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Vajglová, Zuzana
2016

Dostupný z <http://www.nusl.cz/ntk/nusl-263210>

Dílo je chráněno podle autorského zákona č. 121/2000 Sb.

Tento dokument byl stažen z Národního úložiště šedé literatury (NUŠL).

Datum stažení: 19.04.2024

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INDUCED OSCILLATORY BEHAVIOUR DURING 2-METHYLPROPENE (ISOBUTENE) HYDROGENATION IN A PACKED BED MICROREACTOR

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Abstract

For better understanding of the industrial C4 fraction hydrogenation process, a reaction study has been performed in a laboratory environment. Hydrogenation of 2 methylpropene (isobutene, 2MP) over commercial catalyst has been investigated experimentally as a model reaction. This continuous hydrogenation in gas phase has been carried out on the platinum catalyst Cherox 3902 under the temperatures up to 110°C and hydrogen pressure 20 bar.

This contribution focuses on the induced oscillatory behaviour observed during the continuous hydrogenation of 2MP in a packed bed microreactor. Induced reproducible oscillations have been studied using the on-line gas chromatograph (GC-FID/TCD) and a catalyst bed temperature monitoring. Effects of the temperature, thermal conductivity and space velocity on the properties of induced oscillations have been investigated in detail.

The study results revealed extremely high sensitivity of the oscillatory behaviour to the heat transfer conditions in the system. Experimental tests focusing on the space velocity effect revealed a significant influence on the oscillation amplitude height and period phase length with the high reaction rate. Based on the character of the induced oscillations, they have been classified as thermo-kinetic oscillations¹ as they are resulting from the interaction between the exothermic reaction, heat transfer and a reversible decrease in the catalyst activity.

Introduction

Industrial production of olefins (ethylene, propylene), is one of the largest chemical technologies. Production of olefins is based on steam cracking of naphtha and other liquid raw materials. Main product ethylene is a pillar on which stands the follow-organic technology and production of major polymers. Hydrocarbon C4 and C5 fractions are by-products of the process. These fractions are interesting for further processing^{2, 3} and also important in terms of volume (approx. 20%). Due to large-scale production of C4 fractions and complexity of the pyrolysis process any yield improvement, more efficient use of raw materials or by-products or reducing the energy demands of the process results in considerable economic value. Therefore, the knowledge of the reaction kinetics is crucial for the design of C4 (C5) hydrogenation units, their validation and scale-up.

One way to determine the kinetics of the industrial process is to use a down-scaling. Control of the continuous mode at steady state is simpler and at the same time provides constant, precisely defined quality product. Microtechnology and microreactors can be a solution for down-scaling continuous process⁴⁻⁸.

Microdevices are characterized by a small internal dimension with respect to the character of the studied process. Generally, the microdevice might be defined as a device with internal characteristic dimension smaller than 1 mm. Microdevices are widely used in a variety of applications. They are used as micro mixers, micro heat exchangers or microreactors. Knowledge of flow hydrodynamics, reaction kinetics, heat and mass transfer conditions for a specific process is necessary in the case of microreactors for a complete description of their behavior⁹⁻¹³. The basic information for operation, optimization and intensification of the conventional processes in microreactors are shown in Jahnische's et al. study¹⁴.

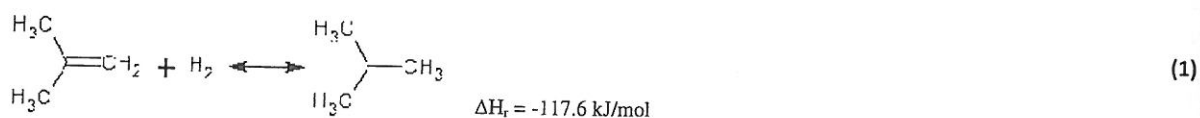
The presence of heat and mass transfer effects in the system might lead to a strong distortion of an intrinsic kinetics of the investigated process. Therefore, these effects should be minimized by selecting the expedient experimental set-up design and optimization of process conditions¹⁵. The necessity of a correct system settings was shown in Ardiaca's et al. study¹⁵ that deals with hydrogenation of 1,3 butadiene and n-butenes in the liquid phase over a Pd catalyst.

