

CHARACTERIZATION OF SUPPORTED RUTHENIUM CATALYSTS BY THERMAL ANALYSIS *

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ABSTRACT

The reduction–oxidation behaviour of unsupported and supported ruthenium components has been examined and the extent of metal–support interaction characterized. The sintering stability of the ruthenium crystallites on alumina and silica supports has been studied through reduction–oxidation cycles by DTA and the influence of the chloride impurities on the reduction–oxidation behaviour has also been examined. Finally, reduction kinetic parameters have been determined by the Freeman–Carroll procedure.

INTRODUCTION

The catalytic properties of ruthenium catalysts have been found to be different when incorporated on different supports, and these differences have been attributed to the varied extent of interaction between the metal component and the supports [1–5]. Usually the extent of metal–support interaction is correlated with the reducibility of the metal component. In other words, strong metal–support interaction is generally associated with low reducibility of the metal component, and weak metal–support interaction usually renders the metal component amenable to easy reduction. Thus, a study of the reduction behaviour of the supported ruthenium catalysts can provide information concerning the extent of metal–support interaction.

To study the reduction behaviour of a supported metallic catalyst, the commonest method is the temperature programmed reduction (TPR) technique. Although this method has a high sensitivity for the detection of reducible species, its sensitivity in quantitative determination is unsatisfactory, and its response is also rather slow [6]. On the other hand, the thermal

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analysis technique has the advantages which are lacking in the TPR method. For this reason, we initiated an investigation to study the reduction behaviour of ruthenium catalysts supported on alumina and silica by the thermal analysis method, and the results are reported in this paper. In this investigation differential thermal analysis (DTA) and thermogravimetry (TG) were employed to study the reduction-oxidation behaviour of unsupported and supported ruthenium components and to characterize the extent of the metal-support interaction. Then the sintering stability of the ruthenium crystallites on alumina and silica supports has been studied through reduction-oxidation cycles by DTA. The influence of the chloride impurities on the reduction-oxidation behaviour has also been examined. Finally, reduction kinetic parameters have been determined by the Freeman-Carroll procedure.

EXPERIMENTAL

Catalysts

All catalysts were prepared by the conventional impregnation method. The supports used were Al_2O_3 (surface area $250 \text{ m}^2 \text{ g}^{-1}$) and SiO_2 (surface area $278 \text{ m}^2 \text{ g}^{-1}$), grain size being 20–40 standard mesh. The supports were impregnated with aqueous RuCl_3 solutions, dried at 120°C in air, then calcined at 480°C for 4 h. Table 1 shows the mean crystallite size of the catalysts determined by electron microscope.

Experimental equipment and conditions

Reduction-oxidation experiments and reduction kinetics determination were performed on the medium temperature DTA unit of a Shimatsu DT-20B thermal analysis equipment. The experimental conditions were as follows

DTA reduction: sensitivity 25 V, heating rate $10^\circ\text{C min}^{-1}$, in H_2 atmosphere.

DTA oxidation: sensitivity 250 V, heating rate $10^\circ\text{C min}^{-1}$, in O_2 atmosphere.

TABLE 1

Crystallite size of supported Ru catalysts

1% Ru/ Al_2O_3	ca. 40 Å
1% Ru/ SiO_2	ca. 50 Å
5% Ru/ Al_2O_3	60–120 Å
5% Ru/ SiO_2	60–100 Å

DTA reduction kinetics: the same as in DTA reduction except suitable adjustment in sensitivity.

TG reduction-oxidation: detection range 5 mg, others were the same as in DTA reduction or oxidation.

Experimental procedure

The once-through reduction-oxidation DTA and TG measurements were carried out according to conventional procedures. The measurement of the reduction-oxidation-reduction cycles were performed in the following manner: first the catalyst sample was reduced in a temperature-programmed reduction mode up to 480 °C (first DTA), then cooled to room temperature. The sample chamber was then evacuated, and oxygen was introduced to oxidize the sample in a temperature-programmed oxidation mode to 200 °C. After this, the sample was again cooled to room temperature and the apparatus evacuated, then hydrogen was introduced, and the sample was reduced again in a temperature-programmed mode, as before, to 480 °C (second DTA). This cyclic procedure was carried out repeatedly by reoxidizing the sample in 300 and 480 °C to obtain the third DTA and fourth DTA data.

