

# Nickel modified ultrananosized diamonds and their application as catalysts in methanol decomposition

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## Abstract

Different ultrananosized diamonds obtained by shock-wave procedure and their nickel modifications were prepared and characterized by nitrogen physisorption, X-ray diffraction, Temperature-programmed reduction and IR spectroscopy. The catalytic behaviour of the modified composites in methanol decomposition to hydrogen, carbon monoxide and methane was also studied. The state of supported nickel particles as well as their reductive and catalytic properties strongly depends on the pretreatment conditions and the composition of the support.

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## 1. Introduction

The new type of carbon materials, the shock-wave synthesized ultrananosized diamonds, possess unique surface characteristics as high adsorption capacity, high specific surface area and large concentration of unsaturated surface carbon atoms usually stabilized by different heteroatoms (O, H and N) [1–5]. It was also reported that like the other types of carbon supports [6], the surface functional groups of the ultrananosized diamonds might act as nucleation centers for generation of highly dispersed metal/metal oxide crystallites [1,7,8]. It is known that the design of these supported composites strongly depends on several factors, such as the choice of metal precursor, the procedure of its deposition, thermal decomposition and reduction. On the other hand, the composition and stability of the support surface has an important role for the formation of the supported metal phase. In the case of diamond-based materials the thermal treatment under various media is found to influence strongly their surface properties [1,4,9–13].

Recently, methanol is expected to become alternative energy source, because it can be synthesized from biomass, coal and

natural gas by well-known technologies [14–16]. Among the various catalytic processes, methanol decomposition to hydrogen, carbon monoxide and methane is often reported as a suitable way for producing ecological fuels for vehicles, gas turbines and fuel cells [17–31]. Methanol decomposition is highly endothermic process and that's why it has attracted growing interest also for recovering waste heat from exhausted gases. However, a significant improvement of the catalysts should be achieved. Catalysts, working at low temperatures with high activity and selectivity are needed. Nickel containing materials, usually supported on silica or other oxides are often reported to be suitable for methanol decomposition [20–23,25,29–31]. It was shown that the catalytic activity of Ni/SiO<sub>2</sub> in methanol decomposition is promoted only by well-crystallized nickel particles, adsorbing strongly hydrogen and carbon monoxide [22]. That's why the preparation method and surface properties of the support seems to be important factor for their catalytic behaviour. It has been demonstrated high catalytic activity and low degree of carbon deposition for nickel modified oxidized diamonds in comparison with the conventional supports for CO<sub>2</sub> reforming of methane, hydrocarbons partial oxidation, methane and methanol decomposition [32–36]. Weak, but significant enough interaction between loaded metal and support surface was revealed to be an important factor in enhancing and prolonging the catalytic activity of these type of materials [32–40]. However, data

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concerning the catalytic properties of modified nanodiamonds obtained by detonation is rarely reported [1,41–43]. In our previous study it was found, that the phase composition, reductive properties and catalytic behaviour in methanol decomposition of iron modified diamond materials are significantly affected by the amount of ultradispersed diamond present in them [44].

The aim of the present paper is to compare the catalytic behaviour in methanol decomposition of nickel supported on different shock-wave synthesized ultrananosized diamonds. The effect of the support phase composition and the pretreatment conditions on the state and reductive properties of nickel species is also studied.

## 2. Experimental

### 2.1. Materials

The shock-wave synthesized ultrananosized diamonds were produced by explosive conversion of TNT/RDX (trinitrotoluene/hexogene) mixture, with negative oxygen balance, in water-cooled combustion chamber with 3 m<sup>3</sup> volume according to the procedure described in [45,46]. The samples denoted as diamond blends contain 7% (DB1) and 40 wt.% (DB2) ultrananosized diamond. Cylindrical or conical charges were used for DB1 and DB2 synthesis, respectively. The sample, denoted as UDD was isolated from DB1 by liquid phase oxidative purification in mixture of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> and H<sub>2</sub>SO<sub>4</sub> at 373–393 K. As a result, ultrananosized diamond powder, containing below 7 wt.% non-diamond carbon was obtained. The final refining of diamond blends and UDD was performed by boiling in diluted hydrochloric acid and by washing with distilled water.