During kinetic studies, we can observe the existence of multiple steady states process (bifurcation) within a certain range of conditions. This applies in particular for highly exothermic reactions^{1,16,17}. The most common type of the observed oscillations are classified as thermo-kinetic oscillations. During these oscillations the reaction occurs either in so called cold or hot state. The cold state of the reaction is generally a steady state under the intrinsic kinetic control regime with low temperature, low reaction rate and the same concentrations of reactants and products on the catalyst surface as in the bulk continuous phase. The hot state of the reaction

is a steady state under the transport phenomena controlled regime with high temperature, high reaction rate and low concentrations of reactants but high concentrations of product on the catalyst surface ^{1,18,19}.

Reaction mechanism of 2-methylpropene hydrogenation

The model reaction was chosen to simplify the development of the experimental procedure and the evaluation of a presence of mass and heat transfer effects. Hydrogenation of 2-methylpropene (2MP) on the commercial Pt catalyst was selected as a model reaction representing total hydrogenation of the C4 fraction. 2-methylpropene was selected on the basis of good availability on the market. Also, the 2MP hydrogenation is the slowest comparing to hydrogenation of other butene isomers in the C4 fraction [20]. Hydrogenation of 2MP to 2-methylpropane (2MPA) is exothermic reversible equilibrium reaction (1) with the reaction enthalpy -117.6 kJ/mol [21].



Experimental

Catalyst

As a catalyst was selected commercial catalyst Pt/ γ -Al₂O₃ „Cherox 3902“ (Euro Support Manufacturing Czechia, s. r. o., Czech Republic). The catalyst was in form of spheres with a diameter of 2 mm, and contained 0.55 wt. % Pt. Pt in the catalyst was homogeneously distributed in the support. This catalyst is commonly used for industrial application study of hydrogenation of the C4 fraction in the reference pilot plant in the Unipetrol Centre of Research and Education, Litvinov in Czech Republic. In order to eliminate the wall fluxes in the laboratory reactor ($D_R/D_{cat} > 10$) [22], the commercial catalyst was crushed and sieved to a fraction with a grain size ranging from 0.1 to 0.36 mm (Table I).

Table I
Catalyst bed properties

Scale	L_{CB}	D_{CB}	D_{cat}	W_{cat}	D_R/D_{cat}
	mm	mm	mm	g	mm/mm
Pilot plant	144	15	2	150	7.5
Laboratory	39	4.8	2	-	2.4
Laboratory	39	4.8	0.1 – 0.36	0.05	21.1

Reactor setup

The main part of the laboratory apparatus (Figure 1) consists of a high temperature high pressure packed bed microreactor with integrated mixer. The microreactor is part of the modular microreactor system (MMRS) developed for the study of chemical processes at the microscale from Ehrfeld Mikrotechnik BTS GmbH in Germany. Detailed description of the apparatus is shown in Stavarek's et al. study ¹⁹.

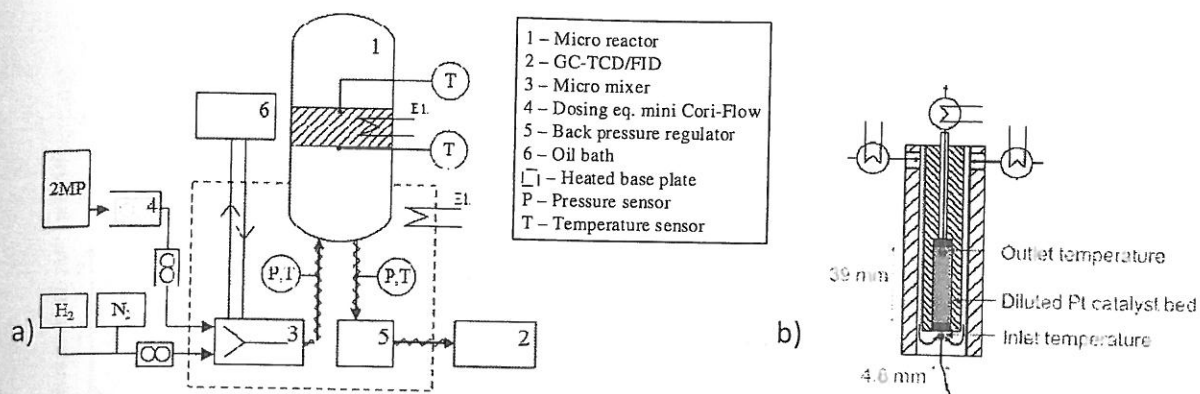


Figure 1. a) scheme of experimental apparatus, b) scheme of the microreactor cartridge with a catalyst bed

