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Water-Gas Shift Reaction over the Carbon-Based Magnetite Catalysts Doped with Ruthenium or Palladium

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The catalytic reaction of carbon monoxide with steam – water-gas shift reaction (WGSR), is a source of hydrogen for the refinery and petrochemical industries, for the nitrogen fertilisers production and for the fuel-cell applications. Typically, the magnetite catalysts obtained by the precipitation method are used in the large-scale WGSR units [1,2]. However, our studies have shown [3–5] that the magnetite crystallites deposited on thermally modified carbon are also very active in the water-gas shift reaction, particularly when promoted with chromium [4].

This communication is devoted to the Fe_3O_4/carbon and Fe_3O_4-Cr_2O_3/carbon catalysts doped additionally with palladium or ruthenium, both noble metals being often used as components of various WGSR systems [6–15]. While palladium does not influence the activity of the carbon-based magnetite catalysts, a strong effect of the ruthenium presence has been found. An enhancement in the WGS reaction upon the Ru addition is accompanied, however, by the methane formation, due to the reaction between hydrogen and carbon monoxide, carbon dioxide, or both. This may lead to the significant decrease in the hydrogen efficiency, especially when the Ru loadings are high.

Two carbon materials, denoted as A and B, were used as supports for the catalysts preparation, both obtained by the high temperature (1900°C, helium) annealing of commercial active carbon (supplied by Norit N.V.), followed by the partial gasification in a CO_2 stream ($C + CO_2 = 2CO$) at about 900°C up to 35 wt. % mass lost – carbon A, or to 48 wt. % mass lost – carbon B. The textural characteristics of the supports is presented in Table 1.

Table 1. Textural parameters of the activated carbon supports; S_{BET} – BET surface area; V_{Hg}, V_{mHg}, S_{Hg} – total volume, volume of pores in the 3–80 nm range and surface are obtained from the mercury porosimetry measurements, respectively.

carbon support	S_{BET} [m^2/g]	V_{Hg} [cm^3/g]	V_{mHg} [cm^3/g]	S_{Hg} [m^2/g]
carbon A	917	0.76	0.32	184
carbon B	1700	1.18	0.83	425

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Iron nitrate – the precursor of the magnetite phase and chromium nitrate – the Cr_2O_3 precursor, were deposited onto the support surface through the impregnation in aqueous solutions [4]. Subsequently, the samples were dried in air at 90°C and calcined at 220°C for 24 h to convert the salts into oxides. Ruthenium carbonyl, ruthenium chloride and palladium nitrate – the noble metals precursors, were introduced by impregnation from acetone ($Ru_3(CO)_{12}$) or aqueous ($RuCl_3 \cdot 0.5H_2O$, $Pd(NO_3)_2$) solutions. Finally, the catalysts were dried in air at 90°C.

The kinetic studies of the WGS reaction were carried out in a flow differential reactor, supplied with a mixture of hydrogen (30%), nitrogen (10%), carbon dioxide (5%), carbon monoxide (1%) and water vapour (54%) [16,17] (the gas composition corresponded to that in final parts of the WGSR industrial reactors installed in ammonia plants). Under steady-state conditions of pressure (25 bar), temperature (330°C, 350°C or 370°C) and gas flow rate (60 dm^3[STP]/h), the concentrations of CO in the inlet and outlet gas streams were monitored by the URAS 10p analyser (Hartman & Braun). The rates of CO conversion were determined from a CO mass balance (inlet-outlet), assuming that the reactor operated as a plug-flow one. An empirical equation proposed by Gołębiowski *et al*. [16]:

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

was used for the approximation of the kinetic data, where: r is the reaction rate, k is the rate constant, a_i are the molar fractions of the reactants and the $(1 - \beta)$ term represents the distance to the equilibrium state. Prior to kinetic examinations, the samples (typically 0.5 g) were activated (stabilized) *in situ* at 400°C for 4 h [5,16,17].