RESULTS AND DISCUSSION

Reduction-oxidation behaviour of unsupported RuCl₃

Since the composition of the catalysts after impregnation is RuCl₃/Al₂O₃ or RuCl₃/SiO₂, we first studied the unsupported RuCl₃ by the thermal

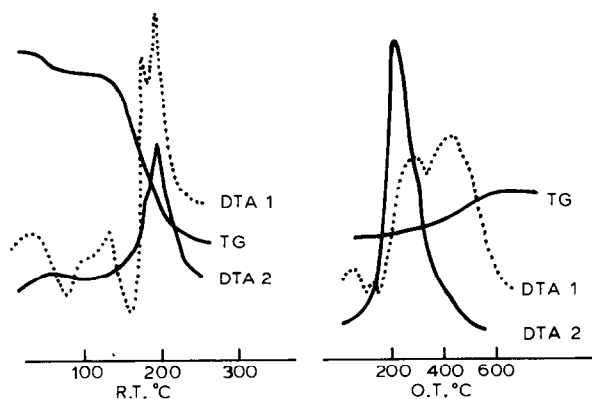
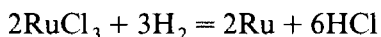


Fig. 1. DTA and TG reduction-oxidation curve of pure RuCl₃. DTA 1, large quantity sample (40 mg); DTA 2, small quantity sample (20 mg).

analysis technique to get some preliminary information. Figure 1 shows the DTA and TG curves in the reduction–oxidation processes of the RuCl_3 sample.

The curve DTA 1 shows an endothermic peak in the temperature range of 32–100°C, and we can see that there is also a corresponding weight-loss in the TG curve. According to the hygroscopic nature of RuCl_3 , this peak can be attributed to water-desorption. In the range 130–215°C the pair of doublet peaks are obviously the reduction peaks of RuCl_3 , the corresponding temperatures for the two peaks being respectively 168 and 193°C. From the TG curve it can be noted that there is a remarkable weight-loss corresponding to these reduction peaks. It is interesting to find that for the small quantity sample (DTA 2 curve), only a single peak appeared at a temperature of 186°C.

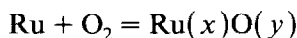
The reduction of RuCl_3 can be represented stoichiometrically by the following equation



Following this equation we confirmed by calculation from the weight-loss data that RuCl_3 is reduced completely to zero-valent ruthenium.

The oxidation curves in Fig. 1 represent the oxidation behaviour of the ruthenium formed from the reduction of RuCl_3 . We can see from the curve DTA 1 that, like the curve of RuCl_3 reduction, the oxidation of the reduced sample also gave a doublet peak, and the corresponding temperatures for the two peaks are 275 and 482°C. Meanwhile, weight-gain appeared in the corresponding TG curve. It is again interesting to find that for the small quantity sample (DTA 2) only one single peak at a temperature of 235°C is obtained.

The oxidation of metallic ruthenium can be represented as follows



Calculation from the weight-gain data allows us to conclude that the oxidation product of metallic ruthenium at these temperatures is RuO_2 .

Reduction–oxidation behaviour of supported RuCl_3

The reduction–oxidation data of pure RuCl_3 are utilized as a basis for the comparison of the reduction–oxidation behaviour of alumina and silica supported RuCl_3 samples, and the results are summarized in Fig. 2 and Table 2.

If the peak temperatures in Table 2 are taken as a measure of the ease of reduction or reoxidation of the Ru species, then the following sequences can be obtained

Reduction: $\text{RuCl}_3 < 1\% \text{ RuCl}_3/\text{SiO}_2 < 1\% \text{ RuCl}_3/\text{Al}_2\text{O}_3$

Oxidation: $\text{RuCl}_3 < 1\% \text{ RuCl}_3/\text{SiO}_2 < 1\% \text{ RuCl}_3/\text{Al}_2\text{O}_3$

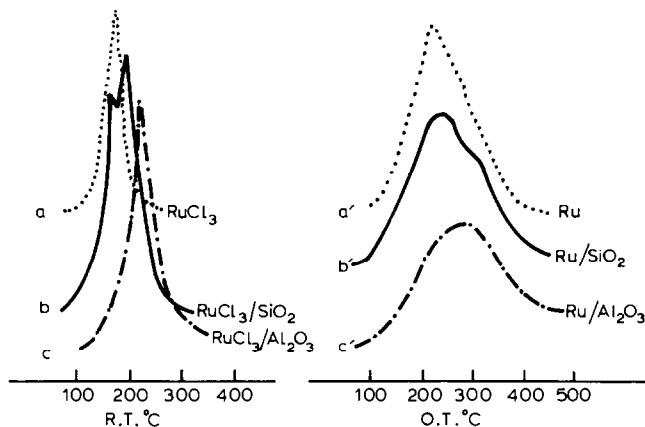


Fig. 2. Reduction-oxidation DTA curve of pure and supported RuCl_3 .

