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Controlled preparation of CoPdSiBEA zeolite catalysts for selective catalytic reduction of NO with methane and their characterisation by XRD, DR UV–vis, TPR, XPS

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ABSTRACT

The $Pd_{0.15}$SiBEA and $Co_xPd_{0.15}$SiBEA zeolites (where $x = 1.0$ and 3.0 wt.% Co) are prepared by a two-step postsynthesis method which allows to control the introduction of palladium and cobalt into zeolite and thus to obtain catalysts with specific bimetallic Pd and Co sites. The effect of Co content on the catalytic activity of $Co_xPd_{0.15}$SiBEA zeolites in the selective catalytic reduction (SCR) of NO with methane is investigated. The nature of the active sites is characterized by diffuse reflectance UV–vis, H_2-TPR and XPS. These techniques allow to show that in both $Co_{1.0}Pd_{0.15}$SiBEA and $Co_{3.0}Pd_{0.15}$SiBEA catalysts the cobalt is present as isolated mononuclear Co(II) species. The catalytic activity of $Co_xPd_{0.15}$SiBEA strongly depends on the content of this particular Co(II) species. When Co content increase from 1.0 to 3.0 wt.% the NO conversion in SCR of NO with methane increase from maximum value of 25% to 55%. The conversion of methane is lower than 15% for $Co_{1.0}Pd_{0.15}$SiBEA over a wide temperature range (230–460 °C) but for $Co_{3.0}Pd_{0.15}$SiBEA is much higher at temperature range between 400 and 500 °C reaching maximum value of 35% at 500 °C.

1. Introduction

In the last decades several technologies have been proposed and used to reduce the emissions of nitrogen oxides (NO_x), major contributor to the acidification of the atmosphere and soil [1,2]. Among these technologies, the selective catalytic reduction (SCR) of nitrogen oxides by hydrocarbons, in presence of excess oxygen, has been extensively studied as a potential process in NO_x emissions control for diesel and lean-burn engines with the advantage of removing the hydrocarbons. The use of methane—in the form of readily available natural gas—as reducing agent is very attractive. However, the use of this hydrocarbon is restricted: the activation of the strong C–H bond often necessitates high reaction temperature. Cobalt and palladium containing zeolite catalysts seems to be capable in doing this [3,4]. Such types of catalysts have been tested and they revealed an increase of activity and stability when compared with monometallic Co catalysts [5–9]. However, they still show a significant loss of activity when water is present in the reaction mixture. Among of zeolites, BEA zeolite attracts many attentions because of the three-dimensional large pore channel system, which may offer numerous advantages in the catalytic processes. The Si/Al framework ratio can be easily controlled between 6.5 and 100, thus providing material with a wide variation in the concentration of the active sites [10]. It has been stressed [11] that a high dispersion of Co in zeolite is required in order to avoid oxidation of the hydrocarbons with O_2 and to maintain the high selectivity towards N_2. Because current postsynthesis methods such as ion exchange or conventional impregnation do not allow to control the speciation of transition metal ions introduced in zeolites, a two-step postsynthesis method was developed which consists first of creating vacant T-atom sites by dealumination of BEA zeolite with nitric acid and then impregnating the resulting SiBEA with metal precursors [12,13].

In the present work, Pd and Co were incorporated in BEA zeolite using this postsynthesis method to obtain bimetallic $Co_xPd_{0.15}$SiBEA catalysts for selective catalytic reduction of NO with methane in excess oxygen. The $Co_xPd_{0.15}$SiBEA catalysts with different Co content have been obtained and characterized by XRD, DR UV–vis, TPR and XPS in order to identify the nature and localization of metallic species.

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2. Experimental

2.1. Catalyst preparation

$Pd_{0.15}$SiBEA and $Co_xPd_{0.15}$SiBEA zeolites (where $x = 1.0$ and 3.0 wt.% Co) were prepared by the two-step postsynthesis method reported earlier [12–14].

To obtain $Pd_{0.15}$SiBEA sample with 0.15 wt.% Pd, 4.5 g of SiBEA zeolite (Si/Al = 1000), obtained by treatment of a tetraethyl ammonium BEA zeolite (Si/Al = 11) in a 13 mol L^{-1} HNO_3 solution (4 h, 80 °C), were stirred for 24 h at 25 °C in aqueous solutions containing 7.8×10^{-3} mol L^{-1} of $Pd(NH_3)_4(NO_3)_2$. Then, the suspensions (pH 4) were stirred for 2 h in air at 80 °C until the water was completely evaporated. The solid was washed three times with distilled water and then dried in air at 80 °C for 24 h. The solid containing 0.15 wt.% Pd was labelled $Pd_{0.15}$SiBEA.

