

COMPLETE BENZENE OXIDATION OVER Co_3O_4 - CeO_2 COMPOSITES PREPARED BY MECHANICAL MIXING

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Abstract

Nowadays many researchers are focused on catalytic oxidation as one of the most efficient ways to reduce the harmful emissions from various chemical industries. The use of appropriate highly active catalysts could decrease the operational costs by significantly lowering the temperature for total oxidation of volatile organic compounds (VOCs). The object of the present study is the complete benzene oxidation, used as a probe reaction for the VOCs abatement, over Co_3O_4 – CeO_2 mixed oxides synthesized via mechanical mixing of cerium hydroxide and cobalt hydroxycarbonate precursors at different time of treatment. The CeO_2 content was 20, 30 and 40 wt.%. All materials were characterized using Brunauer-Emmet-Teller (BET) method, X-ray Diffraction (XRD), and Temperature Programmed Reduction (H_2 -TPR). The mixed oxides exhibited much better catalytic activity in comparison with Co_3O_4 . 100% benzene conversion was reached in the relatively very low temperature range 200 – 250°C, thus confirming the promotional role of ceria. The optimal composition was 70 wt.% Co_3O_4 – 30 wt.% CeO_2 . The catalyst prepared by 1 min mechanical mixing exhibited the best performance, a slightly lower activity was established in the case of 5 min precursors' grinding. Both catalysts with this best composition reached 100% benzene conversion at 200°C, maintaining stable activity at this temperature without any products of incomplete benzene oxidation. The important role of mechanochemical treatment was evidenced by the significantly worst catalytic behavior over the sample with this optimal composition but prepared by manual mixing. The results showed the promising oxidation activity of low-cost noble metal-free composites synthesized by simple method of mechanochemical mixing for effective VOCs elimination.

Key words: volatile organic compounds, complete benzene oxidation, Co_3O_4 – CeO_2 composites

1. INTRODUCTION

One of the most significant problems related to the protection of the environment and human health is the problem of reducing harmful emissions emitted by various industrial gases or from motor vehicles.

Volatile organic compounds (VOCs) represent an important class of air pollutants because of their hazardous and toxic nature. Among them, the aromatic VOCs, including BTX (benzene, toluene and o-xylene), chlorobenzene and others, with high toxicity to human health and “carcinogenic-mutagenic-teratogenic” effect, mainly come from industrial sources [1,2]. VOCs emissions have been regulated by EU legislation since 1999. After the adoption of the UN Framework Convention on Climate Change since 2015 in Paris, the requirements for monitoring of gaseous emissions into the atmosphere have increased every calendar year. The effective and environment-friendly removal of VOCs in the atmosphere is an object of special attention and a serious challenge for the scientific community.

Catalytic combustion to harmless CO_2 and water is the preferred method among existing processes for the purification of toxic VOCs emissions with significant advantages like decrease in energy requirement of the process and decrease in costs [3,4]. It is known that various transition metals, metal oxides and mixed metal-metal oxides have high activity and stability during operation. Of particular importance in the development and preparation of such catalytic systems is the choice of a suitable method of synthesis and the addition of suitable promoters.

Catalysts for combustion of VOCs have been divided into three categories: (i) noble metal catalysts; (ii) non-noble metal catalysts; (iii) mixed-metal catalysts [5]. Noble metals, such as Au, Pd, Pt and Ru, are

often used as catalysts due to their superior activity in combustion of VOCs [6-8]. However, the industrial application of noble metal catalysts for VOCs oxidation is limited by cost and some problems like sintering and susceptibility to poisoning. Non-noble metal oxides through doping, improving the design and synthesis of porous structures have advantages over noble metal catalysts because of their comparably high activity in deep oxidation of VOCs and their much lower cost [9]. Non-noble metal catalysts mainly include single metal oxide catalysts, mixed metal oxide catalysts and perovskite catalysts.

