Polish J. Chem., **76**, 1513–1517 (2002) **COMMUNICATION**

Water-Gas Shift Reaction over the Carbon-Based Magnetite Catalyst Doped with Chromium Oxide

by A. Jedynak-Koczuk and Z. Kowalczyk*

Warsaw University of Technology, Faculty of Chemistry, Noakowskiego 3, 00-664 Warsaw, Poland

(Received June 24th, 2002; revised manuscript July 16th, 2002)

The catalytic water-gas shift reaction ($CO + H_2O = CO_2 + H_2$) is an important step in the large-scale production of hydrogen or hydrogen-nitrogen mixture for ammonia synthesis. Typically, the magnetite-based catalysts, manufactured by the precipitation method, have been used in industrial installations [1–3]. Our recent studies demonstrate [4] that the Fe_3O_4 particles supported on thermally modified carbon also exhibit high activity in the $CO + H_2O$ conversion, especially when finely dispersed.

This paper shows, in turn, that the dispersion of the magnetite crystallites may be enhanced significantly by the chromium oxide addition. However, the surface of the Fe_3O_4 particles doped with Cr_2O_3 was found to be less active than the surface of the pure magnetite phase.

The thermally modified active carbon – a support for the Fe-Cr/C catalysts was obtained by heating of the raw, commercially available active carbon (Norit N.V.) in a helium atmosphere at 1900°C, followed by the partial gasification in flowing carbon dioxide at 900°C [4–6] up to about 48% loss of mass. The BET surface area of the support prepared was 1300 m^2/g and the volume of pores larger than 3 nm in diameter was 1.2 cm^3/g as measured by the nitrogen physisorption and mercury porosimetry methods, respectively. Iron nitrate ($Fe(NO_3)_3 \cdot 9H_2O$) and chromium nitrate ($Cr(NO_3)_3 \cdot 6H_2O$) were the precursors of Fe and Cr oxides, respectively, both introduced simultaneously, according to the single-step co-impregnation procedure from aqueous solutions (procedure A) [7,8] or, alternatively, they were introduced in a sequence: impregnation with iron nitrate, calcination at 220°C, impregnation with chromium nitrate (procedure B). Finally, the materials were heated in air at 220°C to convert nitrates into oxides. The content of iron oxide (Fe_2O_3) in all the calcined samples was 30 wt % and the content of chromium oxide (Cr_2O_3) was 3.5 wt. % or 7 wt. %.

The measurements of the water – gas shift reaction rates were performed in a flow, four-channel differential reactor, operating under the standard conditions of pressure – 25 bar, of temperature – 330°C, 350°C, 370°C and of the gas composition: H_2 – 30%, N_2 – 10%, CO_2 – 5%, CO – 1%, H_2O – 54%; the details of the measurement

*Author for correspondence.

procedure are described in [8]. Prior to tests, the samples of the catalysts (0.5 g) were stabilized *in situ* at 400°C for 4 h [8–10].

The experimentally determined reaction rates were approximated with an empirical equation [9]:

$$r = k \cdot a_{CO} \cdot a_{CO_2}^{-0.3} \cdot a_{H_2}^{-0.15} \cdot a_{H_2O}^{0.1} \cdot (1-\beta) \quad (1)$$

where: r is the reaction rate, k is the rate constant, a_i are the mole fractions of the gaseous components and $(1 - \beta)$ is a factor that represents the distance to the equilibrium state. The values of the k-constants calculated from (1) were used, subsequently, for the comparison of the catalysts activities. The post reaction samples of the catalysts were characterized by the XRD technique. The X-ray diffraction patterns were recorded using a standard Bragg-Brentano focusing geometry (Rigaku Denki) with CuK_α, Ni filtered radiation. The patterns were recorded by the step-by-step technique with a counting time of 10 s and a step size $2\theta = 0.05°$. The average sizes of the magnetite crystallites were calculated from line broadening, according to the Scherrer's formula. Subsequently, the active surface area was calculated, assuming that magnetite forms spherical particles, the diameter of which is equal to the average crystallite size determined from the XRD measurements.

