The influence of alkali metals on the activity of supported ruthenium catalysts for the water–gas shift reaction

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This paper presents the results of the studies on the influence of alkali metals on the activity of ruthenium catalysts, which were supported on the products of α- and δ-iron oxide-hydroxide calcination. Modification of these supports with alkali metals, in particular potassium, rubidium and cesium, prior to deposition of ruthenium was found to increase the activity of Ru/Fe_2O_3 catalysts in the water–gas shift reaction. It was also established that the activity and stability of catalysts prepared on iron oxide obtained from α-FeOOH increased when the latter was modified with sodium ions. The favourable effect of sodium on the activity of the catalysts was shown to appear at a certain proportion of the base to the active component, i.e. ruthenium.

Keywords: ruthenium catalysts, water–gas shift reaction, impregnation with alkali metals, iron oxides and hydroxides

1. Introduction

As follows from our earlier works on supported ruthenium catalysts, their activity in the water–gas shift reaction significantly depends on the character of surface groups formed during the calcination of iron oxide-hydroxides used as a support and on the method of ruthenium deposition [1–3]. A detailed analysis has shown that iron oxides obtained by calcination of oxide-hydroxides of different type differ by the degree of basicity of the surface, decreasing as $\alpha > \delta > \beta > \gamma$ [4]. It has been also established that ruthenium catalysts supported on Fe_2O_3, similar to iron–chromium catalysts, show greater catalytic activity in the high-temperature water–gas shift reaction when they have been prepared with the iron oxides obtained on the basis of α- and δ-type iron oxide-hydroxides [4]. On the other hand, the promoting effect of alkali metals on the catalytic activity of ruthenium supported on different oxides in such reactions of industrial significance as the hydrogenation of CO or synthesis of ammonia, is well known [5–9]. However, the role of basic admixtures introduced into ruthenium catalysts, among others those for water–gas shift reactions, has not been fully explained yet [8].

This paper reports the effect of alkali metals used as admixtures (to the products of calcination of the α- and δ-type iron oxide-hydroxides) for the synthesis of ruthenium catalysts for water–gas shift reactions. Ruthenium, supported on the modified iron oxides, was used in the form of solutions in organic solvents (e.g. solution of $RuCl_3$ in acetone).

2. Experimental

2.1. Preparation of catalysts

Iron oxides used as a support were obtained from α- and δ-FeOOH calcined for 3 h at 600°C in air [2]. The tested alkali metals (as nitrates and Rb as RbCl), were deposited from aqueous solutions at such concentrations that the molar ratio of ruthenium to the alkali metal was 1 : 1. These preparations were dried and calcined once again for 3 h at 600°C and then ruthenium, in the form of a solution of $RuCl_3$ in acetone, was deposited on the support. The catalysts obtained in this way were subjected to calcination at 400°C for 3 h and used in the water–gas shift reaction. A series of reference preparations were iron oxides activated with alkali metals and iron oxides impregnated with ruthenium chloride.

2.2. Catalytic reaction

The catalytic activity for the water–gas shift reaction was measured in a flow reactor. The reaction conditions were as follows: catalyst amount 0.25 g, reaction temperature 300°C, the ratio of $H_2O : CO = 2.5$, flow rate 3.5 dm^3/h. CO of 99.9% purity was purchased from the BOC Limited Special Gases Company, London. The activity of the catalyst was expressed as conversion of CO with steam.The catalytic activities presented in table 1 are averages of three measurements.

Table 1
The effect of alkali metals on the activity of ruthenium catalysts (Me/Ru = 1 : 1 mol) supported on products of calcination of α- and δ-FeOOH at 600°C (N), in the water–gas shift reaction (0.25 g of the catalysts, $T = 300°C$, $H_2O/CO = 2.5$)[a]

Lp.	Catalyst	Concentration (wt%)		Conversion (mol%)	
		Me	Ru	α-FeOOH	δ-FeOOH
1	Fe_2O_3-600 (N)	–	–	6.9[b]	7.6[b]
2	N + Ru-400	–	0.5	8.0	9.0
3	N + Na-600	0.6	–	8.2[b]	8.8[b]
4	N + K-600	1.0	–	8.1[b]	8.6[b]
5	N + Li-600 + Ru-400	0.03	0.5	53.1	7.8
6	N + Na-600 + Ru-400	0.1	0.5	35.7	10.6
7	N + K-600 + Ru-400	0.2	0.5	77.4	60.2
8	N + Rb-600 + Ru-400	0.4	0.5	72.0	60.8
9	N + Cs-600 + Ru-400	0.65	0.5	69.9	63.8

[a] Me: alkali metal; N: support (product of calcination in 600°C of α- or δ-FeOOH); 400, 600: temperatures of calcination.
[b] Temperature of reaction 350°C.

