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CHOICE OF CONDITIONS FOR ACTIVITY MEASUREMENTS OF COMMERCIAL METHANATION CATALYSTS

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A method to choose the conditions of activity measurements for commercial methanation catalysts is suggested.

Предлагается методика выбора условий измерения активности промышленных катализаторов метанирования.

It is known /1/ that catalyst activity is characterized by the reaction rate measured under definite conditions. It is evident that on one hand these conditions must correspond to operating conditions and, on the other hand, must provide the most detailed information regarding the catalyst activity. Therefore measurements should be carried out:

(a) on industrial grains (since in this case all internal diffusion effects are taken into account automatically);

(b) in a gradientless reactor (since only there are direct rate measurements, unperturbed by "apparatus effects", possible /1, 2/).

The reaction rate is a function of the concentration and temperature. The analytical type of this dependence and the majority of its parameters are usually constant for catalysts with the same chemical composition, and all activity differences are well described by the rate constant observed. Therefore, we consider the measure of activity to be the rate constant of CO hydrogenation determined by the flow-circulation technique /2/, effectively used in practice.

It is known /3/ that the accuracy of kinetic parameter determination depends on the measurement conditions.

Measurement errors can be systematic and random. The systematic error of flow-circulation measurements is due to insufficient stirring in the circulation loop /2/. According to Ref. /3/, the relative systematic error Δ_{sys} for the determination of the observed rate constant k is:

$$\Delta_{sys} = \frac{1}{k} \frac{C_o - C}{2N} \frac{\partial k}{\partial C} \text{ x } 100\% \qquad (1)$$

where C_o and C are the initial and final CO concentrations, respectively, and N is the circulation number.

The random error of K determination Δ_{ran} is governed by the final accuracy of the directly measured parameter. According to Ref. /3/, the relative random error is

$$\Delta_{ran} = \frac{1}{k} \sum_{i=1}^{n} (\frac{\partial k}{\partial P_i} \delta P_i)^2 \text{ x } 100\% \qquad (2)$$

where P_i $(i = \overline{1, n})$ are the n directly measured parameters and δ_{P_i} are their absolute errors.

To determine numerical values of Δ_{sys} and Δ_{ran} and thus to choose measurement conditions, the type of the kinetic model must be known. To describe the process of CO hydrogenation, several types of equations are known /4, 5/ but they were obtained for the kinetic region. We have used the following description of the conversion rate observed in porous grains:

$$r = kC^n \qquad (3)$$

To determine the model parameters (k_o, E, n), kinetic measurements on a TO-2 commercial catalyst were carried out in the CO concentration range from 0.025 to 1% and at temperatures ranging from 448 to 523 K. The data obtained were processed on a computer using a special regression analysis for the case when the efficiency function depends on the unknown parameters /6/. The following parameter values have been found: $k_o = 1.4 \pm 0.3$ nm^3 CO s^{-1} kg cat^{-1}, $E = 31\,000 \pm 900$ J/mol, $n = 0.467 \pm 0.008$. As is seen from Fig. 1, the kinetic model (3) with these parameters describes fairly well the experimental data in the temperature and concentration range studied and one can use eqs. (1) and (2) to calculate errors of the experimental setup. Figures 2, 3, 4 and 5 illustrate the calculated systematic (curve 1) and the random (curve 2) errors for the determination of k as a function of the conversion, temperature, initial CO concentration and catalyst weight. Errors of the parameters measured are given in the apparatus certificates. The circulation velocity was taken equal to 800 l/h.

As is seen from Fig. 2, the minimum of Δ_{ran} is attained at the conversion degree of $X \sim 0.6$, and in the range of $X = 0.4$–0.8 it changes insignificantly, which permits to consider this range of conversion as the most appropriate for the activity measurements.

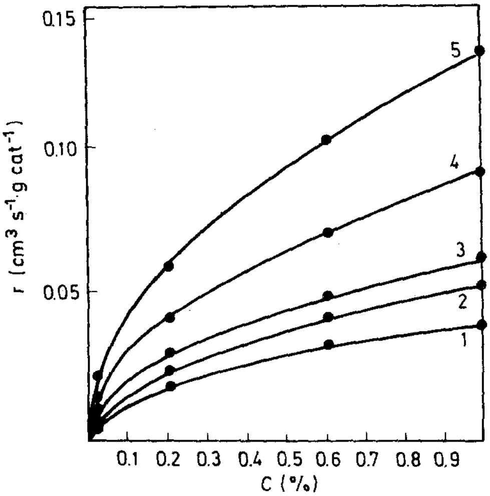

Fig. 1. Reaction rate as a function of CO concentration. 1 – 448 K, 2 – 463 K, 3 – 473 K, 4 – 498 K, 5 – 523 K

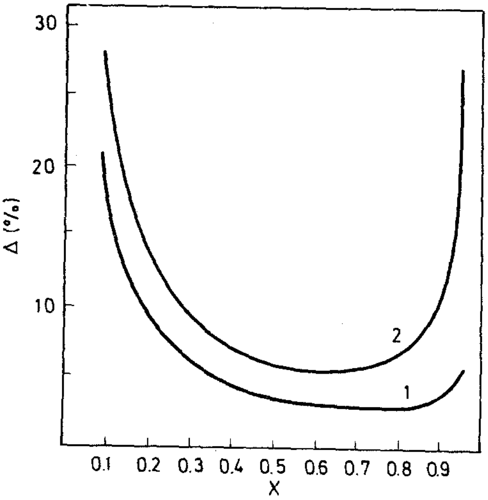

Fig. 2. Systematic (1) and random (2) errors as a function of CO conversion. T = 473 K, $C_O = 1.5\%$, catalyst weight is 2 g

