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HYDROGEN OXIDATION OVER Fe_2O_3 - Al_2O_3 SOLID SOLUTIONS

By

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Abstract

Fe_2O_3 -in- Al_2O_3 solid solution type systems, together with the pure components were prepared by spray-decomposition technique: by thermal decomposition at 500°C of the aerosol of the aqueous solution of the nitrates. Solid state properties were characterized by X-ray analysis, scanning electron-microscopy, IR, visible and EPR spectroscopy.

These systems contain iron in different surroundings. Increasing the concentration, isolated Fe^{3+} ions disappear and develop clusters with increasing iron-iron interaction. The low-temperature preparation technique promotes the formation of oversaturated solid solutions, too.

The effect of surroundings of Fe^{3+} upon the catalytic behaviour was tested in the hydrogen oxidation reaction in a flow-system microreactor. It was concluded that in this reaction the only essential neighbourhood effect is whether Fe^{3+} ions are isolated or not. Above 1 molar % concentration the activity of the samples was proportional to the iron content either in real solid solutions or in hematite phase.

Introduction

The present work has been undertaken to examine Fe_2O_3 - Al_2O_3 solid solution type catalysts, prepared by spray-decomposition technique.

The study of oxide solid solutions as catalysts has developed steadily over the past 10-15 years.^{1,2)} Besides their practical importance these systems serve as useful model substances yielding interpretable experimental data for the elucidation of the nature of catalytic behaviour.

Phase-equilibrium data show that in the Fe_2O_3 - Al_2O_3 system there is a limited mutual solubility of the components: hematite enters into solid solution with corundum up to some 10 molar %. Above this concentration there forms a two-phase solid solution system: hematite in corundum plus corundum in hematite.^{3,4)}

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In the lower iron-concentration range the samples represent Fe^{3+} in various surroundings: dilute samples contain isolated Fe^{3+} , while with increasing concentration develop dipole-dipole and exchange interactions.^{5,6)}

There are several methods for preparation of multicomponent solid systems, the spray-decomposition technique applied here is an uncommon but very promising one. A similar method, spray-drying with subsequent heat-treatment was already studied.⁷⁾ The spray-decomposition method accomplishes the process in a single step by instantaneous thermal decomposition of an aerosol of the solute system. Recently we have prepared various oxide and oxide-salt systems by this technique.^{8~10)}

Experimental

Preparation of the samples

Al_2O_3 , Fe_2O_3 and mixed oxide samples have been prepared by spray-decomposing the aqueous solution of the nitrates at 500°C . The apparatus and the procedure have already been reported.¹⁰⁾ A further standardizing heat treatment was applied at 600°C in a stream of oxygen for 2 hrs.

Samples are denoted as AlFe_x , where x is the iron content in molar percent.

Characterization of the samples

X-ray diffractograms were recorded in a MIKROMETA apparatus by the Guinier — de-Wolf technique. The morphology of the samples is characterized by scanning electron photomicrographs recorded by a JSM-03 JEOL apparatus.

IR spectra were recorded in KBr using a SPECORD IR-75 spectrophotometer over the $2200\sim 400\text{ cm}^{-1}$ range. Diffuse reflectance spectra were obtained by OPTON RA-II. apparatus, in the spectral range $1\cdot 10^4\sim 5\cdot 10^4\text{ cm}^{-1}$. MgO was applied as reference material and for the dilution of the samples. EPR spectra were recorded by an ERS 200 apparatus.

Catalytic activity

The catalytic activity in hydrogen oxidation reaction was measured in a flow-system microreactor coupled with gas-chromatograph (carrier gas: N_2 . Analysis: molecular sieve column for H_2 and O_2 ; Porapack-Q column for H_2O). The reactant was stoichiometric mixture of H_2 and O_2 supplied by constant-current electrolysis of an aqueous Na_2SO_4 solution. The reaction was studied under the following circumstances: $300\sim 500^\circ\text{C}$, $p_{\text{H}_2}=30\sim 60\text{ mmHg}$, conversion less than 25%.

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A 0.09~0.16 mm fraction of the pelleted and repowdered sample was used. Activation: 500°C, 2 hrs in pure N₂. The analysis was performed after 1/2 hr continuous working. In the course of experiments (2~5 hrs) there was no detectable ageing effect.

Results and Discussion

Phase analysis

X-ray analysis and IR spectra show that pure Fe₂O₃ was hematite. Al₂O₃ was roentgen-amorphous but its IR spectrum revealed a broad band with the upper edge at about 1000 cm⁻¹, characteristic for low-temperature alumina modification.