The UDD and diamond blends were modified by impregnation with Ni-acetylacetonate (Ni(AcAc)<sub>2</sub>) in chloroform in order to prepare formulations (Ni/DB1, Ni/DB2 and Ni/UDD) containing 7 wt.% Ni. The salt precursor was decomposed by heating in Ar (10°/min) at two different final temperatures, 650 or 770 K, for 90 min.

### 2.2. Methods of investigation

X-ray powder diffraction (XRD) patterns were collected on Bruker AXS D8 diffractometer (Cu K $\alpha$ ) in  $\theta/\theta$  geometry with a secondary monochromator. The BET surface areas, pore diameters and total pore volumes were determined by N<sub>2</sub> adsorption/desorption isotherms at 77 K on Quantachrome Autosorb 1. The total pore volumes were measured at  $p/p_0 = 0.0995$ . The pore size distributions were calculated using the desorption branch of the N<sub>2</sub> isotherm and the Barret–Joyner–Halenda (BJH) method [47]. The IR spectra (KBr pellets) were recorded on Bruker-Vector 22 FT-IR spectrometer at resolution of 1–2 cm<sup>-1</sup> accumulating 64–128 scans. Thermal gravimetry–temperature programmed reduction (TG–TPR) experiments were performed on Setaram TG 92 microbalance where the temperature programmed profiles of the samples were obtained upon heating in inert and hydrogen atmosphere. Typically, 50 mg of the sample were placed in a microbalance crucible and heated in a flow (100 cm<sup>3</sup>/min) of argon or H<sub>2</sub> (H<sub>2</sub>:Ar = 1) at 10 or 5 K/min,

respectively. Prior to the TPR experiments the samples were treated in-situ in a flow of Ar up to 770 K followed by a hold-up of 1 h. The medium and/or temperature of samples modification treatment were denoted in brackets for each of them where needed for clarity.

### 2.3. Catalytic test

The catalytic experiments were performed in a fixed-bed reactor (0.055 g catalyst) at a methanol partial pressure of 1.57 kPa, argon being used as a carrier gas. The temperature was raised with a rate of 1 K/min in the range of 350–770 K. On-line gas chromatographic analysis was performed on a Porapak Q and a molecular sieve column using an absolute calibration method. Before the catalytic experiments the samples were pretreated in situ in argon at 650 or 770 K for 1 h. In some cases, the samples were additionally reduced with hydrogen at 770 K for 2 h.

## 3. Results and discussion

### 3.1. Structural characterization of the pristine and nickel modified materials

In Figs. 1–3 the XRD patterns of DB1, DB2 and UDD materials and their Ni-modifications are presented. The XRD results indicate that graphite (26.2° 2 $\theta$ ) and diamond (43.8° 2 $\theta$ ) grains compose the diamond blends based materials. An additional typical of cubic diamond-like lattice reflection at 75.2° 2 $\theta$  is also observed in case of UDD. For all samples a halo localized at about 17° 2 $\theta$  is detected, which could be ascribed to small non-diamond carbon clusters [1,5]. The interpretation of XRD patterns of Ni-supported materials is rather complicated due to the overlapping of the strongest reflections of diamond, metallic nickel and NiO. However, Ni/DB1, Ni/DB2 and Ni/UDD, pretreated in Ar at 770 K (Fig. 2), show well-defined reflections, typical of NiO species (37.3°, 43.3° and 62.9° 2 $\theta$ ). They are most strongly pronounced in the case of diamond blend supported samples in comparison with UDD one. Reflections typical of Ni<sup>0</sup> (44.5° and 51.9° 2 $\theta$ ) also appear in the XRD patterns of all

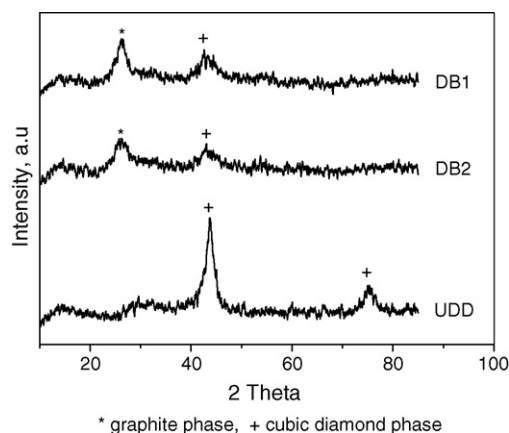


Fig. 1. XRD patterns of pristine ultrananosized diamond containing materials.

