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Abstract

A robust and solvent-free mechanochemical approach for the synthesis of cobalt-nitrogencarbon nanocomposite by simple mixing of cobalt(II) salts, nitrogen-containing ligands and carbon black, followed by thermal treatment is suggested. The catalysts obtained were tested in the oxidative esterification of benzyl alcohol, demonstrating highly competitive performance.

Keywords: Cobalt-nitrogen-carbon catalyst; mechano bemical synthesis; heterogeneous catalysis; oxidative esterification.

Solution

1. Introduction

Carbon materials doped with transition metals (Me = Fe, Co, Ni, Cu, etc) and nitrogen, usually denoted as Me@NC, represent extraordinarily active non-precious metal catalysts which are used in a variety of newly developed green, economic and sustainable catalytic processes. The latter involve hydrogenation of nitroarenes [1-3], reductive amination of carbonyl compounds [4,5], selective oxidation and oxidative esterification of alcohols [6-12], oxidation of amines [13,14], epoxidation of alkenes [15], oxidation of ethylbenzene to acetophenone [16], hydrogen production via electrolysis [17], electrochemical conversion of molecular oxygen [18-22], selective dehydrogenation of formic acid (for hydrogen fuel cells) [23] and also other important applications [24,25].

In particular, cobalt-containing composites, Co@NC have shown the best catalytic performance in the oxidative esterification ci benzyl alcohol with methanol under quite mild conditions, ca. 1 atm O₂ and 20-60 °C [5->,26], which in fact can be used for testing the relative catalytic activity of Co@NC materials octained by different methods.

The most active Co@NC carlysts are commonly produced by the incipient wetness impregnation of carbon black (or carbon nanotubes) with Co(II) complex with 1,10-phenanthroline precursor compound, followed by pyrolysis of the resulting material at 800 °C under inert gas concition [2,6,23]. Another usual technique is the carbonization of cobalt–nitrogen containing meral-organic frameworks (MOFs), such as ZIF-67 [8,9,19-21] and others [7,24] at temperatures in the 600 - 900 °C range, which ensures the formation of Co-N doped graphitic structures. Besides, several other more or less sophisticated approaches toward Co@NC formation have been elaborated [7,16,27-29].

In general, it is considered that the active sites of the Co@NC catalysts could be: a) nanoparticles of cobalt oxide (e.g. Co_3O_4) incorporated into a graphite-like framework with nitrogen-containing heterocyclic fragments [6]; b) nanoparticles with a core of metallic cobalt surrounded by an oxide layer which is embedded in a graphene layer matrix [4]; c) atomic-size

or subnanosize cobalt particles forming chelate complexes with pyridine-like vacancies in Ndoped graphene [2,3].

Currently, there is a dominant perception that highly dispersed single-atom Co centers coordinated to nitrogen (CoN_x sites) or cobalt particles surrounded by a protective graphitic layer play a key role in the catalytic activity of Co@NC materials [16,17,23,25,27,28]. Accordingly, the concurrent formation of Co nanoparticles as part of the catalyst is not really necessary for high catalytic activity [23,27]. It is, therefore, not surprising that Co@NC composites obtained with different approaches can show surprisingly similar retalytic behavior, even though the relative content of cobalt nanoparticles (of the same size d stribution) varies widely, ca. from 3 to 30 wt% [6,9]. Indeed, this is more likely to happen when highly dispersed Co or CoN_x centers supported on carbon consist the real active site. Fu thermore, in recent years, a great deal of research effort has been devoted to the accelopment of environmentally benign and cost-effective procedures of fabricating analytic materials. Among them, the elaboration of mechanochemical methods for the preparation of catalysts has experienced a significant evolution [30-32]. Mechanochemistr, has developed as quite promising and simple methodology able to compete with traditional synthetic protocols for MOFs, nanomaterials and catalysts syntheses, which generally avoive multi-step processes.

