by measuring the H–D exchange between the hydrogen molecules – the homomolecular isotope exchange (homoexchange) of molecular hydrogen, which occurs on the catalyst surface as a result of the reversible dissociative adsorption of hydrogen molecules. In this paper, we applied this method.

2. Experimental

The catalyst was prepared by wet impregnation of a commercial 7 wt% La_2O_3 containing ZrO_2 (MEL-CAT XZ 068/01 MEL Chemicals) [1] by an aqueous solution of $(NH_4)_2CrO_4$, yielding samples with 4.0 wt% Cr. After drying at 120 °C, the catalyst samples were annealed for 2 h in air at 600 °C and reduced at 550 °C in hydrogen in the reactor before starting the DHC test reaction.

The DHC experiments were carried out at atmospheric pressure in a quartz glass annular gap reactor consisting of three concentric tubes. The catalyst (0.5–0.7 mm particle

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size) was filled in the void volume between the 12 mm outer diameter and the 9 mm diameter middle tubes (cross section of the annular gap equals 15 mm^2, height of the catalysts bed usually 20 mm). The educt mixture was preheated in the void volume above the catalyst bed, and the product mixture was taken on top of the middle tube. A thermocouple was positioned in the inner tube.

Standard conditions of the experiments were as follows: 550 °C reaction temperature, 62.5 mmol/h carrier gas, 1.11 mmol/h n-octane, 250 mg catalyst. n-octane was dosed by a saturator at 25 °C, with H_2 or N_2 as carrier gases. The product mixture analysis was performed by on line gas chromatography (HP5890 chromatograph, 30 m capillary column, type SE30).

Exchange experiments were carried out in a static apparatus (218 ml, 1–4 Torr, 5–25 mg sample) with on line MS analysis, using a Baltzers QMG 421 mass spectrometer, equipped with cross beam ion source and channeltron, recipient pressure about 10–7 Torr.

For exchange experiments the pre-treatment of the catalysts included heating under vacuum up to 550 °C, exposure to 10 Torr H_2 during 2 h, cooling down in hydrogen to 300 °C, evacuation at this temperature for 30 min (10–5 Torr), and finally cooling down to the experiment temperature in the evacuated reactor. To get activity differences as high as possible samples were taken from fresh made catalyst as well as after exposing it during 8 h to an N_2/n-octane mixture under conditions described above.

The hydrogen isotopic molecules concentrations were determined by simultaneous measuring of ion current intensities at the mass numbers 2 (HH), 3 (HD) and 4 (DD). The calibration was carried out with an equilibrated mixture of the dihydrogen isotopic molecules (25% HH, 50% HD, 25% DD) with an overall deuterium content of 50%.

3. Isotope exchange

Kinetics of dihydrogen exchange is described in earlier work [6] and will be only briefly outlined in the following.

In an equilibrium system of hydrogen-containing species, we can label one of the species by a deuterium tracer at a distinct time. This tracer will then be transported to the other species by hydrogen or proton transfer reactions occurring between them. The initial non-equilibrium tracer distribution changes to a final equilibrium distribution. Measuring the time dependence of the tracer distribution of, at least, one species of the system, one obtains information about the chemical reactions transporting the tracer.

It is convenient with isotope exchange investigations [7,8] to distinguish between heteromolecular exchange (shortly heteroexchange) and homomolecular exchange (shortly homoexchange). In heteroexchange experiments one species is marked and then its tracer concentration time dependence is measured. Homoexchange experiments aim to measure the tracer movement between the molecules of one species.

In this paper, we exclusively applied homoexchange. In our experiments, the component under observation will be molecular hydrogen containing two equal hydrogen atoms in its molecules. By D labelling three isotopic molecules can be formed: HH, HD and DD.

