Iron–ruthenium catalyst for the water–gas shift reaction

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Received 10 August 1992; accepted 27 November 1992

Iron–ruthenium catalysts prepared by impregnation of calcination products of α-, β, γ- and δ-iron oxide-hydroxides with either ruthenium chloride or ruthenium red were tested for the activity for the water–gas shift reaction. The effect of support, ruthenium containing impregnation agent and thermal treatment on catalyst performance was discussed.

Keywords: Iron–ruthenium catalyst; water–gas shift reaction; oxide impregnation

1. Introduction

The deposition of ruthenium on different supports can result in the formation of catalysts of considerable activity for the water–gas shift reaction [1–3]. Examples of such catalyst are a $[Ru(NH_3)_x(OH)_y(CO)_z]^{n+}$ ($n < 3$) complex formed on a faujasite-type zeolite [1], a $[Ru_3H(CO)_{11}]^-$ cluster anchored to silica via ammonium or pyridinium functional groups [2] or a RuO_2/Al_2O_3 catalyst (0.1–0.2 wt% Ru) [4,5]. All these compounds exhibit higher activity for the low-temperature water–gas shift reaction than the commercially used copper oxide chromium oxide catalyst.

In the case of the RuO_2/Al_2O_3 catalysts the conversion degree increases with an increase in the ruthenium content to 5 wt%, this value being associated with the extent of Ru coverage on Al_2O_3 surface [3].

Our preliminary study on catalysts obtained by impregnation of different modifications of iron(III) oxides with various ruthenium compounds has shown that the iron–ruthenium catalysts can be highly active for the water–gas shift reaction. Since there are no reports on the behaviour of the iron(III) oxide supported ruthenium catalysts in the commercially important water–gas shift reaction, we have undertaken a detailed study of the activity of these catalysts for the above reaction.

2. Experimental

2.1. PREPARATION OF THE CATALYSTS

Iron oxide-hydroxides (α-FeOOH, β-FeOOH, γ-FeOOH) were obtained according to methods described earlier [6].

The iron–ruthenium catalysts were prepared either by impregnation of iron oxide-hydroxides (α-, β-, γ- or δ-FeOOH) with ruthenium compounds or by impregnation of oxides formed by a three-hour calcination of the above oxide-hydroxides at 400°C or 600°C. Aqueous solutions of ruthenium chloride ($RuCl_3 \cdot nH_2O$) or ruthenium red $[(NH_3)_5RuORu(NH_3)_4ORu(NH_3)_5]Cl_6 \cdot 4H_2O$ were used for the impregnation.

The amount of ruthenium in the catalyst was 0.5, 2, 4 or 5 wt%. The impregnation procedure was the following: a solution of a ruthenium compound was added gradually to a dry iron oxide-hydroxide until the sample became wet (incipient wetness impregnation) after which the impregnated samples were dried in an oven at 100°C. After drying, the samples obtained were ground and heated for 3 h at 400 or 600°C. A fraction of particle sizes of 0.2–0.1 mm was used for the catalytic runs. Ruthenium-free iron oxide samples were used as reference catalysts.

2.2. CATALYTIC REACTION

The catalytic activity for the water–gas shift reaction was measured at 350°C in a flow reactor described in detail elsewhere [7]. The reactor was loaded with 0.5 or 0.25 g of a 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).

After condensing the steam in an ice cooled trap, the product gas was analysed by a Giede GCHF 18-3 gaschromatograph equipped with a dosing valve GP-1 and a thermal conductivity detector. The reaction products were separated at 120°C on a 2 m column packed with active carbon (20–35 mesh). Catalysts were subject either to 30 min reduction in the reactor in CO flow or were tested without any preliminary treatment. The reaction products were analyzed after 0.5, 0.1, 1.5, 2.0 and 3 h.