In recent years, intensive efforts have been devoted to the synthesis of transition and rare earth metal oxides as alternatives to the expensive noble metal catalysts for VOCs complete oxidation and for the reduction of the reaction temperature [10-12]. Typical metal oxides used in environmental catalysis are transition metal oxides such as TiO_2 , ZrO_2 , Fe_2O_3 , NiO , MnO_x , and Co_3O_4 . They can be used as catalysts directly or as active components supported on appropriate carriers. There are three types of cobalt oxides: Co_3O_4 (spinel structure), CoO (rocksalt structure), and Co_2O_3 (hexagonal structure). Among them Co_3O_4 is considered as the most useful catalyst for environmental remediation [13]. Co_3O_4 is an active and prevalent catalyst for CO and VOCs catalytic oxidation at low temperatures [14,15]. Even in some cases Co_3O_4 is more reactive than supported Pd or Pt catalysts, which are often the catalysts of choice for VOCs complete oxidation [16].

Ceria is one of the most important rare earth oxides being actively investigated, especially its application in catalysis [17]. CeO_2 doped with specific transition metal ions with the formation of ceria-based solid solution structure or mixed oxides are very promising catalytic materials, widely used for the abatement of various air pollutants including volatile organic compounds. Trovarelli reported for catalytic properties of ceria and CeO_2 -containing materials [18]. Other publications were also focused on the catalytic applications of CeO_2 -based materials [19,20].

Composites consisting of cobalt and cerium oxides have been the subject of intense interest [21]. Xe et al. [22,23] have shown that CeO_2 – Co_3O_4 oxide systems are significantly more active comparing to pure Co_3O_4 and the activation effect of cerium is mainly related to modification of the redox properties of cobalt. Co_3O_4 and Co_3O_4 – CeO_2 composites have been reported as promising systems for total oxidation of VOCs e.g. ethyl acetate [24-26], methanol [27], toluene [28-31], hexane [32], propane [33], propene [34,35].

The complete oxidation of benzene (CBO), one of the most harmful and stable molecule, was chosen as a model reaction in the present study. In the literature Co_3O_4 – CeO_2 and supported Co_3O_4 – CeO_2 mixed oxides have been studied in the reaction of CBO [36- 39].

Carabineiro et al. [31] examined the impact of preparation procedure on the VOCs oxidation performance of Ce – Co mixed oxides at a constant Ce/Co ratio of 0.5. Despite the wide application range of cobalt–ceria binary oxides, there is no a systematic study on the impact of preparation method on the catalytic performance in the reaction of complete benzene oxidation. In general, the simple way of catalyst synthesis by mechanical mixing is less commonly used. Ilieva et al. [40] established that the preparation of Co_3O_4 – CeO_2 supports (10 wt.% Co_3O_4) of gold catalysts by mechanochemical mixing is beneficial for the higher activity in CBO as compared to the co-precipitation method. Liu et al. [41] observed high activity in propane oxidation of highly strained Co_3O_4 catalyst prepared by mechanochemical treatment via prolonged citrate-precursor grinding.

The goal of the present work is to develop well performing in the reaction of complete benzene oxidation and cost effective Co_3O_4 – CeO_2 mixed oxides prepared by mechanical mixing. The role of mechanical treatment, in particular the time of precursors grinding, and the effect of mixed oxides composition (20, 30 and 40 wt.% of ceria) on the oxidation activity is discussed.

2. MATERIALS AND METHODS

2.1. Preparation of Co_3O_4 and CeO_2

CeO_2 and Co_3O_4 were synthesized by precipitation of aqueous solutions of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ($C = 200 \text{ g/L}$), respectively, with a solution of K_2CO_3 ($C = 150 \text{ g/L}$) which was added dropwise at constant temperature, stirring and pH (60°C and $\text{pH} = 9.0$). The resulting precipitate aged for 60 minutes at 60°C under stirring, then it was filtered off and thoroughly washed with warm distilled water (about 50°C) to neutral pH and lack of nitrate ions (checked with diphenylamine indicator). Both precipitates were dried at 80°C under vacuum and then calcined at 400°C for 2 h in air. For comparison, commercial Cobalt (II, III) oxide (Sigma Aldrich) was used. The samples are denoted as Co_3O_4 , CeO_2 and Co_3O_4 (c).

