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Chemical Characterization of a Fused Iron Catalyst for Ammonia Synthesis

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A triply promoted fused iron catalyst was examined by (i) temperature-programmed desorption of hydrogen, (ii) temperature-programmed desorption of nitrogen, (iii) temperature-programmed hydrogenation of preadsorbed nitrogen and (iv) chemisorption of carbon monoxide. The studies demonstrate that all the methods are suitable for characterization of the catalyst, provided that the experimental conditions of the measurements are correctly chosen.

Key words: fused iron catalyst, chemical characterization, temperature-programmed desorption of nitrogen, temperature-programmed hydrogenation of nitrogen

Fused iron catalysts are commonly used in industrial process of ammonia synthesis. In view of the enormous scale of the NH_3 production, extensive studies of the catalysts have been performed to explain their unique properties and to elaborate new catalytic systems that would operate effectively at lower temperature and under low pressure. Nevertheless, in spite of the efforts, a lot of controversies and unsolved problems still remain.

This paper is concerned with the basic problems of chemical characterization of a triply promoted fused iron catalyst. The following methods were applied: temperature-programmed desorption of preadsorbed hydrogen (TPD-H_{ads}), temperature-programmed desorption of preadsorbed nitrogen (TPD-N_{ads}), temperature-programmed hydrogenation of preadsorbed nitrogen (TPH-N_{ads}) and chemisorption of carbon monoxide.

EXPERIMENTAL

Apparatus. The experiments were carried out in a glass flow system equipped with a gradientless microreactor [1,2]. A temperature controller maintained the reactor temperature within 1°C and provided linear temperature programming in the range of –200–800°C. Hydrogen, helium, argon and nitrogen were of 99.999% purity and carbon monoxide was of 99.9% purity. Hydrogen was further purified by a palladium filter. Argon and helium were purified in a series of columns packed with Cu/SiO_2, silica gel and molecular sieves 5 Å. The gas stream required was fed to the measuring system by a four-way valve and, before entering the reactor, it was additionally purified by passing through a MnO/SiO_2 column. In the case of a He stream, the column was maintained at –195°C, which lowered the concentration of impurities below 0.1 ppm. Composition of the gas stream leaving the reactor was followed by a TCD cell and results were collected with a computer-controlled system.

The catalyst. A commercial triply promoted (CaO, Al_2O_3, K_2O) fused iron catalyst, KM I, of a 0.5–0.8 mm grain size was used. The 1 g sample was prereduced *in situ* in a H_2 stream of 1 cm^3/s. The reduction was carried out at slowly increasing temperature so that the concentration of water in the outlet gas did not exceed 1000 ppm. At the terminal temperature, 550°C, the reduction was continued for 48 h, what lowered H_2O concentration in the outlet stream below 1 ppm. Hence, the catalyst was fully reduced when starting the chemical examinations.

Measurements procedure. All the experiments were preceded by an extra reduction in a H_2 stream (0.5 cm^3/s, 540°C, 0.5 h). Afterwards, the sample examined was purged from the adsorbed hydrogen in a He stream (0.5 cm^3/s, 500°C, 0.5 h) and one of the following measurements was then performed:

Temperature-programmed desorption of preadsorbed hydrogen. Preadsorption of hydrogen was carried out in three stages: 1 – initially at constant temperature of 20°C, 150°C or 400°C for 0.25 h, 2 – at gradually decreasing temperature (during 0.5 h) from the initial value to 20°C, and 3 – at constant temperature of 20°C for 0.25 h. Subsequently, the sample was flushed with a He stream (0.5 cm^3/s, 20°C, 0.25 h) to remove the weakly adsorbed hydrogen and the remaining hydrogen was examined by the TPD method. The desorption was carried out in an Ar stream of 0.5 cm^3/s at linearly increasing temperature (0.17°C/s or 0.33°C/s) from –30°C to 550°C. Then, the reactor with examined sample was cooled down to determine the base line and the calibration of the system was performed.

Temperature-programmed desorption of preadsorbed nitrogen. Preadsorption of nitrogen was carried out in two steps: 1 – at 400°C for 0.25 h, and 2 – at gradually decreasing temperature (during 1 h) from the initial temperature to 20°C. Afterwards, the reactor was flushed with a He stream (0.5 cm^3/s, 20°C, 0.25 h) to remove the weakly adsorbed nitrogen and the remaining nitrogen was examined by TPD or TPH method. The TPD runs were performed in a He stream of 0.5 cm^3/s at linearly increasing temperature of 0.17°C/s from 20°C to 550°C, whereupon it was continued at 550°C for 0.33 h.

