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The Evaluation of Oxide Catalysts' Properties in Test Reactions

Wincenty Turek · Agnieszka Sniechota · Jerzy Haber

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Abstract Oxidative dehydrogenation of cyclohexane could be very promising and complementary test reaction to evaluation of redox properties of the catalyst surface, which are very important in the selection of materials for neutralisation of NO_x. The process is autothermic and it runs in significantly lower temperatures than conventional dehydrogenation.

Keywords Test reactions · Dehydrogenation of cyclohexane · Oxidative dehydrogenation of cyclohexane

1 Introduction

Air is one of the most important elements of our environment. It is an essential element for living organisms. Pollutants present in the air have a negative influence on the development and life of plants, animals and people and endanger the global climate system. Nitrogen oxides are one of the most significant groups of compounds causing air pollution. Therefore it is very important to limit their emission to the environment.

The most popular industrial method of nitrogen oxides neutralisation is catalytic selective reduction using ammonia [1, 2]. This method was first introduced in Japan in the 1970's [3], and around 10 years later in the USA, Germany and Australia [4]. However, due to significant drawbacks of the process, new methods of nitrogen oxides neutralisation are investigated. The most important disadvantages of catalytic selective reduction using ammonia are:

- formation of various by-products such as organic cyanides or isocyanides when the amount of ammonia is not controlled,
- use of expensive and highly corrosive and toxic ammonia,
- the contact temperature must be maintained in a narrow range. Too high or too low temperature leads to lower degree of reduction,
- problems with transport and storage of ammonia.

A very promising solution is catalytic selective reduction of NO_x with hydrocarbons (SCR HC) and alcohols. This method is a convenient and cheap process with excess of oxygen, where unreacted hydrocarbons from the fuel are used as reducing agents [5]. Hydrocarbons (mainly methane, propane, propene) and alcohols are easily accessible, exhibit neutral chemical character and give low running costs. Ethyl alcohol, especially, is one of the most promising reducing agents for neutralisation of nitrogen oxides. It is a natural product, non-toxic at low concentrations. It is also much cheaper than ammonia.

Although a satisfactory catalyst has not been found, catalytic decomposition of NO seems to be an attractive and promising method of limiting nitrogen oxides

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W. Turek (✉) · A. Sniechota
The Silesian University of Technology, ul. Strzody 9, 44-100 Gliwice, Poland
e-mail: wincenty.turek@polsl.pl

A. Sniechota
e-mail: agnieszka.sniechota@polsl.pl

J. Haber
Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, Niezapominajek 8, 30-239 Krakow, Poland
e-mail: nchaber@cyf-kr.edu.pl

emission, because it does not require addition of any other reactants and leads only to neutral products. The only disadvantage is the cost of catalyst.

Studies of metal, oxide and zeolite catalysts suitable for this type of applications are carried out [2]. In the case of effective catalyst, hydrocarbons and alcohols should selectively react with NO, and they should not react with adsorbed oxygen or lattice oxygen. In addition, the catalyst must remain active in the presence of SO_2 and H_2O [6, 7].

The most attention was focused on zeolites with metal cations like CuZSM-5 [8, 9]. The activity of the catalyst depends on the metal cation, which is the active centre for the reduction of NO. Zeolites are not hydrothermally stable and are not good practical catalyst; additionally narrow pores in zeolites can limit the diffusion and the rate of reaction [10].

Metals are active only in narrow temperature range and often catalyse oxidation of hydrocarbons. When the reducing agents is fully used the conversion of NO_x falls when increasing the temperature. Moreover, the significant amount of NO is reduced to N_2O, which is also a pollutant [2].

Metal oxides are thermodynamically stable, which is very important for car catalysts often working at high temperatures [11]. Mixtures of more catalysts are often used [12] in order to improve the properties of metal oxides, especially the possibility of application in wide temperature range. Perovskites [13, 14] and spinels [15, 16] are also active in reduction of NO_x. Their advantages include higher selectivity in reduction of NO to N_2 than in the case of simple transition metal oxides and the appropriate mixtures [14–16]. Additionally introducing potassium cations into A positions of perovskites ABO_3 i K_2NiF_4 (A_2BO_4) effectively increases the activity and selectivity of neutralisation of NO_x.

Therefore, metal oxides with redox properties and the structure of spinels or perovskites were chosen. Redox properties of the catalyst surface seem to be very important in the selection of materials for neutralisation of nitrogen oxides.