From the reduction sequence we can see that the two supported samples are more difficult to reduce than pure RuCl_3 ; this suggests that the existence of the supports yields an interaction between the ruthenium component and the supports and makes the reduction more difficult. Similarly, these results also substantiate the fact that when the supporting materials are different, the extent of interaction is also different. Thus, we can conclude from the reduction results that the interaction between the ruthenium component and alumina is stronger than that between the ruthenium component and silica. The reoxidation sequence gives further support to the above conclusions, and it is easy to conceive that the more loosely the Ru crystallites are bound to the support, the easier they will be activated by oxygen molecules.

In order to characterize the exact oxidation states of the supported ruthenium species after calcination in air, TG determination on an alumina-supported ruthenium catalyst with 5% ruthenium loading was performed. The principle and the determination results are illustrated in Fig. 3. The catalyst has first been calcined in air at 480°C for 4 h before the TG determination. The TG curve in Fig. 3 can be explained as comprising three different processes. In the temperature range $38\text{--}220^\circ\text{C}$, the weight-loss of

TABLE 2

DTA results of pure and supported RuCl_3

	RuCl_3		1% $\text{RuCl}_3/\text{Al}_2\text{O}_3$		1% $\text{RuCl}_3/\text{SiO}_2$	
	T.R. ($^\circ\text{C}$)	P.T. ($^\circ\text{C}$)	T.R. ($^\circ\text{C}$)	P.T. ($^\circ\text{C}$)	T.R. ($^\circ\text{C}$)	P.T. ($^\circ\text{C}$)
Reduction	140–228	186	150–290	218	80–248	195
Oxidation	179–450	235	166–396	286	140–367	245

T.R., temperature range; P.T., peak temperature.

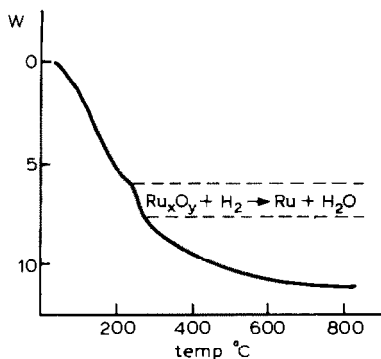


Fig. 3. TG curve during reduction of alumina-supported ruthenium catalyst after calcination in air.

the sample is due to elimination of adsorbed moisture. In the range 220–300°C the weight-loss is caused by the reduction of the ruthenium oxides, as has been shown from data in Table 2. The weight-loss at temperatures higher than 300°C and up to as high as 600°C is quite probably due to the removal of the chloride anions, which have been known to be combined strongly with the alumina support.

From the data of weight-loss in the reduction of ruthenium oxides, we can calculate and assess the oxidation state of the ruthenium oxide component on the supported catalyst, and the results are shown in Table 3. It is evident from the calculated and experimental data that the weight-loss calculated according to the second equation in Table 3 basically coincides with that obtained from experimental determination. Thus we can conclude that the ruthenium oxide on the alumina support after calcination in air at 480°C is RuO_2 .

Reduction–oxidation behaviour of supported RuO_2

Since the ruthenium oxide on the supported catalyst has been determined to be RuO_2 , then we can study the reduction–oxidation behaviour of this supported RuO_2 and compare it with that of unsupported pure RuO_2 . The DTA curves and data are shown in Fig. 4 and Table 4.