3. Results and discussion

The influence of alkali metals on the activity of supported ruthenium catalysts in the high-temperature water–gas shift reaction was studied on the earlier prepared new Ru/Fe_2O_3 type catalysts [1–3]. The activities of the supports obtained by calcination of α- and δ-FeOOH activated by alkali metals, and the catalysts obtained on their basis are collected in table 1. As follows from the results, introduction of alkali metals deposited on the support does not bring significant changes in the activity of the products of calcination of α- and δ-FeOOH. Deposition of ruthenium alone in the amount of 0.5 wt% on the supports studied changes their catalytic properties by one order of magnitude (see table 1, items 1–4). Regarding the high activity of ruthenium catalysts, the effect of alkali metals was studied at 300°C. Among the supported and alkali metal activated ruthenium catalysts, the most active proved to be those obtained by modification of the support with K, Rb and Cs. Moreover, their activity was higher when the product of α-FeOOH calcination was used as a support (see table 1, items 5–9).

This means that the activity of Ru/Fe_2O_3 catalysts can be significantly improved by modification of the iron support with small amounts of alkali metals, especially potassium, rubidium and cesium. At 300°C the degree of conversion was 70%, while at 350°C it exceeded 90%. It is interesting to analyse the effect of ruthenium concentration on the activity of Ru/Fe_2O_3 catalysts obtained on the basis of α- and δ-FeOOH, fig. 1, and the corresponding alkali metal modified catalysts of different Ru concentration on the surface of Fe_2O_3, figs. 2 and 3.

The degree of conversion with an Ru/Fe_2O_3 catalyst prepared on the δ-FeOOH based support containing about 1 wt% Ru is about 70%, whereas, when an analogous catalyst on α-FeOOH is applied, the degree of conversion is only 10%. When the ruthenium concentration is 2 wt%, the difference between the activities of the catalysts is over 25%, and a general tendency is that the activity increases with ruthenium concentration. It is worth noting that the activity of the catalysts prepared on the δ-FeOOH modified support abruptly increases at the ruthenium concentration of 0.7 wt% and then remains relatively constant with a further increase of ruthenium content, whereas the activity of the catalysts prepared on the α-FeOOH modified support is rather low for ruthenium concentrations up to 1 wt%, and only above this value increases significantly (see fig. 1). A particularly pronounced promoting effect of alkali metals was observed for the catalysts obtained from α-FeOOH

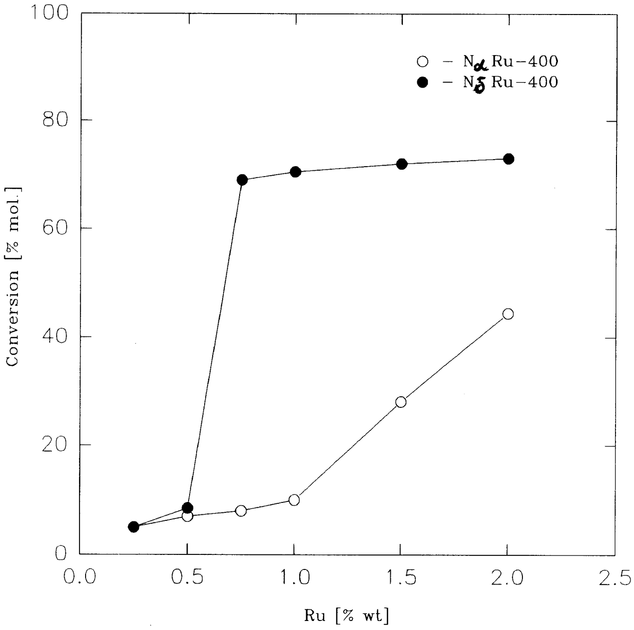

Fig. 1. The influence of ruthenium concentration on the activity of Ru/Fe_2O_3 catalysts, obtained on the basis of α-FeOOH (○) and δ-FeOOH (●), in the water–gas shift reaction. $T = 300°C$, $H_2O/CO = 2.5$. N_α and N_δ denote the supports obtained from α- or δ-FeOOH respectively.