2.2. Preparation of $\text{Co}_3\text{O}_4 - \text{CeO}_2$ mixed oxides

Mixtures of cerium hydroxide and cobalt hydroxycarbonate synthesized from aqueous solutions of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and K_2CO_3 under the conditions described above, but without thermal treatment at 400°C were used as precursors. They were subjected to mechanochemical mixing in an electric mortar (Mortar Grinder RM 200, Retsch) for different time. The calculated amounts of cerium hydroxide and cobalt hydroxycarbonate were fully ground for 1 and 5 minutes, thus two series of mixed oxides with different composition were prepared. The amount of cerium hydroxide was selected to correspond to 20, 30 and 40 wt.% CeO_2 in the mixed oxides after calcination for 2 h at 400°C based on analysis of weight losses at the same temperature. Depending on the amount of ceria and mixing time of preparation, the composites were denoted as: $\text{Co}_{20}\text{Ce}_1$, $\text{Co}_{30}\text{Ce}_1$, $\text{Co}_{40}\text{Ce}_1$, $\text{Co}_{20}\text{Ce}_5$, $\text{Co}_{30}\text{Ce}_5$ and $\text{Co}_{40}\text{Ce}_5$.

For comparison, one sample containing 70 wt.% Co_3O_4 and 30 wt.% CeO_2 was prepared from the same precursors (cerium hydroxide and cobalt hydroxycarbonate) by manually mixing (MM), and then it was calcined for 2 h at 400°C and denoted as $\text{Co}_{30}\text{CeMM}$.

2.3. Catalysts characterization

The specific surface area of all samples was measured by nitrogen adsorption at 77 K using Quantachrome Instruments NOVA 1200e (USA). Prior to the measurements, the catalysts were degassed at 200°C for 2h under vacuum. The obtained results were calculated using the BET equation.

The powder X-ray diffraction (XRD) measurements were carried out on a PANalytical Empyrean apparatus equipped with a multichannel detector (Pixel 3D) using Cu K_α 45 kV-40 mA radiation in the 2θ range $20-115^\circ$ deg. with a scan step of 0.01° for 20 s. The particle size of the crystalline phases and lattice parameters were calculated in powder diffraction analysis software based on the Rietveld method – ReX [42].

The temperature programmed reduction (TPR) measurements were carried out by means of an apparatus described elsewhere [43]. A cooling trap (-40°C) for removing water formed during reduction was mounted in the gas line before the thermal conductivity detector.

A hydrogen–argon mixture (10% H_2), dried over a molecular sieve 5A (-40°C), was used to reduce the samples at a flow rate of 24 mL min^{-1} . The temperature was linearly raised at a rate of $15^\circ\text{C min}^{-1}$. Each sample used had a weight 0.007 g. This was selected by the criterion proposed by Monti and Baiker [44].

2.4. Catalytic activity measurements

The catalytic activity of the samples in the reaction of complete benzene oxidation (CBO), expressed as the degree of benzene conversion, was evaluated over the temperature range $150 - 350^\circ\text{C}$. The activity was measured using a microcatalytic continuous flow fixed bed reactor at atmospheric pressure connected to a Hewlett Packard 5890 series II gas chromatograph, equipped with a flame ionization detector, using capillary HP Plot Q column.

The following conditions were chosen: catalyst bed volume of 0.5 cm^3 (particle size $0.50 - 0.80 \text{ mm}$), inlet benzene concentration 42 g m^{-3} in air, space velocity 4000 h^{-1} . The amount of the catalysts was

charged into the reactor and the particles size of the catalysts was selected to be small enough to avoid diffusion retardation effects. The catalysts were activated “in situ” by purified air for 1 h at 200°C.

Stability tests with Co30Ce1 and Co30Ce5 composites were conducted at 200°C for 24 h.