To obtain bimetallic catalysts with 0.15 wt.% Pd and 1.0 or 3.0 wt.% Co, 2 g of $Pd_{0.15}$SiBEA zeolite were stirred for 24 h at 25 °C in aqueous solutions containing 1.7×10^{-3} or 5.1×10^{-3} mol L^{-1} of $Co(NO_3)_2 \cdot 6\ H_2O$. Then, the suspensions (pH 2.9) were stirred for 2 h in air at 80 °C until the water was evaporated. The solids were washed with distilled water and then dried in air at 80 °C for 24 h. The solids containing 0.15 wt.% Pd and 1.0 or 3.0 wt.% Co were $Co_{1.0}Pd_{0.15}$SiBEA or $Co_{3.0}Pd_{0.15}$SiBEA, respectively.

2.2. Catalyst characterization

Chemical analysis of the samples was performed with inductively coupled plasma atom emission spectroscopy at the CNRS Centre of Chemical Analysis (Vernaison, France).

Powder X-ray diffractograms (XRD) were recorded on a BRUKER D8 Advance diffractometer using the Cu Kα radiation (λ = 154.05 pm).

DR UV–vis spectra were recorded at ambient atmosphere on a Cary 5000 Varian spectrometer equipped with a double integrator with polytetrafluoroethylene as reference.

Temperature-programmed reduction (TPR) experiments were performed in a U-shaped tubular quartz reactor, using 5% H_2 in an Ar flow of 1.8 L h^{-1}. The H_2 consumption is monitored by a thermal conductivity detector (TCD) and prior to reduction, the samples are pretreated at 500 °C (100 °C h^{-1}) in flowing air for 3 h.

X-ray photoelectron spectroscopy (XPS) measurements were performed with a hemispherical analyzer (PHOIBOS 100, SPECS Gmbh) using Al Kα (1486.6 eV) radiation. The power of the X-ray source was 400 W and the energy pass for analyzer was 10 eV, corresponding to a full width at half maximum of 0.9 eV for the $Ag3d_{5/2}$ peak. The area of the analyzed sample was ~3 mm^2. The powder samples were pressed on an indium foil and mounted on a special holder. Binding energy (BE) for Si2p and Co2p was measured by reference to C1s peak at 284.5 eV, corresponding to carbon contamination. Before analysis, the samples were outgassed at room temperature to a pressure of 10^{-7} Pa. All spectra were fitted with a Voigt function (a 70/30 composition of Gaussian and Lorentzian functions) in order to determine the number of components under each XPS peak and to quantify the content of cobalt species from the surface area of the corresponding component.

2.3. Catalyst activity measurements

The catalytic reaction was performed with the following reaction mixture: 150 ppm NO, 7 vol.% O_2, 1500 ppm CH_4, in Ar as balance. Concerning nitrogen oxide, methane and oxygen, this reaction mixture is representative of the concentrations present in the exhaust gases of combined heat powers (CHP) [15]. The NO mixture was supplied by air liquid as 1 vol.% NO, and 99 vol.% Ar (<10 ppm other gases). The O_2 mixture contained 100 vol.% O_2 (air liquid). The CH_4 mixture contained 5 vol.% CH_4, and 95 vol.% Ar (Air Liquid). The total gas flow was maintained at 0.25 L min^{-1} NTP. Each of the gas mixtures was metered using calibrated electronic mass flow controllers (Brooks, Model 5850E).

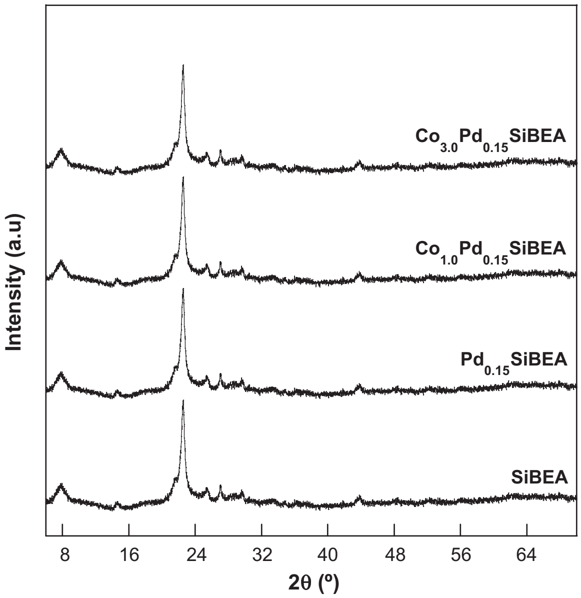

Fig. 1. X-ray diffractograms recorded at room temperature as prepared of SiBEA, $Pd_{0.15}$SiBEA, $Co_{1.0}Pd_{0.15}$SiBEA and $Co_{3.0}Pd_{0.15}$SiBEA.