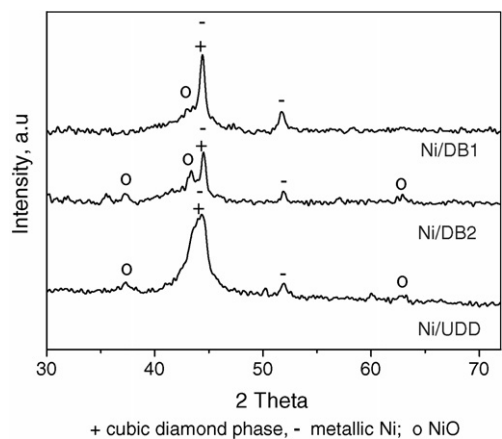


Fig. 2. XRD patterns of nickel modified ultrananosized diamond containing materials treated in Ar at 770 K.

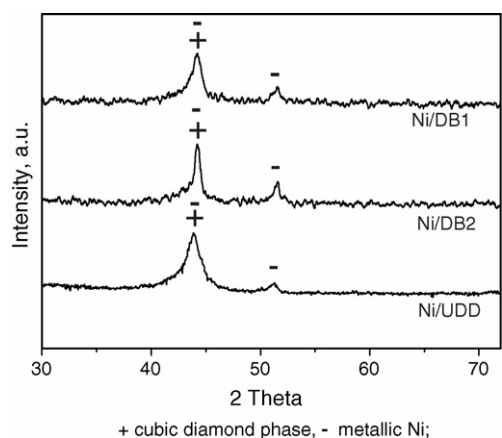


Fig. 3. XRD patterns of reduced Ni modified ultrananosized diamond containing materials.

argon treated at 770 K samples, which are most intense in the case for Ni/DB1.

After the samples reduction with hydrogen at 770 K, no reflections of NiO are observed in XRD patterns for all mate-

Table 1

BET surface area and total pore volume of parent and Ni modified diamond containing materials, pretreated under various conditions

Sample	BET ( $\text{m}^2 \text{g}^{-1}$ )	$V_{\text{pores}}$ ( $\text{cm}^3 \text{g}^{-1}$ )
UDD	269	1.02
DB1	470	1.84
DB2	518	1.77
DB2 (Ar, 770)	552	1.87
Ni/DB2 (Ar, 770)	452	1.56
Ni/DB2 (red)	470	1.55

rials (Fig. 3). The intense and sharp peak at  $51.9^\circ 2\theta$  in the diffractograms of Ni/DB1 and Ni/DB2 samples are indicative for presence of  $\text{Ni}^0$  particles on the diamond blends (Fig. 3). The broader reflection at  $51.9^\circ 2\theta$  for the Ni/UDD (Fig. 3) indicates that more finely dispersed  $\text{Ni}^0$  particles are formed in UDD.

In Fig. 4 and Table 1 are presented data for nitrogen physisorption on the studied pristine materials and selected modified ultrananosized diamond material (DB2). The adsorption isotherms (Fig. 4) of both pristine diamond blends (DB1 and DB2) could not be ascribed definitely to any of the typical types of isotherms according to IUPAC classification. They are characterized with a smooth condensation step above  $0.7 p/p_0$  with a H1 type hysteresis loop. These peculiarities could be assigned to porous materials with a prevailing presence of textural mesopores (BJH pore diameter of about 9 nm). Practically, no significant changes in the textural characteristics are found after the diamond blends pretreatment in Ar even at 770 K (Table 1, Fig. 4), indicative of structure preservation under these conditions. However a significant decrease in the pore volume and BET surface area is observed after samples modification with nickel. This could be an evidence of nickel particles location predominantly into the support mesopores. Significantly different course of the nitrogen isotherms is observed for the UDD sample (Fig. 4). Here, the nitrogen uptake is clearly seen just above relative pressure of 0.9 and not very well pronounced hysteresis loop is also registered in this case. It could be assigned to