In the mixed oxide systems there was no detectable hematite phase, although on the basis of earlier data referring to hematite-corundum system its presence would be predictable above 10 molar % iron content.^{3,4} This discrepancy may have two different reasons;

- i) solubility limits determined for hematite-corundum system are not valid for hematite dissolved in a low-temperature alumina modification,
- ii) the applied special preparation technique (low temperature, very rapid thermal decomposition) might have promoted the formation of over-saturated solid solutions.

Further experiments support an explanation combining both effects: an increase in solubility (up to some 15%) and formation of oversaturated solid solutions above this concentration. As it is illustrated by the IR spectra on Fig. 1, after heat treatment at 900°C in AlFe20, AlFe25 and AlFe30 samples developed hematite phase, while AlFe10 and AlFe15 remained unchanged. 900°C was chosen as a temperature high enough to enhance self-diffusion "melting" the frozen-in non-equilibrium situation, but low enough to prevent formation of corundum phase.

Morphology

Fig. 2 shows ball-shaped particles with approximately monodisperse size-distribution (1.5~2.0 μm). Comparing the diameter of these particles with that of the droplets of the aerosol we can conclude by a simple calculation that these particles were formed by the decomposition of a single droplet of the aerosol.

Comparing, on the other hand, the BET surfaces (Table 1) with the calculated geometric surface of these balls, turns out that the elementary particles have some pore-structure, since the BET/geometric surface ratio is about 30.

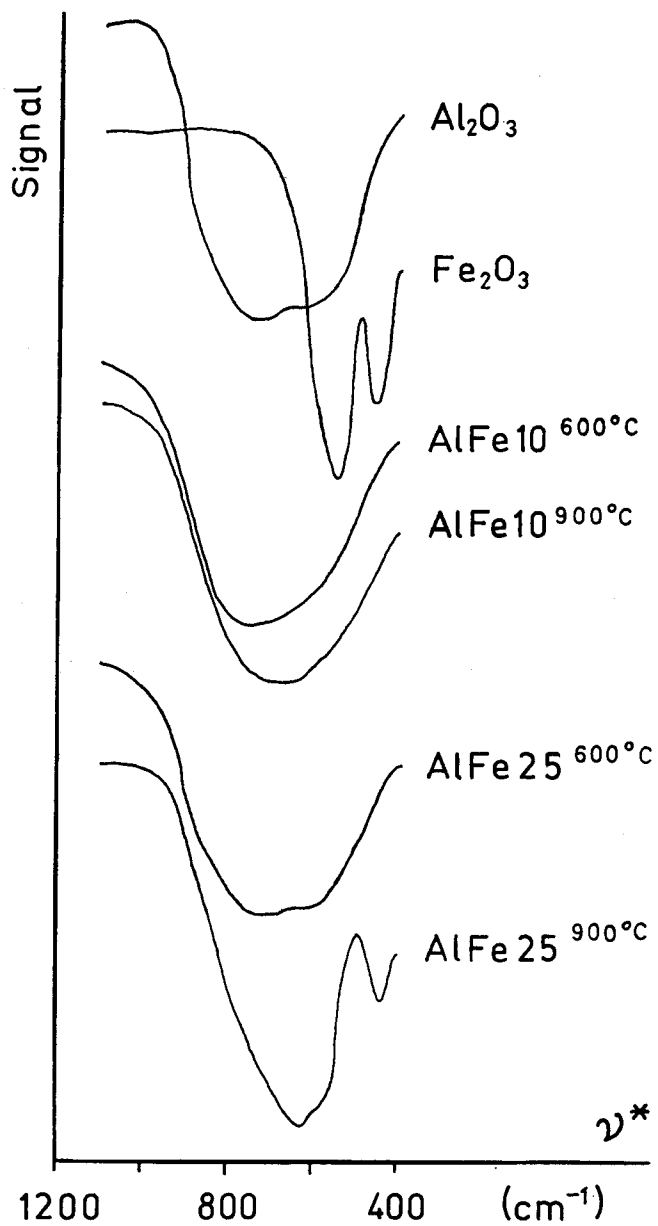


Fig. 1. IR spectra illustrating the effect of heat treatment at 900°C.

Upon heat treatment at 900°C the behaviour of AlFe15 was similar to that of AlFe10, while the behaviour of AlFe20 and AlFe30 was analogous to that of AlFe25.