3. RESULTS AND DISCUSSION

The catalytic activity results in CBO over the studied samples as a function of the reaction temperature are illustrated in Fig. 1A and B. Complete benzene oxidation was observed and no intermediate products of mild oxidation were detected over all mixed oxides materials. The best performance demonstrated both samples Co30Ce1 and Co30Ce5 – total oxidation was reached at 200°C, while all other mixed oxides attained it at 250°C. It is important to underline significantly higher activity of all mixed oxides compositions in comparison with pure Co₃O₄. 100% benzene conversion was not achieved over pure Co₃O₄ even at 350°C, thus revealing the role of ceria as an active phase in oxidation reactions.

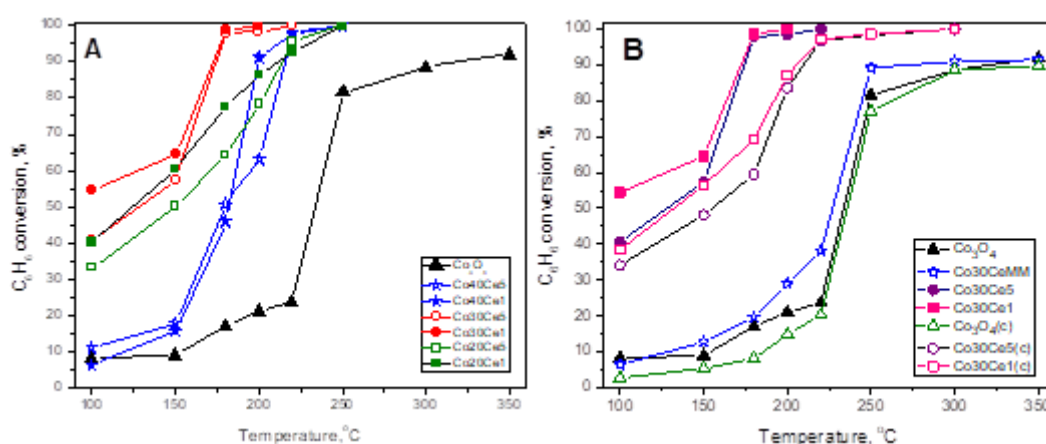


Fig. 1. Temperature dependence of CBO according to: (A) mixed oxides composition; (B) method of mixing and precursor used

In Fig. 1 A the catalytic activity of the mixed Co – Ce oxides prepared by mechanical mixing of cerium hydroxide and cobalt hydroxycarbonate precursors is compared with the activity of laboratory prepared Co₃O₄ as a reference material. Co₃O₄ exhibited the lowest CBO activity and benzene conversion around 90% was registered at 350°C.

The promotional role of ceria is clearly evidenced as in the presence of mixed oxides the 100% benzene conversion was observed in the range 200 – 250°C. These temperatures for benzene combustion are relatively very low in respect to noble metal-free catalysts. Regardless the milling duration, the samples with the highest Co₃O₄ content, Co20Ce1 and Co20Ce5 showed substantially higher catalytic activity than that of Co40Ce1 and Co40Ce5 (both with similar activity) in the low temperature range up to 175°C. However, at 200°C the samples treated 1 min (Co40Ce1 and Co20Ce1) exhibited over 85% benzene conversion, while those milled 5 min, Co20Ce5 and Co40Ce5, demonstrated lower catalytic activity. The performance of samples with 60 and 80 wt.% Co₃O₄, was very similar in higher temperature range 200 – 250°C, all of these samples reached 100% benzene conversion at 250°C.

The established optimal composition of the mixed oxides is 70 wt.% Co₃O₄ – 30 wt.% CeO₂. Very high benzene conversion (55% at 100°C and 100% at 200°C) was obtained using sample preparation by 1 min mechanical treatment and this catalyst, namely Co30Ce1, demonstrated the best catalytic activity among the studied samples throughout the all temperature range. The catalytic activity of Co30Ce5 catalyst was slightly lower. Both catalysts maintained stable activity during the stability tests and no loss of catalytic activity and products of mild oxidation were registered.

