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NANOCOMPOSITE OXIDE SYSTEMS FOR OXIDATION OF CO AND VOLATILE ORGANIC COMPOUNDS IN GASEOUS PHASE

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Abstract

In the present study bulk NiOx and supported NiOx/ZrO_2 catalysts were prepared. The bulk NiOx was synthesized using the precipitation-oxidation method with reverse order of precipitation while deposition-precipitation method technique was applied for the preparation of zirconia supported catalyst. The catalytic activity and selectivity of as-prepared oxide catalysts were studied in reaction of complete oxidation of CO, dimethyl ether and methanol. Strong influence of the support on the catalytic activity of NiOx/ZrO_2 was observed. Experimental results demonstrated complete oxidation of these compounds at different temperatures.

Key words: *NiO_x and NiO_x/ZrO_2 catalysts, heterogeneous catalytic oxidation, CO, methanol, dimethyl ether, waste gases*

1. INTRODUCTION

In the last years, huge amounts of carbon monoxide (CO) and volatile organic compounds (VOCs) such as methanol and dimethyl ether (DME) are emitted in the atmosphere, mainly from transport, chemical industry and domestic activities (Schneidemesser et al., 2010). Due to its high affinity to hemoglobin, CO is a very toxic gas for human beings; moreover it is also a precursor of the ground level ozone which can raise serious health problems. In addition to CO, DME is widely used as an aerosol propellant to replace chloro- and fluorocarbons that can destroy the ozone layer of the atmosphere (Baker et al., 2008). Methanol is also found in the atmosphere due to its increasing role as a low-cost fuel with low NO emissions. All of these reasons render the abatement of CO, DME and methanol before discharging into the atmosphere an important issue and needs highly efficient low-cost processes.

Recently much attention has been focused on the synthesis of low-molecular, highly efficient, selective, stable and low-cost catalysts for the complete oxidation of CO, CH_3OH and $(CH_3)_2O$ (Baker et al., 2008; Tabakova et al., 2013). Although the high activity of noble metals as catalysts in oxidation processes, due to their high price they have limited application for solving ecological problems related to gas emissions purification from CO и VOCs. The solution of problems connected with the environment protection in the future is connected with the development of new oxide catalyst systems of transition metals.

It is known that the composition, structure and surface properties of the catalysts, which are of utmost importance for their catalytic activity, selectivity and thermal stability depend on the applied synthesis procedures. A number of methods exist for the synthesis of nanosized oxide systems as laser methods, plasma methods using various plasma discharges, electrodispersion, thermal combustion, mechanical grinding, sol-gel reactions, solid-phase reactions, etc. These syntheses are carried out at high temperatures leading to the formation of oxides with large particles sizes and worse homogeneity. It is known that the ideal product of nanotechnologies should be obtained with 100% reproducibility and should possess unique properties making it applicable for special purposes.

The practical application of oxide catalytic systems is related to their deposition on proper supports; improvement of the acid-base and oxi-reduction properties of the supports. The nature of the supports affects strongly the catalyst activity and selectivity due to their ability to disperse the active phase in various ways (the authors prove that porous supports increase the dispersity of the active phase and the contact between the active centers and the reagents. γ-Al_2O_3 is one of the most widely used supports for nickel catalysts, due to its high thermal stability (800 ^oC) and high specific surface 200-250 m^2/g^{-1} (Li et al., 2008).

Cerium (CeO_2) and zirconium (ZrO_2) oxides find also wide application as supports of nickel catalysts. The presence of centers with basic properties in ZrO_2 increases the activity of the immobilized phase. The role of