With N being the total amount of hydrogen molecules

$$N = {}^{\mathrm{HH}}N + {}^{\mathrm{HD}}N + {}^{\mathrm{DD}}N,$$

and ${}^{\mathrm{HH}}X$, ${}^{\mathrm{HD}}X$ and ${}^{\mathrm{DD}}X$ being the relative concentrations of the possible three isotopic molecules of hydrogen,

$${}^{ii}X = \frac{{}^{ii}N}{N},$$

we get three independent components for describing the state of the molecular hydrogen system. If we regard this system as being closed (constant N), there remain two free parameters to describe it unambiguously. Using the concentrations of the isotopic molecules, we get non-linear differential equations of their time dependences even for simple exchange reactions [9].

Therefore, it is preferable to use another parameter system, namely the tracer content α and the decline y of the single traced molecules concentration from the equilibrium (binominal) distribution value at given α:

$$\alpha = \frac{{}^{\mathrm{HD}}N + 2\,{}^{\mathrm{DD}}N}{2({}^{\mathrm{HH}}N + {}^{\mathrm{HD}}N + {}^{\mathrm{DD}}N)},$$
$$y = {}^{\mathrm{HD}}X - 2\alpha(1-\alpha).$$

Now we can describe the isotopic molecules concentrations by α and y:

$${}^{\mathrm{HH}}X = (1-\alpha)^2 - y/2, \qquad {}^{\mathrm{HD}}X = 2\alpha(1-\alpha) + y,$$
$${}^{\mathrm{DD}}X = \alpha^2 - y/2$$

and get linear differential equations for the time dependence of α [6,7] during heteroexchange experiments. If the experimental conditions are chosen in such a way that α is nearly constant, we also obtain a linear differential equation for the deuterium homoexchange of the molecular hydrogen,

$$N\frac{\mathrm{d}y}{\mathrm{d}t} = -ky,$$

with the product of N and k being the dissociation rate of dihydrogen, if assuming a dissociation mechanism with moveable H species at the catalyst surface [6]:

$$\mathrm{H_2 + Z + [\,] \rightleftharpoons HZ + [H]}$$
$$\mathrm{HZ + [\,] \rightleftharpoons Z + [H]}$$

4. Results

4.1. Dehydrocyclisation

As already shown in [3] and [10], the deactivation during n-octane DHC is rather fast in nitrogen atmosphere and slower in H_2 atmosphere. But even in pure hydrogen, the

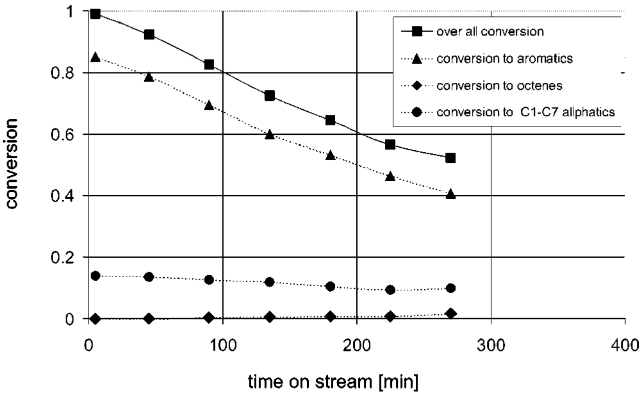

Figure 1. n-octane conversion and parts of conversion into aromatics, octenes and C_1–C_7 aliphatics as a function of time on stream (coke not taken into account).

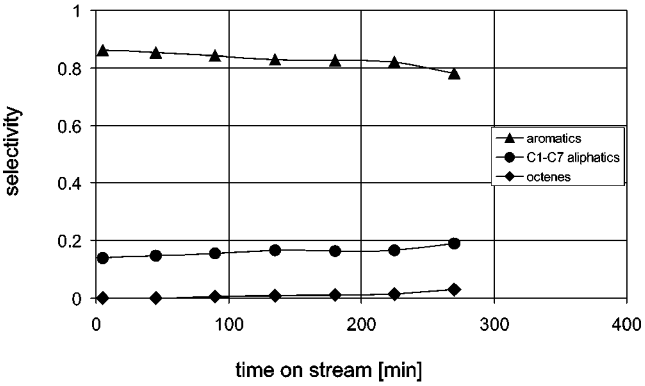

Figure 2. Selectivities as a function of time on stream (coke not taken into account).