Analysis

For the on-line analysis of the reaction mixture we used two-channel gas chromatograph 7890A (Agilent Technology, USA) with thermal conductivity detector (TCD) and flame ionization detector (FID). The first channel (for TCD) was used for the separation of permanent gases (N_2 , H_2) in a column paraPLOT Q (Agilent Technologies, USA) and 5A molecular sieve with an inner diameter of 2 mm (Restek Corporation, USA). The second channel (for FID) was used for the separation of hydrocarbons (2MP, 2MPA) in a column GS-Gaspro 30 m x 320 μ m x 0 μ m (Agilent Technologies, USA). Continuous GC analysis was programmed with sampling frequency of 12 min.

Discussion and result analysis

This paper focuses on the study of 2MP hydrogenation on the diluted catalyst bed with alumina (Sasol γ - Al_2O_3) as an inert material in a volumetric ratio of 1/5.9 and 1/9.5, respectively (denoted as CB2 and CB3). During the hydrogenation the induced oscillations were observed on this diluted beds (CB2, CB3).

In the early phase of experimental campaign with the diluted beds the 100% conversion of 2MP has been observed for more than 60 hours on stream under the operating conditions similar to the industrial process (inlet temperature of 80 $^{\circ}C$ and pressure of 20 bar). Following experimental measurements were therefore carried out at lower inlet temperature, i.e. about 40 $^{\circ}C$.

Effect of the catalyst bed (CB) type

For four different types of the catalyst beds (Table II) but with the same catalyst amount (50 mg) the identical set of experiments was performed focusing on the dynamic behavior of the system (Figure 2). The hydrogenation experiments were carried out as a continuous campaign duration approximately two months on stream without interruption.

Table II
Type of catalyst bed (CB)

	W_{cat} g	Inert -	Pt/Inert ml/ml	V_{CB} ml	L_{CB} mm	λ_{CB} W/m/K	ϵ_{CB} -
CB1	0.5	-	-	0.067	3.7	0.22	0.35
CB2	0.5	Al_2O_3	1/5.9	0.402	22.2	0.22	0.35
CB3	0.5	Al_2O_3	1/9.5	0.705	39.0	0.22	0.35
CB4	0.5	SiC	1/9.5	0.705	39.0	2.03	0.42

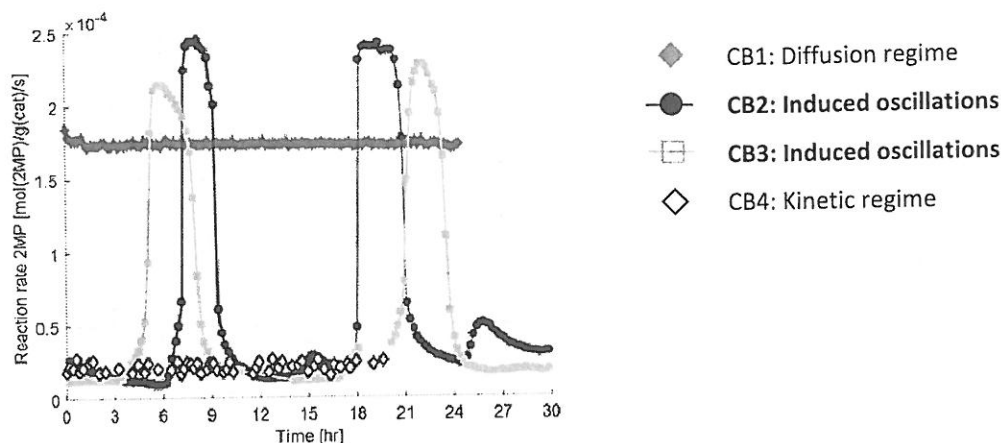


Figure 2. Effect of the catalyst bed type, conditions: WHSV = 50 g(2MP)/g(cat.)/hr, $Q_{tot} = 270$ NmL/min, $T_{in} = 50 - 80$ °C, $T_{out} = 55 - 133$ °C, $p = 20$ bar

The results with the catalyst bed CB1 (see Table II) show the hot state due to high reaction rate that indicates transport phenomena limited regime. Conversely, the results with the diluted catalyst bed with silicon carbide of high thermal conductivity CB4 (see Table II) show the cold state due to low reaction rate that indicates the intrinsic kinetic control regime. It has to be noted that the inlet temperature in both cases was the same (80 °C) while the catalyst bed temperature was 133 °C for CB1 and 107 °C for CB4.