Taking in account a catalyst density (0.3 g cm^{-3}), the gas hours space velocity (GHSV) was 40,000 h^{-1}. Catalytic experiments were carried out in a glass microreactor containing quartz wool supporting the sample. The bed temperature was measured using K-type thermocouple affixed to the outer reactor surface. The temperature was controlled using an electronic controller (Eurotherm 2408). The reactor outflow was analyzed using a set of specific detectors. An Eco Physics CLD 700 AL NO_x chemiluminescence analyzer (for NO and total NO_x (i.e. NO + NO_2)) allowed the simultaneous detection of NO, NO_2 and NO_x. An Ultramat 6 IR analyzer was used to monitor N_2O and a FID detector was used to follow the total concentration of hydrocarbons (HC). Isothermal steady-state reaction was measured at different temperatures, ranging from 200 to 500 °C, in decreasing the temperature to avoid all the desorption effects. The NO and methane conversions were calculated from measured concentration of NO and methane, respectively.

3. Results and discussion

3.1. Evidence for incorporation of Pd and Co as isolated mononuclear species

3.1.1. X-ray diffraction

Fig. 1 shows the XRD patterns of SiBEA, $Pd_{0.15}$SiBEA, $Co_{1.0}Pd_{0.15}$SiBEA and $Co_{3.0}Pd_{0.15}$SiBEA, typical of the BEA zeolite. The crystallinity of SiBEA zeolite is preserved after incorporation of Pd and Co ions and the catalysts do not show any evidence of extra lattice crystalline compounds or long-range amorphization of the zeolite structure. It suggests that Pd and Co species are well dispersed in the zeolite framework as isolated mononuclear species.

3.1.2. Diffuse reflectance UV–vis spectroscopy

The $Pd_{0.15}$SiBEA sample exhibits only one broad band at around 300 nm (Fig. 2) assigned to oxygen-to-metal charge transfer (CT) transition in line with earlier work of Weckhuysen et al. [16].

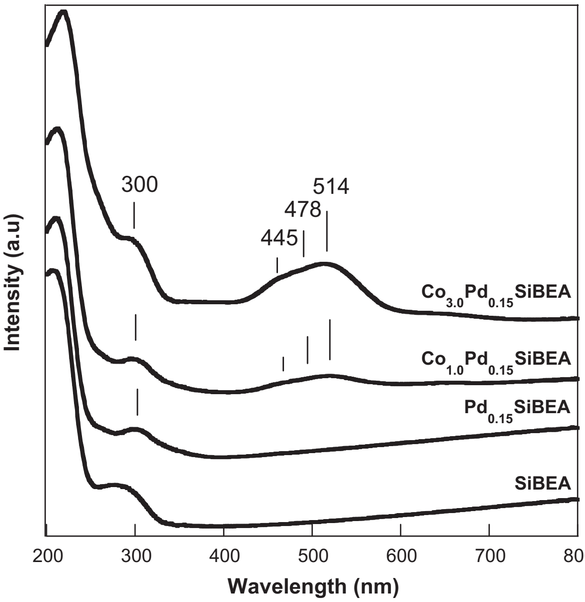

Fig. 2. DR UV–vis spectra recorded at room temperature and ambient atmosphere of as-prepared SiBEA, $Pd_{0.15}SiBEA$, $Co_{1.0}Pd_{0.15}SiBEA$ and $Co_{3.0}Pd_{0.15}SiBEA$.