ZrO_2 as a support is due to its ability to be easily reduced at high temperatures releasing oxygen (Wei et al., 2013). Cerium oxide and ceria-supported catalysts are widely used in variety of catalytic reactions (Ma et al., 2014; Kim et al., 2012; Avgouropoulos et al., 2008; Ilieva et al., 2010). These applications take advantage of the excellent redox properties and high oxygen storage capacity of ceria. The ability of ceria to change the oxidation state of the cation between (+3) and (+4) depending on the redox conditions, results in rapid formation and elimination of oxygen vacancy defects (Tabakova et al., 2013). Moreover, one of the most important applications of the CeO_2 is its use in the three-way catalyst for automotive gas treatment (Kašpar et al., 1999). Promising results in CO catalytic oxidation reaction of gold catalysts supported on CeO_2 doped by some rare-earth or transition metals have been recently reported (Laguna et al., 2010; Karpenko et al., 2007; Hernández et al., 2010;). Tabakova et al. investigated that 100 % conversion degree of CO and CH_3OH were achieved at 25^OC and 40^OC respectively, using AuCeCo catalyst. It has been concluded in the same work that the catalytic activity towards the oxidation of CO and methanol was in the following order: AuCeCo>AuCe>AuCeFe>AuCeMn (Tabakova et al., 2013). Wootsch et al. found that Pt/CeO_2 catalysts with different Pt concentrations were more active than Pt/Al_2O_3 in CO oxidation. The effect of the temperature in the range 90 – 300 ^OC has been also studied and four reaction mechanisms were suggested (Wootsch et al., 2004). Nanosize effect of ZrO_2 in Au/ZrO_2 catalyst has been studied by deposition-precipitation of Au nanoparticles with size 4-5 nm on ZrO_2 nanoparticles of varying sizes. Nanocomposite Au/ZrO_2 catalysts with sized 5-15 nm ZrO_2 particles have been found more promising over those containing larger (40-200 nm) ZrO_2 particles for CO oxidation (Zhang et al., 2005). However, the increasing price of the noble metals limits their applications as catalysts for industrial use.

Catalytic performance for CO oxidation over different spinel mixed oxides and perovskites has been compared in a review article (Royer et al., 2010). Dependence between the size and catalytic activity of different type CeO_2 nanocrystals towards CO oxidation was also found (Wu et al., 2012). Measurements have been performed on the dynamics of CO oxidation reaction over fresh and aged mixed CeO_2-ZrO_2 catalysts with different composition. The oxidizing process has been carried out under "anaerobic" conditions. It has been found that under these conditions catalytic activity strongly depends on surface area and thus, highest effectiveness was achieved with pure ceria. It has been noted that in contrast with ceria, the low-temperature activity of the mixed CeO_2-ZrO_2 solid solution for CO oxidation under "anaerobic" conditions is dependent on the degree of reduction of the material (Boaro et al., 2000). It is also shown that the bulk diffusion is two orders of magnitude higher for CeO_2-ZrO_2 than for CeO_2 and this fact can be responsible for the enhancement of CO conversion observed for CeO_2-ZrO_2 catalysts in respect to ceria catalyst.

Our preliminary investigations revealed that the physicochemical and catalytic properties of the nickel-oxide catalysts supported on ZrO_2 depend on the way of synthesis, the type of the precipitation reagent (NaOH, Na_2CO_3, NH_4OH) and on the temperature of thermal treatment.

The aim of this paper is twofold (i) to synthesize novel bulk and supported on ZrO_2 NiO_x (fresh and calcinated) catalytic systems; (ii) to investigate their catalytic activity and selectivity towards reactions of complete oxidation of CO, DME and methanol.

2. EXPERIMENTAL PART

2.1. Preparation of catalysts

The bulk NiO_x (hereafter denoted as NiO_x-fresh) catalyst was synthesized by non-conventional ultrasound assisted precipitation-oxidation method with a reverse order of precipitation. Ultrasonic treatment, realized by using ultrasound homogenizer UP100H, facilitates obtaining of highly dispersed and nano-sized catalysts. Detailed description of the synthesis procedure is given in our previous paper (Stoyanova et al., 2003). Deposition-precipitation method was applied for the preparation of the supported catalyst NiO_x/ZrO_2. Solid ZrO_2 (Merck) suspended in fixed volume of 0.1 M aqueous solution of $Ni(NO_3)_2.6H_2O$, so as to keep an atomic ratio of Ni:Zr=1:1, followed by dropwise addition of a mixture of 4 M NaOH and NaOCl under continuous stirring by the ultrasonic homogenizer to yield a black precipitate. The latter was kept in the mother solution for 24 hours, followed by filtration, washing with distilled water to neutral pH and negative reaction towards Cl^-. The precipitate was dried at 105^oC to constant mass (the sample was marked as NiO_x/ZrO_2 –fresh). Part of the as-prepared catalysts was calcined in air at 450^oC for 4 hours in a program-controlled electric furnace LM312.11C at a heating rate of 2^oC/min. The thermally treated samples were denoted as NiO_x– 450 and NiO_x/ZrO_2 – 450, respectively.

2.2. Characterization of the catalytic systems

The bulk and supported catalysts – fresh and thermally treated at 450°C were characterized by means of powder X-ray diffraction (XRD), FTIR spectroscopy, XPS, EPR, TEM, SAED and chemical analysis. Results obtained from these analyses and their interpretations are described in details in other our paper (Christoskova et al., 1995). In this study we present the results of the chemical analysis, which include determination of the total (O*) and surface active oxygen active oxygen (O_s*) content expressed in % and g-at.g^{-1}.