Table 1
Time on stream dependence of coke deposition and coking selectivity in H_2/n-octane.

Time on stream (min)	n-octane conversion (%)	Coke content of catalyst (wt%)	C-selectivity of coking (%)
0			
5	98	0.2	5.7
15	93	0.6	5.7
30	90	1.0	4.1
180	64	2.6	2.0
360	48	3.4	1.0

rate of n-octane DHC on our $CrO_x/La_2O_3/ZrO_2$ catalyst clearly depends on the time on stream (figure 1). Selectivities are not influenced to a considerable extent (figure 2).

As shown in table 1, the deactivation is accompanied by coke deposition. The coking selectivity starts at 5.7% of the n-octane conversion and then decreases with increasing time on stream.

4.2. Dihydrogen dissociation

As already mentioned, we measured the H_2 homoexchange rate to characterise the dehydrogenation capability of the catalyst.

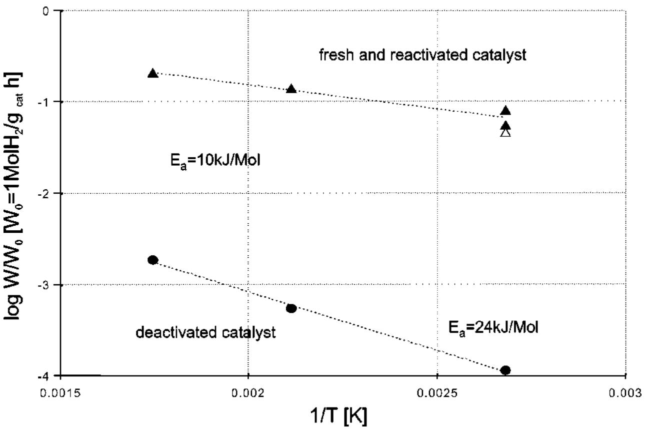

Figure 3. Temperature dependence of hydrogen H–D homoexchange rates on fresh and deactivated catalyst (the empty triangle symbol belongs to the regenerated sample).

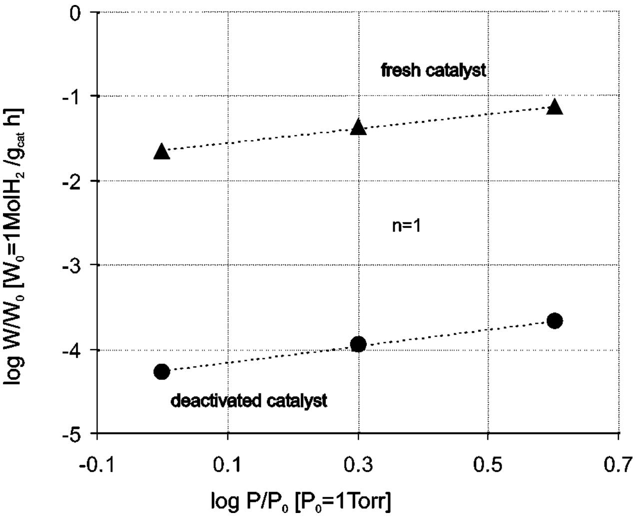

Figure 4. Pressure dependence of hydrogen H–D homoexchange rates on fresh and deactivated catalyst.

To get a sufficient activity difference between fresh and used catalyst samples, the used (deactivated) samples were prepared by exposing the catalyst for 8 h to an N_2/n-octane atmosphere at 550 °C, where deactivation proceeds significantly faster than in H_2/n-octane [3]. The conversion was observed to decrease from 96 to 21% and the coke content reached 6 wt%.