In this study, ve report a rather technologically convenient, solvent-free and green synthesize Co@NC physical (mechanochemical way to composites by the mixing grinding) of solid starting components, such as cobalt(II) salts, nitrogen-containing ligands and carbon support, followed by thermal treatment. Despite this fairly simple the obtained materials had displayed a remarkable catalytic activity, wellpreparation, compared with that of the state-of-the-art Co@NC catalysts [6,9] in the oxidative esterification of benzyl alcohol, which is used here as a probe reaction.

2. Experimental

2.1. Catalysts preparation

(*i*) Co@NC-Phen. A solution of Co(OAc)₂.4H₂O (25 mg, 0.1 mmol) and 1,10phenanthroline monohydrate (46 mg, 0.2 mmol) in 10 mL of ethanol was stirred for 30 min at room temperature. Then, 138 mg of VulcanXC72R carbon powder (provided by Cabot Ltd) was added to form a suspension, which was heated under reflux with agitation for 4 h. After cooling the mixture to room temperature, the solvent was removed in vacuum, and the solid obtained was further dried at 6¹ °C/5 Torr for 12 h, ground to powder, and then annealed at 800 ± 10 °C (heating rate 5 °C min⁻¹) for 2 h under flowing Ar gas at 10 cm³ min⁻¹ (*cf.* ref. [6]).

(*ii*) Co@NC-ZIF. ZIF-67 was obtained in the form of a blue-violet finely crystalline powder via the reaction of 2-methylimid are (97%, Alfa Aesar) with cobalt(II) nitrate hexahydrate (extra pure, SLR, Fisher Themical) by the procedure described earlier [9,26]. A Co@NC-ZIF sample in the torm of a homogeneous black powder possessing paramagnetic properties was produced by carbonization of ZIF-67 at 850 ± 10 °C (heating rate 5 °C min⁻¹) in flow of argon gas in the course of 2 h.

(*iii*) Co@NC-Gr1-6,8,5 (typical procedure). A mixture of cobalt(II) salt (1 mmol scale; see Table 1 for eagent loadings) and VulcanXC72R carbon powder was thoroughly hand-ground with a restle in an open mortar at room temperature for 10 min. Then, the corresponding nitrogen ligand was added to the mass obtained, and the grinding was continued for additional 10 min until the mixture became moist and turned eventually into a homogeneous paste. The reaction mixture was dried under air flow in the hood within a few hours. The resultant material was placed in a ceramic crucible and heat treated under conditions indicated in Table 1 to offer the final material.

(*iv*) Co@NC-Gr7. A mixture of $Co(NO_3)_2.6H_2O$ (291 mg, 1 mmol) and 2methylimidazole (164 mg, 2 mmol) was hand-ground with a pestle in an open mortar at

room temperature for 20 min to afford a bright purple wet residue which was left to dry under a fume hood overnight. The obtained material was mixed with VulcanXC72R (455 mg), and the process of grinding was continued for another 20 min using a FRITSCH Mortar Grinder Pulverisette 2 (Germany) equipped with agate bowl and pestle (contact pressure ~23.8 daN), followed by heat treatment.

2.2 Catalysts characterization techniques

(*i*) Brunauer–Emmett–Teller (BET) specific surfac area. The porous structure parameters were determined from N₂ adsorption is the ns at 77 K on ASAP-2400 (Micromeritics, USA) analyzer after degassing the camples at 150 °C to a residual pressure of 30 mTorr (4 Pa). The total accessible surface area by the BET method, and the total volume of pores with effective sizes u_1 to 100–200 nm (V_{total}) were estimated from the amount of adsorption at the relative vitrogen pressure of ~ 0.99. A micropore volume and surface areas of mesopores and vicropores were calculated by the standard software provided by the instrument.