Fig. 1 shows the post-reaction XRD patterns of the Cr-Fe/C specimens that contained 3.5% chromium oxide. It should be noticed first that magnetite is the only phase in both materials. It is also seen that the preparation procedure is essential for the structure of the magnetite particles. In case of the B procedure, the reflections

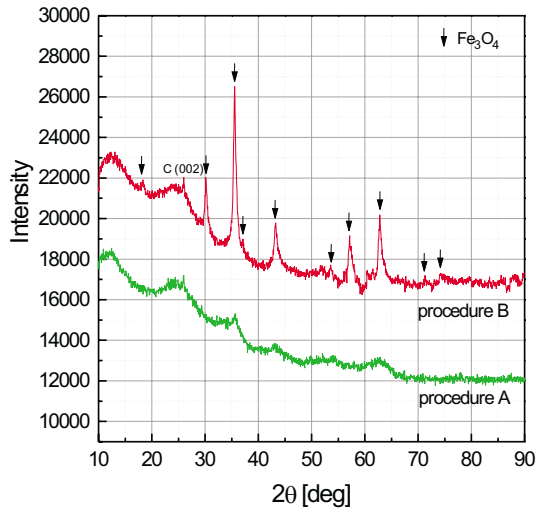

Figure 1. XRD patterns of the post-reaction Cr-Fe/C samples containing 3.5 wt. % Cr_2O_3.

from Fe_3O_4 are distinct, thus indicating the crystallites to be large. In contrast, the pattern corresponding to procedure A is diffused, characteristic for the specimens of high dispersion. The patterns obtained for the 7% Cr_2O_3-Fe/C samples were analogous, respectively, to those described above. The average Fe_3O_4 crystallite sizes in all of the samples as well as corresponding surface areas are collected in Table 1.

Table 1. Average Fe_3O_4 crystallite size (d) in the catalysts and specific surface area of the magnetite phase (S).

Catalyst	d [nm]	S [$m^2/g_{cat.}$]
Fe_3O_4/carbon	18	49
3.5% Cr_2O_3 – Fe_3O_4/carbon (A)	3	116
3.5% Cr_2O_3 – Fe_3O_4/carbon (B)	20	17.4
7% Cr_2O_3 – Fe_3O_4/carbon (A)	3	116
7% Cr_2O_3 – Fe_3O_4/carbon (B)	18	20.5

The kinetic data obtained for the catalysts studied in the water-gas shift reaction are shown in Figs 2 and 3, the activity (k-constant) being referred to the catalyst mass. Fig. 2 presents the effect of the preparation procedure (A and B) on the activity of the samples containing 3.5 wt % Cr_2O_3. As one may notice (Fig. 2), procedure A is significantly more advantageous than procedure B. Over the whole temperature range, the A catalyst is almost twice as active as B and about 20% more active than the catalyst free from chromium oxide (Fe_3O_4/C), used in the studies as a reference material. In the case of higher Cr_2O_3 loading (7%), the effect of the preparation procedure is even more pronounced (see Fig. 3). The Cr_2O_3–Fe_3O_4/C system prepared according to the co-impregnation method (A) shows the activity similar to that of the unpromoted one,

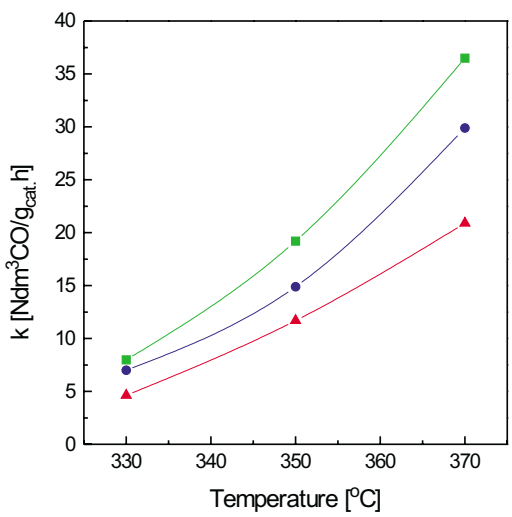

Figure 2. Weight-based activities (k-constant) of the chromium doped catalysts (3.5 wt. % Cr_2O_3) *vs.* temperature; ■ – procedure A, ▲ – procedure B; ● – catalyst free from chromium oxide.