The analysis of the effect of mixed oxides composition on the CBO demonstrated that 70 wt.% Co_3O_4 and 30 wt.% CeO_2 has favourable role in achieving high oxidation activity. The catalytic behavior of laboratory prepared and commercial Co_3O_4 is very similar. However the composites containing 70% of commercial Co_3O_4 (Co30Ce1(c) and Co30Ce5(c)) showed noticeably lower activity (100% benzene conversion at 300°C). The longer treatment caused again slightly lower activity. A crucial role for the observed high CBO activity of mixed Co – Ce oxides plays the way of preparation. In order to rationale the influence of mixing procedure the catalytic behaviour of Co30Ce1 and Co30Ce5 was compared with that of Co30CeMM prepared by manual mixing (Fig. 1 B). The Co30CeMM sample synthesized from the same precursors (cerium hydroxide and cobalt hydroxycarbonate) by manually mixing contributed to only small CBO activity increasing as compared to that of mono Co_3O_4 .

The results clearly show that the sample preparation by mechanical mixing of cerium hydroxide and cobalt hydroxycarbonate precursors has a favourable effect on the catalytic activity of mixed Co_3O_4 – CeO_2 oxides. These catalysts were the object of subsequent sample characterization.

The obtained values of specific surface area (SSA) estimated by BET method are given in Table 1. A tendency of higher SSA values with increasing of CeO_2 amount as compared to mono Co_3O_4 is seen for mixed oxides prepared by 1 min mechanical mixing. This finding is in agreement with the trend of Co_3O_4 particle size lowering, while the ceria particles size is in the range 4.8 – 5.2 nm. The longer time of mechanical mixing did not lead to higher surface area, in particular SSA of $\text{Co30Ce1} > \text{SSA}$ of Co30Ce5 , nevertheless the lower values of both $D_{\text{Co}_3\text{O}_4}$ and D_{CeO_2} .

The crystal phase composition of mono Co_3O_4 , CeO_2 and studied Co – Ce mixed oxides prepared by mechanical mixing of cerium hydroxide and cobalt hydroxycarbonate precursors were analyzed by powder XRD as illustrated in Fig. 2.

For pristine CeO_2 the typical for cubic fluorite structure diffraction peaks at $2\theta = 28.5$ (peak with the highest intensity characteristic for Ce (111)), 33.1, 47.4, 56.3, 59.0, 69.4, 76.6 and 79.9° (Ref. Code ICSD: 98-015-5605; 98-016-4225; 98-016-9029; 98-015-5604; 98-015-5605; 98-026-2755; 98-062-1707) were registered.

The commercial and as-prepared Co_3O_4 showed identical XRD patterns at $2\theta = 18.9, 31.3, 36.9^\circ$ (the most intense peak of Co_3O_4 (311)), 38.6, 44.9, 55.8, 59.5, 65.5, 77.5, 78.6, 82.6 and 82.9° , corresponding to the spinel crystalline Co_3O_4 phase (Ref. Code ICSD: 98-002-4210; 98-002-7498; 98-002-7498; 98-002-7498; 98-062-4573; 98-017-3832; 98-015-5604; 98-017-3832; 98-015-0805; 98-003-6256), [45].

The coexistence of the same Co_3O_4 and CeO_2 phases is visible in the XRD patterns of the studied mixed oxides. The estimated average size of CeO_2 (D_{CeO_2}) and Co_3O_4 particles ($D_{\text{Co}_3\text{O}_4}$) as well as the lattice parameter of CeO_2 (a_{CeO_2}) and Co_3O_4 ($a_{\text{Co}_3\text{O}_4}$) are listed in Table 1. The obtained lattice parameter of pure CeO_2 is similar to that of stoichiometric ceria (5.41 Å) [46,47]. A decrease of ceria lattice parameter, e.g. a tendency of lattice contraction with increasing Co_3O_4 amount is visible for Co – Ce mixed oxides prepared by 1 min mechanical mixing (Table 1).

Table 1. Specific surface area, average size of CeO_2 and Co_3O_4 particles and lattice parameter of CeO_2 and Co_3O_4 estimated by XRD.

