

## PULSE DYNAMIC MEASUREMENTS OF OXYGEN CHEMISORPTION ON SULPHIDED Co-Mo/Al<sub>2</sub>O<sub>3</sub> CATALYST — EFFECT OF EXPERIMENTAL CONDITIONS

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The effects of temperature and time regime of individual steps of the methodic procedure (*i.e.* catalyst drying, sulphidation, purification of the sulphided surface by inert gas, and chemisorption) on pulse dynamic measurements of oxygen chemisorption on commercial sulphided Co-Mo/Al<sub>2</sub>O<sub>3</sub> catalyst have been studied. The strongest effect was exerted by the chemisorption temperature and by the temperature and time of purification of the surface of sulphided catalyst. Optimum experimental conditions for testing catalysts of this type by the described chemisorption method are proposed.

Specific chemisorption of oxygen on cobalt-molybdenum hydrorefining catalysts has widely been studied and used as one of the methods for characterizing surface properties of the catalysts of this type. It is applicable for both the reduced un sulphided and sulphided catalysts. Chemisorption on reduced un sulphided catalysts has been the subject of many studies, and the method has been extensively standardized. This does not hold for the chemisorption on sulphided catalysts, the surface of which is chemically more complex and chemisorption measurements are more sensitive to a great number of experimental variables. As different authors have used different conditions in chemisorption measurements and different pretreatment of the catalysts, comparison of the results reported for sulphided catalysts by different authors is very difficult.

In chemisorption measurements with sulphided catalysts, the pulse dynamic arrangement of the experiment is prevailing. In comparison with static methods, the advantage of which is high precision of the measurement, dynamic methods are less elaborate and less time-consuming. Furthermore, using a flow apparatus, one can easily perform catalytic reaction and chemisorption measurements in the same instrument, which enables to characterize catalyst surface in the working state.

In pulse dynamic measurements on sulphided catalysts, it is most important to find appropriate temperature of chemisorption. Chemisorption capacity depends on temperature over broad range<sup>1</sup>. Kinetic factor which makes possible to suppress sub-surface reaction with oxygen at higher temperatures, limits the use of low temperatures suitable for performance of static methods. At -78°C, the dynamic method afforded much lower values for sulphided catalysts compared to the static method<sup>1</sup>, likely due to kinetics of the process. Very good agreement was found between the values measured by static method at -78°C and data obtained by dynamic method at 25°C (refs<sup>1,2</sup>). Chemisorption data at 25°C were successfully correlated with catalytic activity<sup>3-6</sup>. However, Cornet *et al.*<sup>6,7</sup> found for sulphided nickel catalysts that the slope of temperature dependence of chemisorption around 25°C is relatively high. The region in which the de-

pendence on temperature was negligible was around 60°C, and data obtained at this temperature correlated well with catalytic activity.

A number of contradictory results obtained with comparable catalytic systems has been explained by differences in pretreatment of catalysts. The activation regime represents, however, rather equivalent subject of research, and its necessary standardization for practical testing of the catalysts should at present be considered as optional.

Another question is, however, purification of the catalyst surface from the molecules adsorbed reversibly during previous catalyst pretreatment; the purification is made by a stream of inert gas prior to chemisorption measurement. Conditions used vary from 15 min at 25°C (ref.<sup>3</sup>) to 2 h at 420°C (ref.<sup>6</sup>) and authors differ in their views on the necessary time and temperature of flushing. When studying this problem, Bodrero and Bartholomew<sup>1</sup> have found that the decrease of purification temperature from 300–400°C to 25°C affects strongly oxygen consumptions, and that the changes are different for pure MoS<sub>2</sub> and the supported catalysts. In the case of sulphided nickel catalysts<sup>6</sup>, chemisorption data were independent of the time of purification of the catalyst with helium only at times longer than 2 h at 420°C.

In our laboratory, the pulse dynamic method of oxygen chemisorption was applied to characterization of HDS catalysts and to correlation of chemisorption data with activity of the catalysts. We examined first reduced catalysts<sup>8–10</sup> and then sulphided ones<sup>11</sup>. For the latter catalysts chemisorption experiments showed worse reproducibility compared to the reduced catalysts<sup>10</sup>, in which case the results of repeated measurements lied within 10 per cent range. For this reason we resumed the more detailed investigation of individual steps of the methodic procedure. The major part of our previous study was made with Czechoslovak commercial Co–Mo/Al<sub>2</sub>O<sub>3</sub> catalyst. Therefore, we worked out methodology of chemisorption measurements for this catalyst. In spite of this fact, we consider the results obtained as useful in more general way. With the catalyst chosen, the aim of this work was to examine (i) the dependence of chemisorption capacity on temperature and (ii) the effect of procedure conditions of individual steps of the method (drying, sulphidation, purification of catalyst surface by inert gas and tempering, chemisorption) on oxygen consumption data and their reproducibility.