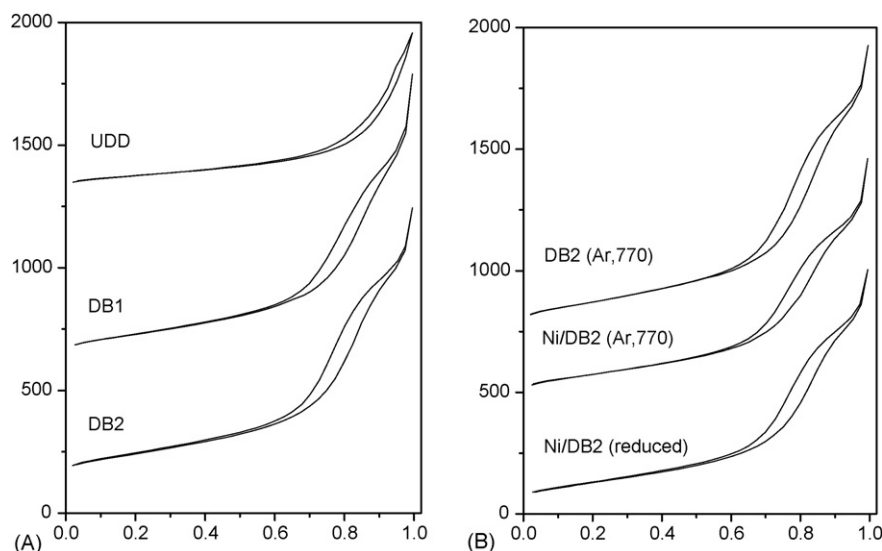


Fig. 4. Nitrogen physisorption isotherms (shifted in y-direction in order to prevent overlapping) for the pristine (A) and differently modified DB2 materials (B).

a much lower degree of mesoporosity in UDD. This assumption is also confirmed by the registered lower values of BET surface area and pore volume (Table 1). The structural characteristics of UDD are also not influenced by the pretreatment at different temperatures. Here, only about 10 % decrease in the pore volume is observed after the sample modification with nickel.

The FT-IR spectra (not shown) reveal absorption bands illustrating the presence of surface functional groups in various modes and ratio on all studied samples. The absorption bands with maxima at 2982 and 2866  $\text{cm}^{-1}$ , as well as 2929 and 2859  $\text{cm}^{-1}$  detected predominantly for diamond blend samples could be ascribed to the  $\text{CH}_3$  and  $\text{CH}_2$  groups. The surface  $\text{CH}_3$  groups prevail in the case of DB2. In contrast, the spectra of UDD reveal the typical bands of acid-purified nanodiamonds carbonyl

(1730  $\text{cm}^{-1}$ ) and hydroxyl (1640  $\text{cm}^{-1}$ ) fragments [9,10] that were completely missing in case of both diamond blends [1,4,5].

### 3.2. TG and TPR study

In Fig. 5 the results from the thermogravimetric study for the pristine supports (Fig. 5A) and their Ni modifications (Fig. 5B) heated in Ar up to 770 K are displayed. Both, pristine diamond blends and UDD, reveal a sharp peak (not shown) at about 360 K due to elimination of physically adsorbed  $\text{H}_2\text{O}$  and gases. In the higher temperature region, progressive weight loss (about 3 and 4 wt.% for diamond blends and UDD, respectively), most probably due to evolution of hydrocarbon containing fragments is observed (Fig. 5A). Considering the position of  $T_{\text{max}}$  of DTG curves it is evident that the surface integrity of diamond blends

