Chlorine-free iron–ruthenium catalyst for the water–gas shift reaction

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Received 28 April 1993; accepted 21 July 1993

We present results of studies on the activity of chlorine-free iron–ruthenium catalysts in the water–gas shift reaction. The catalysts were prepared by impregnation of calcination products of α-, β-, γ-, δ-iron oxide-hydroxides with $Ru_3(CO)_{12}$. For two iron oxides (from α- and δ-FeOOH) the reaction rate constants are considerably higher than those of reactions with other catalysts based on $RuCl_3$. Among the catalysts used, those obtained by impregnation of δ-FeOOH calcination product with $Ru_3(CO)_{12}$ appeared to be the most active.

Keywords: Ruthenium catalysts; alloy catalysts; water–gas shift reactions

1. Introduction

It was proved in our previous paper [1] that ruthenium can be a very attractive component of iron catalysts used in the high-temperature water–gas shift reaction. In this case the most favorable carriers of iron–ruthenium catalysts were the products of calcination of δ- and α-FeOOH type iron oxide-hydroxides, which have the highest concentration of surface basic centers [2]. In these studies, the problem of unfavorable effect of chlorine impurities originating from the catalysts synthesis, was disregarded. As it is well known such residues of chlorine might be located on the surface of metallic ruthenium or on a carrier [3–8] and besides, they may exert unfavorable effect on the water–gas shift reaction. Therefore, to avoid the inhibiting effect of chlorine we have examined the synthesis of chlorine-free iron–ruthenium catalysts from $Ru_3(CO)_{12}$.

This paper gives the results of our studies on the activity of iron–ruthenium catalysts, obtained via impregnation of calcination products of iron oxide-hydroxides with $Ru_3(CO)_{12}$, in the water–gas shift reaction.

2. Experimental

2.1. PREPARATION OF THE CATALYSTS

Iron oxide-hydroxides (α-, γ- and δ-FeOOH) were obtained according to methods described earlier [9]. β-FeOOH was obtained by oxidation with air (24 h) of a solution containing 333.6 g $FeSO_4 \cdot 7H_2O$ pure for analysis and 296.3 g NH_4F pure for analysis in 8.0 dm^3 H_2O. The precipitate was continuously washed out till the ions (SO_4^{2-}, F^-, Cl^-) were no longer detected and then dried.

Iron–ruthenium catalysts were prepared via impregnation of iron oxides obtained as a result of a three-hour thermal activation (at 600°C in air) of iron oxide-hydroxides (α-, β-, γ-, and δ-FeOOH) with $Ru_3(CO)_{12}$ solution. A solution of $Ru_3(CO)_{12}$ in toluene was used for the impregnation. The impregnation process was run in a vacuum evaporator at the atmosphere of dry nitrogen at 70°C for 60 min. Towards the end of this process, the temperature was elevated in order to evaporate the solvent completely. Thus obtained dry catalyst was then subjected to a three-hour thermal treatment at 600°C. A fraction of particle sizes of 0.2–0.1 mm was used for the catalytic runs.

2.2. CATALYTIC REACTION

The catalytic activity for the water–gas shift reaction was measured at 350°C in a flow reactor. A scheme of the applied apparatus was presented before [10]. The reactor was loaded with 0.25 g of the catalyst and the reaction mixture (with the ratio of $H_2O : CO = 2.5$) was passed through at a flow rate of 3.5 dm^3/h. CO of 99.97% purity was purchased from the BOC Limited Special Gases Company, London. Distilled H_2O was used. The conditions for running the reaction, product analysis, and determination of rate constants were discussed before [1]. The results of determination of catalytic activity in the water–gas shift reaction are averages of three measurements. Reproducibility of the results was within 2%.

k values for iron–ruthenium catalysts from $RuCl_3$, given for the sake of comparison, were determined by extrapolation over a range of Ru contents from the results presented in the previous paper [1].

3. Results and discussion

As follows from the results given in table 1, the most active of the chlorine-free iron–ruthenium catalysts obtained via impregnation of calcination products of iron oxide-hydroxides with $Ru_3(CO)_{12}$ are definitely more favourable for the water–gas shift reaction than the corresponding catalysts obtained from $RuCl_3$ [1]. The above conclusion is supported by a comparison of some of the rate constants given in table 1.

Table 1
Activity (k, TOF) in the water–gas shift reaction of iron–ruthenium catalysts obtained by impregnation of calcination products of iron oxide-hydroxides (of the α-, β-, γ- and δ-FeOOH type) by $Ru_3(CO)_{12}$ (ruthenium was expressed in wt%). (0.25 g of the catalyst; reaction temp. 350°C, reaction time 3 h)

Catalyst	Activity of catalysts (after 3 h)		
	k ($cm^3\,g^{-1}\,min^{-1}$)	TOF (mol-CO/at-Ru s)	k_{RuCl_3} [a] ($cm^3\,g^{-1}\,min^{-1}$)
Fe_2O_3-α-600 (A)	26.6	–	–
A + 0.25% Ru-600	30.8	0.7	15.6
A + 1% Ru-600	234.8	0.9	63.1
Fe_2O_3-β-600 (B)	0.0	–	–
B + 1% Ru-600	0.0	0.0	2.5
Fe_2O_3-γ-600 (C)	30.0	–	–
C + 1% Ru-600	21.0	0.12	28.0
Fe_2O_3-δ-600 (D)	31.1	–	–
D + 0.05% Ru-600	54.7	5.87	–
D + 0.2% Ru-600	461.9	6.07	38.1
D + 0.25% Ru-600	663.2	5.24	50.3
D + 1% Ru-600	1593.5	1.42	145.2