## EXPERIMENTAL

### Chemicals

Czechoslovak commercial catalyst Cherox 36-01 (Chemopetrol, Chemical Works Litvínov). Chemical composition according to the producer: 14.1 wt. % MoO<sub>3</sub>, 3.55 wt. % CoO. Textural properties of the oxide catalyst (determined by Sorptomatic Carlo Erba, *cf.*<sup>11,12</sup>); BET area 170 m<sup>2</sup> g<sup>-1</sup>, pore volume 0.56 cm<sup>3</sup> g<sup>-1</sup>, the most frequent pore radius 2.2 nm. Helium (Messer Griesheim, Austria), 99.996% purity (according to the producer) was freed from oxygen by passing the gas through deoxidizing agent of the composition 42 wt. % MnO<sub>2</sub>, 52.8 wt. % MgO, 5.2 wt. % Cr<sub>2</sub>O<sub>3</sub> which was activated by the reduction with hydrogen at 400°C; then, helium was dried by Calsit 5A molecular sieve. Hydrogen, electrolytic (Technoplyn, Prague), was freed from eventual admixtures of oxygen by passing over Cherox 40-00 palladium catalyst and dried

by Calsit 5A molecular sieve. Hydrogen sulphide (Merck, Darmstadt, F.R.G.), 99.6% purity (according to the producer), was used in supplied form.

### Apparatus

The apparatus allows to measure oxygen chemisorption by pulse chromatographic method on reduced or sulphided catalysts as well as to test their activity in hydrogenation reaction (*cf.*<sup>10,13</sup>). The catalyst is placed in a glass U-reactor of 4 mm internal diameter; the reactor can be placed either in the furnace equipped with thyristor temperature controller or in the corresponding cooling bath. Change-over switch on the reactor inlet serves to connection of the reactor alternately to one of the separate gas ways. Gases are taken from pressure cylinders and led through purification units and flow meters. By the first gas way, nitrogen, hydrogen, hydrogen sulphide or gaseous reaction components mixed in arbitrary ratio can be fed. The second gas way serves for feeding helium into which oxygen can be added in discrete pulses *via* six-way valve with the loop of 0.22 ml-volume. The dosing valve is controlled pneumatically by the time switch. Helium is introduced into the reactor through the reference cell of a thermal conductivity detector. After the reactor outlet, the system of two change-over switches makes possible to lead gases directly to the outgas, to the chromatograph equipped with a flame ionization detector (when analyzing reaction products, *cf.*<sup>10,13</sup>) or to the measuring cell of the thermal conductivity detector (when detecting the amount of adsorbed oxygen). The apparatus outlet is connected with a checking bubble flow meter. The signals from detectors are transmitted to a linear recorder and the results are evaluated from the graphical record.

### Example of the Procedure

The catalyst supplied in the form of pellets was crushed and screened to 0.16–0.315 mm particle size. A total of 0.5 g of the catalyst was mixed with the same volume of fine glass balls and charged to the reactor. The residual volume of the reactor was filled with fine glass balls. In the standard procedure, the sample was warmed up to 400°C in 15 min in a stream of helium (50 ml min<sup>-1</sup>) and dried at this temperature for 1 h. Then, it was sulphided with a mixture of hydrogen and hydrogen sulphide in 10 : 1 ratio (hydrogen 50 ml min<sup>-1</sup>, hydrogen sulphide 5 ml min<sup>-1</sup>) at 400°C for 1 h and at the same temperature it was flushed with the helium for another hour (50 ml min<sup>-1</sup>). After this period, the reactor was removed from the furnace and tempered at room temperature for another hour; 20 min before tempering was finished, the helium stream from the reactor was being introduced into the measuring cell of the detector. Helium flow rate was adjusted to 30 ml min<sup>-1</sup> and at the same time, oxygen was introduced into the dosing loop. Oxygen pulses were fed to helium stream at one minute intervals. The height of the peaks in the graphical record has reached constant value (equating to 0.22 ml min<sup>-1</sup>) after 20 to 22 min. All the volumes reported in this study are those at 20°C and 100 kPa.

