Unraveling a Biomass-Derived Multiphase Catalyst for the Dehydrogenative Coupling of Silanes with Alcohols under Aerobic Conditions

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ABSTRACT: Herein, a novel silver and chromium nanostructured N-doped carbonaceous material has been synthesized by a biomass-annealing approach using readily available chitosan as a raw material. The resulting catalyst AgCr@CN-800 has been applied for the dehydrogenative coupling reaction of various silanes with different alcohols to obtain the corresponding silyl ethers under aerobic and mild conditions. Besides excellent activity and selectivity, the as-prepared catalyst exhibits good stability and reusability. Characterization by XRD, XPS, ICP-MS, HRTEM, in combination with careful examination of the structure with Cs-corrected HAADF-STEM revealed that catalyst AgCr@CN-800 comprises Ag and CrN aggregated particles, as well as highly dispersed Ag-N_x and Cr-N_x sites embedded in N-doped graphitic structures. A comparative catalytic study using structure-related catalysts in combination with acid-leaching treatments has shown that the most active species are the Ag particles, and that their activity is boosted by the presence of Cr-derived species. By *in-situ* Raman spectroscopy experiments, it has been found that the dehydrogenative coupling of silanes with alcohols in the presence of catalyst AgCr@CN-800 takes place through an oxygen-assisted mechanism.

KEYWORDS: Chitosan, Silanes, Alcohols, Dehydrogenative coupling, Silyl ethers, Oxygen activation, *in-situ* Raman spectroscopy

INTRODUCTION

Silyl ethers are valuable raw materials for the silicon industry as well as important commodity reagents and protecting groups for alcohols in organic synthesis on laboratory scale.[1-5] In addition, these compounds have also attracted the attention of scientists from the perspective of material science because of their use as reagents for surface coating and modification,[6-13] as well as for the preparation of hybrid organic–inorganic materials.[14-16]

Traditionally, silyl ethers have been synthetized by reaction of halosilanes with alcohols in the presence of a base, thus resulting in the formation of stoichiometric amounts of undesired halide salts.[17-20] In this context, the catalytic dehydrogenative coupling of hydrosilanes with alcohols represents a more atom-economical, and hence, a more environmental-friendly synthetic route.[21-22] Advantageously, since hydrogen is the only generated by-product, this reaction is also relevant for H_2-generation. In fact, the system based on alcohol/silane pairs has been considered as a potential liquid organic hydrogen carrier (LOHCs) that releases H_2 at low temperatures.[23-24] However, although this coupling reaction is thermodynamically favored, the presence of a catalyst is required to improve the reaction kinetics under mild conditions.

To date, a wide variety of transition-metal-based complexes,[25-36] alkaline earth metals,[37] and alkali metal bases[38-39] have been reported as catalysts for the dehydrogenative coupling of hydrosilanes with alcohols. Moreover, metal-free boron-based Lewis acids[40-43] and N-heterocyclic carbenes[44] have also efficiently catalyzed this reaction. Nevertheless, despite good activity and selectivity toward the production of silyl ethers achieved by these catalysts, the use of reusable heterogeneous systems is more advantageous from an environmental point of view.

In recent times, with the aim of dealing with global challenges related to sustainability, the scientific community has paid much attention toward the use of metal nanoparticles (NPs) modified by N-doped carbon as catalysts for innovative organic synthesis because of their good activity and controllable selectivity.[45] Different strategies have been developed for the preparation of this kind of nanostructured materials.[46] Among them, the *in-situ* formation of both metal NPs and the N-doped graphitic material is a well-established methodology. Here, non-volatile molecularly defined metal-amine ligated complexes impregnated on different supports,[47-81] metal-organic frameworks (MOFs),[82-92] or coordination polymers[93-95] are typically used as self-sacrificial templates to obtain metal NPs embedded in a carbonaceous matrix after pyrolysis under an inert gas.