TABLE 3

Assessment of the oxidation state of the Ru species in the Al_2O_3 -supported Ru catalyst

Reduction process	Weight-loss (mg)	
	Theoretical	Experimental
$\text{Ru}_2\text{O}_3 + 3\text{H}_2 = 2\text{Ru} + 3\text{H}_2\text{O}$	0.24	0.34
$\text{RuO}_2 + 2\text{H}_2 = \text{Ru} + 2\text{H}_2\text{O}$	0.32	0.34

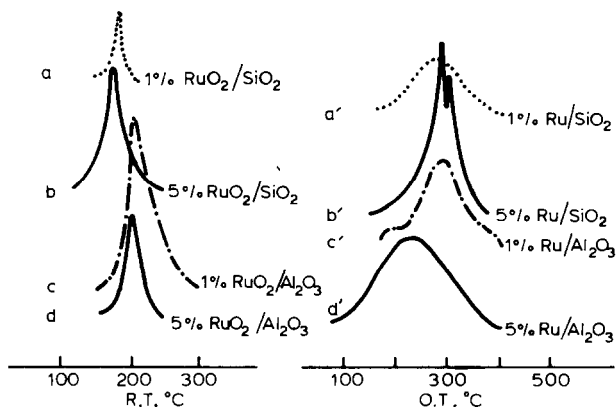


Fig. 4. Reduction-oxidation DTA curve of pure and supported RuO_2 .

Again, when we take the peak temperature as a measure of the ease of reduction or oxidation, we get the following sequences

Reduction: RuO_2 (160°C) < $\text{RuO}_2/\text{SiO}_2$ (177°C) < $\text{RuO}_2/\text{Al}_2\text{O}_3$ (200°C)

Oxidation: Ru (205°C) < Ru/SiO_2 (275°C) < $\text{Ru}/\text{Al}_2\text{O}_3$ (297°C)

The above sequences and data are in complete agreement with the foregoing RuCl_3 results, which indicates that unsupported RuO_2 is more easily reduced than the supported samples, and the reduced Ru is more easily reoxidized. Furthermore, of the two supports, silica has a weaker interaction with the ruthenium component, and thus undergoes reduction or reoxidation more easily than the alumina-supported catalyst.

Reducibility of supported ruthenium catalysts after repeated oxidation treatment

In order to study the sintering stability of the ruthenium component, alumina- and silica-supported ruthenium catalysts with 1% and 5% metal loadings were investigated by DTA reduction procedure after repeated oxidations. The results are shown in Figs. 5–8 and Tables 5 and 6.

TABLE 4

Reduction-oxidation DTA results of pure and supported RuO_2

	RuO_2		$\text{RuO}_2/\text{Al}_2\text{O}_3$		$\text{RuO}_2/\text{SiO}_2$	
	T.R. ($^\circ\text{C}$)	P.T. ($^\circ\text{C}$)	T.R. ($^\circ\text{C}$)	P.T. ($^\circ\text{C}$)	T.R. ($^\circ\text{C}$)	P.T. ($^\circ\text{C}$)
Reduction	130–280	160	178–265	200	167–198	177
Oxidation	150–380	235	235–400	297	165–355	275

Metal loading of the supported catalysts is 1% Ru ; T.R., temperature range; P.T., peak temperature.

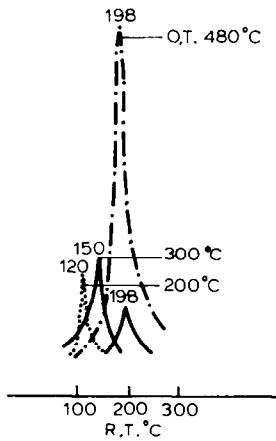


Fig. 5. Reduction DTA curve of 1% Ru/Al₂O₃.

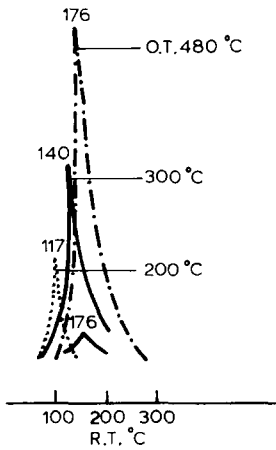


Fig. 6. Reduction DTA curve of 1% Ru/SiO₂.

TABLE 5

DTA reduction results of supported 1% Ru catalysts

Oxidation temperature (°C)	Ru/Al ₂ O ₃		Ru/SiO ₂	
	T.R. (°C)	P.T. (°C)	T.R. (°C)	P.T. (°C)
Initial sample	165–231	198	160–209	176
200	115–143	120	90–104	117
300	112–191	150	104–200	140
480	156–271	198	132–263	176

T.R., temperature range; P.T., peak temperature.