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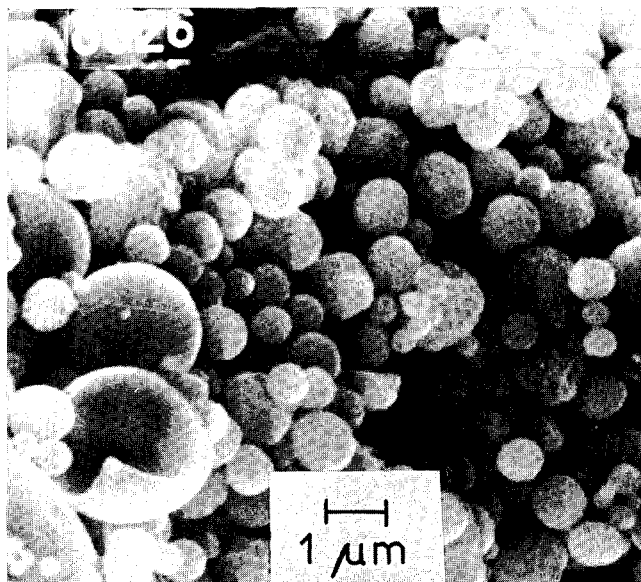


Fig. 2. Scanning electron photo-micrograph of Fe₂O₃.

TABLE 1. BET surface areas

Sample	BET surface area (m ² g ⁻¹)
Al ₂ O ₃	29
AlFe1	33
AlFe3	31
AlFe5	33
AlFe10	30
AlFe15	27
Fe ₂ O ₃	34

It is interesting to note that spray-drying with subsequent heat treatment produced a hematite sample with very similar morphology.⁷⁾

EPR spectroscopy

The EPR spectra of hematite dissolved in γ -Al₂O₃ and corundum have been analyzed.^{5,6)} As it was expectable on the basis of phase analysis, our spectra correspond to those measured in hematite- γ -Al₂O₃ system. In AlFe1 we could also detect β and α spectra characteristic for isolated Fe³⁺ in octahedral and tetrahedral sites. With increasing iron content these spec-

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tra gradually diminish and there forms a broad, so called ϕ spectrum, characteristic for clusters containing more than two Fe^{3+} ions being in dipole-dipole and exchange interaction with each other. In AlFe_{10} practically all amount of iron is in such clusters, although there remain some traces of