Sample	SSA ($\text{m}^2 \text{g}^{-1}$)	$a_{\text{Co}_3\text{O}_4}$ (Å)	$D_{\text{Co}_3\text{O}_4}$ (nm)	a_{CeO_2} (Å)	D_{CeO_2} (nm)
Co_3O_4	44	8.0868(7)	18.0(2)	-	-
$\text{Co}_3\text{O}_4(\text{c})$	49	8.0680(5)	18.7(3)	-	-
CeO_2	61	-	-	5.4118(2)	5.0(4)
Co20Ce1	54	8.0717(4)	18.0(2)	5.4093(2)	5.1(2)
Co30Ce1	64	8.0630(6)	17.0(4)	5.4043(5)	5.2(3)
Co40Ce1	67	8.0557(4)	16.0(4)	5.3980(4)	4.8(2)

Co20Ce5	56	8.0735(2)	17.8(4)	5.4076(5)	4.6(2)
Co30Ce5	51	8.0793(5)	13.0(2)	5.4156(3)	4.0(1)
Co40Ce5	66	8.0783(5)	14.6(2)	5.4128(5)	4.4(4)

It could be explained by the supposition of Co ions involving in ceria lattice having in mind the larger radius of the Ce^{4+} cation (1.01 Å) as compared to that of the Co^{2+} cation (0.79 Å). There is no such clear trend for the samples synthesized by 5 min mechanical treatment. The observed lattice parameter of laboratory prepared Co_3O_4 is closed to the given in the literature value of 8.08 Å for stoichiometric Co_3O_4 [48]. A tendency of lattice contraction with increasing ceria content is clearly expressed for the mixed Co – Ce oxides prepared by 1 min mechanical mixing.

Studying highly active in total oxidation of propane cobalt oxide synthesized by grinding of citrate-precursor Liu et al. [41] observed lattice contraction as compared to the Co_3O_4 catalysts prepared by co-precipitation or sol-gel method. The authors explained this observation by a high degree of lattice distortion in cobalt oxide spinels caused by the grinding procedure of preparation. In the present case for the mixed Co – Ce oxides synthesized via longer time of mechanical treatment (5 min) the difference from the pure Co_3O_4 lattice constant value is less significant and there is no a clear dependence on ceria content as for the above commented case of 1 min treatment. A plausible explanation could be related to the additional effect of incorporation of some limited amount of cerium ions with larger radius into the Co_3O_4 lattice. It caused the opposite effect of lattice expansion as reported by Zou et al. investigating Co – Ce oxides for catalytic oxidation of diesel soot [49].

In general, it could be concluded that the preparation of mixed Co – Ce oxides using mechanical mixing of the corresponding cerium hydroxide and cobalt hydroxycarbonate precursors make possible formation of defective catalyst surface with strained Co_3O_4 and CeO_2 nanocrystals in close interaction. The reducibility of Co_3O_4 and the studied Co – Ce mixed oxides was investigated by H_2 -TPR. The TPR pattern of Co_3O_4 is usually characterized by two TPR peaks: the low temperature peak is related to $\text{Co}^{3+} \rightarrow \text{Co}^{2+}$ and the next one to $\text{Co}^{2+} \rightarrow \text{Co}^0$ transition, as reported by Yao [50] and many other researchers. The registered position of the peaks is in the range up to 500°C depending on different factors. Particle size is mainly addressed - the lower temperatures are registered for Co oxides with higher dispersion [26]. The reduction of ceria is characterized by surface layers reduction at around 500°C and bulk reduction over 800°C [51]. Positive effect of ceria on the reducibility of Co_3O_4 with existing of optimal Co/Ce ratio is often reported in the literature for mixed oxides prepared by different methods [52,53].