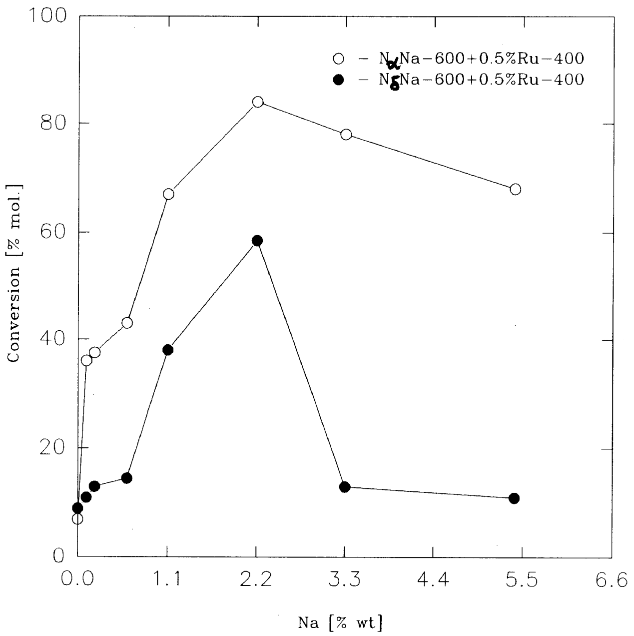

Fig. 2. The effect of sodium ion concentration on the activity of ruthenium catalysts (0.5% Ru) obtained on the basis of α-FeOOH (○) and δ-FeOOH (●), in the water–gas shift reaction. $T = 300°C$, $H_2O/CO = 2.5$. N_α and N_δ denote the supports obtained from α- or δ-FeOOH respectively.

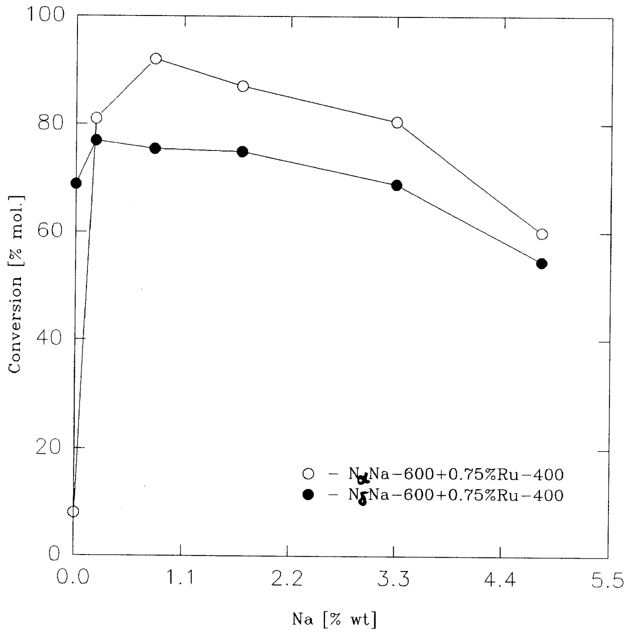

Fig. 3. The effect of sodium ion concentration on the activity of ruthenium catalysts (0.75% Ru) obtained on the basis of α-FeOOH (○) and δ-FeOOH (●), in the water–gas shift reaction. $T = 300°C$, $H_2O/CO = 2.5$. N_α and N_δ denote the supports obtained from α- or δ-FeOOH respectively.

modified with sodium. We report only the results (figs. 2 and 3) illustrating the effect of Na^+ on the catalysts with 0.5 and 0.75 wt% of ruthenium. For both ruthenium concentrations studied, the effect of sodium is particularly favourable.

The catalysts prepared in this way show a much higher activity and stability when compared with their analogues prepared on the basis of the products of δ-FeOOH calcination. The optimum activity of the former is observed for a ruthenium concentration of 0.75 wt%. As follows from the results of our studies, an increase of concentration of the basic admixture has either no effect or an unfavourable effect on the catalytic activity. Also, no evidence has been obtained to support the thesis that an increase of the catalytic activity is proportional to increasing atomic weight of the alkali metal admixture [7]. In general it has been found that the activity of the catalysts reaches a maximum for a certain concentration of the base and ruthenium.

In conclusion, it has been established that a small amount of alkali metal admixture to the supports obtained by calcination of iron oxide-hydroxides allows preparation of ruthenium catalysts showing relatively high activity and stability at low concentrations of ruthenium. Additions of potassium, cesium and rubidium to the ruthenium catalysts (prepared by modification of α- or δ-FeOOH) show the greatest activity. Sodium has been proved to exert a favourable effect on the activity of the catalysts at a certain proportion of the base to the active agent, that is ruthenium, and small amounts of sodium are probably necessary for neutralisation of the surface acidic centres. At concentrations higher than a certain threshold value, sodium can cause a drastic decrease of Ru/Fe_2O_3 activity in the high-temperature water–gas shift reaction. Further studies on the effect of alkali metals on the activity of catalysts obtained by various methods, aimed at explaining the mechanism of their activity, are under way.

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