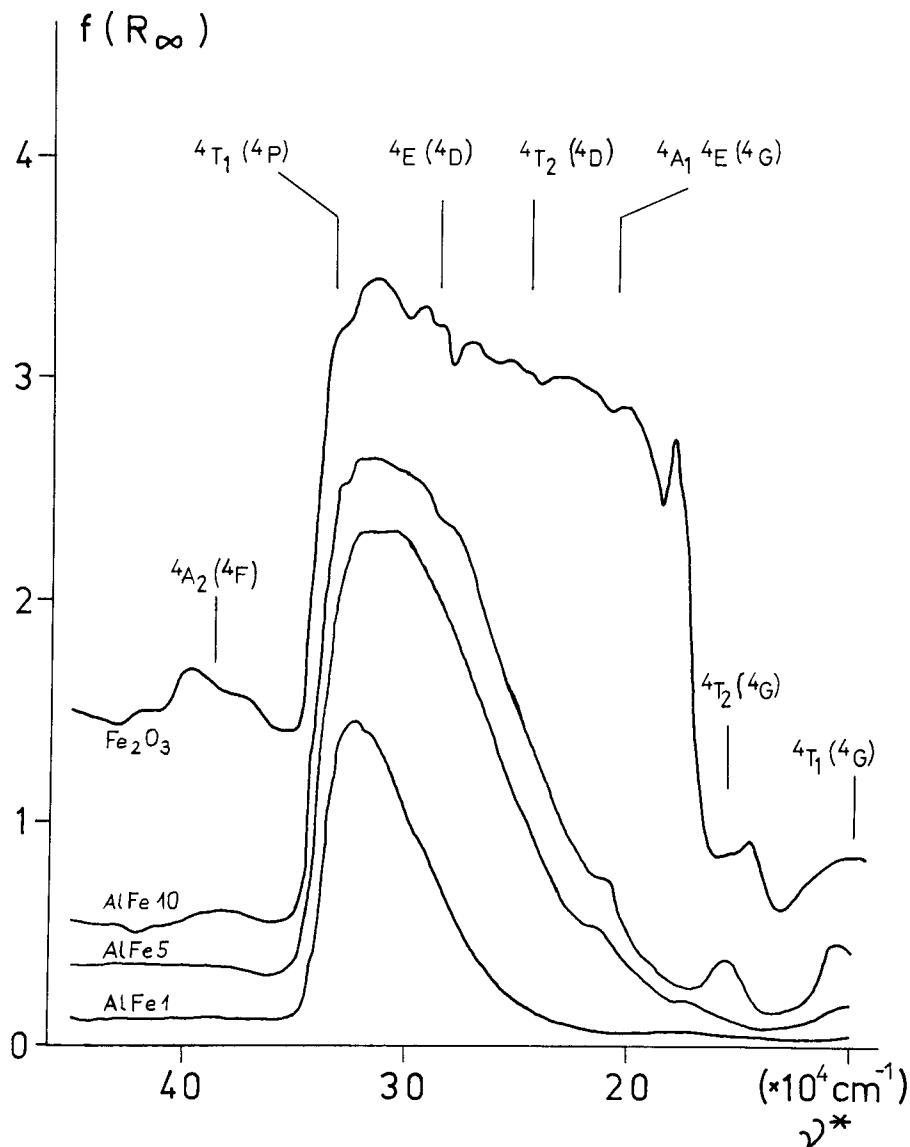


Fig. 3. Diffuse reflectance spectra of the samples. The assignments are based on the results of Ref. (11).

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isolated Fe³⁺, just above the level of detectability.

Diffuse reflectance spectra

The visible spectra of the samples are electronic transition spectra of Fe³⁺ ions and similarly to the EPR spectra they are affected by neighbourhood effects, especially by iron-iron interactions. The assignation and the interpretation of the recorded spectra (Fig. 3) were performed utilizing earlier works, where the behaviour of Fe³⁺ in various mixed oxide lattices was investigated and dependence of some of the transitions on the neighbourhood was found.¹⁰ It was concluded on this basis that, in accordance with the EPR results, there are isolated Fe³⁺ ions in AlFeI and with increasing concentration iron-iron interactions develop. Comparing the spectra of the mixed oxide samples with that of the hematite, there is also an indication of their solid solution nature, in agreement with the X-ray and IR results.

Catalytic activity

Preliminary experiments showed that under the applied experimental circumstances the reaction was of first order with respect to H₂ and zero order with respect to O₂. On this basis catalytic activity was characterized by first order velocity constants: k ($\mu\text{mole}_{\text{H}_2\text{O}} \cdot \text{g}^{-1} \cdot \text{s}^{-1} \cdot \text{mmHg}_{\text{H}_2}^{-1}$)*).

Fig. 4 represents Arrhenius plots. An effect of the iron content upon the activity is apparent. As a further analysis characteristic temperatures can be determined where the velocity constants of the samples reach a fixed value. As Fig. 4 shows if $\log k = -1$ is chosen, the minimum extrapolation of the Arrhenius lines beyond the temperature range of the experiments is necessary.

On Fig. 5 the pattern of these characteristic temperatures indicates that with increasing iron content the activity increases. It is difficult to judge, however, whether the change in activity is controlled by the iron content alone, or the different surroundings have also an effect.

To answer this question further transformation of the data is necessary. The activity of pure Al₂O₃ is also taken into account introducing a new quantity:

$$R = \frac{k_{\text{meas.}}}{k_{\text{add.}}}$$

where $k_{\text{meas.}}$ means the measured velocity constant and $k_{\text{add.}}$ is an additive velocity constant calculated assuming that the activity of the sample is a

*) The BET surface areas being not very different, the velocity constants are related to unit mass.