Evaluation of catalysts for particular reactions and determination of certain properties of catalysts, carriers and adsorbents is carried out using catalytic test reactions. Reduction of nitrogen oxides with hydrocarbons is usually performed in the temperature range 500–750 K, so the evaluation of the catalyst and its redox properties should be based on test reactions that proceed at similar temperatures [6, 7]. It seems that a suitable reaction for this purpose can be dehydrogenation of cyclohexane, which occurs at adequately high temperature. This test reaction can be more reliable in evaluation of redox properties of the surface of the catalyst for the reduction of nitrogen oxides than the conversion of isopropyl alcohol which is widely used to determine redox and acid–base properties of the surface [17].

There are processes, which are used in the global industrial scale. There are oxidative dehydrogenation of organic compounds. They are used for production formaldehyde from methanol, ethane and ethene in the oxidative coupling of the methane, and they also could be used for production styrene from ethylbenzene [18–20]. Oxidative dehydrogenation of cyclohexane is very promising test reaction to evaluation of redox properties of oxysalts. This process is autothermic, it runs in significantly lower temperatures than conventional dehydrogenation of cyclohexane and for this reason the reduction of catalysts is impossible.

The aim of our studies was to determine which test reaction: dehydrogenation of cyclohexane or oxidative dehydrogenation of cyclohexane can be more useful in the description of redox properties of oxide catalysts for neutralisation of nitrogen oxides: catalytic reduction by ethanol and catalytic conversion NO_x. The catalysts chosen for detailed studies were: $NiCo_2O_4$, $NiFe_2O_4$ and $NiMoO_4$.

2 Experimental

Materials: The materials for catalysts' preparation ($Ni(NO_3)_2 \cdot 6H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, $FeCl_3$ sodium hydroxide, ammonia solution 25%) and cyclohexane, used for test reactions, were obtained from POCh (Poland) and were pure grade.

2.1 Synthesis of Catalysts

2.1.1 Synthesis of $NiCo_2O_4$

$NiCo_2O_4$ was obtained by co-precipitation of solutions of $Ni(NO_3)_2 \cdot 6H_2O$ and $Co(NO_3)_2 \cdot 6H_2O$ with aqueous solution of sodium hydroxide. The precipitate was filtered, dried and calcined at around 600 K for 10 h [21].

2.1.2 Synthesis of $NiFe_2O_4$

$NiFe_2O_4$ was obtained by co-precipitation of solution of $Ni(NO_3)_2 \cdot 6H_2O$ and $FeCl_3$ with aqueous solution of sodium hydroxide and subsequent drying and calcination for 5 h at around 1,000 K [22].

2.1.3 Synthesis of $NiMoO_4$

$NiMoO_4$ was obtained by precipitation of solution of $Ni(NO_3)_2 \cdot 6H_2O$ and $(NH_4)_6Mo_7O_{24} \cdot 7H_2O$ with aqueous solution of ammonia at 343 K, drying and calcination at around 800 K for 15 h [23].

2.2 Physico-chemical Studies

2.2.1 Studies of Specific Area

Measurements of the specific area using a BET method were carried out by adsorbing nitrogen at 77.4 K in ASAP 2010 apparatus.

2.2.2 Studies of X-ray Diffraction (XRD)

Measurements of the XRD were carried out in Siemens D5005 (Bruker-AXS, Germany) diffractometer, used Cu K_α radiation and a graphite monochromator.

2.2.3 Studies of Catalytic Activity

Oxide catalysts were studied in two test reactions: dehydrogenation of cyclohexane and oxidative dehydrogenation of cyclohexane. The main product of cyclohexane dehydrogenation is benzene. At high temperatures some cyclohexene can also be formed. The reaction is reversible. The temperature over which the reaction occurs is 570 K, according to the available data. Below this temperature the hydrogenation of benzene proceeds.

The main product of cyclohexane oxidative dehydrogenation is also benzene, but some other processes such as full oxidation of cyclohexane (in the case of very active catalysts) and non-destructive oxidation of cyclohexane can also proceed.

Kinetic measurements were performed in a glass reactor with the inside diameter of 18 mm. The reaction substrate—cyclohexane was diluted with nitrogen. Dehydrogenation of cyclohexane was carried out at the mole fraction of the reactant equal to 0.0310. During the measurements in oxidative dehydrogenation of cyclohexane, the mole fraction of cyclohexane was 0.01897 and the mole fraction of oxygen was 0.03784. These values were chosen to ensure that cyclohexane and oxygen could not form an explosive mixture.