During the experiments on CB2 and CB3 it has been observed a gradual extinction of hydrogenation reaction (reaction rate dropped to 0). Spontaneous extinction reaction was observed without changing the external operating conditions. To prevent the complete extinction of the reaction, the inlet temperature of the reaction mixture was increased stepwise by small increments (0.2 °C each 3 – 15 hours). This thermal impulse occasionally also caused the observed (induced) oscillations.

The induced oscillations were observed only for catalyst beds diluted with alumina CB2-3 (See Table II). The induced oscillations were initiated by a forced reactor temperature increase. The induced oscillations observed on the both diluted catalyst beds with alumina show a similar character of oscillatory behavior with only minor differences. The results comparison shows that increasing the dilution ratio from 1/5.9 (CB2) to 1/9.5 (CB3) resulted in smoother and approximately 2× slower transition between the hot and cold reaction state (from 4 hours (CB2) to 8 hours (CB3), Figure 2.

Effect of the space velocity (WHSV)

Experimental tests to reveal the space velocity (WHSV: weight hourly space velocity) influence on the course of induced oscillations detected the change in amplitude height and length of the oscillation period phase with a high reaction rate (3 – 15 hours, Figure 3). The induced oscillations were initiated by a forced reactor temperature increase in range of 0.2 – 2 °C. It is seen that the phase of the period with the high reaction rate, i.e. the so-called hot state, extends with decreasing space velocity.

The high sensitivity of the properties of nonisothermal induced oscillations to the linear flow rate at constant concentration of reactants in the reactor can indicate the thermo-kinetic nature of the oscillations. This type of oscillations is also very sensitive to the heat transfer conditions in the system¹⁸.

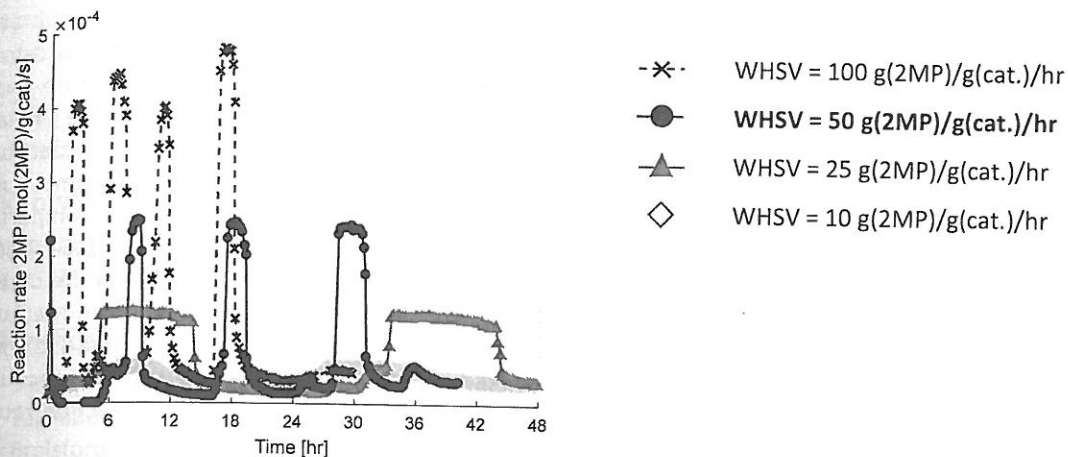


Figure 3. Time development of induced oscillations, conditions: CB2, 2MP/H₂/N₂ = 1/3/13, WHSV = 10 – 100 g(2MP)/g(cat.)/hr, Q_{tot} = 68 – 540 NmL/min, T_{in} = 40 – 60 °C, T_{out} = 48 – 85 °C, p = 20 bar