## RESULTS AND DISCUSSION

### *Dependence of Oxygen Consumption on Chemisorption Conditions*

*Effect of temperature.* The procedure described in the previous chapter was used and the chemisorption was measured at temperatures -78, 0, 20, 40, and 60°C. However, the catalyst tempering after flushing with helium was made in such a way that after 15 min-cooling at room temperature, the reactor was placed into cooling

bath ( $-78^{\circ}\text{C}$ ; ethanol-solid  $\text{CO}_2$ ,  $0^{\circ}\text{C}$ ; water-ice) or into the furnace. The results of these measurements are shown in Fig. 1.

It is seen that in the region from  $-78$  up to c.  $20^{\circ}\text{C}$ , the chemisorption is not complete and oxygen consumption increases non-linearly with temperature. Apparently, the oxygen uptake in this region is determined predominantly by kinetic factors, *i.e.* by the rate of chemisorption and its temperature dependence. At  $-78^{\circ}\text{C}$ , the reproducibility of measurements was the worst.

Between  $20$  and  $40^{\circ}\text{C}$ , one finds a certain delay in the chemisorption curve. Over the range of twenty grades, the average oxygen consumption increases only by 10 per cent. The region of room temperature was therefore investigated in more detail. The initial series of data lied randomly within  $0.95$ – $1.04$   $\text{ml g}^{-1}$ , the average value being  $1.00$   $\text{ml g}^{-1}$ . In the course of further study, the measurements in this region were repeated ten times in the period of several months, using temperatures from  $19.5$  to  $26^{\circ}\text{C}$ . Experimental values are presented in Table I. The average oxygen

TABLE I  
Oxygen uptake determined at room temperature

Temp., $^{\circ}\text{C}$	Oxygen uptake $\text{ml g}^{-1}$	Temp., $^{\circ}\text{C}$	Oxygen uptake $\text{ml g}^{-1}$
19.5	0.94	24	0.98
20	1.01	24	0.94
20	1.04	24	0.98
23	0.95	26	1.06
23.5	1.03	26	1.04

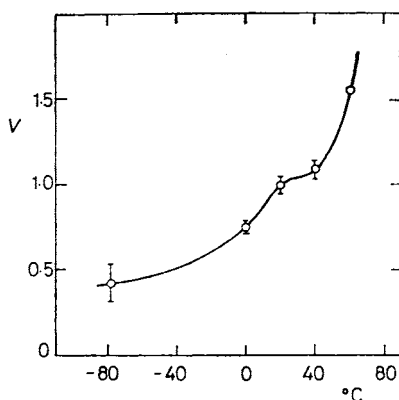


FIG. 1  
Dependence of oxygen uptake  $V$  ( $\text{ml g}^{-1}$ ) on temperature of chemisorption ( $^{\circ}\text{C}$ ). Points are the average values of three measurements, the abscissae show maximum deviations. The point found at  $60^{\circ}\text{C}$  is illustrative only, because of the increase of oxygen uptake with time

consumption was again  $1.00 \text{ ml g}^{-1}$  and all the values lied within 12 per cent range, without being distinctly dependent on temperature.

At  $40^\circ\text{C}$ , the oxygen consumption still achieved reliably a constant value and was well reproducible (10% range). At  $60^\circ\text{C}$ , however, the oxygen uptake increased steeply, the constant value was not achieved even after 45 min-titration, although this increase was very slow after 30 minutes.

The region of slow chemisorption ( $-78$  and  $0^\circ\text{C}$ ) was subjected to further examination, the chemisorption experiment being complemented by the additional titration at room temperature. After the first titration had been completed, the reactor was removed from the bath and tempered again at room temperature for 90 min after chemisorption at  $-78^\circ\text{C}$  and for 60 min after that at  $0^\circ\text{C}$ . After this tempering, oxygen was again allowed to chemisorb on catalyst surface. The results of the additional titration were very well reproducible. The values of the first and second titration were summed up. The highest total oxygen uptakes obtained by the additional titration after chemisorption either at  $-78^\circ\text{C}$  or at  $0^\circ\text{C}$  did not differ essentially from the lowest values determined directly at  $20^\circ\text{C}$ .