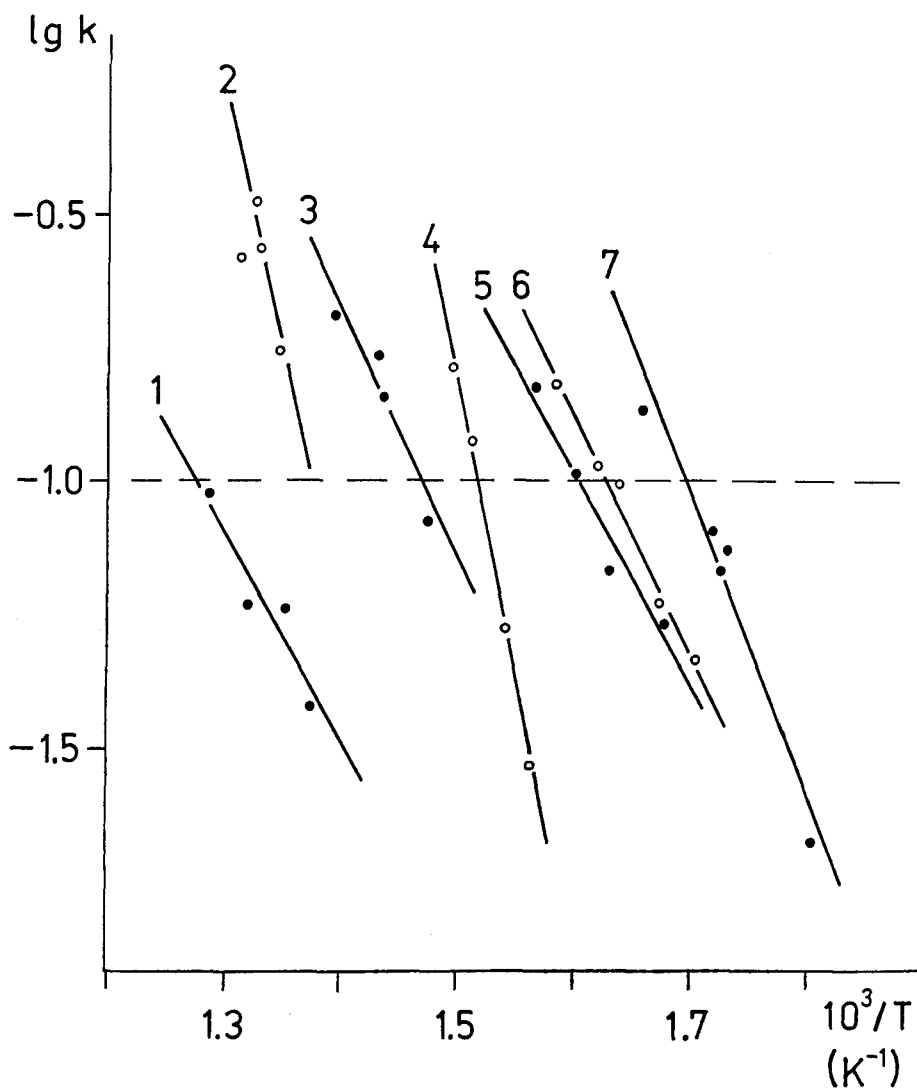


Fig. 4. Arrhenius plots of the rate constants of hydrogen oxidation reaction.

k is in $\mu\text{mole}_{\text{H}_2}\cdot\text{g}^{-1}\cdot\text{s}^{-1}\cdot\text{mmHg}_{\text{H}_2}^{-1}$, 1: Al_2O_3 , 2: AlFe1 , 3: AlFe3 , 4: AlFe5 , 5: AlFe10 , 6: AlFe15 , 7: Fe_2O_3 .

sum of the activities of its Al_2O_3 and Fe_2O_3 content. Deviation of the value of R from unity reveals possible neighbourhood effects. Fig. 6 shows $\log R$, calculated for 375°C as a function of iron content.

This type of analysis is to be accepted with some criticism, since for

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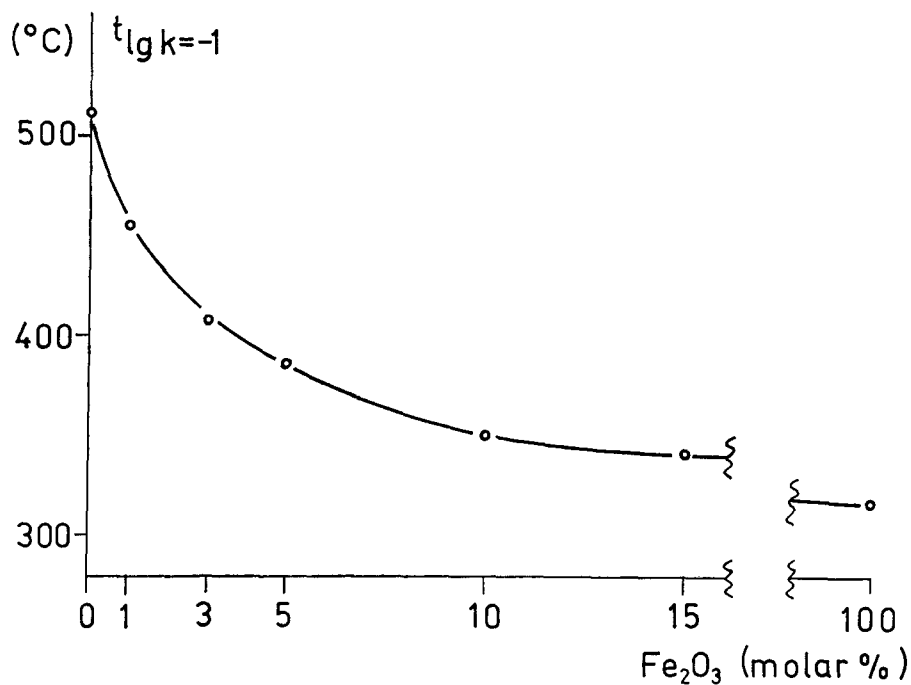