Changing the space velocity has a significant influence on the size of the temperature impulse required to initiate oscillations, i.e. to move from the cold state with a low reaction rate to the hot state with a high reaction rate. During the experiments with the high space velocity 100 g_{2MP}/g_{cat}/hr, temperature impulse for initiating of induced oscillations was only of 0.2 °C. Whereas during experiments with low space velocity 10 g_{2MP}/g_{cat}/hr, the temperature impulse for initiating the induced oscillations was about 2 °C. The value of thermal impulse also increased with increasing inlet temperature of the reaction mixture. Increasing the volumetric dilution ratio Pt-catalyst and the alumina 1/5.9 (CB2) to 1/9.5 (CB3) has only a minor influence on the observed oscillations. The minor effect can be attributed to a very low thermal conductivity of γ-Al₂O₃.

Effect of the thermal conductivity of the reaction mixture

Figure 4 shows experiments with different thermal conductivity of the reaction mixture (λ_f) in the range of 0.02 – 0.17 W/m/K with constant initial concentration of 2MP and constant total volumetric flow. Changing the thermal conductivity of the fluid was realized by higher excess of H₂ instead of N₂ (2MP/H₂/N₂: from 1/3/13 to 1/16/0).

During the experiments with 8× higher thermal conductivity of the reaction mixture (0.17 W/m/K) the disappearance of induced oscillations occurred together with stabilization of the reaction in the hot state. The results of these experiments confirmed a high sensitivity of the system to the conditions of heat transfer. This is also another characteristic feature of the nonisothermal thermo-kinetic oscillations [18].

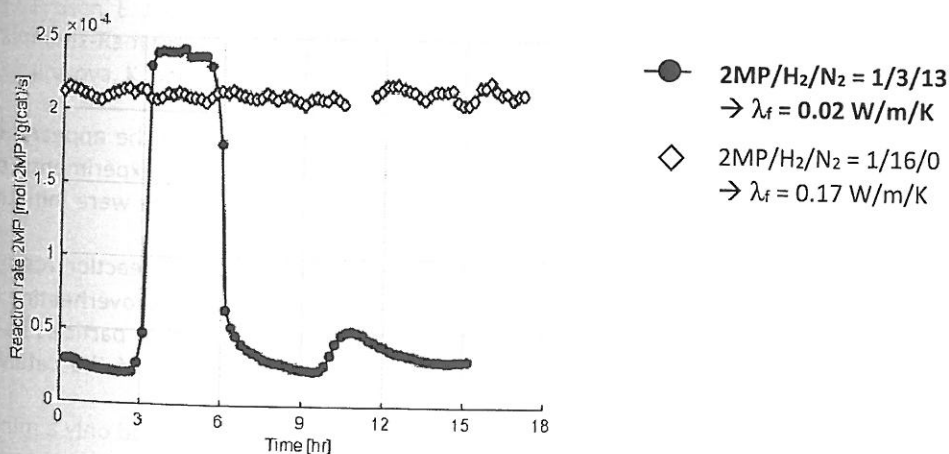


Figure 4. Effect of the thermal conductivity of the reaction mixture, conditions: CB2, WHSV = 50 g(2MP)/g(cat.)/hr, Q_{tot} = 270 NmL/min, T_{in} = 52 – 58 °C, T_{out} = 58 – 82 °C, p = 20 bar

Reaction hot zone moving through the catalytic bed

A detailed record of the course of reaction rate 2MP, inlet and outlet temperatures of the catalytic bed at the time is shown in Figure 5. Figure 5 clearly shows that both oscillation peaks of 2MP reaction rate

(conversion) are accompanied by an unusual U-shaped peak of bed temperature. This specific temperature curve during oscillation can be explained by the presence of the reaction zone, which moves along the catalyst bed. The length of the catalyst bed was 22.2 mm (CB2, Table II).

Development of moving the reaction zone could be described as follows: thermal impulse initiates the hydrogenation reaction which initially takes place in the whole volume of the bed, but due to its exothermicity and poor heat dissipation rapidly forms a hot zone at the beginning of the bed. Thermocouple, which is located at the outlet of the bed recorded sharp maximum and the temperature was temporarily stabilized at between 70 to 75 °C (first peak of bed temperature). Due to a feedback mechanism [16-18] local deactivation of the catalyst occurs, which leads to slow movement of the reaction zone through the catalyst bed in the flow direction of the reaction mixture towards to thermocouple at the end of the bed. Measured temperature increases slightly when the reaction zone is approaching the thermocouple. Second maximum of the temperature of oscillating peak indicates that the reaction zone is located near the thermocouple. The reaction zone slowly extinguishes due to deactivation of the most of catalyst bed, while the reaction rate of 2MP decreases as well as the temperature measured at the output.