The results allow to make the following conclusions: For the catalyst chosen, the temperature region of good reproducibility of the measurements is from  $0$  to  $40^\circ\text{C}$ , the region of the minimal temperature effect being from  $20$  to  $40^\circ\text{C}$ . Room temperature ( $20$ – $25^\circ\text{C}$ ) was proved as suitable for dynamic measurements and thus was used in the study of effects of other factors. Our results obtained at  $-78$  and  $0^\circ\text{C}$  with the additional chemisorption at  $20^\circ\text{C}$  agree well with data reported by Bodrero and Bartholomew<sup>1</sup>. At these low temperatures, the chemisorption in pulse dynamic arrangement does not proceed completely because of kinetic reasons and can continue at higher temperature on the same surface to attain saturation, in which case oxygen uptake resumes the constant value. Contrary to this, above  $40^\circ\text{C}$ , sub-surface reaction of the catalyst with oxygen is obviously taking place and the oxygen uptake does not attain a constant value.

*The effect of flow rate of carrier gas.* In addition to the temperature dependence of chemisorption, we have also studied the effect of flow rate of the carrier gas. Using the constant volume of oxygen pulses and the constant interval between them, we have performed measurements with three different values of helium flow rate. The following data were obtained:

Flow rate, $\text{ml min}^{-1}$	15	30	60
$\text{O}_2$ uptake, $\text{ml g}^{-1}$	0.99	1.00	1.00

The reported oxygen consumptions represent the average of three measurements. Individual experimental values lied again within 10% range and the general feature of the graphical record in the decisive region of the initial peaks has not been changed either, only the time needed to complete the saturation of catalyst surface changed

in the corresponding way – at the lower flow rate this time decreased by 3 minutes in average, at the higher flow rate it increased by 5 minutes. This provides information about kinetics of the process, but it is unessential for estimating the chemisorption capacity. Therefore, for the conditions of the standard experiment, we have chosen the helium flow rate  $30 \text{ ml min}^{-1}$ , 0.22 ml-pulses of oxygen being fed into helium stream at one minute intervals.

#### *Dependence of Oxygen Consumption on Conditions of Catalyst Pretreatment*

*Catalyst drying.* The catalyst contained a certain amount of moisture and had to be dried in inert gas at elevated temperature. In previous work<sup>11</sup> we used nitrogen (for economic reasons) which was purified and dried in the same way as helium. However, we found later that already simple replacement of nitrogen by helium led to improved reproducibility of the results. Therefore, we decided to use helium as the inert gas in the whole procedure.

To obtain maximum values of chemisorption ( $\text{O}_2$  uptake) under standard conditions of the other steps of the procedure, the catalyst drying at least for 1 h at  $300^\circ\text{C}$  was necessary. At 400 and  $500^\circ\text{C}$ , sample drying for 30 min was sufficient. The prolonged drying over 1 h at 300 and  $400^\circ\text{C}$  did not change the values; at  $500^\circ\text{C}$  the prolonged drying caused mild increase in chemisorption values. We believe that in this case the increase is caused by the change in the extent of support calcination. For the standard procedure we have chosen drying at  $400^\circ\text{C}$  for 1 h, in view of the advantage which is represented by the use of the same temperature for the subsequent activation.

*Sulphidation conditions.* In our earlier work<sup>11</sup> we examined the dependence of oxygen chemisorption on temperature and on time of the preceding catalyst sulphidation. The curve of temperature dependence was relatively flat within  $350\text{--}450^\circ\text{C}$  region, with maximum around  $450^\circ\text{C}$ . Above  $450^\circ\text{C}$ , the values began to decrease; the decrease indicates that the catalyst in the activated state is sensitive to high temperature and apparently undergoes sintering. The curve of time dependence rises steeply for all the temperatures investigated (300, 400, and  $500^\circ\text{C}$ ) up to 30 min, then the values become independent of time of the sulphidation. As the standard experimental procedure in this work we chose sulphidation at  $400^\circ\text{C}$  for 1 h, *i.e.* temperature of the flat part of the curve slightly below maximum.

Another factor in the sulphidation process which may affect the chemisorption capacity is space velocity of the sulphidation mixture. In the work<sup>11</sup> we used  $200 \text{ ml}^{-1} \cdot \text{min}^{-1}$ , in order to preserve activation conditions used in parallel investigations of other aspects of the activation process. In the chemisorption measurements on reduced catalysts<sup>10</sup>, the space velocity of hydrogen  $100 \text{ ml g}^{-1} \text{ min}^{-1}$  was used. With respect to our further intentions we considered this value as more suitable. In the experiments in which half the flow rate of the sulphidation mixture was used,

we found that even this relatively small change influences somewhat the chemisorption of oxygen. For purposes of comparison we present the following data:

Space velocity, ml g <sup>-1</sup>	100	200
O <sub>2</sub> consumption, ml g <sup>-1</sup>	1.00	1.09

The oxygen consumption at the higher flow rate of the gas mixture is the average of three measurements, at the lower one, the average of all ten measurements carried out under standard conditions. With both space velocities of the sulphidation mixture, the oxygen consumption was well reproducible. For the standard procedure, we chose the space velocity 100 ml g<sup>-1</sup> min<sup>-1</sup>. The higher space velocity used in our previous work<sup>11</sup> is obviously one of the reasons of the higher absolute values of chemisorption found for the same catalyst.