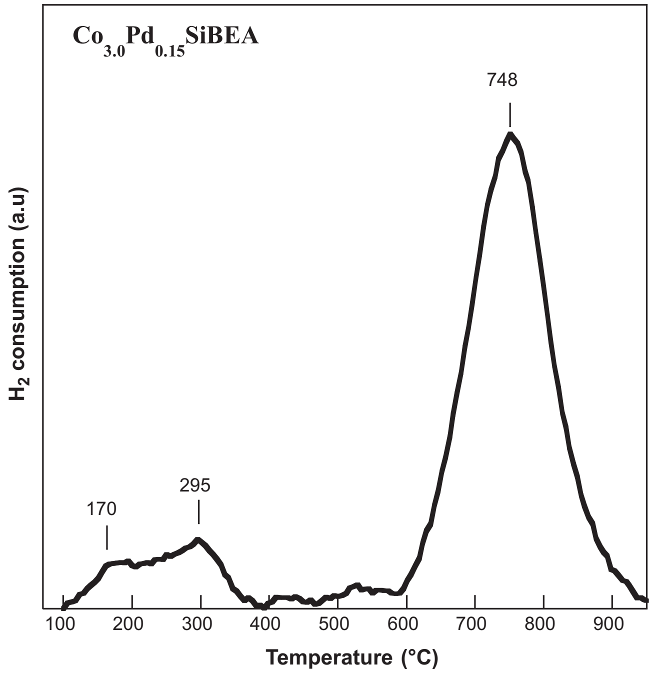

Fig. 3. TPR pattern of $Co_{3.0}Pd_{0.15}SiBEA$ calcined at 500°C (100°C h^{-1}) for 3h in flowing air.

In contrast, the $Co_{1.0}Pd_{0.15}SiBEA$ and $Co_{3.0}Pd_{0.15}SiBEA$ samples exhibit in addition three DR UV–vis bands at around 445, 478 and 514 nm (Fig. 2) assigned to isolated mononuclear Co(II) in octahedral coordination, in line with earlier report on Co-MFI [17] and CoSiBEA [18] zeolites.

The intensity of these bands increase with Co content. The absence of the DR UV–vis bands between 340 and 440 nm characteristic of cobalt oxides [19], suggests that the latter are not present in both $Co_{1.0}Pd_{0.15}SiBEA$ and $Co_{3.0}Pd_{0.15}SiBEA$ samples.

3.1.3. Temperature programmed reduction

TPR pattern of $Co_{3.0}Pd_{0.15}SiBEA$ pretreated at 500 °C exhibits one main reduction peak (Fig. 3) at relatively high temperature (748 °C). It may be attributed to the reduction of a well dispersed mononuclear Co(II) species being in a strong interaction with the zeolite framework, in line with earlier work [20]. Additional two very small peaks appeared at 170 and 295 °C can be attributed to the reduction of cobalt oxide [21]. The much lower reduction temperature of this cobalt oxide species suggests that they are in weaker interaction with the BEA structure, probably present in extra-lattice position. However, the majority of Co species in this catalyst is present as isolated mononuclear Co(II) species. These species are in strong interaction with BEA zeolite and very resistant to reduction.

Table 1
XPS data of $Co_{3.0}Pd_{0.15}SiBEA$ calcined at 500 °C for 3 h in flowing air.

Peak	Binding energy (eV)
$Co2p_{3/2}$	781.9
$Co2p_{3/2}$	779.7
Satelite	786.5
$Co2p_{1/2}$	798.5
$Co2p_{1/2}$	795.6
Satelite	803.4
O1s	532.7
Si2p	103.4
$Pd3d_{5/2}$	337.0

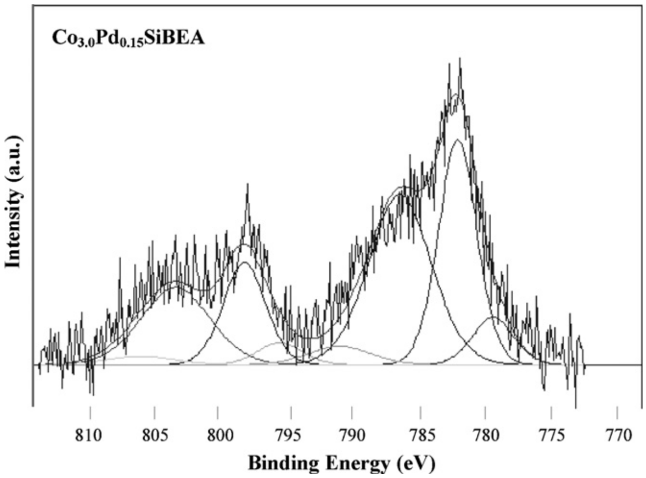

Fig. 4. XPS pattern of Co_{2p} on $Co_{3.0}Pd_{0.15}SiBEA$ calcined at 500 °C (100 °C h^{-1}) for 3 h in flowing air.