The results in Figs. 5 and 6 and Table 5 shows that after repeated oxidation with progressively higher temperatures between reductions, the DTA peak temperatures of both alumina- and silica-supported catalysts of 1% Ru increased with the temperature of oxidation treatments. This seems to imply that lower oxidation temperatures can only oxidize the outer crust of the ruthenium particles. However, when the reoxidation was performed at 480 °C, that is, the same temperature as the initial catalyst was calcined in air, the reduction DTA peak temperature coincides with that of the initial reduction peak. This reveals that the crystallites of the ruthenium component in the 1% Ru catalysts is very stable, so that even repeated reoxidation treatments will not change their dispersion or particle size very much. However, the DTA peak areas have been found to increase with increased number of reoxidation treatments, and the peak area after reoxidation at 480 °C has been found to increase remarkably compared to the initial reduction peak. This may very probably be due to the fact that in the initially reduced sample, a fairly large amount of chloride impurity was left in the RuO₂, and this chloride impurity was removed progressively with the repeated oxidation and reduction processes, yielding more and more clean ruthenium crystallites which are more susceptible to reduction.

It is also important to point out that under the same reoxidation temperature, the reduction peak temperature of the Ru/Al₂O₃ catalyst is always higher than that of the Ru/SiO₂ catalyst. This again confirms the foregoing conclusion that the interaction between the ruthenium component and alumina is stronger than that between the ruthenium component and silica.

Figures 7, 8 and Table 6 summarize the results of similar determinations on 5% ruthenium-loading catalysts supported on alumina and silica. From

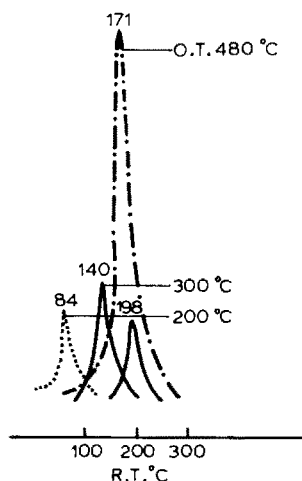


Fig. 7. DTA reduction curve of 5% Ru/Al₂O₃ catalyst.

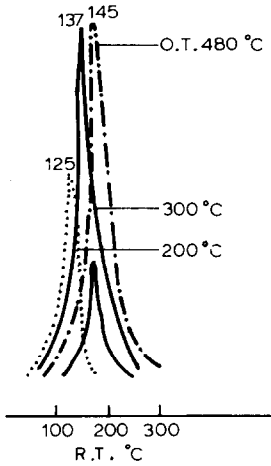


Fig. 8. DTA reduction curve of 5% Ru/SiO₂ catalyst.

these results it can be noted that the DTA reduction peak temperatures also increase with the increase in reoxidation temperatures. However, unlike the 1% Ru catalysts, when the reoxidation temperature was 480°C, i.e., the same as the calcining temperature of the initial sample, the DTA reduction peak temperature could not return to the peak temperature of the initial sample. This is probably because increasing the metal loading from 1% to 5% will cause the dispersion of the ruthenium component to decrease, resulting in larger particle sizes of the crystallites, so that agglomeration occurred during repeated reduction and oxidation treatments. This implies that compared with the 1% Ru catalysts, the sintering stability of the 5% catalysts is inferior.

Finally, it is noteworthy that the rate of increment in the DTA peak areas of the ruthenium component with the number of reoxidations is different for different supports irrespective of metal loading, and it has been found that the DTA peak areas in silica-supported catalysts increased faster than those

TABLE 6

DTA reduction results after repeated oxidation of supported 5% Ru catalysts

Oxidation temperature (°C)	5%Ru/Al ₂ O ₃		5%Ru/SiO ₂	
	T.R. (°C)	P.T. (°C)	T.R. (°C)	P.T. (°C)
Initial sample	140–217	198	57–265	173
200	50–120	84	52–172	125
300	60–220	140	60–242	137
480	70–260	171	60–258	145

T.R., temperature range; P.T., peak temperature.

of the alumina-supported catalysts. This can be explained by the removal of the chloride impurity being easier in silica-supported catalysts than in alumina-supported ones.