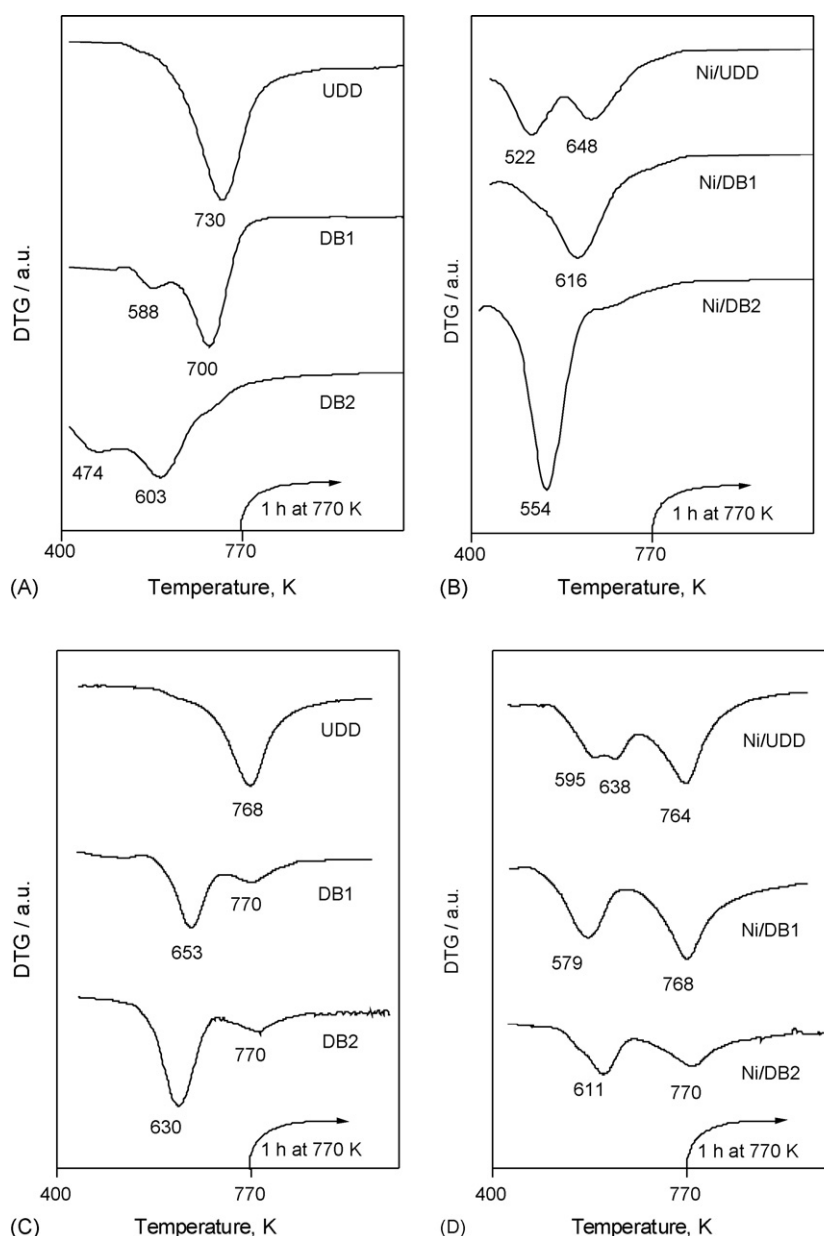


Fig. 5. Temperature programmed desorption profiles in Ar (A and B) and temperature programmed reduction profiles after pretreatment in Ar at 650 K (C and D) of pristine and Ni modified UDD containing materials.

and UDD differs and less easily removable species leave the surface of the latter. According to [1,48] mostly  $\text{CH}_4$  and  $\text{H}_2$  desorb from diamond blend materials, while  $\text{CO}_2$  is the main product evolved from the surface of UDD.

Only one, high temperature peak with maxima at 554 and 616 K is registered for Ni/DB2 and Ni/DB1, respectively (Fig. 5B). In contrast, two desorption effects in the same temperature interval are seen in case of Ni/UDD. Obviously, the observed DTG curves features are due to the salt decomposition and the acetylacetonate ligands replacement and point to a diverse mode of interaction of the precursor with the surface of the different diamond based materials as it is proposed for Ni/(AcAc)<sub>2</sub> supported on  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  [49].