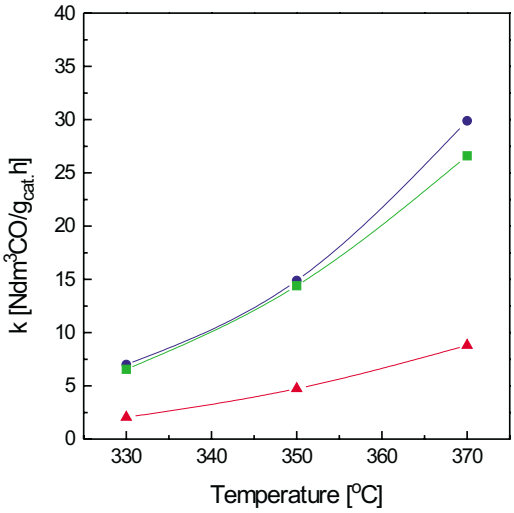

Figure 3. Weight-based activities (k-constant) of chromium doped catalysts (7 wt. % Cr_2O_3) *vs*. temperature; ■ - procedure A, ▲ – procedure B; ● – catalyst free from chromium oxide.

both materials being about three times more active than the catalyst prepared by step-by-step technique (B).

The above comparison, based on the reaction rates related to the mass of the catalysts, seems to be valid for the industrial applications. From the scientific point of view, however, the effect of chromium oxide on the catalytic properties of the Fe_3O_4 surfaces is essential. Table 2 presents the reaction rates (k_1-constants) at 370°C, as referred to the active surface areas. It is clearly seen (Table 2) that the Fe_3O_4 surfaces doped with chromium oxide are less active than those of pure magnetite. The difference may exceed a factor of 6. Hence, two independent effects are observed after the chromium oxide addition to the Fe_3O_4/C system: the Fe_3O_4 surface becomes less active and the dispersion of magnetite may increase significantly when the co-impregnation procedure is applied. It should be added in the end that all the catalysts deposited on carbon exhibited a very high selectivity. Any by-products, such as methane, have not been observed in the outlet gas stream when operating.

Table 2. Surface activity (k_1-constant at 370°C) of the catalysts in the WGS reaction.

Catalyst	k_1[Nl CO/$m^2_{Fe_3O_4}$ h]
Fe_3O_4/carbon	1.5
3.5% Cr_2O_3 – Fe_3O_4/carbon (A)	0.31
3.5% Cr_2O_3 – Fe_3O_4/carbon (B)	1.1
7% Cr_2O_3 – Fe_3O_4/carbon (A)	0.23
7% Cr_2O_3 – Fe_3O_4/carbon (B)	0.43

REFERENCES

1. Catalyst Handbook, Second Edition, ed. Martyn V. Twigg, Wolfe Publishing Ltd, London (1989).
2. Carstensen J.H., Bogild-Hansen J. and Pedersen P.S., *Hydrocarbon Processing*, 57 (1990).
3. Evans T., *Nitrogen & Methanol*, **232**, 41 (1998).
4. Kowalczyk Z., Sentek J., Diduszko R., Presz A., Tetrzyk A., Kucharski Z. and Suwalski J., *Carbon*, **34**, 403 (1996).
5. Kowalczyk Z., Jodzis S., Raróg W., Zieliński J., Pielaszek J. and Presz A., *Appl. Catal., A: General*, **184**, 95 (1999).
6. Raróg W., Lenarcik I., Kowalczyk Z., Sentek J., Krukowski M. and Zieliński J., *Polish J. Chem*., **74**, 1473 (2000).
7. Jedynak A., Sentek J., Kowalczyk Z., Pielaszek J. and Stołecki K., *Polish J. Chem*., **74**, 1803 (2000).
8. Jedynak A., Sentek J., Kowalczyk Z., Pielaszek J. and Stołecki K., *Przem. Chem*., **80/9**, 398 (2001).
9. Gołębiowski A., Stołecki K. and Magdziarz S., *Przem. Chem*., **67**, 470 (1988).
10. Gołębiowski A. and Stołecki K., *Chemik*, **3**, 73 (1998).