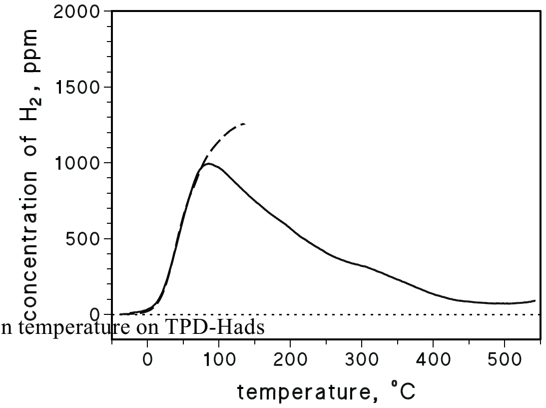
Temperature-programmed hydrogenation of preadsorbed nitrogen. The hydrogenation was carried out in a H_2 stream of 0.5 cm^3/s at linearly increasing temperature (0.17°C/s) from 20°C to 550°C, whereupon it was continued at 550°C for 0.33 h. Since the stream leaving the reactor contained not only ammonia but also nitrogen, two parallel experiments, A and B, were performed to determine the concentration of both components. In experiment A a summed up response from both NH_3 and N_2 was recorded. In experiment B ammonia was condensed in a trap at –195°C and the concentration of nitrogen alone was monitored.

Adsorption of carbon monoxide. The measurement was carried out by the pulse method, introducing every 180 s portions of 4.5 μmol CO into a He stream (0.5 cm^3/s) flowing over the sample maintained at 20°C.

RESULTS AND DISCUSSION

Temperature-programmed desorption of preadsorbed hydrogen. Fig. 1 shows the TPD spectra of hydrogen preadsorbed at various (initial) temperatures. The spectra represent broad profiles that begin close to the flushing temperature, 20°C, and decay near to the purging temperature, 500°C. Such a broad range of H_2 desorption indicates that: (i) various adsorption sites participate in the adsorption/desorption process and (ii) the flushing temperature is a crucial parameter in measurement the amount of hydrogen adsorption. The flushing temperature 20°C was chosen on the basis of the extensive experience in characterization of supported metal catalysts, which have shown that irreversible adsorption of hydrogen at room temperature is suitable for the calculation of the amount of surface metal atoms.

Fig. 1 demonstrates also the effect of initial temperature of hydrogen preadsorption on the shape of the $TPDSH_{ads}$ spectra. The low-temperature side of the spectra is independent of the preadsorption temperature, whereas the high-tem-

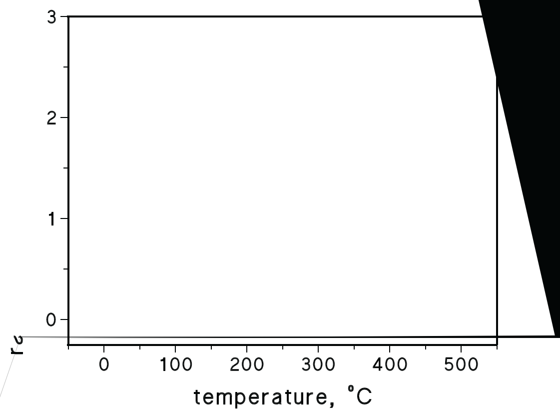


Effect of preadsorption temperature on TPD-Hads

Figure 1.