Active oxygen is the amount of over-stoichiometrical oxygen in the oxide above that corresponding to the lowest stable oxidation state. The total active oxygen content of the catalysts was determined iodometrically (Nakagava et al., 1962). A known amount catalyst 0.1 g ± 0.001 was added to 25 cm^3 dilute (1:10) sulfuric acid containing 2g of potassium iodide in a flask supplied with a ground stopper. After complete dissolution of the sample, the solution is allowed to stand for 10 min and the liberated iodine is titrated with 0.1 N sodium thiosulfate solution using starch as indicator. The relative standard deviation of the method is 4.71%.

The total active oxygen content in g-at.g^{-1} and % was determined according to the equations:

$$O^* = \frac{N \times V \times mgE_{O_2}}{m \times 16}, g-at/g \qquad O^* = \frac{N \times V \times mgE_{O_2}}{m} \times 100,\%$$

where N – normality of the titrant; V – volume of the consumed titrant solution, cm^3; m- catalyst amount, g; $mgE_{O_2} = 0.008$, miligram equivalent O_2.

The content of surface active oxygen has been determined by the hydrazine method (Ushijima et al., 1967). The relative standard deviation of the method is 5.02%.

2.3. Catalytic activity measurements

Considering that the aim of the investigation was to synthesize catalysts for CO oxidation in cigarette smoke as well as for abatement of industrial gas emissions from various industries containing CO and VOC's, a comparative study on the activity and selectivity of both fresh and thermally treated catalytic systems was carried out.

The catalytic activity of the samples in CO and CH_3OH oxidation was measured using continuous flow equipment with fixed bed stainless steel reactor at atmospheric pressure. The following conditions were chosen: catalyst bed volume- 0.5 cm^3 (particle size 0.6-1.0 mm), inlet CO and CH_3OH concentrations- 2.0% balanced with air and space velocity 20000 h^{-1}.

Two types of equipments for DME oxidation measurements were used: (i) flow-line equipment with an isothermal reactor, allowing precise control of the methanol dehydration to $(CH_3)_2O$ on Al_2O_3 and (ii) flow-line equipment with stainless steel reactor for deep oxidation of the preliminarily purified DME. The feed gas was 1.0% DME balanced with air and the space velocity was 20000 h^{-1}.

The reactant and product gases were analyzed by HP 5890 Series II gas-chromatograph, equipped with flame ionization and thermal conductivity detectors and Porapak Q and MS-5A columns. The activity of the catalytic system was evaluated on the basis of organic substrates conversion degree (α, %), calculated after the equation:

$$\alpha = \frac{C^o - C}{C^o} \times 100,\%$$

where C^o and C are the inlet and outlet concentration of the substrate, respectively.

3. RESULTS AND DISCUSSION

3.1. Chemical analysis

Data of the chemical analysis show that the fresh bulk sample of NiO_x is characterized by high content of active oxygen (7–8%), which being highly reactive and is responsible for the heterogeneous substrate oxidation even at room temperature. The content of the total active oxygen in the $NiOx/ZrO_2$ sample is lower (2.6 %), which is due the lower weight content of the active phase. The surface-active oxygen O_S^* constitutes 80% от the total active oxygen in the fresh-oxide catalytic systems. The O* content of the thermally treated samples as well as those of the NiO_x-fresh after depletive oxidation of CO to 160°C is below 1%. The chemical analysis reveals also that the pure ZrO_2 does not contain active oxygen.

The presence of O* in the obtained catalysts is a result of the applied modified synthesis whose basic moment is the obtaining of the precursor $Ni(OH)_2$ and its subsequent oxidation with NaOCl. The electronic transfer between the hydroxide and the oxygen of the oxidizer leads to effects of great significance for the catalysts in the reactions of complete oxidation:

* the level of metal ions oxidation increases;

* provides high concentration of the ionic oxygen species (O^-, O_2^{2-}, O^{2-}), i. e. of super-stoichiometric (active) oxygen on the surface of the oxide catalytic system, which play a major role in the oxidation catalysis.

3.2. Catalytic activity and selectivityof NiO_x and $NiOx/ZrO_2$ during the oxidation of CO, MeOH и DME.

3.2.1 Oxidation of CO

The data of the comparative study on the catalytic oxidation of CO, MeOH и DME under the experimental conditions as described in Chapter 2 in the presence of the synthesized catalytic systems as well as on and on the support (ZrO_2) are presented in Figs. 2-4.

