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Nanosized cobalt oxides modified with palladium for oxidation of methane and carbon monoxide

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Nanosized Co_3O_4 oxide was prepared and modified with palladium. Catalyst samples were characterized by X-ray diffraction, X-ray photoelectron spectroscopy, transmission electron microscopy, temperature-programmed reduction, and diffuse reflectance infrared spectroscopy. The catalytic performance of the as synthesized materials was examined in the reactions of methane combustion and CO oxidation. Finely divided PdO particles were formed on the surface of the modified cobalt oxides.

Based on diffuse reflectance infrared spectroscopy investigations a Langmuir-Hinshelwood mechanism was proposed for the oxidation of carbon monoxide on the studied samples up to 150°C. A linearly adsorbed CO species was formed and involved in the reaction over Pd/Co_3O_4 under these conditions. At a higher temperature, the palladium surface was mainly covered by dissociatively adsorbed oxygen and the reaction proceeded through the Eley-Rideal mechanism: chemisorbed oxygen atoms react with gaseous carbon monoxide. A Mars-van Krevelen mechanism cannot be excluded as well. Carbon dioxide was detected after introduction of a $CO+N_2$ mixture into the cell, which indicates that CO oxidation proceeded most probably due to a reaction between carbon monoxide and lattice oxygen from PdO and/or Co_3O_4

Keywords: Pd-modified nanosized Co_3O_4 oxide, mechanism of CO oxidation, methane combustion**.**

INTRODUCTION

The design of an effective and less expensive catalytic system for complete oxidation of methane and carbon monoxide is an important problem of modern environmental catalysis. Methane makes the second largest contribution to the global warming after carbon dioxide [1, 2]. Methane catalytic combustion has been extensively studied for emission control and power generation during the last decades. CO oxidation at low temperatures has attracted great attention because of its wide applications in exhaust gas treatment, automotive emission control, and CO preferential oxidation in hydrogen feed for use in proton exchange membrane fuel cells [3].

Supported palladium catalysts are widely accepted as the most active catalysts for both catalytic combustion of methane and low temperature oxidation of CO [3, 4]. Palladium has been used in three-way catalysts because of its superior oxidation properties in comparison with platinum and rhodium. Concerning the methane oxidation reaction, the main drawback of the palladium catalysts is their deactivation at high temperatures. Thus, efforts are directed toward searching novel materials or for improving existing catalysts by better dispersion of Pd on catalytically active supports, such as premodified alumina, hexaaluminates, etc. [5–7].

The activity of palladium in the reaction of CO oxidation is dependent on particle size, morphology, and Pd-support interactions. Highly dispersed species are considered more active than large particles. The interfaces between metal and metal oxide phases probably provide active sites. The support could play a role as an oxygen-storage material and may take part in the reaction [8–10]. Recently, Jin *et al.* [11] reported a preparation technique for very active catalysts by depositing palladium on different mesoporous oxides.

The present work is aimed at developing highly active catalysts for CO oxidation and methane combustion by a suitable combination between Pd and nanosized cobalt oxide of controlled size, shape, and morphology.

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EXPERIMENTAL

2.1 Synthesis of nanosized Co_3O_4

Cobalt acetate was added to a mixture of double distilled water and ethanol at a 1:10 ratio in a beaker and the new mixture was stirred to get a clear solution. Liquor ammonia was added to this clear solution. It was then treated hydrothermally at 150°C for 3 h. The black colour precipitate was washed twice with ethanol and finally dried at 70°C [12].

2.2. Synthesis of Pd/Co_3O_4

Cobalt oxide was modified with palladium to improve the catalytic activity. Before Pd deposition, the metal oxide was calcined in air at 450°C for 2 h. Samples were prepared by introduction of the metal oxide to an aqueous solution of $Pd(NO_3)_2.2H_2O$ to achieve 0.5 wt.% Pd/Co_3O_4. After the impregnation, a quick evaporation of the solvent was applied in order to coat the metal oxide particles by a thin layer of palladium [13]. The samples were finally calcined in air at 450°C for 2 h.

2.3. Catalyst characterization

The specific surface area of the supported catalyst samples was determined by low temperature adsorption of nitrogen according to the BET method using a Nova 1200 (Quantachrome) apparatus. Prior to measurements, the samples were degassed for 5 h at temperatures in the interval 70–150°C.