An activity test lasted usually for 3 h but the most active catalyst was tested for 20 h. The measurement results are given in terms of conversion and reaction rate constant, k, calculated according to the first-order rate equation [8]

$$k = \frac{F_T}{w} \ln \frac{\alpha_{eq}}{\alpha_{eq} - \alpha} \text{ cm}^3 \text{ g}^{-1} \text{ min}^{-1}, \tag{1}$$

where α is the conversion, α_{eq} is the equilibrium conversion at 350°C, $\alpha_{eq} = 0.928$

(calculated for the parameters applied), F_T is the flow rate of reaction gases under normal conditions (cm^3/min) and w is the catalyst mass (g).

3. Results and discussion

The first series of catalysts was prepared by impregnation of α- and δ-iron oxide-hydroxides with $RuCl_3$ solution (table 1). It has been shown earlier [9] that the above oxide-hydroxides are the best precursors of the water–gas shift reaction catalysts. We have found that the activity of catalysts obtained in such a way without pretreatment with CO is very high, e.g., in the case of catalysts supported on δ-FeOOH, the activity reaches up to about 90%, while their rate constants exceed 300 cm^3 g^{-1} min^{-1} (table 1). It is also worth to add that the activity of catalyst calcined at 400°C, with Ru content of 2 wt% is similar to that shown by a catalyst of 5 wt% Ru content, calcined at 600°C. The same catalysts, when subjected to a 30 min pretreatment with CO, show considerably lower activity. Their corresponding rate constants are not higher than 130 cm^3 g^{-1} min^{-1}.

The process of preliminary reduction involves an appropriate activation of Fe_3O_4 present in catalysts for the high-temperature water–gas shift reaction [10], i.e. the pretreatment should be carried out in the way preventing the reduction to metallic Fe, which catalyzes the highly exothermic side reaction of methanation. In the case of catalysts prepared on the basis of iron oxide-hydroxides with underdeveloped oxide structure [11,12] the undesired process of

Table 1
Conversion degree (%) in the water–gas shift reaction, $RuCl_3$-impregnated iron oxide-hydroxide catalysts (α- and δ-FeOOH); 0.5 g of the catalyst, reaction temperature 350°C

Catalyst	Conversion degree after 3 h on stream			
	with 30 min CO pretreatment		without CO pretreatment	
	(%)	k (cm^3 g^{-1} min^{-1})	(%)	k (cm^3 g^{-1} min^{-1})
α-FeOOH-400	13.4	18.2		
α + 0.5%Ru-400	5.2	6.7	53.1	99.0
α + 2%Ru-400	19.5	27.5	70.0	163.7
α + 5%Ru-400	42.4	71.2	73.4	182.5
α-FeOOH-600	20.3	28.8	20.5	29.1
α + 0.5%Ru-600	19.0	26.7	33.1	51.4
α + 5%Ru-600	62.1	129.0	82.6	257.5
δ + 2%Ru-400	36.2	57.7	89.7	396.3
δ + 5%Ru-400	54.2	102.3	82.2	253.0
δ + 2%Ru-600	58.1	114.7	87.6	336.0
δ + 5%Ru-600	64.1	136.8	89.0	372.6

Table 2
Activity (k, turnover frequency) of iron–ruthenium catalysts for water–gas shift reaction after 3 h; $RuCl_3$ – or ruthenium red – impregnated calcination products of iron oxide-hydroxides (α-, β-, γ- and δ-FeOOH; 0.25 g of the catalyst, reaction temperature 350°C

Catalyst	Activity of catalysts [a]			
	impregnated with $RuCl_3$		impregnated with ruthenium red	
	k [b]	(mol CO/at Ru s)	k [b]	(mol CO/at Ru s)
Fe_2O_3-α-600 (A)	19.9			
A+0.5%Ru-600	23.5	0.27	30.3	0.34
A+2%Ru-600	175.6	0.37	77.0	0.20
A+4%Ru-600	285.3	0.25	263.3	0.24
A+5%Ru-600	475.2	0.24	323.3	0.21
Fe_2O_3-β-600 (B)				
B+0.5%Ru-600	1.9	0.02		0.00
B+2%Ru-600	3.8	0.01	5.9	0.02
B+4%Ru-600	17.8	0.03	24.1	0.03
B+5%Ru-600	53.7	0.06	18.8	0.02
Fe_2O_3-γ-600 (C)	18.0			
C+0.5%Ru-600	29.4	0.33	29.4	0.33
C+2%Ru-600	26.3	0.08	28.1	0.08
C+4%Ru-600	26.3	0.04	26.0	0.04
C+5%Ru-600	14.5	0.02	24.4	0.03
Fe_2O_3-δ-600 (D)	27.4			
D+0.5%Ru-600	109.6	1.05	54.4	0.58
D+2%Ru-600	236.9	0.45	333.6	0.53
D+4%Ru-600	539.0	0.32	482.9	0.31
D+5%Ru-600	745.2	0.27	612.9	0.26