The flow rate in the catalytic reactor was equal to 20 dm^3/h. Measurements were carried out in the conversion range below 25% in the steady state. Approximately 3 g of the catalyst was used in each catalytic tests. Before the reaction all the catalysts were conditioned in the reactor at 130 °C for 1 h in the nitrogen flow. Products of the reaction were analysed by gas chromatography (two parallel acid-resistant steel columns, 3 m long, 3 mm internal diameter, packed with 4% Carbowax 20 M on Chromosorb G, AW, DMCS, 80/100 mesh, chromatograph equipped with a FID detector). Based on the results of catalytic experiments, specific rates of the reactions taking place in the systems, their activation energies were calculated.

3 Results and Discussion

3.1 Studies of Specific Area

Values of specific area of investigated catalysts are shown in Table 1.

The values of specific area of the catalysts were used to calculate specific rates of test reactions.

3.2 Studies of X-ray Diffraction

XRD measurements were performed to verify the phase purity and identification of crystalline phases of oxide catalysts studied.

Figures 1–3 show X-ray diffraction patterns of investigated catalysts.

The diffraction pattern of the sample contains only signals characteristic of the spinel $NiCo_2O_4$ and no other signals indicating the presence of other phases. The sample contains phase pure regular $NiCo_2O_4$ (spinel). The parameters of the elementary cell of $NiCo_2O_4$: a = 8,114(14) Å, Z = 8, space group: $Fd\bar{3}m$.

The diffraction pattern contains signals characteristic of regular $NiFe_2O_4$ with a small amount of trigonal Fe_2O_3 (hematite).

Parameters of the elementary cell of $NiFe_2O_4$: a = 8,3379(3) Å, Z = 8, space group: $Fd\bar{3}m$. Parameters of the elementary cell of Fe_2O_3: a = 5,0285(7) Å, c = 13,736 Å, $\gamma = 120°$, Z = 6, space group: $R\bar{3}c$.