X-ray diffraction (XRD) patterns were obtained on a TUR M62 apparatus, HZG-4 goniometer with Bragg-Brentano geometry, CoKα radiation, and Fe filter. XRD data processing was performed using the X'Pert HighScore program.

Temperature-programmed reduction (TPR) was carried out using a flow mixture of 10% H_2 in argon at a flow rate of 10 $ml.min^{-1}$ and a temperature ramp of 10 $deg.min^{-1}$ up to 700°C. Prior to the TPR experiments, the samples were treated in argon flow at 150°C for 1 h.

X-ray photoelectron measurements were carried out on an ESCALAB MkII (VG Scientific) electron spectrometer at a base pressure in the analysis chamber of 5×10^{-10} mbar using a twin anode MgKα/AlKα X-ray source with excitation energies of 1253.6 and 1486.6 eV, respectively. The spectra were recorded at a total instrumental resolution (as it was measured by the FWHM of Ag $3d_{5/2}$ photoelectron line) of 1.06 and 1.18 eV for MgKα and AlKα excitation sources, respectively. The energy scale has been calibrated by normalizing the C 1s line of adsorbed adventitious hydrocarbons to 285.0 eV. Spectra processing included a subtraction of X-ray satellites and Shirley-type background [14]. Peak positions and areas were evaluated by a symmetrical Gaussian-Lorentzian curve fitting. The relative concentrations of the different chemical species were determined based on normalization of the peak areas to their photoionization cross-sections, calculated by Scofield [15].

High-resolution transmission electron microscopy (HRTEM) studies were carried out by using a FEI Technai G^2 20 (200 kV) instrument. The samples were prepared by dispersion in ethanol and loading on a holey copper grid.

Carbon monoxide adsorption on Pd/Co_3O_4 catalysts was studied *in situ* by diffuse reflectance infrared spectroscopy (DRIRS) using a Nicolet 6700 spectrometer equipped with a high temperature vacuum chamber installed in the Collector II accessory (Thermo Spectra-Tech). CO was adsorbed from $CO+N_2$ or $CO+O_2+N_2$ mixture flows at room temperature. Experiments were carried out on oxidized (‘as prepared’) catalysts pretreated in nitrogen at 350°C for 1 h.

2.4. Catalyst characterization

Catalytic activity tests were performed using an integrated quartz micro-reactor and mass spectrometer analysis system (CATLAB, Hiden Analytical, UK). Reactant gases were supplied through electronic mass flow controllers. The catalysts (particle sizes of 0.3–0.6 mm) were held between plugs of quartz wool in a quartz tubular vertical flow reactor (ø = 6 mm). CO and methane inlet concentrations in air were kept 600 and 900 ppm, respectively. External mass transfer limitations were minimized by working at gas hourly space velocities (GHSV) of 60 000 h^{-1}.

RESULTS AND DISCUSSION

Powder X-ray diffraction studies of the metal oxide nanoparticles suggest the formation of a cubic phase for cobalt oxide (PDF 01-080-1539) (Fig. 1).

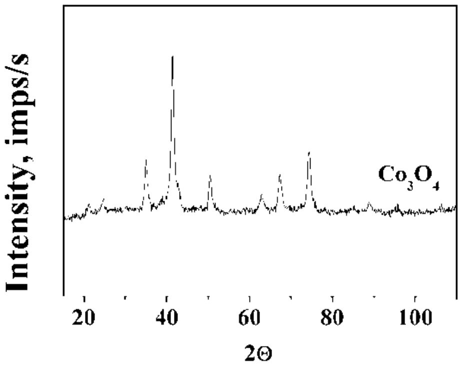

Fig. 1. XRD pattern of as synthesized metal oxide before calcination.

The size and morphology of the metal oxide were studied by TEM and the image shown in figure 2 reveals the formation of cube-shaped particles of cobalt oxide of ~8–10-nm size. These materials are characterised by high surface area of ~125 $m^2.g^{-1}$ value, which makes them ideal for catalytic reactions.