*Purification of the sulphided surface by inert gas.* We have examined several regimes of surface purification by inert gas. The experiments can be divided into two groups: (i) investigation of the influence of the flushing time in the temperature region of chemisorption measurements (20–25°C) and (ii) investigation of the influence of time and temperature of flushing in the temperature region 300–500°C. Catalyst drying and sulphidation was carried out by the standard procedure. In the first group of experiments, the reactor was removed from the furnace after completion of the activation and then the catalyst was flushed with the stream of the sulphidation mixture or of helium for 30 min during cooling. In some cases, further flushing with helium at room temperature was performed and the chemisorption was then measured. The results are summarized in Table II. In the second group of experiments, helium was introduced into the reactor after completion of the activation, and the temperature was adjusted in ten minutes to the chosen temperature of

TABLE II

Dependence of oxygen uptake on time of flushing with helium at chemisorption temperature without previous flushing at elevated temperatures

Gas used to cooling after sulphidation	Time of further helium flushing at room temp., min	Oxygen uptake ml g <sup>-1</sup>
Sulphidation mixture	20	1.42
Sulphidation mixture	60	1.19
Helium	0	1.41
Helium	60	1.18

flushing. After the appropriate time, the reactor was removed from the furnace and after 15 min-cooling to room temperature it was tempered in a stream of helium for another 1 hour. The results are presented in Table III. The oxygen consumptions given in both tables are again the average of three experimental values lying within 10% range.

Comparison of the oxygen consumption found by the standard method ( $1.00 \text{ ml} \cdot \text{g}^{-1}$ ) with that given in Table II shows that flushing of the catalyst with inert gas only at the temperature of chemisorption measurements leads clearly to the distortion of the results toward the higher values and depends on the time of this flushing. In the cases in which flushing with the inert gas did not exceed 30 min, the values were increased by c. 40% even in the case where the flushing was started at activation temperature. The results in Table III show that at 1 h-flushing at  $300^\circ\text{C}$  the oxygen consumption was still mildly increased. At  $400^\circ\text{C}$ , prolongation of flushing time did not result in further decrease in oxygen uptake. At  $500^\circ\text{C}$ , relatively significant decrease of oxygen uptake was observed after 1 h-flushing, while after 30 min-flushing, data agreed well with the results obtained with flushing at  $400^\circ\text{C}$ . It seems likely that the surface of the sulphided active components of the catalyst used undergoes sintering when exposed to the temperature of  $500^\circ\text{C}$  for the time longer than 30 min.

As the standard experiment conditions we chose flushing with helium for 1 h at  $400^\circ\text{C}$  and 1 h-tempering under helium stream at the temperature of the measurement. The purification procedure of the sulphided surface by inert gas used in our work<sup>11</sup> was obviously one of the sources of our difficulties with reproducibility of the results. We used flushing at  $500^\circ\text{C}$  for 30 min, and the total time of cooling and tempering was another 30 min. This means that the catalyst was exposed to thermal conditions close to those at which sintering began to operate. This seems

TABLE III

Dependence of oxygen uptake on time and temperature of catalyst flushing with helium in  $300\text{--}500^\circ\text{C}$  region

Flushing with helium		Oxygen uptake $\text{ml g}^{-1}$
temp., $^\circ\text{C}$	time, min	
300	60	1.11
400	60	1.00
400	120	0.99
500	30	1.01
500	60	0.79



to be the cause of the necessity of exclusion of several experiments from calculation of average values because of sudden deviation toward lower values. The overall short time of flushing and tempering of the reactor was at the same time one of the reasons of the higher absolute value of the average oxygen uptake. Nevertheless, trends in the dependences reported in the work<sup>11</sup> can still be considered as correct ones. On the other hand, for purposes of comparison with other results, the absolute values of reported oxygen consumptions should be considered as increased due to the effect of the procedure used.