Table 1 Values of specific area of catalysts

Catalyst	S_{BET} [m^2/g]
$NiCo_2O_4$	2.50
$NiFe_2O_4$	7.70
$NiMoO_4$	11.60

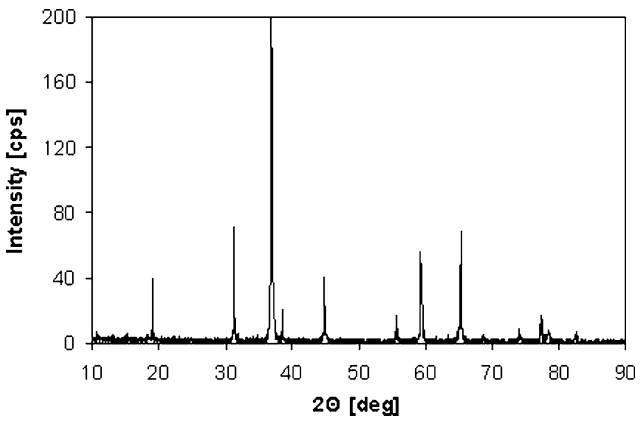

Fig. 1 X-ray diffraction patterns of $NiCo_2O_4$

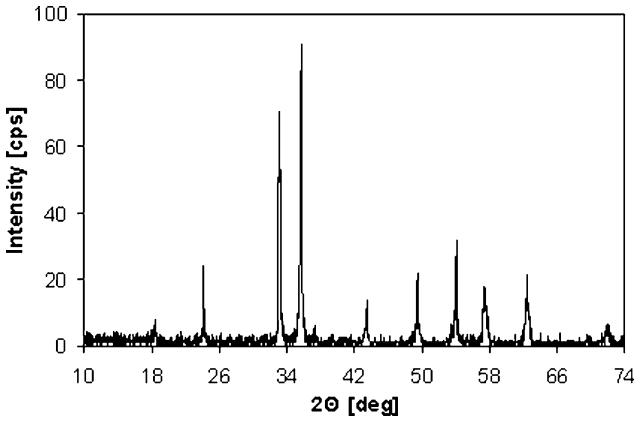

Fig. 2 X-ray diffraction patterns of $NiFe_2O_4$

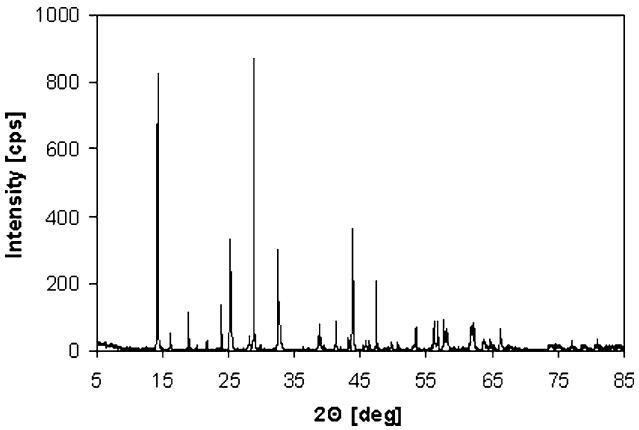

Fig. 3 X-ray diffraction patterns of $NiMoO_4$

The diffraction pattern of the sample contains only signals characteristic of monoclinic α -$NiMoO_4$. Parameters: a = 9,566(1) Å, b = 8,734(1) Å, c = 7,649(1) Å, β = 114,22(1)°, Z = 8, space group: C2/m.

The diffraction patterns confirm that the sample are pure phases and small amounts of impurities (in the case of $NiFe_2O_4$) do not influence further studies.

3.3 Studies of Catalytic Activity

The results of test reactions—dehydrogenation of cyclohexane to benzene and oxidative dehydrogenation of cyclohexane to benzene and steam, were used to calculate specific reaction rates and mole fractions of each product for the catalysts studied. From these data Arrhenius plots showing the dependence of logarithm of the reaction rate on 1/T were prepared (Figs. 4 and 5).

On the basis of Arrhenius plots, activation energies of cyclohexane dehydrogenation to benzene and oxidative dehydrogenation of cyclohexane to benzene and steam over the investigated catalysts were calculated and the results are shown in Tables 2 and 3.

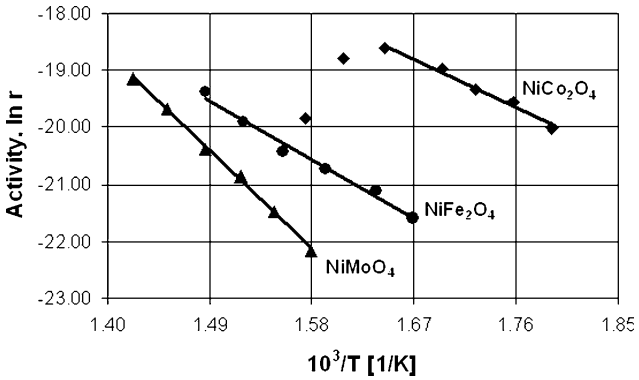

Fig. 4 Dehydrogenation of cyclohexane to benzene

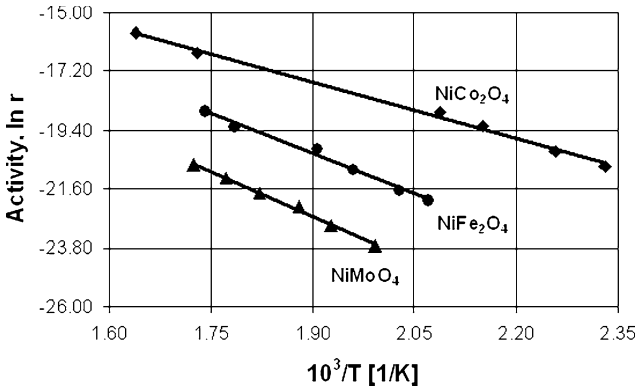

Fig. 5 Oxidative dehydrogenation of cyclohexane to benzene and steam

Table 2 Activation energies dehydrogenation of cyclohexane

Catalyst	E_a [kJ/mol]
$NiCo_2O_4$	79.3 ± 13.8
$NiFe_2O_4$	95.6 ± 16.2
$NiMoO_4$	158.9 ± 9.8

Table 3 Activation energies of oxidative dehydrogenation of cyclohexane

Catalyst	E_a [kJ/mol]
$NiCo_2O_4$	58.5 ± 5.6
$NiFe_2O_4$	83.6 ± 11.6
$NiMoO_4$	137.3 ± 9.2

Test reactions over all the catalysts proceed in the kinetic region, which is confirmed by linear Arrhenius plots. Such relationship can be obtained at low conversion in the test reactions (less than 25%).