Table 2 illustrates the effect of both noble metals (Pd, Ru) on the activity of the magnetite-rich Fe_xO_y*/carbon A* catalyst (45wt. % Fe_2O_3 in the calcined specimen), the activity being expressed in terms of k – constants. As one may notice, the effect of palladium is of rather minor importance. The catalyst of a low Pd loading (0.5 wt. %) is less active than that of a higher Pd loading (1.0 wt. %), the k – constants for both catalysts being close, however, to the k – constants for the Pd-free reference sample.

Table 2. Activity (k – constant) of the Fe_xO_y/carbon A catalysts doped with palladium or ruthenium; all the catalysts contained 45 wt. % Fe_2O_3 after calcination.

catalyst symbol	noble metal precursor	noble metal content	activity (k) $[dm^3_{CO}$ [STP]/$(g_{cat} \cdot h)]$		
		[wt. %]	330°C	350°C	370°C
Fe_2O_3/carbon A	–	–	6.38	11.7	23.8
Ru0.46-Fe_2O_3/carbon A	$RuCl_3 \cdot 0.5H_2O$	0.46	5.44	7.8	12.4
Ru0.46-Fe_2O_3/carbon A	$Ru_3(CO)_{12}$	0.46	35.3	50.1	68.2
Pd0.5-Fe_2O_3/carbon A	$Pd(NO_3)_2$	0.5	–	10.6	20.6
Pd1.0-Fe_2O_3/carbon A	$Pd(NO_3)_2$	1.0	–	16.3	27.1

The effect of ruthenium depends strongly, in turn, on the choice of the Ru precursor. The sample impregnated with ruthenium carbonyl is considerably more active (significantly higher rate constants) than the undoped sample, whereas the catalyst impregnated with ruthenium chloride is less active, compared to Fe_xO_y/carbon. It is supposed, that chlorine acts as a deactivating agent for the system – small amounts of chlorine always remain on the surface of the catalyst after its preliminary activation, thus, leading to the poisoning of active sites. For this reason, a more detailed study of the Ru-doped Fe_xO_y/carbon catalysts was performed with the samples based on the carbonyl precursor only.

Fig. 1 shows the variations of the rate constant (k) *vs* the ruthenium content in the material ($Ru_3(CO)_{12}$ precursor was used). All the catalysts tested in this series of experiments were deposited on carbon A and contained 30 wt. % Fe_2O_3 after calcination. Generally, ruthenium seems to be an advantageous component of the Fe_xO_y/carbon systems prepared. The most active sample (0.75 wt. % Ru) exhibits by several times higher rate of CO conversion (k constant) than the Ru-free material, results from the data collected in Fig. 1, the difference being especially pronounced at a lower temperature of 330°C. There is one doubt, however. The rate constants (k) presented in Fig. 1, as well as those in Table 2, were determined under the assumption, that carbon monoxide reacted with water vapour only ($CO + H_2O = CO_2 + H_2$; WGSR), *i.e.* the contribution of the $CO + 3H_2 = CH_4 + H_2O$ reaction to the overall