The results of Fig. 2 demonstrating the temperature conversion of CO on NiOx-fresh, $NiOx/ZrO_2$ – fresh and with the participation of the pure ZrO_2 show that:

- the average conversion degree of CO on ZrO_2 in the studied temperature range 40 - 280^{0}C is approximately 10%.

- a practically complete oxidation of carbon monoxide (α=100%) both on the NiOx-fresh, and on the supported catalyst is achieved at temperature $\geq$ 220^{o}C.

- the curves profile reflecting the temperature dependence of α in the range 160-280^{0}C are absolutely identical for the both catalytic systems.

- the pattern of the curve demonstrating α = f(T) for the bulk catalyst in the temperature range 40-160^{0}C differs from that of $NiOx/ZrO_2$. The maximum in the curve α = f(T) at temperature 120^{o}C for NiOx-fresh with α = 20%, as well as the lower conversion of CO on the supported catalytic system in the same temperature interval is attributed to the oxidation of CO to 160^{o}C by the active oxygen of the catalytic systems This is confirmed by the results illustrated in Fig. 2, which shows the temperature dependence of α in the range 20-160^{o}C at depletive oxidation (without blowing of oxygen through the catalytic layer) of CO in the presence of NiOx-fresh. This finding is supported by the results from the comparison of the FTIR spectra of NiOx-fresh and of the catalytic system after the depletive oxidation to 160^{o}C (Stoyanova et al., 2003). The absorption band at 576 см$^{-1}$ in the IR spectrum of NiOx-fresh, due to the stretching vibrations of the Me-O bond and considering the presence of active oxygen in the catalyst is absent in the IR spectrum of the catalytic system after the CO oxidation to 160^{o}C. These results are in agreement with the data of the chemical analysis for the content of active oxygen in the studied samples. According to literature data, the character of bonding in the oxide is IR distinguishable. The vibrations of the Me = O bond, which is stronger than the Me-O bond is registered the range 600-900 см$^{-1}$ (Christoskova et al., 1995) It is seen from Fig. 2 that the degree of CO conversion sharply rises at temperatures higher than 160^{0}C for the two catalytic systems and reaches 100% at temperatures higher than 220^{o}C.

The mechanism of depletive oxidation of CO, as well as that with atmospheric oxygen participation is shown in Fig. 1.

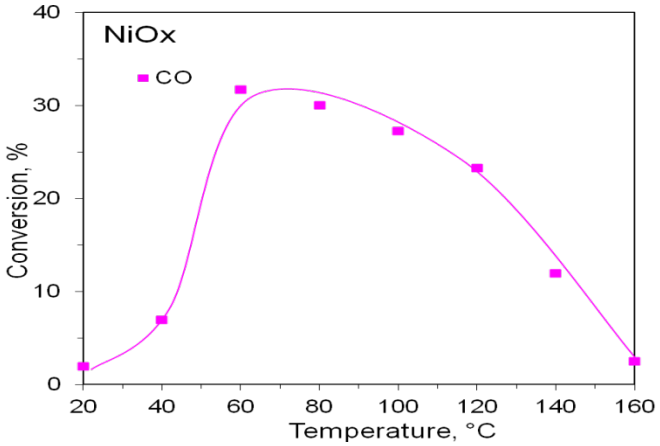


Fig.1. Depletive oxidation of CO over NiOx fresh

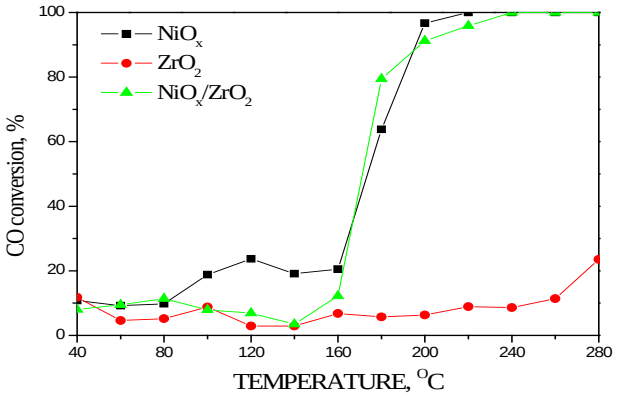


Fig.2. Conversion of CO as a function of temperature in the course of catalytic oxidation over NiOx, $NiOx/ZrO_2$ and ZrO_2

3.2.2. Oxidation of methanol

The activity of the studied catalysts in the reaction of methanol oxidation is evaluated by the degree of conversion α %. The temperature dependence of α in the same reaction is illustrated in Fig. 3.