TPR profiles of pristine and Ni modified materials are presented in Fig. 5C and D. As the calculations show, the subsequent reduction of both types of pristine samples in  $\text{H}_2$  after Ar pretreatment leads to an additional 2–4 wt.% loss. The detected effect may be connected, according to the IR investigations of many authors [1,41], to transformations and decomposition of different surface functional groups in presence of hydrogen. Two reductive peaks are registered for both blends, independently on their diamond content. The low temperature peak ( $T_{\text{max}}$  at 653 and 630 K for DB1 and DB2, respectively) can be attributed to the replacement of more loosely connected functional groups existing on the diamond blend surface. At the same time, only one peak with  $T_{\text{max}}$  at 768 K, is observed for UDD and it is situated at approximately the same position to the high temperature peak in TPR profiles of the diamond blends.

The TPR profiles of the corresponding Ni-modifications seem to be a superposition of complex transformations taking place under hydrogen medium, concerning both the functional groups changes and the nickel oxide reduction (Fig. 5D). Two reductive peaks could be distinguished in the TPR curves of all nickel modified materials. A significant increase in the relative part of the high temperature peak ( $T_{\text{max}}$  about 770 K) is the main observed effect for the Ni/DB1 and Ni/DB2 in comparison with the corresponding non-modified materials (Fig. 5C and D). This could be

partially ascribed to the reduction of highly dispersed NiO particles, strongly interacting with the support. In our opinion, the main loosely connected part of NiO particles seem to be already reduced during the samples pretreatment in Ar at 770 K. This assumption is also confirmed by the XRD patterns for the Ar pretreated Ni/DB1 and Ni/DB2, where metallic nickel in significant amount is registered (Fig. 2). In case of Ni/UDD appearance of new doublet-like peak at 570–650 K in its TPR profile is registered. Here predominant reduction of homogeneously dispersed NiO particles, weakly interacting with the support is assumed. Practically no changes in the high temperature region in comparison with the corresponding pristine material are observed. This effect could be ascribed again to evolution of the diamond surface hydrogenation products.

### 3.3. Catalytic study

The temperature dependencies of methanol decomposition on Ni modified diamond blends and UDD materials, pretreated under various conditions are compared in Figs. 6–8. At the same time, all pristine materials show low catalytic activity to methanol decomposition only just above 650–700 K (not shown). In contrast, for the modified materials pretreated in Ar methanol decomposition is observed already at 520–550 K. Carbon monoxide and methane are the only registered carbon containing products in all cases (Figs. 6 and 7). However, despite the temperature pretreatment in Ar, higher catalytic activity and lower selectivity to methane were registered for Ni/UDD in comparison with the diamond blend-based modifications. The catalytic behaviour of the latter is rather similar when the lower pretreatment temperature (650 K) is realized (Fig. 6). Some differences in methane selectivity, being higher in the case of Ni/DB1, is only registered in this case. The catalytic behaviour of the samples changes in different way with the temperature pretreatment increase (Fig. 7). A decrease in catalytic activity is observed both for Ni/UDD and for Ni/DB2, characterized with higher content of UDD, while in contrast, it significantly