(ii) Powder X-ray difference in A powder X-ray difference (XRD) analysis was performed on a Siemen. D500 instrument with CuKa radiation and θ -2 θ focusing geometry. The instrumen was equipped with a graphite monochromator in the reflected beam, which made *j* possible to diminish the contribution from the cobalt fluorescence the copper radiation. A scintillation detector was used for signal detection. under Measurements were made in the scanning mode at 20 angles in the $10-70^{\circ}$ range at a step of 0.05° and accumulation duration at a point of 3 s. The analysis was made with a Bruker EVA software package contained in the hardware-software complex. The X-ray diffraction patterns were interpreted by the aid of the ICDD (International Center for Diffraction Data) PDF-2 database.

(*iii*) High-resolution transmission electron microscopy (HRTEM). Micrographs were obtained with JEM-2010 (JEOL, Japan) instrument with lattice resolution 0.14 nm and accelerating voltage 200 kV. The samples were prepared by ultrasonic dispersing in ethanol and consequent deposition of the suspension upon a "holey" carbon film supported on a copper grid. Local elemental analysis was performed with the EDX method on an Energy-dispersive X-ray spectrometer «QUANTAX 200-TEM» (Bruker, Germany) equipped with XFLASH detector with energy resolution ~ 130 eV.

(*iv*) X-ray fluorescence (XRF). The content of \bigcirc element in the samples was measured by XRF using a sequential spectrometer Al'L 'erform'X with a Rh anode X-ray tube.

(v) X-ray photoelectron spectroscopy ("PS. X-ray photoelectron spectra were recorded on a SPECS (Germany) phote electron spectrometer using a hemispherical PHOIBOS-150-MCD-9 analyzer (Al κ i. diation, hv = 1486.6 eV, 150 W). The binding energy (BE) scale was pre-calibrated using the positions of the peaks of $Au4f_{7/2}$ (BE = 84.0 eV) and Cu2p_{3/2} (BE = 9.2.67 eV) core levels. The binding energy value of peaks consider the sample charging by referencing to the C1s (284.5 eV, was corrected to internal standard). The same in the form of powder was loaded onto a conducting double-sided copper scot h. The survey spectrum and the narrow spectra (C 1s, N 1s, O 1s and Co 2p) were registered at the analyzer pass energy of 20 eV. Atomic ratios of the elements were calculated from the integral photoelectron peak intensities, which were corrected by corresponding sensitivity factors based on Scofield photoionization crosssections. Analysis of the data was carried out by the software of XPS Peak 4.1 provided by the instrument.

2.3 Catalytic performance tests

In accordance with the typical procedure, the oxidative esterification of benzyl alcohol was carried out in an oxygen-filled 10-mL Schlenk flask connected to an oxygen-filled balloon (1 atm). The flask was charged with benzyl alcohol (250 mg, 2.3 mmol), methanol (4 mL), K₂CO₃ (37 mg, 0.27 mmol) and catalyst (40 mg). The reaction mixture was magnetically stirred (800 rpm) at 60 °C (temperature of thermostatic oil-bath). At appropriate time intervals, stirring was stopped and, after catalyst settling, samples from analysed by GC (flame-ionization. detector) on an LKhM-8MD the reactor were chromatograph equipped with 0.03×1.2 m metallic column with HayeSep Q sorbent (Chrompack). With the purpose of additional c_{nu} the quantification of the analytes was further verified using 1 H NMR measurem nts [33].

3. Results and discussion

The reference catalyst samples denoted as Co@NC-Phen and Co@NC-ZIF, were prepared as described in the literature, by the main prime wetness impregnation of VulcanXC72R carbon with the Co(II) complex with 1,10 phenanthroline [6], and through a separate ZIF-67 synthesis [9,26], respectively. The samples arouted as Co@NC-Gr were obtained from the use of dry grinding method. Table 1 compares the catalytic performances of these samples in the oxidative esterification of benzyl alcohol. In contrast to previous studies [6,9], the catalyst loading (relative to benzyl alcohol) was lowered by half, to 14 wt%, even though the reaction time was reduced from 24 to 12 h. This has enabled a more accurate comparison of the catalytic activity under applied reaction conditions (atmospheric pressure of oxygen and 60 $^{\circ}$ C). Also, for a number of catalysts, benzyl alcohol conversion as a function of reaction time is shown in Fig. S1 (Electronic Supplementary Information, ESI).