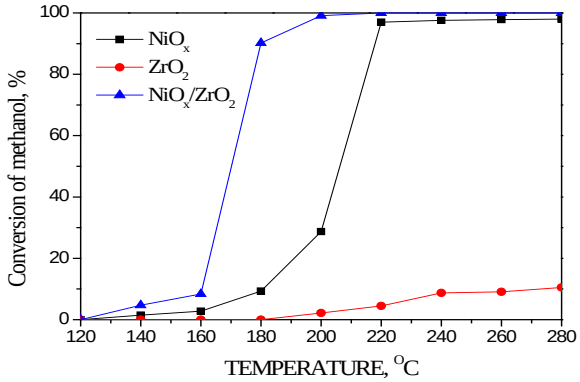


Fig.3. Temperature dependence of α during the catalytic oxidation of methanol

The results show that the oxidation of methanol to 180°C does not proceed on the pure support. In the temperature interval 200-280°C is observed a very low degree of conversion ~10%. At temperatures higher than 160°C the oxidation of methanol on $NiOx/ZrO_2$-fresh and NiOx-fresh sharply increases. At temperatures higher than 220°C a practically complete oxidation of methanol (α=100%) is achieved. It should be noted that the gas-chromatographic analysis does not register the formation of intermediate products.

- the ZrO_2 support has a great impact on the catalytic efficiency of the supported catalyst and the latter is not due to the synergism of the activities of the support and the immobilized phase in the studied reaction.

- the supported catalyst represents a new catalytic system characterized by a much higher activity in the temperature range 160-200°C (although the active phase of the supported catalyst is only 30 % wt.).

It is seen that at 180°C the conversion of methanol on NiOx-fresh is 5-6%, whereas for the supported catalysts α ~ 90%, and α = 100% at 200°C, respectively. α is only 30% in the presence of the bulk catalyst at the same temperature. The effect of the support on the catalytic activity of the supported catalyst most probably is due to the creation of new active centers on the surface of the catalytic system where the oxidation of methanol takes place.

3.2.3. Oxidation of dimethyl ether

The effect of the support on the catalytic oxidation of dimethyl ether is demonstrated by the data in Fig. 4.

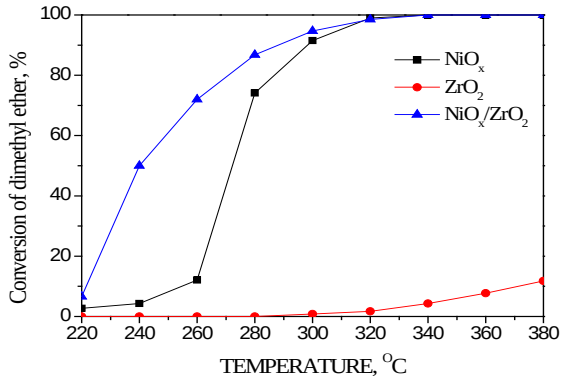


Fig.4. Temperature dependence of the conversion degree (α, %) of dimethyl ether

The comparison of the figures for the oxidation of CO and methanol with that for the oxidation of dimethyl ether reveals that the oxidation of the latter proceeds at higher temperatures than that of methanol and CO on the same catalytic systems. The oxidation of dimethyl ether starts at 220°C (at this temperature is reached 100% degree of conversion of methanol and CO with the same catalytic systems). Complete oxidation of dimethyl ether by the two catalysts is achieved at T ≥ 320°C. The supported catalyst to 280°C exhibits much higher activity as compared to the bulk catalyst although the active phase on ZrO_2 is only 30%. At the oxidation of dimethyl ether is also not observed a synergism of the activities of ZrO_2 and NiO_x – fresh.