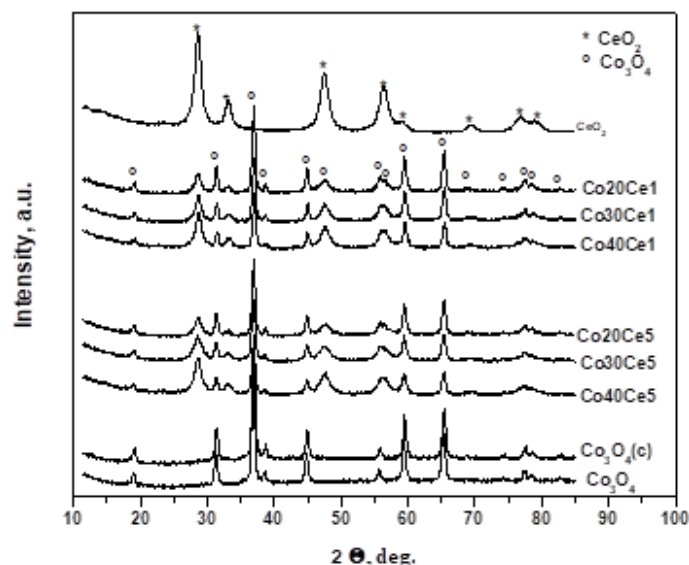


Fig. 2. XRD patterns of the studied samples

However, studying the reduction behavior of $\text{CeO}_2 - \text{Co}_3\text{O}_4$ (molar ratio $\text{Ce}/\text{Co} = 2/8$) by TPR [54] and by *in situ* XRD [55] no effect of ceria on the $\text{Co}^{3+} \rightarrow \text{Co}^{2+}$ transition and $\text{Co}^{2+} \rightarrow \text{Co}^0$ reduction at higher temperature as compared to bare Co oxide was found. The observed in the present study TPR profiles are compared in Fig. 3.