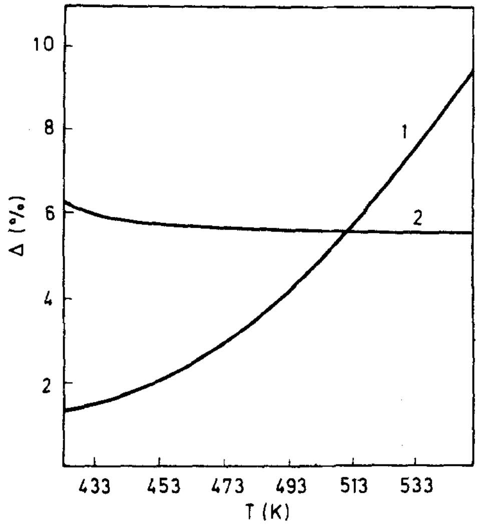

Fig. 3. Systematic (1) and random (2) errors as a function of temperature. $C_0 = 1.5\%$, $X = 0.6$, catalyst weight is 2 g

With increasing temperature (Fig. 3), the random error slightly decreases, whereas the systematic error increases so that at a definite temperature (~ 513 K) it exceeds the random error. This can be attributed to the fact that with increasing temperature the reaction rate rises and in order to maintain the constant conversion level, the inlet stream should be raised. In turn this decreases the circulation number. Up to the temperature of 513 K the systematic is lower than the random error, i.e. it is statistically insignificant. Assuming that the systematic error must be at least by 50% lower than the random error, and judging from Fig. 2, measurements should be carried out at ~ 473 K.

The same situation is also observed when the catalyst weight is increased. Figure 5 shows that the measurements must be performed at a catalyst weight of not more than 2 g (i.e. 10 grains). According to Ref. /7/ the number of simultaneously tested grains stipulates the reliability of the average activity determination within the batch. For 10 grains the relative confidence interval for the average activity determination is 7–9%.

The increase of the initial CO concentration decreases both the systematic and the random errors. The decrease of the former is attributed to the decreased inlet stream (to maintain the specified conversion level). The drop of the random error can be attributed to the increased difference of C_0 and C (since the accuracy of the C_0 and C measurements is constant, the relative error of their difference deter-

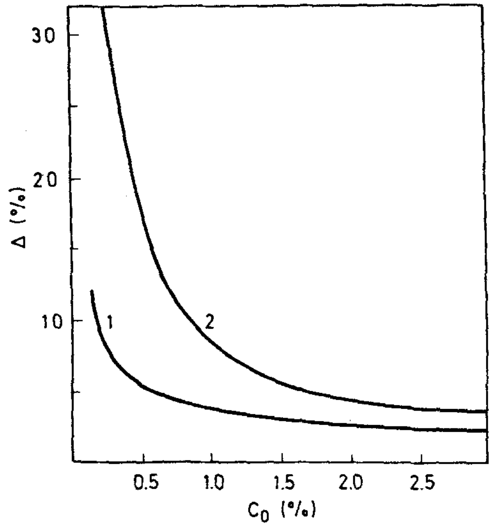

Fig. 4. Systematic (1) and random (2) errors as a function of the inlet CO concentration. T = 473 K, X = 0.6, catalyst weight is 2 g

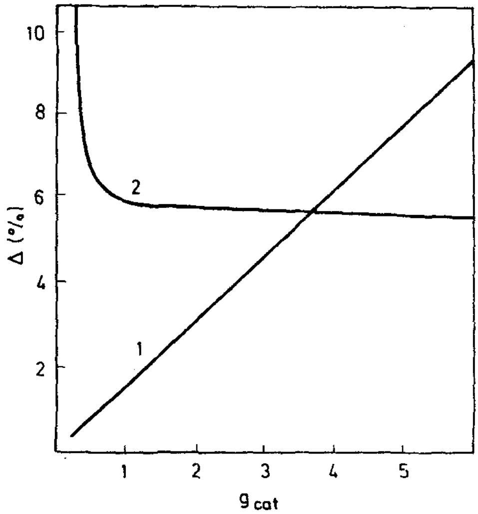

Fig. 5. Systematic (1) and random (2) errors as a function of the catalyst weight. T = 473 K, C_0 = 1.5%, X = 0.6

mination must decrease with the C_o–C increase). Assuming that Δ_{sys} is at least 50% lower than Δ_{ran} and the CO concentration in the loop (C) must be within its industrial range (up to 1%), it can be predicted that C_o must be no more than 1.5%. In this case at $X = 0.4–0.8$ the CO concentration in the loop will be 0.9–0.3%.

So it is recommended to measure the activity of the TO-2 commercial methanation catalyst under the conditions: $C_o = 1.5\%$, $T = 473$ K, $X = 0.4–0.8$, catalyst weight of 2 g and circulation velocity of no less than 800 l/h.

Under these conditions the K measurement error will not be higher than 6–7%. This means that for the discrimination of two catalyst samples by this method, their activity must differ by not less than 7–8%.

The suggested method can be used to choose the test conditions for other types of methanation and other catalysts.

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