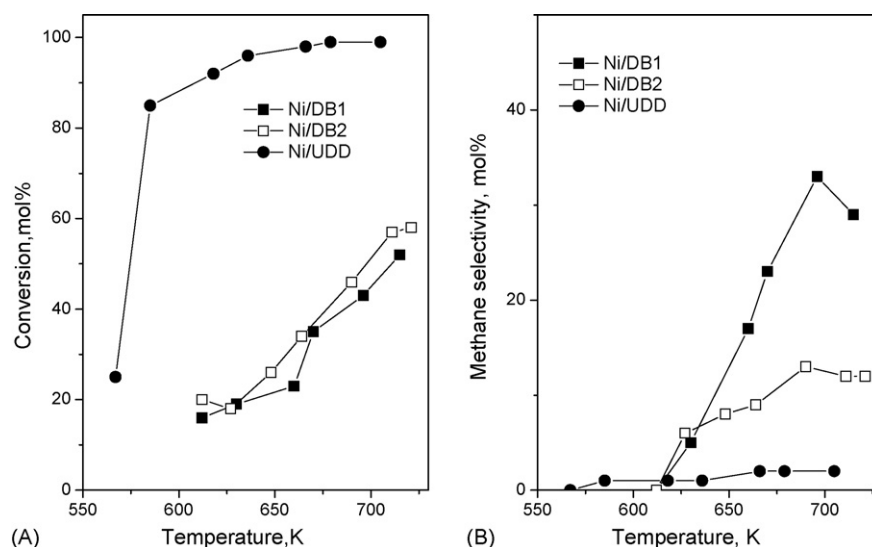


Fig. 6. Methanol conversion (A) and methane selectivity (B) vs. temperature for the pretreated in Ar at 650 K various ultrananosized diamond containing materials.

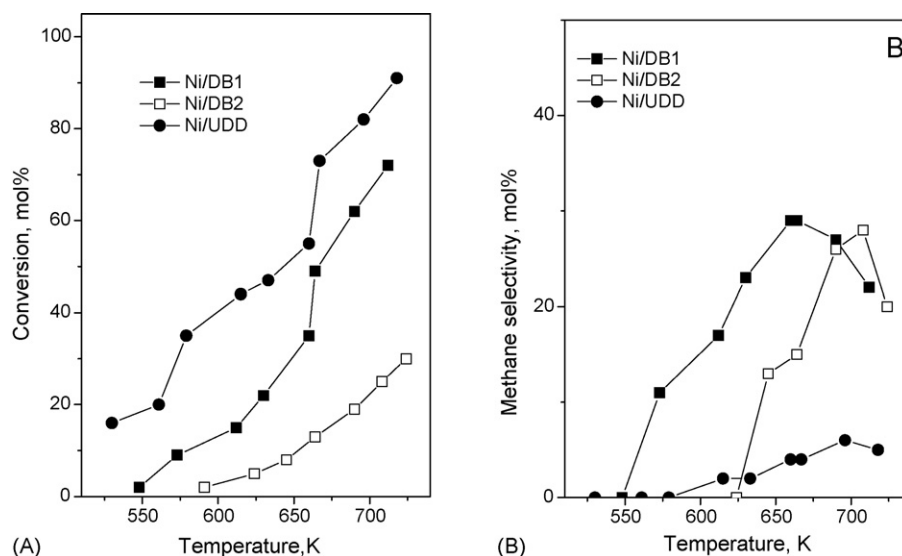


Fig. 7. Methanol conversion (A) and methane selectivity (B) vs. temperature for the pretreated in Ar at 770 K various ultrananosized diamond containing materials.

increases for Ni/DB1. Moreover, methane selectivity increase was observed for all materials in this case, but this effect is very small for Ni/UDD and highest for Ni/DB1. So, some significant changes with the Ni species could be expected under samples pretreatment in Ar. Both agglomeration processes as well as reductive transformations of the nickel particles due to the influence of precursor decomposition products [50] and the support are possible. The reductive effect of the support seems to be more significant in the case of diamond blend with higher content of non-diamond carbon in it (Ni/DB1). This is also confirmed by XRD patterns obtained after samples pretreatment in Ar, where most clearly defined signal of metallic nickel was observed for Ni/DB1 (Fig. 2). In order to ignore these complex nickel phase transformations and also to prove this assumption, some experiments with preliminary reduced in hydrogen materials were performed (Fig. 8). As a whole, the catalytic activity of the samples significantly increase in comparison with the

non-reduced ones. Here methanol decomposition starts at lower temperatures, but this effect is most notable for Ni/UDD. Both diamond blends exhibit less pronounced increase in the catalytic activity and it is close for both materials in all temperature interval. At the same time, an increase in methane selectivity is observed for all materials after the hydrogen pretreatment, but this is most essential once again for Ni/UDD. The obtained results are in accordance with our assumption (see Sections 3.1 and 3.2), that more homogeneously dispersed Ni particles, not so strongly interacting with the support, exist in UDD. Based on the data of our previous investigation [51], Ni/UDD exhibits close catalytic activity, but higher selectivity to methane formation in methanol decomposition in comparison with Ni modified mesoporous silicas with different porous structures. In our opinion, formation of nickel particles with optimal size and well-defined crystalline structure are formed in UDD due to the weaker nickel interaction with the support (Ni–O–C mode). As it was already