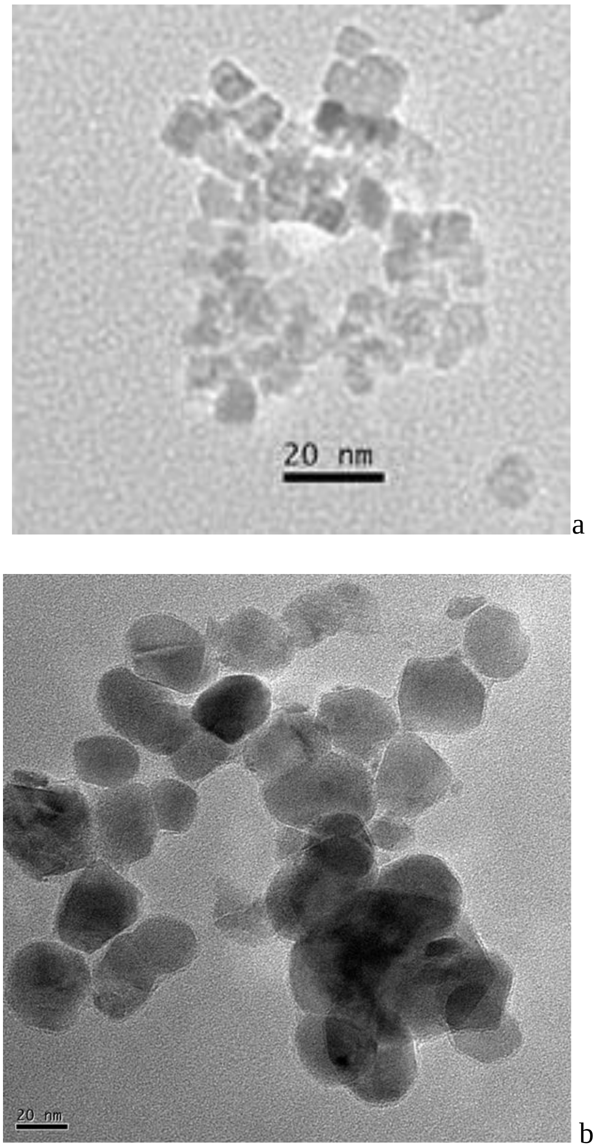

Fig. 2. TEM images of cobalt oxide nanosized particles: a. as synthesized', b. after calcination

Palladium or palladium oxide were not detected in the XRD patterns after Pd deposition and following calcination. Co_3O_4 particle size calculation, according to Scherrer equation and TEM images (Fig. 2B), showed about a two-fold increase in particle mean diameter after calcination. No additional increase in Co_3O_4 particle sizes was observed after Pd deposition and following calcination (Table 1). A decrease in the specific surface area was found after treatment in air at 450°C for 2 h.

TPR profiles of the pure metal oxide after calcination and after Pd deposition are presented in figure 3.

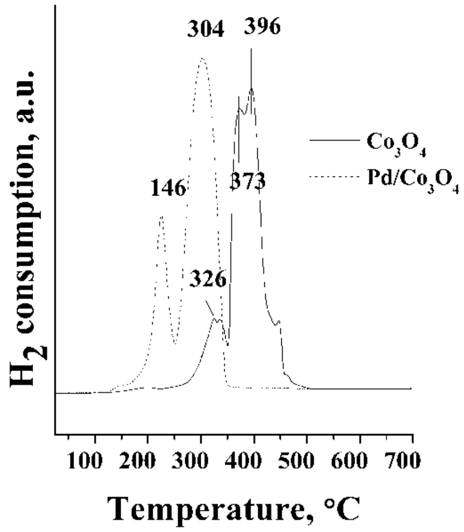

Fig. 3. TPR profile of cobalt oxides before and after palladium modification.

The reduction profile of pure cobalt oxide consists of two overlapping peaks at 326 and 336°C and other two peaks with maxima at about 373 and 396°C, accordingly. The reduction profiles of the Co_3O_4 sample fit well within the stepwise reduction of the metal oxide ($Co_3O_4 \rightarrow CoO \rightarrow Co$) [16]. Two reduction peaks, registered in both intervals, could be a result of a bimodal distribution of the cobalt oxide particles. A particle size effect on the TPR reduction profile was established: the smaller the particle size the lower the registered reduction temperature is. Okamoto et al. have found the same tendency for reduction of silica-supported Co_3O_4 of different size [17].