Fig. 5. Activity pattern represented by characteristic temperatures, where the activity reaches a fixed value.

$$k = 0.1 \mu\text{mole}_{\text{H}_2\text{O}} \cdot \text{g}^{-1} \cdot \text{s}^{-1} \cdot \text{mmHg}_{\text{H}_2}^{-1}$$

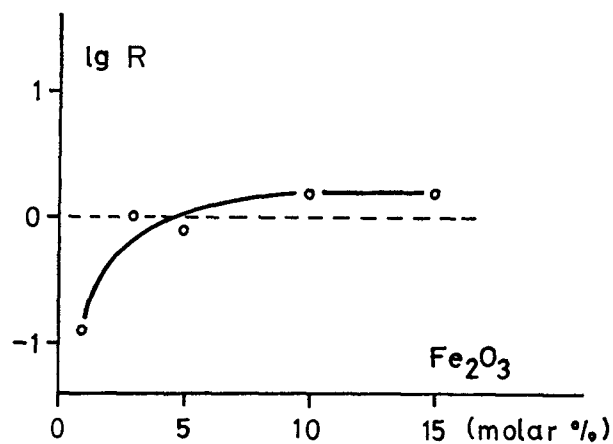


Fig. 6. Logarithm of R calculated for 375°C plotted against the iron content of the samples. For R , see the text.

calculation of k_{add} . Arrhenius plots of pure Al_2O_3 and Fe_2O_3 are extrapolated far beyond the experimental temperature range. We think, however, that large deviation of R from unity can be considered as a sign of significant difference of the state of iron in the given sample from that in hematite. As it is seen on Fig. 6 this situation occurs only at AlFe1. It can be concluded that isolated Fe^{3+} ions are less active in this reaction than Fe^{3+} ions in the lattice of hematite. Taken into account the regularities of the reactivity of solids this is not very surprising. It is interesting, however, that R values of the rest of the samples indicate that in this reaction it is much the same whether iron is present in a real solid solution or in hematite phase, providing that the concentration is high enough to allow iron-iron interaction.

As for the discussion of the present investigations in comparison with literature data Table 2 shows earlier results calculated for a chosen temperature and hydrogen pressure, assuming first order kinetics with respect to H_2 and zero order with respect to O_2 .

The found agreement of specific activities within one order of magnitude can be considered as satisfactory taken into account the uncertainties of such re-calculations of earlier data.

Hematite-corundum solid solutions were studied in hydrogen oxydation reaction recently.¹⁹⁾ The applied preparation technique was the calcination of the coprecipitate of hydroxides at 1350°C . This high temperature might have been necessary for formation of real solid solutions, but a comparison of the measured activities with the present results and with literature data (Table 2) shows that the samples were highly deactivated as catalysts. Activity measured on Al_2O_3 agrees well with that measured by us, but surpris-

TABLE 2. Comparison of specific activities measured by various authors in hydrogen oxidation over hematite

Ref.	Tempr. range of measurements	Apparent energy of activation	$\log r^*$
	$^\circ\text{C}$	kJoule. mole^{-1}	
12)	225-279	63	-1.62
13)	225-279	80	-2.0
14)	260-380	84	-1.1
present data	285-325	100	-1.98

* at 300°C and $p_{\text{H}_2} = 6.1 \text{ mmHg}$; $[r] = \mu\text{mole}_{\text{H}_2}\text{O} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$.

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ingly, the activity of hematite does not exceed it significantly and it is 2~3 orders of magnitude smaller than data in Table 2. On this basis we think that—at least in this reaction— study of solid solutions calcined at high temperatures can be misleading at interpretation of catalytic behaviour of active iron catalysts. This underlines at the same time the applicability of spray-decomposition as a technique for preparation of solid solution type catalysts.

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