The H_2 homoexchange rates of the samples, fresh and used in DHC, are shown in figures 3 and 4. At 100 °C, there is a difference of more than two orders of magnitude between the activities of fresh and used catalyst samples. For both fresh and used samples, the apparent reaction order n is about “1” with respect to hydrogen. The apparent activation energies of homoexchange amount to 10 kJ/mol for fresh and 24 kJ/mol for used samples, respectively.

If the deactivated sample is treated in air at 10 Torr absolute pressure at 600 °C to burn off the coke and then subjected to the normal pre-treatment in hydrogen and vacuum, it exhibits the same exchange rates as the fresh catalyst (figure 3).

5. Discussion

Obviously, the catalyst deactivation is caused by coke: The activity loss with time on stream is accompanied by increasing coke content. High-temperature treatment in air burns off the coke and fully restores the catalytic activity in DHC [10] and in H_2 dissociation (figure 3).

The amount of coke deposited on the catalyst surface is high enough to cause active sites poisoning as well as pore blocking. After 180 min time on stream, we found 26 mg-carbon/g-catalyst. This amount corresponds to about one carbon monolayer (a monolayer calculated with about 10^{19} C-atoms/m^2) on the catalyst (BET surface 110 m^2/g) and is sufficient to cause the observed decrease of n-octane conversion from 98 to 64% by covering or poisoning active sites. On the other hand, this coke being concentrated in the pores near the surface could also act as an effective diffusion barrier for C_8 hydrocarbons.

First information about the mechanism of deactivation can be obtained from the insignificant time dependence of selectivities. If, additionally to the rate-limiting dissociative adsorption of n-octane [5], the deactivation caused further limitations on later reaction steps (for example, on the stage olefins to diolefins), one should expect severe changes in selectivities. In our example chosen in figure 1, i.e., in view of the activity decline from 98 to 64% after 3 h, the octenes selectivity should exceed the aromatics selectivity. But, in fact, the selectivities to aromatics remain almost constant at about 80% and only a few percent of octene selectivity is found after 270 min on stream (figure 2).

Thus, an additional limitation of later steps of the DHC reaction chain seems to be improbable. Either the dissociative n-octane adsorption or the mass transport to the active sizes must be influenced by coking.

If a pre-catalytic mass transport limitation was responsible for the DHC activity decrease, one should observe only weak or no influence of the samples state (fresh or used) on the H_2 homoexchange rates. But, in fact, together with the decrease in n-octane conversion from 96 to 27% (after 8 h in N_2/n-octane) we also found differences in the H_2 homoexchange rates of two orders of magnitude between fresh and deactivated samples (figures 2 and 3).

The increase of the activation energy E_a from 10 to 24 kJ/mol is an additional argument against deactivation by a mass transport limitation. An E_a value of 10 kJ/mol on the fresh catalyst is typical for rate limitations by diffusion. On the used catalyst the H_2 dissociation is strongly decreased. It becomes rate limiting and the E_a value rises up to 24 kJ/mol. The formal H_2 reaction of order $n = 1$ remains the same on fresh and deactivated samples, because this value is typical for both diffusion-limited and dissociation-limited processes.

All our experimental data indicate that the catalyst deactivation observed during n-octane DHC must be due to loss of the number and/or activity of those active sites which are responsible for the dissociative adsorption of hydrocarbons and of molecular hydrogen, too. This conclusion is in good agreement with the results of ESR [3], which showed a decrease of chromium(III) signals with increasing deactivation and coke deposition.

6. Conclusions

- The homomolecular H–D exchange of molecular hydrogen is a suitable test reaction to characterise the H_2 dissociation and thus to prove the dehydrogenation capability of catalysts.
- Deactivation of $CrO_x/La_2O_3/ZrO_2$ catalysts during n-octane dehydrocyclisation is caused by a loss or modification of active sites responsible for the dissociative adsorption of the paraffin molecules.

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