3.1.4. X-ray photoelectron spectroscopy

The XPS measurements performed in the BE region corresponding to Si2p, O1s, Pd3d, Co2p on the samples calcined at 500 °C for 3 h in flowing air are presented in Table 1 and Fig. 4. The Si2p BE value (103.4 eV) is close to that reported earlier for others zeolites [22,23]. The O1s BE value (532.7 eV) is very similar to that already observed for zeolites and silica [24]. Because of very low Pd content in $Co_{3.0}Pd_{0.15}SiBEA$, it is very difficult to see the peaks corresponding to this metal. Probably, very small peak appear at 337 eV (not shown) corresponds to Pd^{2+} ion [25].

As shown in Fig. 4 and Table 1, for $Co_{3.0}Pd_{0.15}SiBEA$, the core level BE of $Co2p_{3/2}$ is at 781.9 eV. This value is very close to that reported elsewhere for Co^{2+} ions [25] and observed for highly dispersed Co species in Co-ZSM-5 [26] (BE value of 783.2 eV) with cobalt coordinated to lattice oxygen. It suggests that in $Co_{3.0}Pd_{0.15}SiBEA$, the Co^{2+} ions are well dispersed in zeolite framework and strongly bound to the zeolite. For this sample, the core level BE of $Co2p_{1/2}$ is at 798.5 eV. This value is close to that reported earlier for Co^{2+} ions in CoSiBEA zeolite [20].

In addition to these spin-orbital peaks, the satellites for $2p_{3/2}$ and $2p_{1/2}$ are also observed, respectively at 786.5 and 803.4 eV for

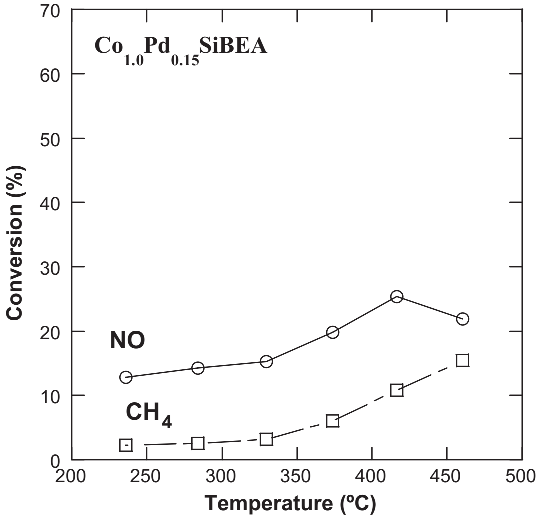

Fig. 5. Temperature-dependence of methane and NO conversions in SCR of NO with methane on $Co_{1.0}Pd_{0.15}SiBEA$.

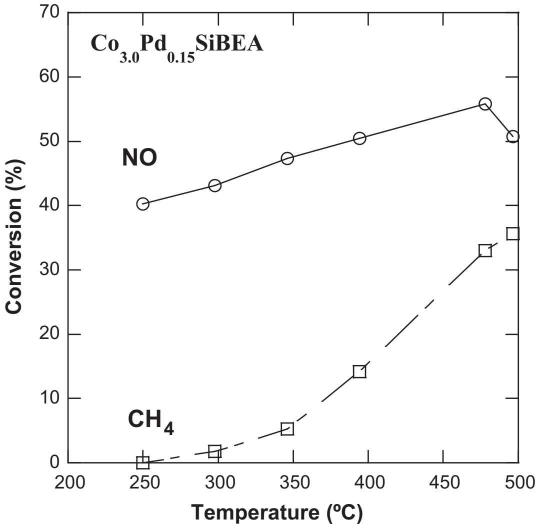

Fig. 6. Temperature-dependence of methane and NO conversions in SCR of NO with methane on $Co_{3.0}Pd_{0.15}SiBEA$.

$Co_{3.0}Pd_{0.15}SiBEA$ confirming that in this sample cobalt is mainly present in (II) oxidation state [27].

Moreover, the second value of BE for $Co2p_{3/2}$ and $Co2p_{1/2}$ at 779.7 and 795.6 eV, respectively, reveal that very small amounts of cobalt is present as cobalt oxides. The BE of $Co2p_{3/2}$ are very close to that observed for Co_3O_4 (BE value of 779.6 eV) and $Co(OH)_2$ (BE value of 781.0 eV) [28]. The XPS results confirm TPR data and evidence the presence of isolated mononuclear Co(II) as main species in $Co_{3.0}Pd_{0.15}SiBEA$.