Palladium introduction led to a significant decrease of the reduction temperature of Co_3O_4. Two major reduction peaks were detected during the reduction of a Pd/Co_3O_4 sample. It is well known that a noble metal added to a metal oxide catalyst accelerates the reduction of the latter by supplying hydrogen via spillover from the prereduced noble metal particles to the metal oxide [18, 19]. It should be noted that a separate peak corresponding to the reduction of Pd oxide (if formed as a separate phase during the calcination) was not observed in our TPR experiments. Usually, a TPR peak of noble metal reduction in supported catalysts is registered at a temperature below 50°C and even well below the room temperature. Our results could be due to a low Pd content and a high Co_3O_4/Pd ratio resulting in a very small hydrogen consumption by the palladium oxide compared to that detected with another metal oxide.

The chemical state of palladium and cobalt and the atomic concentrations of the different elements on the catalyst surface were studied by X-ray photoelectron spectroscopy (Figs. 4a and 4b). The XPS spectrum of Pd/Co_3O_4 in the Co 2p region manifests a binding energy at 780.5 eV and a $2p_{3/2}$-$2p_{1/2}$ splitting of 15.4 eV that are characteristic of octahedral Co^{3+} ions [20].

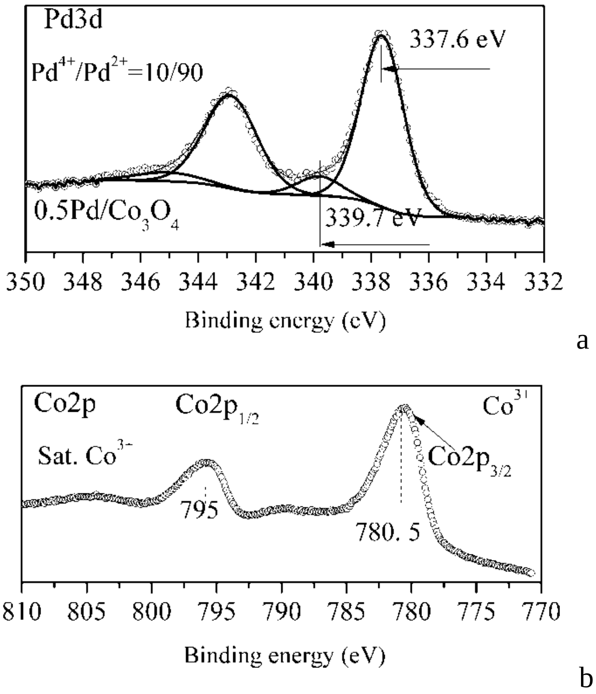

Fig. 4. XPS spectra of a sample after deposition of palladium and calcination at 450°C for 2 h: a. Pd 3d region; b. Co 2p.

The binding energy in the range of 337.2–337.6 eV for a palladium-modified sample indicates the presence of PdO [21, 22]. A third component at 339.6 eV was observed for all samples. It was smaller than other detected components and contributed by 10–12% to the total Pd signal. This peak may be associated with Pd^{4+} from PdO_2 [22]. Pd^{4+} ions in PdO_2 are highly unstable, but according to Barr [23] the palladium metal particles, exposed long enough to air, form palladium oxide with outermost layers of PdO_2 or $Pd(OH)_4$ on their surface.

In situ DRIRS was used as one of the most powerful methods to obtain information about the type of the active sites, their stability and reactivity, chemical state of the surface under static and dynamic conditions in a wide temperature interval, and after various pretreatments. The most frequently used probe molecule to study supported catalysts is carbon monoxide due to the sensitivity of the stretching ν(C−O) vibration to the chemical state of the metal atom(s) to which it is coordinated. The IR spectra provide knowledge of the relative adsorption strength that is closely related to the catalytic activity of the respective sites and allow understanding of the CO oxidation reaction mechanism [24, 25]. DRIRS experiments were carried out to investigate both the CO adsorption on the surface of Pd supported on cobalt oxide and the behaviour of adsorbed CO surface species in flow mixtures of $CO+N_2$ and $CO+N_2+O_2$. Infrared spectra of CO adsorbed on Pd/Co_3O_4 samples are displayed in figures 5 and 7 and the assignment of the IR bands is given in Table 2.