Very good repeatability of induced oscillations and course of bed pointing to the presence of moving reaction zone thus indirectly confirms the presence of a feedback mechanism, which is also characteristic of the thermo-kinetic oscillations [1, 18].

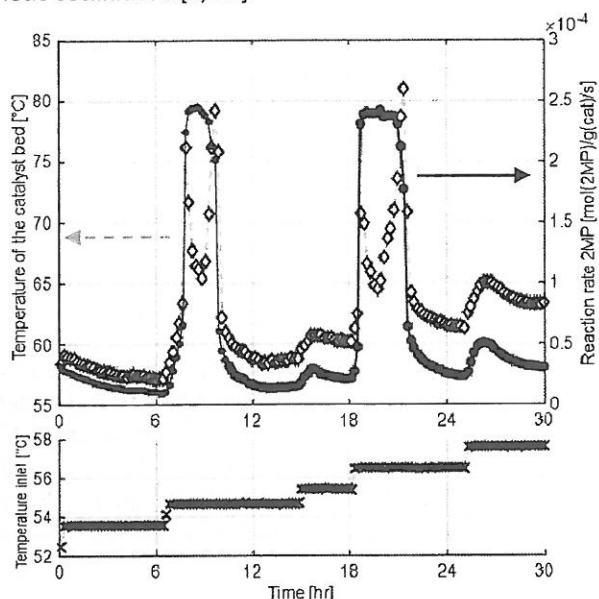


Figure 5. Moving hot zone, conditions: CB2, WHSV = 50 g(2MP)/g(cat.)/hr, $Q_{tot} = 270$ Nml/min, $2MP/H_2/N_2 = 1/3/13$, $T_{in} = 52 - 58$ °C, $T_{out} = 58 - 82$ °C, $p = 20$ bar, $X_{2MP} = 0 - 100$ %

Conclusions

Experimental study of the hydrogenation of 2-methylpropene in the microreactor revealed the appearance of induced oscillatory behaviour. The oscillations of reaction were only observed during experiments on the diluted catalyst bed with alumina at temperatures less than 80 °C. The induced oscillations were initiated by forced reactor temperature increase in range of 0.2 – 2 °C each 3 – 15 hours.

A possible explanation for the observed ignition and extinction phenomena during exothermic reaction rests in low thermal conductivity of alumina ($\lambda = 0.22$ W/m/K [23]) used for dilution, allowing the local overheating of the catalyst particles and insufficient heat removal from bed. Dilution caused that some catalyst particles have lost contact with a well-cooled reactor wall. It apparently also contributed to overheating of the catalyst particles.

Increasing the volumetric dilution ratio Pt-catalyst and the alumina 1/5.9 (CB2) to 1/9.5 (CB3) had only a minor influence on the observed oscillations. The minor effect can also be attributed to a very low thermal conductivity of catalyst bed.

Effect of increasing space velocity (WHSV) revealed higher amplitude height of temperature oscillations and shorter period phase length with high reaction rate. Effect of higher thermal conductivity of fluid revealed oscillation disappearance. The results of these experiments proved the extremely high sensitivity of the oscillatory behaviour to the heat transfer conditions in the system. The reproducible oscillation peaks of 2MP conversion (reaction rate) were accompanied by an unusual U-shaped peak of bed temperature. This specific

temperature curve during oscillation can be explained by the presence of the reaction zone, which moves along the catalyst bed.

Based on the character of the induced oscillations, they have been classified as thermo-kinetic oscillations resulting from the interactions of exothermic, non-linear reactions with the transport phenomena, particularly the insufficient heat removal from the catalyst bed.

Acknowledgement

The publication was created using the infrastructure supported by the UniCRE project (reg. no. CZ.1.05/2.1.00/03.0071), funded by the EU Structural Funds and the state budget of the Czech Republic.

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