perature part grows considerably when the initial temperature of H_2 preadsorption increases. Consequently, the total uptake of hydrogen increases with the initial preadsorption temperature (see the data in Fig. 1). The observed effect might be explained as follows: Adsorption of dihydrogen on clean iron surface is, as a rule, a non-activated process. However, the surface of a fused iron catalyst is partly covered with the promoter oxides [3,4]. It is suggested that at low temperature (20°C) hydrogen is adsorbed for the most part on the clean, *i.e.* uncovered Fe sites, while at high temperature it is adsorbed additionally on the Fe sites modified by promoter (CaO, Al_2O_3) species. That explains why the amount of H_2 preadsorbed at high (initial) temperature is considerably larger than at 20°C. Besides, due to the presence of various Fe sites, the temperature-programmed desorption of hydrogen appears to be a complex process. Hydrogen desorption is accompanied not only by readsorption but also by surface diffusion, both the phenomena being responsible for the shape of individual profiles presented in Fig. 1. Accordingly, the obtained TPD-H_{ads} spectra hardly characterise the state of hydrogen just after the preadsorption, but they correctly reflect the amount of hydrogen adsorbed. More specifically, the integrated spectrum obtained after preadsorption at 20°C yields the amount of hydrogen preadsorbed mainly on clean iron sites, whereas the spectra recorded after higher temperature of preadsorption corresponds to both the clean iron sites and to the sites decorated with the promoters.

Fig. 2 gives a comparison between the TPD-H_{ads} spectrum (relative rates) obtained for KM I catalyst and the spectrum recorded for carbon supported iron catalyst promoted with K_2O (but free of CaO and Al_2O_3). As seen, the latter spectrum represents a well-shaped single peak, which implies that only clean iron sites participate in adsorption and desorption of hydrogen. The comparison suggests that: (i) the low temperature part of the spectrum for KM I catalyst represents the desorption from clean Fe sites and (ii) the high-temperature part reflects the desorption perturbed by the transient hydrogen adsorption on the promoters covered Fe sites, that bind hydrogen more strongly than the clean sites.



TPD of preadsorbed nitrogen. Adsorption of nitrogen on fused iron catalysts is known to be an activated process. Preliminary experiments (not presented in this paper) showed that the process proceeds with a measurable rate above 150°C. The amount of adsorbed nitrogen attains a maximum value at about 350°C. Fig. 3 presents the TPD-N_{ads} spectrum for the fused catalyst studied. Absence of the N_2 signal below 300°C indicates that nitrogen is strongly adsorbed on the Fe surface. Above that temperature a well-shaped profile centred at 467°C appears. The spectrum is similar to those recorded by Muhler *et al.* [5] for the same catalyst. Some differences, which concern the shape of the N_2 signal and position of its maximum, most likely result from differences in the experimental procedures applied. In the experiments performed by the Ertl's group [5], nitrogen was adsorbed just after the ammonia synthesis and the resultant TPD spectra probably reflected not only nitrogen preadsorbed but also nitrogen originated from ammonia species retained after ammonia synthesis. Since the species could not occur in our experiment, the TPD-N_{ads} spectrum recorded in this work (Fig. 3) corresponds solely to preadsorbed nitrogen.

Figure 3. TPD-N_{ads} spectrum for the fused iron catalyst.

The shape of TPD-N_{ads} spectrum presented in Fig. 3 indicates that considerable amounts of nitrogen evolve at temperature as high as 550°C. This indicates that the latter part of evolved nitrogen is especially strongly adsorbed, in accordance with [6], or that nitrogen is bound by other but Fe surface sites and desorbs only at high temperatures.

TPH of preadsorbed nitrogen. Fig. 4 shows the temperature-programmed hydrogenation of the preadsorbed nitrogen. It is clearly seen that beside ammonia a significant amount of nitrogen evolves at high temperature. Complementary calculations showed the N_2/NH_3 ratio is close to the thermodynamic equilibrium in the gas phase. The presence of nitrogen in the exit gas has not been reported so far. According to [7], nitrogen preadsorbed on fused iron catalysts is almost fully converted to ammonia in a H_2 stream at 300°C. Consequently, the integrated NH_3 signal has been used to determine the amount of preadsorbed nitrogen [7,8]. Our results show, however, that both ammonia and nitrogen should be taken into account when counting the number of surface Fe atoms accessible for nitrogen.

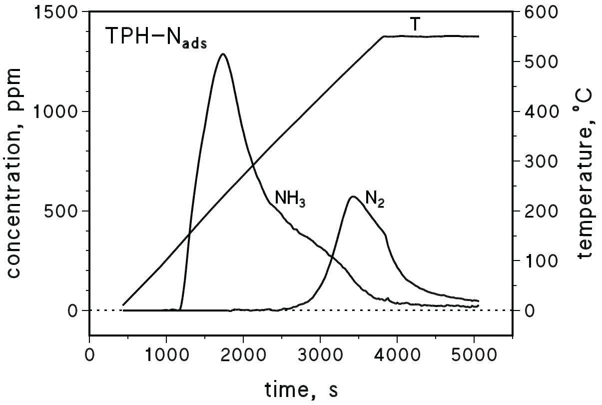


Figure 4. Evolution of NH_3 and N_2 during the TPH-N_{ads} test for fused iron catalyst.