[a] Values obtained for appropriate ruthenium catalyst from $RuCl_3$, TOF – turnover frequency. $k = (F_T/w)\ln[\alpha_{eq}/(\alpha_{eq} - \alpha)]$ ($cm^3\,g^{-1}\,min^{-1}$), where k is the rate constant, α conversion degree, α_{eq} is the equilibrium conversion at 350°C ($\alpha_{eq} = 0.928$), F_T is the flow rate of substrate under normal conditions (cm^3/min), w is catalyst weight (g).

It should be pointed out here that depending on the type of iron oxide-hydroxides used in the catalyst preparation, the series of activity is similar as in the case of respective catalysts obtained by impregnation with $RuCl_3$ [1]. The highest values of the reaction rate constants are related to catalysts obtained from calcination products of α- and δ-iron oxide-hydroxides impregnated with ruthenium carbonyl. The only exception to the above is observed in the case of a catalyst obtained by impregnating β-FeOOH calcination products by a low concentration of ruthenium, as at such a low concentration of Ru this chlorine-free catalyst does not reveal any catalytic activity.

The activity of chlorine-free catalysts prepared on the basis of δ- and α-FeOOH is distinctly higher than that of the corresponding catalysts based on $RuCl_3$ discussed extensively elsewhere [1]. For example, the reaction rate constant determined for D + 1% Ru-600 catalyst (see table 1) is ten times higher than the corresponding constant calculated for a catalyst of the same concentration of ruthenium, but based on $RuCl_3$, and it is two times higher than the rate constant determined for a catalyst obtained by impregnation of the same carrier by $RuCl_3$ with a 5% content of ruthenium. Similarly, catalysts obtained by δ-FeOOH impregnation with lower concentration of ruthenium prove clearly more active, even at 0.05 wt% of Ru. In this case, an almost double increase in the rate constant in comparison with the activity of pure iron oxide (from δ-FeOOH) is observed.

Such a high activity of the chlorine-free catalysts, obtained by impregnation with ruthenium carbonyl, is related not only to a lack of chlorine impurities. Another cause to this effect is a more favorable dispersion of metallic phase of ruthenium generated by decomposition of carbonyls on iron oxides of different origin. That the preparation method using $Ru_3(CO)_{12}$ is more favorable was reported earlier [11], also attributing it to a higher metal dispersion.

On the basis of the obtained results, the degree of ruthenium usage in the water–gas shift reaction was estimated by expressing the activity per one Ru atom (turnover frequency). It was found that in the case of the most active catalysts obtained from calcination products of δ-FeOOH the TOF value clearly decreases with increasing concentration of ruthenium. This testified to a decreasing usage of ruthenium in the water–gas shift reaction. Yet, a higher load of ruthenium leads to an increased catalytic activity.

It turns out that the activity of the catalysts under study is affected by both the removal of chlorine from the iron–ruthenium catalysts and specific interactions of ruthenium with iron oxides differing in the nature of surface groups [2,12,13]. Undoubtedly, the nature of surface groups of iron oxides obtained as a result of oxide-hydroxides calcination has an effect on $Ru_3(CO)_{12}$ adsorption. It was shown in previous papers that adsorption of $Ru_3(CO)_{12}$ on the carrier's surface results in formation of various intermediate compounds, depending on the basic–acidic properties of the carrier's surface [14]. In the case of acid oxides, interaction of their surface with $Ru_3(CO)_{12}$ is weak (physical adsorption), while $Ru_3(CO)_{12}$ with basic OH groups (in the case of oxides with basic surfaces) may form compounds of the $[HRu_3(CO)_{11}]^-$ type.

In our investigation it was reported that the observed activity of iron–ruthenium catalysts in the water–gas shift reaction clearly correlates with the basicity of the surface of oxides obtained from iron oxide-hydroxides, which decreases in the following order: $\delta > \alpha >> \beta > \gamma$. No wonder then that iron–ruthenium catalysts obtained from iron oxides of the δ- and α-type are the most active. A similar effect of the basic character of surface groups was observed for the ruthenium catalyst obtained for ammonia [15].

From our studies, the activity of iron–ruthenium catalysts obtained via impregnation of calcination products of iron oxides of δ- and α-FeOOH type with $Ru_3(CO)_{12}$ in the water–gas shift reaction is distinctively high, much higher than that reported for the previously applied iron–chromium catalysts or Mo–Co–Cr–K catalyst (BASF) with activity $k = 243\ cm^3\ g^{-1}\ min^{-1}$ [16] and iron–ruthenium catalysts based on $RuCl_3$ [1]. The most interesting is the catalyst containing 1% Ru made from $Ru_3(CO)_{12}$ and from iron oxide obtained from δ-FeOOH, as its activity surpasses all catalytic properties of the catalysts applied so far in the water–gas shift reaction. Problems associated with the nature of interactions of ruthenium carbonyl with surface groups, occurring with different ferric oxide preparations, are the subject of further studies currently carried out.

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