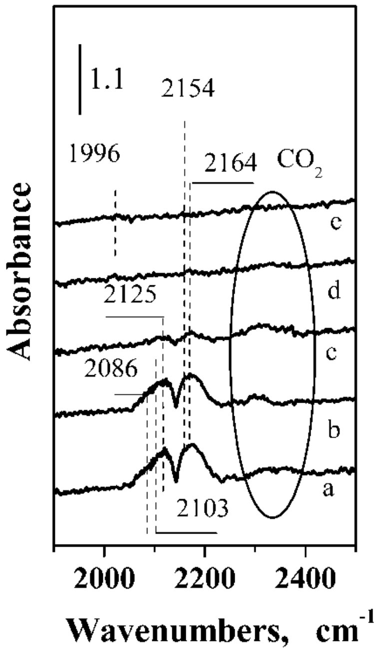

Fig. 5. DRIRS spectra of Pd/Co_3O_4 after: a. 10 min in a flow mixture of 10% CO in nitrogen at room temperature; b. a stay for 2 h in a mixture of 10% CO in nitrogen at room temperature; c. a stay for 18 h in a mixture of 10% CO in nitrogen at room temperature; d. desorption of CO for 1 min in nitrogen flow; e. desorption for 11 min in nitrogen flow.

Table 2. Assignment of IR bands (νC–O) of adsorbed CO species [26, 30].

Sample	Infrared band assignment			
	Pd^{2+}–CO	Pd^{1+}–CO	Pd^0–CO	$(Pd^0)_2$–CO
Pd/Co_3O_4	2154 cm^{-1}	2125 cm^{-1}	2086 cm^{-1} 2103 cm^{-1}	1996 cm^{-1}

Bands at 2154, 2125, 2086, 2103, and 1996 cm^{-1} were registered in the IR spectra of the calcined Pd/Co_3O_4 sample after admission of the flow mixture at room temperature. They could be assigned to linearly bonded CO species on Pd^{2+}, Pd^+, and Pd^0 and bridge bonded CO to Pd^0, respectively [26–29]. According to literature data, the formation of mono carbonyl CO–Pd^0 species is manifested by a band in the frequency interval of 2100–2050 cm^{-1} [26–29]. In our experiments, this band appeared at a slightly higher frequency of 2103 cm^{-1}. One possible explanation is that Pd has a partial positive charge (Pd$^{\delta+}$) due to a strong interaction between finely divided palladium and the support. CO adsorption on metallic palladium with weak electron-donor properties shifts the band to higher wavenumbers. A band at the same position has been observed for CO adsorption on Pd-ZSM-5 [30]. The bands of linearly bonded CO to Pd^{2+} and Pd$^+$ species at 2154 and 2125 cm^{-1}, respectively, are overlapped by those of the gaseous CO (Figs. 5 and 7). In all spectra, the bands in the region 2300–2400 cm^{-1} are assigned to gaseous carbon dioxide. XPS data obtained for the catalysts before CO adsorption revealed that the main state of palladium was Pd^{2+} and partly that of Pd^{4+}. IR bands due to CO adsorbed on Pd$^+$ and Pd^0 after introduction of a CO+N$_2$ mixture indicate a partial reduction of the palladium surface even at room temperature. However, under these conditions the reduction of the palladium particles in the outermost layer(s) of their surface was not complete which was confirmed by very low intensity of the bands at about 1996 cm^{-1} ascribed to bridge-bonded CO to Pd^0 in the spectra of Pd/Co$_3$O$_4$. A non-well resolved band at ~2164 cm^{-1} in the IR spectrum of Pd/Co$_3$O$_4$ has been assigned to CO adsorbed on Co^{2+} ions [31]. Weak bands due to CO$_2$ in the gas phase registered in the spectra of cobalt oxide in Figs. 5a and 5b suggest some reduction process not only with Pd on the surface of the catalyst but, also, to some extent with Co^{3+} to Co^{2+}.