For reliable evaluation of the activity of oxide catalysts the temperatures at which the rate of dehydrogenation of cyclohexane to benzene and oxidative dehydrogenation of cyclohexane to benzene and steam reaches a constant value

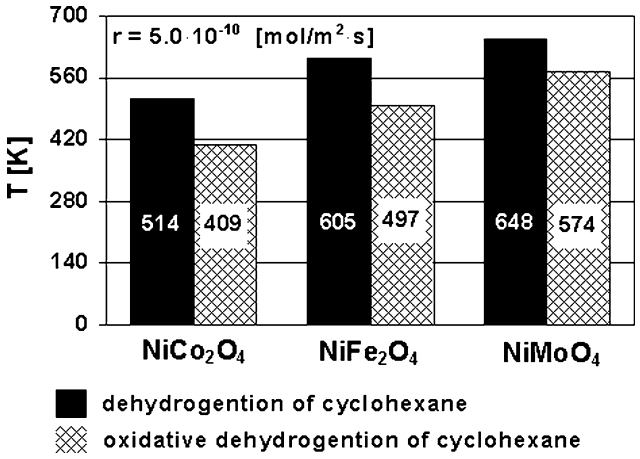

Fig. 6 Temperatures, in which the rate of reactions is constants

equal $r = 5.0 \times 10^{-10}$ mol/m^2 s were found. The results are shown in Fig. 6.

The main objective of test reactions is to determine catalytic activities of catalysts. Such measurements are very important because they give information about the kinetics of reactions—specific reaction rates and activation energies. In this way catalysts for various processes can be chosen. The processes studied by our group are catalytic reduction of NO_x with hydrocarbons and alcohols and catalytic conversion of NO_x to molecular nitrogen and oxygen.

It is not easy to find a good catalyst for these reactions. The reactions do not proceed over catalysts with weak redox properties and the catalyst with strong redox properties are easily deactivated due to the chemisorption of oxygen. The catalysts chosen for detailed studies were: $NiCo_2O_4$, $NiFe_2O_4$ and $NiMoO_4$. Their activity was determined on the basis of two test reactions.

Dehydrogenation of cyclohexane to benzene should be a more reliable test reaction, because it is usually carried out in the temperature range 570–750 K, which is the same as the temperature of nitrogen oxides reduction [6, 7]. However, it has some disadvantages such as endothermic character, while the conversion and reduction of NO_x is exothermic. The second test reaction—oxidative dehydrogenation of cyclohexane to benzene is exothermic. The advantage of the second reaction is also the lack of reduction of catalysts ($NiCo_2O_4$) (Fig. 5), which could be observed in the case of conventional dehydrogenation of cyclohexane (Fig. 4).

The analysis of activation energies of both reactions (Tables 2 and 3) for investigated oxide catalysts shows that these values, in the case of oxidative dehydrogenation of cyclohexane can be a good measure of redox properties of catalysts. These values are lower than the respective values of activation energies in the case of dehydrogenation of cyclohexane.

The activity of catalysts arises in the following order: $NiMoO_4 < NiFe_2O_4 < NiCo_2O_4$.

In the Fig. 6, it could be noticed that the temperatures, at which the reaction rate has a constant value for each catalyst, are significantly higher in the case of first test reaction than the respective temperatures in the case of second test reaction, because dehydrogenation of cyclohexane occurs at higher temperatures. The activity of catalysts arises in the same order: $NiMoO_4 < NiFe_2O_4 < NiCo_2O_4$. Catalyst $NiCo_2O_4$ shows the strongest redox properties, $NiFe_2O_4$—strong and $NiMoO_4$ shows average redox properties.

Because of unambiguous determination of redox properties of catalyst surface, oxidative dehydrogenation of cyclohexane could be very promising and complementary test reaction. It can also supplement TPD NO in investigations of catalysts for nitrogen oxides neutralisation in exhaust gases from power plants and chemical industry.

4 Conclusions

Diffraction patterns of investigated catalysts show that the samples are pure phases and small amounts of impurities (in the case of $NiFe_2O_4$) have no influence on further experiments. The results obtained in this study indicate that test reactions – dehydrogenation of cyclohexane and oxidative dehydrogenation of cyclohexane can be used to study catalysts' activities, which show properties, for reduction and conversion of nitrogen oxides. It was found that oxidative dehydrogenation of cyclohexane is the more accurate reaction to examine the catalysts in view of applications for neutralisation of NO. The most active catalyst, which exhibits the strongest redox properties is $NiCo_2O_4$ and $NiFe_2O_4$ and less active catalyst with average redox properties is $NiMoO_4$.

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