It is noteworthy that the mechanochemically derived catalysts have demonstrated considerable activity. Moreover, Co@NC-Gr3 and Co@NC-Gr7 have shown quite comparative

or even much better performances relative to Co@NC-Phen and Co@NC-ZIF samples (Table 1, entries 5 and 10). Only Co@NC-Gr4 sample turned out to be inactive, which, however, might be attributed to its low porosity (Table S1, ESI).

To assess the reusability of the catalysts, several recycles were conducted with the most active Co@NC-Gr7 sample to compare it with the recycling properties of Co@NC-Phen [6] and Co@NC-ZIF [9]. In fact, Co@NC-Gr7 is successfully recycled without significant loss of activity, remaining as active as a fresh sample of Co@NC-Phen, even after two runs (Fig. S2, ESI). These results validate the achievement of the sinder catalytic behavior for Co@NC samples obtained by the simpler mechanochemical approach. Considering the lack of optimized preparation conditions at present, we think that many possibilities exist to enhance further the performance of Co@NC-Gr. For example, the us of the automatic grinding in the preparation of Co@NC-Gr7 significantly improved the catalytic activity (Table 1, entry 10). Likewise, the source of Co(II), as well as the nature c^c narogen ligand, seem to be not so essential (*cf.* ref. 6), which would also facilitate elaboration of the Co@NC-Gr catalysts.

In order to gain insight into the tright of the catalytic behavior of the Co@CN-Gr samples, a series of characterization techniques was applied to qualify the catalysts. As shown in Table 1, neither content of cobalt, ranging from 5 to 47 w%, nor the values of total specific surface area of Co@NC have no able effect on the conversion of benzyl alcohol and selectivity to methyl benzoate (1) (see, how ever, Table S1 for the influence of meso- and micro-porosity). This may suggest that the real active sites for the oxidative esterification are highly dispersed Co or CoN_x centers supported on carbon, in agreement with the earlier viewpoints [2,3,17,23,25,27,29].

Powder XRD was used to determine a possible difference in the composition of the large particles in selected samples. As shown in Fig. 1, all the catalysts, including inactive Co@NC-Gr4 sample, contain graphitic carbon (a broad peak at 25°). It should be noted that according to XRD, VulcanXC72R carbon itself has an intermediate (turbostratic) structure between amorphous and graphitic [34,35]. Next, the catalysts contain metallic cobalt (peaks at ~ 44, 52,

and 76° 2theta (not shown)) and small amounts of CoO (peak at ~ 43° 2theta). The latter peak may also be attributed to the in-plane (100) and (101) reflections of carbon [35]. The clearly detectable particles of Co_3O_4 (JCPDS 42-1467) are present only in Co@NC-ZIF, and their role as active catalytic sites is therefore doubtful.

The morphology and metal dispersion in the most active Co@NC-Gr7 catalyst and in the "parent" Co@NC-ZIF sample were investigated using HRTEM (Fig. 2), combined with local elemental analysis performed with EDX (Figs. S3 and S4, ESI). As shown in Fig. 2, cobalt nanoparticles of ~ 10–30 nm are uniformly distributed in a porous graphite-like carbon matrix in both the catalysts. The only notable difference between the sesamples is the higher proportion of Co nanoparticles in the less active Co@NC-ZIF catalyst, in agreement with the relative contents of Co measured by the X-ray fluorescence met of Table 1). Hence, the cobalt nanoparticles observable with TEM are not intrinsically connected with the catalytic activity, thus again supporting the view that it might be that the higher section Co or CoN_x centers play a decisive role in the reaction process.