The TPH-N_{ads} spectrum obtained (Fig. 4) as well as the spectra reported previously [7] exhibit a characteristic sharp onset of the ammonia evolution at the beginning of the examination. Similar onset of ammonia was recently observed for supported ruthenium catalysts [9]. The sharp onset of ammonia formation has been attributed to the autocatalytic mechanism [7], according to which ammonia desorption creates free sites for hydrogen adsorption. Once the NH_3 desorption has started, the number of sites accessible for hydrogen adsorption increases, so a self-accelerating effect is observed [7]. To verify the above hypothesis, a supplementary TPH-N_{ads} experiment was performed with the sample of lower (about 73%) coverage of nitrogen. The coverage was achieved by the partial desorption of preadsorbed nitrogen to a He stream prior to the TPH-N_{ads} run. The studies demonstrate (see Fig. 5) that coverage of nitrogen has no effect on the spectra, as far as the shape of the NH_3 onset is concerned. For both runs the onset is equally sharp which indicates that the autocatalytic mechanism is not essential. Thus these examinations as well as

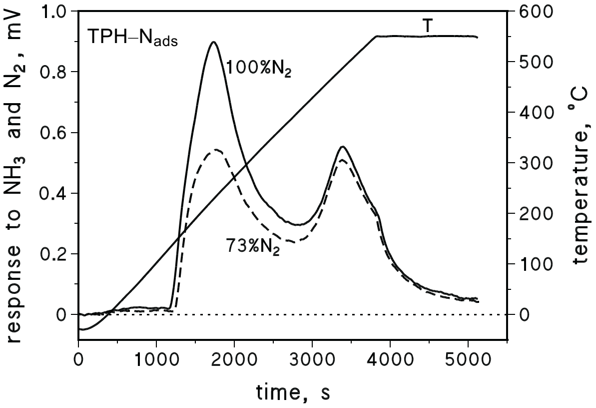


Figure 5. Effect of the nitrogen precoverage on the TPH-N$_{ads}$ spectrum for the fused iron catalyst.

previous reports [7,8] suggest that both chemical reactions on Fe surface and desorption of ammonia from catalyst surface participate in the formation of low-temperature part of the NH_3 profile. Further studies, however, are necessary to explain this problem.

Adsorption of carbon monoxide. Surface area of iron. The state of carbon monoxide adsorbed on metal surface depends considerably on the applied way of CO adsorption. At low pressure/exposure, characteristic for the pulse method, adsorption of CO is fast until the CO_{ads}/Fe_s ratio of about 0.5. All the above temperature-programmed studies were also used to determine the surface area of dispersed iron. The stoichiometries assumed in the calculations were taken from [7]. In the case of the hydrogen chemisorption, however, a $H_{ads}/Fe_s = 1$ stoichiometry was used instead of $H_{ads}/Fe_s = 2$ [7]. The modification is connected with the difference in applied flushing temperature, *i.e.* 20°C in this work and –195°C in [7]. The results of the calculations are collected in Table 1. Excellent agreement between the numbers of surface iron indicates that all the chemisorption methods, *i.e.* TPD-H$_{ads}$, TPD-N$_{ads}$, TPH-N$_{ads}$ and CO adsorption are applicable for the characterization of fused iron catalysts.

Table 1. Characteristics of the fused iron catalyst by chemisorption techniques.

Measurement	Adsorption, evolution [μ mol/g]	Stoichiometry of adsorption	Quantity of surface iron, [μmol/g]
TPD-H$_{ads}$	25.5 H_2	$H_{ads}/Fe_s = 1$	51.0
TPD-N$_{ads}$	27.4 N_2	$N_{ads}/Fe_s = 1$	53.3
TPH-N$_{ads}$	29.4 NH_3 + 11.3 N_2	$N_{ads}/Fe_s = 1$	52.0
ads. CO	27.6 CO	$CO_{ads}/Fe_s = 0.5$	55.2

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