[a] Catalysts not subjected to pretreatment with CO.
[b] k in $cm^3\ g^{-1}\ min^{-1}$.

reduction to metallic Fe proceeds more easily and thus conversions in the water–gas shift reaction are lower. This implies that catalysts which were not subject to CO-pretreatment but were contacted with the mixture of steam and CO are not reduced to metallic Fe and retain high activity (table 1).

The second series of catalysts was prepared by impregnation of the calcination products of iron oxide-hydroxides of α-, β-, γ- and δ-type (table 2) with ruthenium compounds ($RuCl_3$ or ruthenium red). Our studies have shown that more active catalysts were obtained when ruthenium was introduced as $RuCl_3$ rather than as ruthenium red.

All the catalysts investigated within this series can be divided into two groups: one comprises very active catalysts based on the calcination products of δ-FeOOH and of α-FeOOH whereas the others, less active ones, are based on the calcination products of β-FeOOH and γ-FeOOH. The catalysts prepared on the basis of γ-FeOOH, which have a significantly higher surface acidity [9] than those based on products of the calcination of other iron oxide-hydroxides, show a decrease in the catalytic activity with increasing concentration of ruthenium, while in all the other cases the increase in Ru load increases the catalytic activity (table 2). Of all the catalysts studied the catalysts obtained by calcination of δ-FeOOH at 600°C and impregnation with $RuCl_3$ proved to be the most active ones. For example, the rate constant for δ-600–5 wt% Ru-600 catalyst is equal to 745.2 $cm^3\ g^{-1}\ min^{-1}$. The catalyst is active for the time-on-stream of 20 h. Not a much less activity was recorded for a catalyst with a 4 wt% Ru content. On the ground of the results obtained an attempt was made to evaluate the use of ruthenium in the water–gas shift reaction by calculating the activity per 1 atom of the supported ruthenium (turnover frequency). It has been found that very active catalysts obtained on the basis of α- and δ-FeOOH undergo a significant decrease in activity (expressed in terms of a turnover frequency) with increasing ruthenium content. The drop in activity suggests that ruthenium becomes less accessible to the reactants, probably due to an increase in its aggregation with an increased Ru load, and the usefulness of this element is considerably less efficient in catalysts of higher ruthenium content.

It follows from the studies performed that ruthenium can be a very useful component in iron oxide catalysts for the water–gas shift reaction. Depending on the type of iron oxide-hydroxide used for the catalyst preparation, the sequence of activity for the water–gas shift reaction decreases as follows: $\delta > \alpha \gg \beta > \gamma$. The observed decrease in the activity of the catalysts is analogous to the previously reported increase in the concentration of acid surface centres [13,14]. Therefore the activity of iron–ruthenium catalysts depends not only on the chemical composition of catalysts but also on the way of pretreatment and on the modification of initial iron oxides obtained as a result of thermal treatment of iron oxide-hydroxides. The most effective iron–ruthenium catalysts are the calcination products of δ- and α-iron oxide-hydroxides which, as it was found earlier [14], show the highest concentration of surface basic centres. The results of the present study are in agreement with those reported in the literature [9] where it has been proved that calcination products of α- and δ-FeOOH can be successfully used in the preparation of active iron–thorium catalysts. A properly prepared iron–ruthenium catalyst is much more active than currently used catalysts for the water–gas shift reaction. The study on explaining the catalytic role of ruthenium and the nature of active centres of iron–ruthenium catalysts is under way.

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