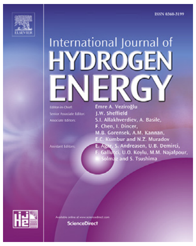
Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/he



The influence of the support composition and structure ($M_XZr_{1-X}O_{2-\delta}$) of bimetallic catalysts on the activity in methanol steam reforming

A.A. Lytkina [a], N.V. Orekhova [a], M.M. Ermilova [a], A.B. Yaroslavtsev [a,b,*]

[a] A.V.Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Moscow, 119991, Leninsky Prospect 29, Russian Federation
[b] N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Moscow, 119991, Leninsky Prospect 31, Russian Federation

ARTICLE INFO

Article history:
Received 24 August 2017
Received in revised form
11 October 2017
Accepted 14 October 2017
Available online 1 December 2017

Keywords:
Hydrogen production
Methanol steam reforming
Bimetallic catalyst
Stabilized zirconia
Support effect

ABSTRACT

Metal oxide-stabilized zirconia supports ($M_xZr_{1-x}O_{2-\delta}$) with different dopants (M = Y, La, Ce) were prepared by coprecipitation method. Bimetallic Cu–Ni and Ru–Rh catalysts supported on $M_xZr_{1-x}O_{2-\delta}$ were prepared by the sequential wetness impregnation method, for use in hydrogen production by methanol steam reforming. The effect of the nature and quantity of the dopant cation (M = Y, Ce) on the catalytic performance of zirconia supported metal catalysts was investigated. The activity of Ni–Cu/$Y_xZr_{1-x}O_{2-(x/2)}$ ($x = 0.1$–0.3) samples increases with an increase in yttrium concentration due to the formation of oxygen vacancies. The dependence of the catalytic activity on the ceria concentration was not monotonous. The sample containing 10% of cerium oxide showed the highest activity. The performance of a Ni–Cu/$La_{0\cdot1}Zr_{0,9}O_{1.95}$ sample was compared with the performance of a Y and Ce containing samples with the same quantity of dopant cation (10%). The La doped catalyst was more active than the yttria-containing composites, but its selectivity was lower. The catalyst based on Ru–Rh alloy differed with significantly higher activity and lower selectivity compared with Ni–Cu samples. The selectivity of the process was not less than 99.5% for all catalysts even at the high temperatures. At the same time, the improved activity of the catalyst also results in an increase in carbon monoxide formation while the hydrogen selectivity decreases. The optimal characteristics, such as rather high hydrogen yield, good selectivity and stability were shown by the catalyst with $Ce_{0\cdot1}Zr_{0\cdot9}O_{2-\delta}$ support.

Introduction

The search for new sources of clean energy is becoming more and more important due to the problem of environmental pollution caused by fuel combustion products. One of the most promising clean technologies is the production of electricity with the use of fuel cells. The fuel cells with proton exchange membranes (PEMFC) are considered to be the most promising systems of autonomous power supply, energy storage and for transportation applications [1,2]. For this reason hydrogen becomes one of the most popular products for alternative energy [3–5]. However, the storage and the transportation of hydrogen are a complicated task. The most

---

* *Corresponding author*. A.V.Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Moscow, 119991, Leninsky prospect 29, Russian Federation.
E-mail address: yaroslav@igic.ras.ru (A.B. Yaroslavtsev).

https://doi.org/10.1016/j.ijhydene.2017.10.182
0360-3199/

convenient way to store hydrogen, perhaps, is the use of metal hydrides, but the capacity of the storage systems based on them is insufficient [6]. The steam or dry reforming of natural gas, coal, hydrocarbons and various alcohols allows producing hydrogen *in situ*, which solves the above mentioned problems [7–10].

Currently, methane is the main material used for the production of hydrogen, however, the high stability of its molecule leads to the relatively high temperature of its processing and therefore a low selectivity; hydrogen produced in this way requires a complex purification [11–13]. The reforming of alcohols, which are considerably more active than methane, occurs at significantly lower temperatures and with higher selectivity [14–17]. More importantly, the alcohols produced from the biomass (bio-alcohols) may be considered as renewable raw materials [18–21]. Compared with other types of fuel, methanol has a number of benefits as a precursor for the hydrogen production. The absence of the C–C bonds provides the reforming flow at relatively low temperatures (200-300° C). Furthermore, the hydrogen content in methanol is rather high, and it is a liquid at a room temperature, which greatly facilitates the storage and the transportation [6,22–24]. From an environmental viewpoint the production and the use of methanol results in a reduced “carbon footprint” compared with conventional synthetic fuels derived from coal [25–27].

The purpose of the methanol steam reforming (MSR) reaction is hydrogen production; however, some other products are formed during the process, and they also need to be taken into account.