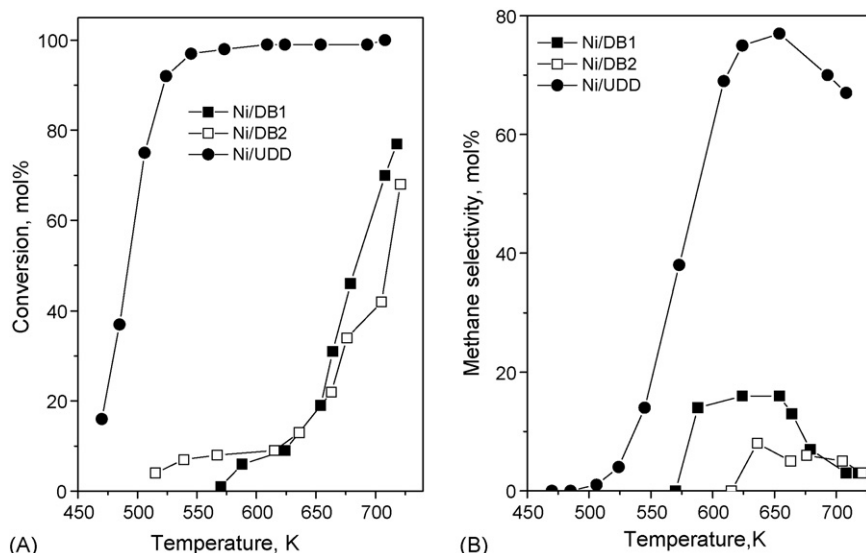


Fig. 8. Methanol conversion (A) and methane selectivity (B) vs. temperature for the reduced in hydrogen various ultrananosized diamond containing materials.

mentioned in Section 1 [41,52], this factor seems to be very significant for the strength of CO and hydrogen interaction with the nickel surface and could essentially increase the methanol decomposition. These peculiarities probably favour the further transformations of the initial products (CO and H<sub>2</sub>) to methane as well. An alternative reaction mechanism with direct methane formation from methanol due to the preferential scission of the C–O bond in the strongly adsorbed methanol molecule is not excluded [53,54]. It can be supposed also that the interaction between methanol molecules and surface O-containing groups, which dominate in UDD (see Section 3.1), results in an increase of the reactant concentration around the nickel species, and in this way, an additional increase in the catalytic activity is realized. It is interesting to stress also that the catalytic behaviour of both diamond blends is very similar under certain conditions (Figs. 6 and 8), despite the significant differences in the diamond carbon content in them. These results confirm the literature data for the complex structure of the diamond blend composites [1]. According to them, the diamond blend could not be assumed as a simple mixture of diamond and non-diamond (carbon clusters and graphite) carbon containing modifications. The observed significant reductive ability of the non-diamond carbon determines the differences in the catalytic behaviour of the samples pretreated in Ar at higher (770 K) temperature. In this relation, methanol decomposition could be assumed as a suitable, fast and informative test for the diamond phase composition elucidation as it was already found for the iron modifications of diamond blend materials in our previous study [44].

#### 4. Conclusion

The preparation procedure and the further treatments in different media allow ultrananosized diamond materials with various phase compositions, textural mesoporosity and surface functionality to be obtained. On the basis of these materials, Ni modified composites with different state of nickel particles could be prepared from the corresponding acetylacetonate precursor. Their catalytic behaviour in methanol decomposition strongly depends on the ultrananosized diamond content as well as on the pretreatment conditions. The absence of clearly defined tendency in the physicochemical and catalytic properties changes with the phase composition of the studied materials suggests that they are not a simple mixture of condensed carbon materials in different state.

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