Carbon dioxide detected in the cell after introduction of the CO+N$_2$ mixture indicates that CO oxidation occurred at room temperature most probably due to a reaction between CO and lattice oxygen from PdO and/or cobalt oxide. The increase in intensity of the bands due to gaseous CO$_2$ accompanied by an intensity decrease and even disappearance of the bands of the various adsorbed CO species is visible in the IR spectra of the catalyst during a 20-h stay of the samples in a mixture of CO+N$_2$ (Fig. 5c). This experiment was carried out to follow the stability of the CO species adsorbed on the surface metal ions in the Pd/Co$_3$O$_4$ catalyst and proved their low stability. The bands assigned to CO-Pd^{1+} and CO-Pd^{2+} species (2125 and 2154 cm^{-1}, respectively) disappeared completely in nitrogen flow at room temperature.

The catalytic properties of palladium-modified cobalt oxide in the reactions of CO oxidation and complete oxidation of methane are illustrated in figure 6. The catalytic activity of the pure cobalt oxide in both reactions is given for comparison. H$_2$O and CO$_2$ were the only detectable reaction products of the methane oxidation. In a recent investigation [32] we established that the catalytic performance of Pd/Al$_2$O$_3$ in methane combustion could be improved significantly by addition of metal oxides of Ni, Co and mixed Co-Ce, Co-Mn binary oxides. This effect was attributed to formation of highly dispersed and well-stabilized Pd or PdO clusters on the support. A close contact between the palladium and a metal oxide may increase the concentration of surface oxygen species around the palladium thus stabilizing PdO on the surface. We established that the most promising catalysts were those that contain cobalt and nickel. Results of the present study supplement our previous statement, namely, that a combination between palladium and cobalt oxide could be used to prepare highly active catalysts for methane combustion.

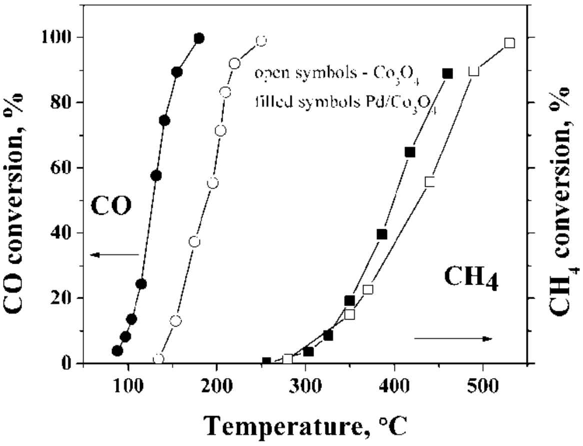

Fig. 6. Carbon monoxide and methane oxidation over Co$_3$O$_4$ and Pd/Co$_3$O$_4$ catalysts.

In order to through some light on the reaction mechanism, DRIRS was used to examine the oxidation of carbon monoxide in a flow of CO+O$_2$+N$_2$ (1% CO, 10% O$_2$) mixture at various temperatures (Fig. 7). During the flow experiments at room temperature, the CO oxidation over Pd/Co$_3$O$_4$ produced only one band due to linear CO–Pd^0 species. The bands of gaseous CO$_2$ were hardly noticeable under these conditions and their intensity increased above 150°C.

It is known that slow reaction rates of CO oxidation over supported Pd catalysts at a low temperature are a result of strong CO adsorption, which inhibits oxygen dissociative adsorption on the same sites [26, 33]. To enhance the catalytic activity at a lower temperature, supports like CeO$_2$, SnO$_2$, and MnO$_x$, which can supply active oxygen under these conditions, have been used. Thus, noble metals supported on these supports exhibited a higher activity at low temperatures, which was suggested to be a result of oxygen provided by the support to the metal [33].

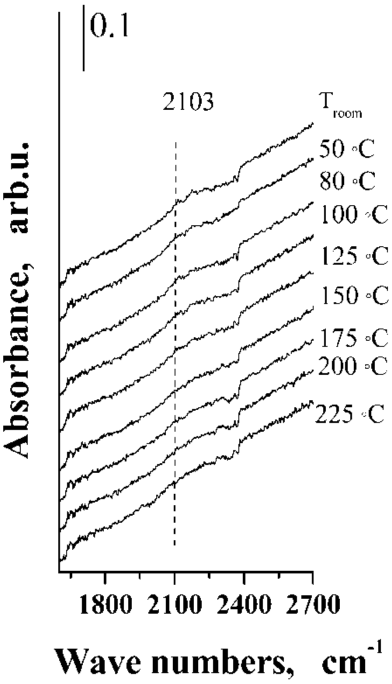

Fig. 7. DRIRS spectra of CO adsorption on Pd/Co_3O_4 in a flow mixture of 1% CO + 10% O_2 in nitrogen at various temperatures.