Calculation of the reduction kinetic parameters for supported RuO₂ catalysts

The foregoing conclusions that different supports can exert different extents of interaction on the ruthenium component, which in turn can affect the reducibilities of the ruthenium oxides and the ease of chloride removal, can be further verified by the results of the reduction kinetic treatments from the DTA data. For this purpose, the Freeman–Carroll method is employed to calculate the kinetic parameters from the DTA data of the initial reduction process as well as the reduction process after reoxidation at 480 °C for the supported RuO₂ catalysts. The linearized equation of this method is as follows

$$\Delta \log(dc/dt)/\Delta \log(1 - c) = n - E/2.303R\Delta(1/T)/\Delta \log(1 - c)$$

where n stands for reaction order, c for conversion, E for reaction activation energy, R for gas constant, t for time and T for temperature.

In order to confirm that the treatment of the DTA data obtained in our equipment by the Freeman–Carroll method is justified, we first use this method to calculate the DTA data of the decomposition of calcium formate, as the kinetic parameters are known from the literature. Figure 9 is a plot of $\Delta \log (dc/dt)/\Delta \log(1 - c)$ vs. $\Delta (1/T)/\Delta \log(1 - c)$, and the activation energy was calculated from the slope of the straight lines. Then the reaction orders were obtained from the intercepts. The results so obtained are compared with those from the literature, as shown in Table 7.

From the comparison in Table 7 we can see that the employment of the

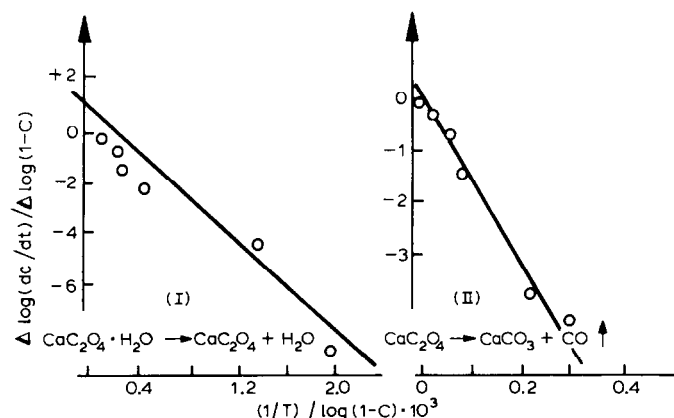


Fig. 9. Linear plots of calcium formate decomposition data.

TABLE 7

Comparison of kinetic parameters of the decomposition of calcium formate

		Freeman–Carroll [7]	Gurrieri et al. [8]	This work
Method		TG	DTG	DTA
Step I	<i>n</i>	1		1
	<i>E</i>	22	21.1	20.7
Step II	<i>n</i>	0.7		0.7
	<i>E</i>	74	73.5	74.1

Freeman–Carroll method to treat the DTA data from our determination is consistent with those reported in the literature.

Accordingly, the same procedure was employed to calculate the DTA data of the supported RuO₂ catalysts, and the results are shown in Table 8. These results show that all the reductions, irrespective of metal loadings and treating conditions, have a reaction order of 1. The activation energy, however, is not the same for catalysts with different supports or different metal loadings. First, we note that for catalysts with the same metal loading, the alumina-supported catalysts always have activation energies higher than those of the silica-supported counterparts. This is consistent with the foregoing conclusions in that the metal–support interaction is stronger for the alumina-supported catalysts than in the case of the silica-supported catalysts, so that higher energy will be needed to accomplish the reduction process of the alumina-supported RuO₂. As for the same support, it is rather interesting to find that, with one exception, the 5% Ru catalysts all have higher activation energies than the 1% catalysts. This may be related to the higher amount of chloride impurity remaining in the 5% Ru catalysts which hinders the reactivity of the RuO₂ species with hydrogen. Finally, as an exception, the reduction activation energy of the reoxidized silica-supported 5% catalyst turned out to be nearly the same as the silica-supported 1% catalyst. This can be explained as further evidence that the chloride impurity is easily removed during the course of repeated reduction and oxidation.

TABLE 8

Kinetic parameters from DTA reduction of supported RuO₂ catalysts

	RuO ₂ /Al ₂ O ₃				RuO ₂ /SiO ₂			
	Initial		Reoxid.		Initial		Reoxid.	
	<i>n</i>	<i>E</i>	<i>n</i>	<i>E</i>	<i>n</i>	<i>E</i>	<i>n</i>	<i>E</i>
1% Ru	1	30.50	1	19.95	1	22.90	1	13.64
5% Ru	1	63.38	1	27.46	1	35.19	1	13.10

Initial, reduction of the initial sample; Reoxid., reduction after reoxidation at 480 °C.

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