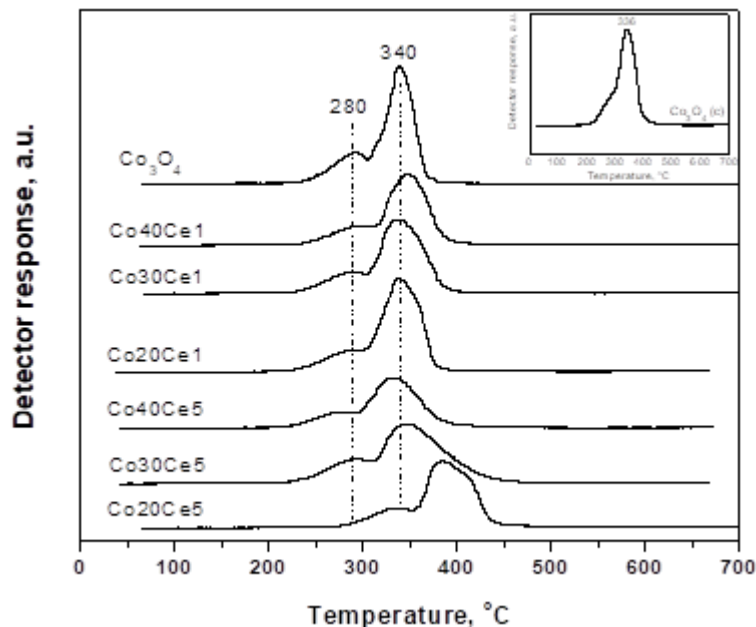


Fig. 3. H_2 -TPR profiles of the studied samples

The TPR peaks of laboratory prepared and commercial Co_3O_4 (inset in Fig. 3) are located in the same temperature range in agreement with the similar average Co_3O_4 particle size (18.0 and correspondingly 18.7 nm as established by XRD). The $\text{Co}^{3+} \rightarrow \text{Co}^{2+}$ reduction in the case of commercial oxide takes place at slightly higher temperatures and it is seen like a shoulder of the peak assigned to the metallic cobalt formation. This could explain the slightly lower activity of $\text{Co}_3\text{O}_4(\text{c})$ as compared to laboratory prepared Co_3O_4 (Fig. 1 B). The TPR peaks of Co – Ce mixed oxides prepared by 1 min mechanical treatment were registered at temperatures similar to those of bare Co_3O_4 (nevertheless its significantly lower CBO activity): T_{max} around 280°C for $\text{Co}^{3+} \rightarrow \text{Co}^{2+}$ transition and 340°C - for $\text{Co}^{2+} \rightarrow \text{Co}^0$ and ceria surface layer reduction. The enhanced reducibility of ceria surface layers below 500 °C has to be considered due to the close contact with Co phase and spill-over of hydrogen [31,32,35,37]. All TPR peaks positions are quite similar regardless of the different (60, 70 and 80 wt.%) Co_3O_4 content. A slightly higher is the T_{max} of the second TPR peak in the profile of $\text{Co}_{40}\text{Ce}_1$ and this sample exhibited lower catalytic activity as compared to $\text{Co}_{20}\text{Ce}_1$ and $\text{Co}_{30}\text{Ce}_1$ in the range up to 175°C. At higher temperature the activity of $\text{Co}_{40}\text{Ce}_1$ became similar to that of $\text{Co}_{20}\text{Ce}_1$ but lower as compared to the best performing $\text{Co}_{30}\text{Ce}_1$ catalyst. The longer time of mechanical treatment causes the most noticeable shift of both reduction steps to higher temperatures for $\text{Co}_{20}\text{Ce}_5$ catalyst. In accordance, it exhibited lower activity than that of $\text{Co}_{20}\text{Ce}_1$ sample up to 220°C. However, no correlation between CBO activity and reducibility in this range was established if $\text{Co}_{20}\text{Ce}_5$ is compared with $\text{Co}_{40}\text{Ce}_1$ having worse performance. This observation is especially well expressed in comparison with the lowest active Co_3O_4 (at all temperatures studied). Both $\text{Co}_{40}\text{Ce}_1$ and Co_3O_4 samples exhibited better reducibility than $\text{Co}_{20}\text{Ce}_5$ one.

In general, no clear correlation between catalyst reducibility and catalytic activity in CBO was observed. The TPR profiles of Co – Ce mixed oxides did not differ significantly than those of mono Co_3O_4 but the later exhibited very substantially lower catalytic activity. The possible explanation could be related to prevailing surface catalyst modification caused by the applied method for mixed oxides synthesis. The availability of active oxygen species plays a crucial role for the oxidation activity. However, the

differences in oxygen mobility of the samples prepared by mechanical mixing concern only the near-surface regions. Further surface-oriented catalyst characterization could explain the positive role of ceria and in particular the optimal 70 wt.% Co_3O_4 – 30 wt.% CeO_2 composition. X-ray photoelectron spectroscopy (XPS) and UV resonance Raman spectroscopy measurements are in progress.

CONCLUSION

Co_3O_4 – CeO_2 mixed oxides were synthesized using mechanochemical mixing of cerium hydroxide and cobalt hydroxycarbonate in an electric mortar during 1 and 5 minutes. The CeO_2 content was 20, 30 and 40 wt.%. These catalytic materials were tested in complete benzene oxidation as a model reaction for VOCs abatement. Significantly higher activity of all mixed oxides in comparison with pure Co_3O_4 was observed - mixed oxides attained 100% benzene conversion in the range 200-250°C, relatively very low temperatures in respect to noble metal-free catalysts. These results clearly confirmed the promotional role of ceria. The composition 70 wt.% Co_3O_4 – 30 wt.% CeO_2 was established as optimal one. The catalyst prepared by 5 minutes mechanical mixing exhibited slightly lower activity as compared to the best performing in all temperature range sample synthesized by 1 minute precursors' grinding. Both catalysts with this best composition reached 100% benzene conversion at 200°C and maintained stable activity at this temperature over a period of 24 h without any harmful by-products of incomplete oxidation. The much worst catalytic behaviour of sample with such optimal composition but prepared by manual mixing evidenced the important role of simple mechanical treatment. To make possible formation of highly active mixed oxide catalysts with strained Co_3O_4 and CeO_2 nanocrystals in close interaction. Future research efforts will be directed to optimize the Co_3O_4 – CeO_2 mixed oxides performance by addition of small noble metal amount aiming supplemental lowering of the temperature for complete VOCs oxidation, accordingly decreasing of the operating costs for VOCs abatement.

ACKNOWLEDGEMENTS

Authors affiliated at Institute of Catalysis-BAS gratefully acknowledge the financial support by Bulgarian National Science Fund (grant number KII-06-KOCT/4/2018). This article is based upon work from COST Action INDAIRPOLLNET CA17136, supported by COST (European Cooperation in Science and Technology).

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