## CONCLUSIONS

With the use of the apparatus for pulse dynamic measurements of oxygen chemisorption, well reproducible results were obtained for sulphided HDS catalyst, the time needed to perform the experiment by the standard procedure being 6 h. Based on these experiments, the following conditions were chosen for the standard procedure: Catalyst drying in helium (space velocity  $100 \text{ ml g}^{-1} \text{ min}^{-1}$ ) for 1 h at  $400^\circ\text{C}$ , sulphidation at  $400^\circ\text{C}$  for 1 h ( $\text{H}_2 : \text{H}_2\text{S}$  ratio = 10 : 1, space velocity of the mixture  $100 \text{ ml g}^{-1} \text{ min}^{-1}$ ), flushing with helium at  $400^\circ\text{C}$  for 1 h (space velocity  $100 \text{ ml g}^{-1} \text{ min}^{-1}$ ), tempering in helium for 1 hour at room temperature ( $20\text{--}25^\circ\text{C}$ , space velocity  $100 \text{ ml g}^{-1} \text{ min}^{-1}$ ), oxygen chemisorption at room temperature, helium space velocity  $60 \text{ ml g}^{-1} \text{ min}^{-1}$  and oxygen pulses  $0.22 \text{ ml}$  fed at 1 min-intervals.

Not for all the factors on which the chemisorption capacity is dependent one can find the region in which oxygen uptake is constant within certain range (chemisorption temperature, activation temperature). Similarly, the quality of commercially produced catalyst is not perfectly uniform. The reproducibility of measurements, characterized by ten up to twelve per cent range of individual experimental values, cannot be obviously improved, considering the above circumstances. Provided that the characteristics of the catalyst determined by this method is the equivalent molybdenum area EMA, as defined by Parekh and Weller<sup>14</sup>, and its calculation is made with the use of the conversion factor  $13.6 \text{ m}^2 \text{ ml}^{-1}$  reported by these authors<sup>14</sup>, then one obtains for the average oxygen uptake  $1.00 \text{ ml g}^{-1}$  on Cherox 36-01 the value of EMA  $13.6 \text{ m}^2 \text{ g}^{-1}$  and for boundary conditions  $12.8$  and  $14.4 \text{ m}^2 \text{ g}^{-1}$ , respectively. This documents that the results of one measurement can be regarded only as the starting values and that for obtaining the more precise information the average of several measurements, at least two or three, is needed, which, furthermore, should lie within 10% range at maximum.

The method of oxygen chemisorption in the experimental arrangement reported in this work is thus the acceptable compromise for the evaluation of surface properties of HDS catalysts of Co-Mo/ $\text{Al}_2\text{O}_3$  type. However, the method is not suitable for conclusive characterization of such changes of surface properties of the catalyst which lead to the difference in EMA smaller than 15 per cent.

At present, we extend the study of the activation process of Co-Mo/Al<sub>2</sub>O<sub>3</sub> catalyst with intention to verify the correlation of the chemisorption capacity controlled by the activation regime with the catalytic activity in hydrogenation reaction<sup>13</sup>.

#### REFERENCES

1. Bodrero T. A., Bartholomew C H.: *J. Catal.* **84**, 145 (1983).
2. Bodrero T. A., Bartholomew C. H., Pratt K. C.: *J. Catal.* **78**, 253 (1982).
3. Tauster S. J., Pecoraro T. A., Chianelli R. R.: *J. Catal.* **63**, 515 (1980).
4. Tauster S. J., Riley K. L.: *J. Catal.* **67**, 250 (1981).
5. Tauster S. J., Riley K. L.: *J. Catal.* **70**, 230 (1981).
6. Bachelier J., Duchet J. C., Cornet D.: *J. Phys. Chem.* **84**, 1925 (1980).
7. Bachelier J., Duchet J. C., Cornet D.: *Bull. Soc. Chim. Belg.* **90**, 1301 (1981).
8. Vyskočil V., Tomanová D.: *React. Kinet. Catal. Lett.* **10**, 37 (1979).
9. Uchytíl J., Beránek L., Zahradníková H., Kraus M.: *Appl. Catal.* **4**, 233 (1982).
10. Zahradníková H., Kárník V., Beránek L.: *Collect. Czech. Chem. Commun.* **50**, 1573 (1985).
11. Stuchlý V., Zahradníková H., Beránek L.: *Appl. Catal.*, in press.
12. Stuchlý V., Beránek L.: *Appl. Catal.*, in press.
13. Zahradníková H., Beránek L.: *Collect. Czech. Chem. Commun.*, to be published.
14. Parekh B. S., Weller S. W.: *J. Catal.* **47**, 100 (1983).

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