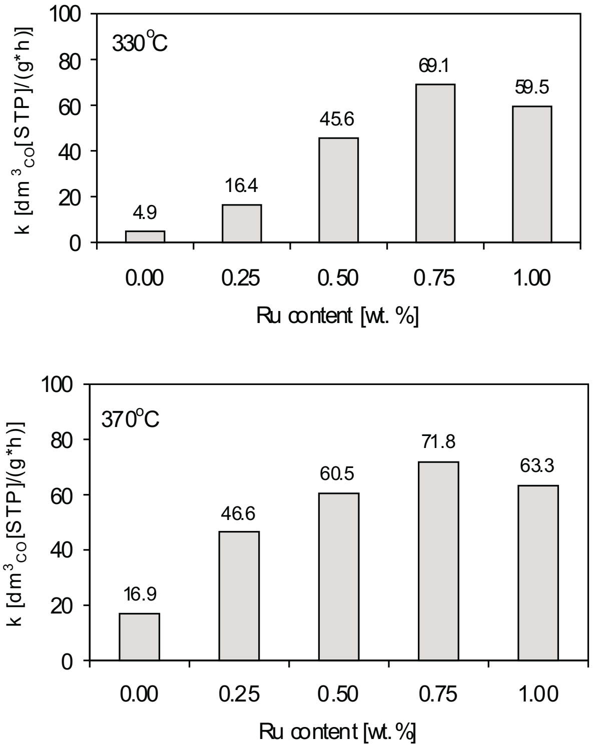

Figure 1. Effect of the ruthenium content ($Ru_3(CO)_{12}$ precursor) on the activity (k) of the Fe_xO_y/carbon A catalysts; all the samples contained 30 wt. % Fe_2O_3 after calcination.

conversion of carbon monoxide was assumed to be negligible. Although the magnetite catalysts, including those supported on carbon [3–5], are known to be very selective in the WGS reaction, the ruthenium presence might lead to nonnegligible methane formation. For this reason, in the subsequent kinetic experiments, the CO conversion measurements were supplemented, with simultaneous measurements of the CH_4 concentration in the outlet gas. Methane formation was monitored chromatographically, by the PU-4500 Philips instrument. Table 3 gives both: overall CO conversion rates determined from the carbon monoxide mass balance and mean (integral) rates of methane formation, all the rates being obtained at 370°C. Apart from the Ru-Fe_xO_y/carbon A and Ru-Fe_xO_y/carbon B catalysts, the chromium-containing systems (Ru-Fe_xO_y-Cr_2O_3/carbon B) was also examined.

Table 3. Rates of CO conversion and integral rates of CH_4 formation over the Ru-doped catalysts at 370°C; all catalysts contained 30 wt. % Fe_2O_3 after calcination; ruthenium was introduced as $Ru_3(CO)_{12}$.

catalyst symbol	CO conversion rate $[dm^3_{CO}\,[STP]/(g_{cat}\cdot h)]$	CH_4 formation rate $[dm^3_{CH4}\,[STP]/(g_{cat}\cdot h)]$
Fe_2O_3/carbon A	0.29	0.00
Ru0.25-Fe_2O_3/carbon A	0.58	0.08
Ru0.50-Fe_2O_3/carbon A	0.63	0.76
Ru0.75-Fe_2O_3/carbon A	0.74	1.21
Ru1.0-Fe_2O_3/carbon A	0.65	1.23
Fe_2O_3/carbon B	0.39	0.00
Ru0.25-Fe_2O_3/carbon B	1.38	0.33
Ru0.50-Fe_2O_3/carbon B	1.57	1.00
Fe_2O_3-Cr_2O_3/carbon B	0.49	0.00
Ru0.25-Fe_2O_3-Cr_2O_3/carbon B	1.59	0.47

It is clearly seen in Table 3, that the enhancement in the CO conversion rate upon the ruthenium addition is accompanied by CH_4 formation. In the range of 0.25–0.75 wt. % Ru, the rate of methanation increases *vs* the Ru loading. For the low ruthenium content (0.25 wt. %), the rates of methanation are, however, by several times smaller than those of CO conversion, regardless of the catalyst kind (Fe_xO_y/carbon, Fe_xO_y-Cr_2O_3/carbon). Consequently, the rates of the water gas shift reaction over the Ru-containing systems (0.25 wt. % Ru) are still significantly higher than those over the ruthenium-free specimens, even if assuming that methane is formed from carbon monoxide only. In the case of higher Ru loadings, the contribution of the carbon monoxide methanation to the overall CO conversion may be large or even very large. Some of the Ru-doped samples (0.75 wt. % Ru or 1.0 wt. % Ru, see Table 3) generate considerable amounts of methane; $r_{CH_4} > r_{CO}$. This means, that a considerable portion of methane results from the reaction of hydrogen with CO_2. Unfortunately, it is impossible to distinguish, from the available data, between the CH_4 formation from CO and that from CO_2. One can say only that both methanation reactions lead to the lowering of hydrogen efficiency.

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