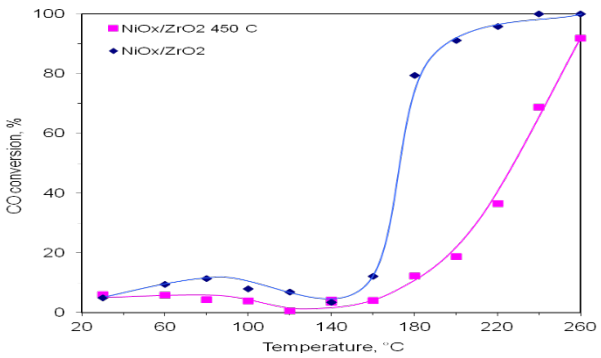


Fig.5. Effect of temperature on the degree of CO catalytic conversion over fresh and calcinated NiOx/ZrO_2

3.3. Oxidation of CO, dimethyl ether and methanol on NiOx-450 and NiOx/ZrO_2-450.

Regarding the potential practical application of the studied catalytic systems for purification of gas emissions from chemical industry containing CO и VOC's (for example the manufacture of formaldehyde), it is necessary to study the catalytic activity after thermal reduction of the catalysts at 450°C. The results of the comparative study of the catalytic activity of fresh and reduced catalytic systems at the oxidation of CO, methanol and dimethyl ether at different temperatures are presented in Figs. 5 – 7.

Data on the catalytic conversion of CO in the temperature range 20-260°C are illustrated in Fig. 5.

It is seen that the activity of the fresh catalytic system is much higher than that of NiOx/ZrO_2-450 in the investigated temperature range. Using the system NiOx/ZrO_2-fresh at T ≥ 220°C is achieved practically complete oxidation of CO, whereas in the presence of the reduced catalytic system at the same temperature α is about 40%. Similar trend is observed also at the oxidation of methanol and diethyl ether by the same catalytic systems but in other temperature intervals as shown in Fig. 6 and 7.

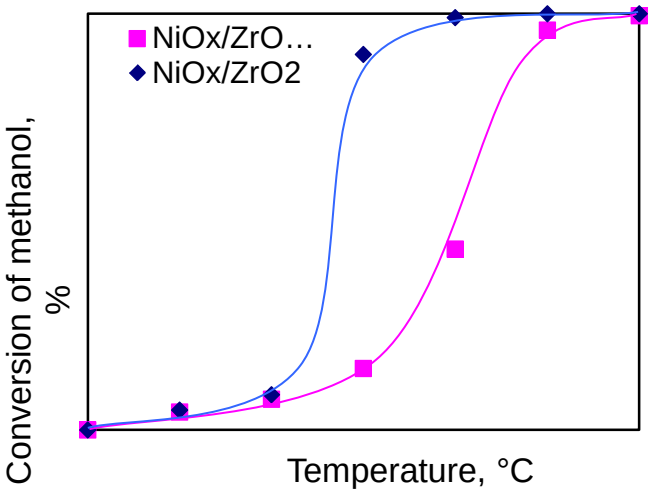


Fig.6. Effect of temperature on the degree of methanol catalytic conversion over fresh and calcinated $NiOx/ZrO_2$

It is seen from Fig. 6 that efficient oxidation of methanol is performed at temperatures higher than 160°C, in the presence of air oxygen. It is also evident that in the temperature range of 180-220°C the fresh $NiOx/ZrO_2$ displays much higher activity. At 200°C using this catalytic system is achieved complete oxidation of methanol, while with the thermally reduced catalytic system at the same temperature α ~ 45%. At 240°C the activities of the two catalytic systems become close and α = 100%.

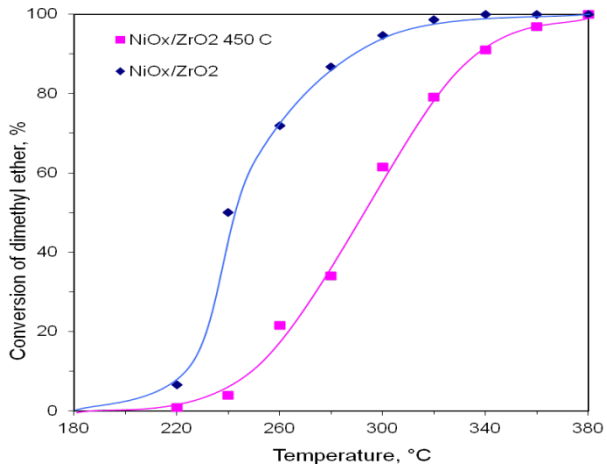


Fig.7. Effect of temperature on the degree of dimethyl ether catalytic conversion

The results of Fig. 7 show that in the temperature range of 180-380°C, $NiOx/ZrO_2$ -fresh is much more active towards the oxidation of dimethyl ether. At temperatures higher than 360°C the activities of the two catalytic systems become close and completely oxidize dimethyl ether. A maximum degree of conversion α = 100% is reached without the registration of intermediate compounds.

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