DRIRS data on CO adsorption from a mixture of 10 vol.% CO in nitrogen or 1 vol.% CO + 10 vol.% O_2 in nitrogen indicate the following. Firstly, the CO adsorption on Pd/Co_3O_4 is not stable at ambient temperature because the bands of different surface carbonyls disappeared shortly after blowing purge in nitrogen flow), and secondly part of the palladium is in reduced (Pd^0) state under oxidation conditions.

The Langmuir-Hinshelwood (L-H) mechanism has been well established as the dominant reaction pathway when CO is the main surface species [34]. The rate-determining step is reaction between adsorbed CO and oxygen species. As was mentioned above, linear bonded CO species were observed in the IR spectra of a Pd/Co_3O_4 sample during CO oxidation up to a temperature of 150°C. Based on this it is possible to suggest that the reaction mechanism is of L-H type including these linearly adsorbed CO species and oxygen species. The CO species are not stable at elevated temperatures; hence, a larger part of the Pd surface will be accessible for O_2 adsorption and next dissociation. Thus, the chemisorbed oxygen atoms will react with the gaseous CO through an Eley-Rideal (E-R) type mechanism. A Mars van Krevelen reaction mechanism involving interaction between CO adsorbed on a noble metal and oxygen from the oxide components is also possible as was demonstrated in our DRIRS experiments with reaction mixtures of different nature: reduction ($CO+N_2$) and oxidizing ($CO+O_2+N_2$) combinations that give rise to carbon dioxide in the gas phase.

CONCLUSION

Finely divided PdO particles have been found to occur on the surface of Co_3O_4. A DRIRS investigation revealed three possible reaction mechanisms of CO oxidation over the studied catalysts: a Langmuir-Hinshelwood pathway, an Eley-Rideal mode, and a bifunctional reaction path involving an interaction between CO species adsorbed on the noble metal and oxygen entities from a metal oxide (PdO and/or Co_3O_4). The Langmuir-Hinshelwood mechanism was proposed for CO oxidation over the studied samples at temperatures up to 150°C. Linearly adsorbed CO species are formed and involved in the reaction over Pd/Co_3O_4.

At a higher temperature, the palladium surface is covered predominantly by dissociatively adsorbed oxygen and the reaction proceeds through the E-R mechanism: chemisorbed oxygen atoms react with gaseous carbon monoxide.

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НАНОРАЗМЕРЕН КОБАЛТОВ ОКСИД МОДИФИЦИРАН С ПАЛАДИЙ ЗА ОКИСЛЕНИЕ НА МЕТАН И ВЪГЛЕРОДЕН ОКСИД

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(Резюме)

Нано размерен Co_3O_4 е получен посредством утаяване на кобалтов ацетат с амониев хидроксид и следваща хидротермална обработка. Така приготвеният оксид е накален и модифициран с паладий. Катализаторните образци са охарактеризирани с рентгенова дифракция, рентгенова фотоелектронна спектроскопия, трансмисионна електронна микроскопия, температурно програмирана редукция и дифузионно отражателна инфрачервена спектроскопия. Каталитичните свойства на синтезираните материали са изследвани в реакциите на пълно окисление на метан и въглероден оксид. Установено е образуване на финодисперсен PdO на повърхността на кобалтовия оксид.

Въз основа на изследвания с инфрачервена спектроскопия е предположено, че реакцията на окисление на CO при температури до 150°C протича по механизъм на Ленгмюир-Хиншелууд, включващ линейно свързани с паладия молекули на въглеродния оксид. При по-висока температура паладиевата повърхност е покрита главно от дисоциативно адсорбиран кислород и реакцията продължава чрез механизма на Или-Ридил: хемисорбирани кислородни атоми реагират с газообразен въглероден оксид. Не е изключен и механизмът на Марс ван Кревелен, поради факта, че се регистрира въглероден диоксид след пропускане на смес от $CO+N_2$ (без кислород), което показва, че най-вероятно въглеродният оксид взаимодейства с решетъчен кислород от PdO и/или Co_3O_4.