The MSR process proceeds according to the reaction:

$$CH_3OH + H_2O \leftrightarrow CO_2 + 3H_2, \quad \Delta H^0_{298\ K} = 49.7 kJmol^{-1} \tag{1}$$

The main side processes are the reactions of methanol decomposition (2) and water-gas shift (WGS) reaction (3):

$$CH_3OH \leftrightarrow CO + 2H_2, \quad \Delta H^0_{298k} = 90.2\ kJmol^{-1} \tag{2}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2, \ \Delta H^0_{298k} = -41.2\ kJmol^{-1} \tag{3}$$

The reactions (1) and (2) are endothermic, and the reaction (3) is exothermic.

The reaction mixture consists of hydrogen, carbon oxides, unreacted water and methanol. The majority of applications, including low-temperature fuel cells, require the high hydrogen purity degree, and the admixtures of carbon monoxide should be minimized [28]. Copper and metals from the VIIIB-group are the most widely used catalysts, characterized by high activity and selectivity towards hydrogen [29–35]. One of the ways to improve the stability and to reduce the cost of such catalysts is the addition of a second metal [36–38].

The catalytic systems used are presented mainly by a metal catalyst and a support, which often consists of oxides [30–33,39]. At the same time, an importance of a support choice is highlighted by an essential dependence of the products yields and the process selectivity upon its nature and even structure [40,41]. From this point of view zirconia, which can be obtained in several crystalline modifications, can be considered as an interesting example of the support [16,31,42–45]. It is possible to obtain one or another structure by adjusting the temperature of the treatment, nature and concentration of a dopant.

The cubic fluorite type modification c-ZrO_2 exists only at high temperatures, when thermal fluctuations in the crystal lattice are significant. This modification transforms to the tetragonal t-ZrO_2 with a distorted fluorite structure when the temperature decreases and then in the monoclinic m-ZrO_2 with a baddeleyite structure. A stabilization of the high-temperature modification can be achieved by substitution of several zirconium atoms by ions with higher radii (Ce^{4+}, Th^{4+}) or by means of vacancies formation in the anionic sublattice by ions with lower valency (Mg^{2+}, Ca^{2+}, Y^{3+}, Sc^{3+}) [16,42].

Earlier Ni–Cu catalysts based on zirconia with the tetragonal and monoclinic structures were investigated [41]. The purpose of this work was the development of bimetallic Ni–Cu and Ru–Rh catalysts on the zirconia support, doped with yttrium, lanthanum and cerium, as well as the study of obtained catalysts' efficiency in the MSR process. It was interesting to compare the activity of catalysts based on the noble metals and copper with nickel alloys. However, because of the difference in the metals activity and cost, the investigated Ru–Rh and Ni–Cu catalysts contained different quantities of metals (5% and 20% respectively).

Experimental

Catalysts and supports preparation

$Y_xZr_{1-x}O_{2-(x/2)}$ (x = 0.1, 0.2, 0.3), $La_xZr_{1-x}O_{2-(x/2)}$ (x = 0.1) and $Ce_xZr_{1-x}O_{2-\delta}$ (x = 0.05, 0.1, 0.15, 0.2) samples were prepared by coprecipitation from zirconium oxynitrate $ZrO(NO_3)_2$ (99% ALDRICH), yttrium nitrate $Y(NO_3)_3{\cdot}6H_2O$ (chemically pure), lanthanum nitrate $La(NO_3)_3{\cdot}6H_2O$ (chemically pure) and cerium nitrate $Ce(NO_3)_3{\cdot}6H_2O$ (99,995%) solutions using the procedure described in Ref. [46]. Hydrated oxides, obtained on the first step, were annealed for 5 h at the temperature of 600 °C to form a solid solution of oxides with the fluorite structure. The resulting samples were sequentially impregnated with the aqueous solutions of $Cu(NO_3)_2{\cdot}3H_2O$ (>98%) and $Ni(NO_3)_2{\cdot}6H_2O$ (≥98.5% ALDRICH) in the quantities calculated so that the total metal content was 20% of the support weight. The ratio of nickel and copper in the samples was 1: 4 (previously it has been shown that this ratio is close to optimal for the Ni–Cu system [41]). The prepared suspension was dispersed by an ultrasonic homogenizer US Soniprep for 1 h and then the excess water was evaporated at 100 °C in the oven. The resulting catalysts were annealed in an air stream at 400 °C for 3 h in a muffle furnace and then kept in a H_2 (5%)/Ar (20 ml/min) flow for 3 h at 350 °C for metal reduction.

The sample containing Ru–Rh (5%) was prepared in a similar way. As the metal precursors ruthenium chloride (III) and rhodium (III) chloride were used in this case.

Shorthand notations of all the studied catalysts are reported in Table 1.

Materials characterization

The specific surface area and pore sizes of the obtained catalysts and supports were investigated by BET method