The combined XRD, DR UV–vis, TPR and XPS results show that cobalt is incorporated into the BEA framework mainly as isolated mononuclear Co(II) species being in strong interaction with the zeolite. Only very small amount of cobalt is present in the $Co_{3.0}Pd_{0.15}SiBEA$ as extra-framework cobalt oxides, less strongly interacting with zeolite and more easily reducible than isolated mononuclear Co(II) species.

3.2. Effect of the Co content on catalytic activity of $Co_xPd_{0.15}SiBEA$ catalysts

On $Pd_{0.15}SiBEA$, less than 5% of NO_x and CH_4 conversions were observed. Figs. 5 and 6 show the conversions of NO and CH_4 in SCR of NO with methane in excess oxygen on $Co_{1.0}Pd_{0.15}SiBEA$ and $Co_{3.0}Pd_{0.15}SiBEA$ catalysts, respectively. As we can see, the catalytic activity of this type of catalysts strongly depends on the Co content.

For $Co_{1.0}Pd_{0.15}SiBEA$, the conversion of CH_4 in this reaction is lower than 15% over a wide temperature range (230–460 °C), which corresponds to 225 ppm of methane activated. In contrast, the conversion of NO is higher and reaches maximum value of 35% at 425 °C, which corresponds to 52.5 ppm of NO_x (Fig. 5).

For $Co_{3.0}Pd_{0.15}SiBEA$, the conversion of CH_4 is low (<10%) at the temperature range between 250 and 350 °C (Fig. 6) but much higher at temperature range between 400 and 500 °C and reaches maximum value of 35% at 500 °C. At the same time, for this catalyst, the conversion of NO is high, exceeding 40% in the wide temperature range (Fig. 6) and reaches maximum value 56% at 475 °C. It suggests that $Co_{3.0}Pd_{0.15}SiBEA$ catalyst is much active in SCR of NO with methane that $Co_{1.0}Pd_{0.15}SiBEA$.

It seems that catalytic activity of these catalysts is related to the presence of isolated mononuclear Co(II) species evidenced by DR UV–vis, TPR and XPS which amount is higher for $Co_{3.0}Pd_{0.15}SiBEA$ than $Co_{1.0}Pd_{0.15}SiBEA$. The activity of both catalysts in SCR of NO with methane is much higher than that found for SCR of NO by methane on alumina supported cobalt palladium catalyst $Co(0.57)Pd(0.14)/Al_2O_3$) reported earlier [15], with less than 15% of NO conversion. As already reported in the literature, one can suppose that on such kind of material, presenting coordinated unsaturated sites "CUS" a three function model can be applied, in which (i) NO is oxidized to NO_2, (ii) methane is partially oxidized by NO_2, and (iii) NO is reduced by this oxidized species [29–31].

4. Conclusions

XRD, DR UV–vis, TPR and XPS investigations show that the two-step postsynthesis method allows to control the introduction of palladium and cobalt into BEA zeolite and to obtain catalysts with specific bimetallic Pd and Co sites, well dispersed in zeolite framework.

DR UV–vis, TPR and XPS investigations show that in both $Co_{1.0}Pd_{0.15}SiBEA$ and $Co_{3.0}Pd_{0.15}SiBEA$ catalysts the cobalt is present as isolated mononuclear Co(II) species.

The catalytic activity of these catalysts in SCR of NO with methane strongly depends on the content of this particular Co(II) species. When Co content increase from 1.0 to 3 wt.%, the NO conversion in SCR of NO with methane increase from maximum value of 25% to 55%. The conversion of methane is lower than 15% for $Co_{1.0}Pd_{0.15}SiBEA$ over a wide temperature range (230–460 °C) but for $Co_{3.0}Pd_{0.15}SiBEA$ is much higher at temperature range between 400 and 500 °C reaching maximum value of 35% at 500 °C.

The isolated mononuclear Co(II) species are able to catalyse effectively SCR of NO with methane without participation of acidic centres removed upon the first step of postsynthesis procedure (Si/Al = 1000).

Further studies are undertaken to better description of Pd and Co sites present in CoPdBEA system, particularly with X-ray absorption spectroscopy, and understanding a role of these sites in SCR of NO with methane.

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