For a more detailed comparative characterization of the catalysts, XPS investigation of their surface chemical composition was performed. The elements of Co, C, N and O could be found in the full survey spectra (F_{12} , 35, ESI) of Co@NC-Phen, Co@NC-ZIF, Co@NC-Gr3 and Co@NC-Gr7, revealing the relative contents of these elements (Tables S2 and S3, ESI). In the Co 2p region (Fig. 3a), all the samples exhibit similar spectra consisting of two major peaks at 780.6 and ~ 796 eV, which are related to Co $2p_{3/2}$ and Co $2p_{1/2}$, and weaker satellite peaks, which together can be assigned to oxidized forms of cobalt (Co²⁺). Well notable additional peak located at ~ 778 eV is assigned to metallic Co⁰. From the high-resolution C 1s spectrum (Fig. 3b), three peaks at the binding energies of 284.5, 285.8 and 288.1 eV are assigned to graphitic carbon, carbon-nitrogen bonds and C=O or COOH groups, respectively, while a weak peak at 290.2 eV can be assigned to carbonates. Regarding the N 1s spectrum (Fig. 3c), three distinct peaks can be observed with electron binding energies of pyridinic N (398.9 eV),

pyrrolic/graphitic N (400.8 eV), and nitrogen within the NO_x functionalities (402.5, 405.4 eV). It is found, however, that the relative contribution of these different nitrogen forms (Table S4, ESI), and likewise different carbon species (Table S5, ESI), does not correlate with the catalytic activity of the samples. But overall, the XPS characteristics are quite consistent with those of the Co@NC materials obtained previously through different methods [6,9,16,27,28,29].

It is apparent that the high temperature graphitization of a carbon-containing material (regardless if it is a carbon black or an organic compound), occurring in the presence of Co(II) and N-heteroarenes, leads eventually to a uniform form tion of the Co-N-doped graphite composites, which are filled with a greater or lesser mount of Co-nanoparticles (*cf.* refs. 23,27,28). It appears that this process, not so much $le_{\mu} \circ \mu_{e}$ and the initial procedures, aimed at ensuring better deposition/distribution of the Co(II)-N complexes inside a carbon matrix. As can be seen, in its simplest implementation, such is position can be even performed by the physical mixing of solid starting components π_{e}^{+} host obvious negative consequences on the resulting catalytic behavior.

4. Conclusions

We have synthesized , set of Co@NC nanocomposites through a new, atom-efficient, solvent-free, mechanc her ical approach based on simple physical mixing of solid cobalt(II) salts, N-heteroarenes *e* id carbon black, followed by thermal treatment. The catalytic behavior of the obtained materials was illustrated by the example of the low-temperature oxidative esterification of benzyl alcohol. It is demonstrated that the method developed can lead to catalysts with activity well-compared with that of the known analogues, obtained previously through the preliminary preparation of cobalt-nitrogen-containing MOFs or by means of successive wet impregnation of carbon materials with cobalt salts and N-ligands. Therefore, it could be concluded that the graphitization process rather than the preparatory stage is the key for the successful formation of desirable Co@NC materials. Considering that besides Co itself

many other transition metals assist the controllable carbonization/graphitization of organics [28], a similar approach can be followed in the future for the facile preparation of related highperformance Me@NC catalysts to promote their practical use.

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Conflicts of interest

The authors declare no conflicts of interest.

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		$\begin{array}{r} \text{OH} \\ + \text{ CH}_3\text{OH} \\ \hline 1 \text{ atm O}_2, \text{ K}_2\text{CO}_3, 60 ^{\text{O}}\text{C}, 12 \text{ h} \end{array}$			`осн _{з+}	о н 2			
Entry	Catalyst	Cobalt salt/L ^b	Carbon	Pyrolysis	Co	S _{BET}	Conversion ^d	Selectivity ^d	
			support (° C, h, gas)		(w%)	$(m^2 g^{-1})$	(%)	(%)	
			(wt%) ^c					1	2
1	Blank ^e	-	-	-	-	-	<1	-	-
2	Co@NC-Phen ^f	Co1/L1 = 1:2	65	800, 2, Ar	5.1	168	76	97	3
3	$Co@NC-Gr1^{g}$	Co1/L1 = 1:2	65	800, 2, Ar	5.0	93	58	91	9
4	$Co@NC-Gr2^{g}$	Co1/L1 = 1:2	25	800, 2, A	.9	148	57	86	14
5	$Co@NC-Gr3^{g}$	Co1/L1 = 1:2.5	65	800, ² , Ar	4.8	104	72	93	7
6	$Co@NC-Gr4^{g}$	Co1/L1 = 1:5	25	8 10, 2, Ar	6.0	134	1	0	90
7	$Co@NC-Gr5^{g}$	Co2/L1 = 1:2	65	800, 2, Ar	5.6	140	62	89	11
8	$Co@NC-ZIF^{h,i}$	Co2/L2 = 1:40	-	850, 2, Ar	32.8	174	64	88	12
9	$Co@NC-Gr6^{g,i}$	Co2/L2 = 1:2	10	850, 2, Ar	46.5	233	63	87	13
10	$Co@NC-Gr7^{j,k}$	Co2/L2 = 1:2	50	850, 2, Ar	12.5	274	88	96	4
11	$Co@NC-Gr8^{g,i}$	Co2/L2 = 1.5	20	850, 2, Ar	19.1	391	67	83	17
12	$Co@NC-Gr9^{g,i}$	Co1/L 2 1.5	20	850, 2, Ar	19.4	272	55	80	20

Table 1. Catalytic performance of Co@NC catalysts in the oxidative esterification of benzylalcohol with methanol.^a

^{*a*} Reaction conditions: .50 mg of benzyl alcohol, 4 mL of CH₃OH, 37 mg of K₂CO₃, 40 mg of catalyst, 1 atm O₂ (balloon), 60 $^{\circ}$ C, 12 h.

^b Molar ratio. Salts: $Co1 = Co(OAc)_2 \times 4H_2O$; $Co2 = Co(NO_3)_2 \times 6H_2O$. Ligands: L1 = 1,10-phenanthroline $\times 1H_2O$; L2 = 2-methylimidazole.

^c VulcanXC72R, weight content before heat treatment.

^d Determined by GC.

- ^e Without a catalyst and K₂CO₃.
- f The wet impregnated sample (*cf.* ref. 6).
- ^{*g*} The sample is obtained by dry grinding method.
- ^h A MOF-derived sample obtained by wet preparation method (cf. refs. 9, 26).
- ^{*i*} The sample exhibits strong magnetic properties.
- ^{*j*} The sample is obtained by dry grinding using a FRITSCH Mortar Grinder Pulverisette 2.

^k The sample exhibits moderate magnetic properties.

Fig. 1. Powder XRD patterns of (a) Co@NC-Phen and related samples, (b) Co@NC-ZIF and related samples.

Fig. 2. TEM images of Co@NC-ZIF (a), (b) and Co@NC-Gr7 (c), (d).

Fig. 3. XPS of (a) Co 2p, (b) C 1s and (c) N 1s of Co@NC-ZIF, Co@NC-Phen, Co@NC-Gr7 and Co@NC-Gr3 (from bottom to top).

Credit Author Statement

Tatiana V. Astrakova: conducting a research process, performing the experiments. Vladimir I. Sobolev: Supervision. Konstantin Yu. Koltunov: data curation, writing and reviewing.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.









Fig. 2

Solution







Fig. 3



Graphical Abstract:

Co(II) salt 1) Physical mixing Co@NC 2) 850 °C, Ar, 2h Carbon black

Some

- A simple, mechanochemical approach for fabricating Co@NC nanocomposites is suggested.
- The Co@NC materials thus obtained exhibit the state of the art catalytic behavior.
- The oxidative esterification of benzyl alcohol on Co@NC was used as a probe reaction.