Alternatively, in order to avoid the use of sophisticated organic ligands and synthetically demanding routes of sacrificial template materials, pyrolysis of renewable and available biomass in combination with metal salts represents a more practical catalyst preparation approach.[96-105] In this respect, the natural biopolymer chitosan, which is obtained from industrial fishery bio-waste by deacetylation of shrimp or crab shell-derived chitin, is especially useful.[106] Chitosan has been proposed as an attractive precursor for obtaining N-doped carbon materials.[107-122] In addition, its particular structure containing amino- and hydroxyl-coordinating groups has made possible its application as a chelating agent for transition-metals.[123-128]

Taking advantage of these properties of chitosan, Garcia and co-workers synthesized Cu NPs supported on N-doped graphene by firstly preparing a homogeneous solution of a Cu salt and chitosan, followed by pyrolysis and sonication.[129] Later, the same group developed a series of facet-oriented Cu_2O,[130-132] Au,[133] Pt,[134] and Ag[135] NPs on (N-doped) graphene films prepared by pyrolysis of nanometer-thick films of chitosan embedding the corresponding transition-metal salt and deposited on a quartz substrate. Importantly, a variation or even a completely removal of the N content was reported depending on the pyrolysis temperature and the metal nature. Meanwhile, Beller and co-workers prepared Co-based N-doped carbon heterogeneous catalysts by using an adapted synthetic methodology, in which chitosan acts as a solid adsorbent for transition metals instead of being used in solution before pyrolysis.[136-139] In addition to these seminal works, other catalytic materials synthesized following a similar preparation approach have also been reported.[140-149]

In general, metal-based materials prepared by pyrolysis tend to be heterogeneous in composition and particle size. In fact, the resulting materials are typically constituted by metal species of different nature, such as metallic and/or metal oxide NPs. Moreover, the formation of isolated single-atom sites (ISAS) is also feasible when using supports or self-sacrificial templates that have a strong coordination ability with metal atoms.[150-158] Concretely, this is the case of chitosan, in which its unique structure containing amino- and hydroxyl-coordinating groups can promote the formation of ISAS embedded in the N-doped carbon matrix besides other multiple metal species formed by agglomeration during uncontrolled pyrolysis.[159-160] This heterogeneity in chitosan-derived N-doped carbon-based materials makes challenging the identification of active species when they are used in catalysis, however, it is an essential task for future development of catalysts with enhanced efficiency.

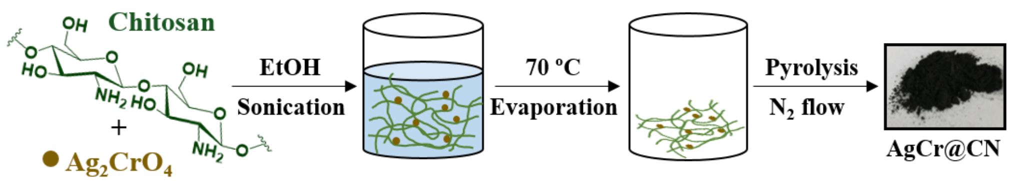
With regard to the use of heterogeneous catalysts for the dehydrogenative coupling reaction of hydrosilanes with alcohols, among various available heterogeneous systems,[36, 161-179] metal catalysts modified by (doped) graphitic carbon have shown promising results. Cu NPs supported on doped (-boron and/or -nitrogen) graphene,[129] Cu_2O[130] or Ag[135] facet-oriented nanoplatelets on graphene films, as well as, atomically dispersed Co species anchored on ultrathin two-dimensional N-doped carbon[180] have been proved to be active catalysts for the title reaction. In addition, the use of a metal-free hierarchically porous N and S co-doped carbon is also noteworthy.[181] Despite these findings, the relatively high temperature, long reaction times, the need to perform the reaction under inert atmosphere, and/or the difficulty of preparing catalysts with higher metal loading offer room for improvement.

In this contribution, we report the preparation of a N-doped carbonaceous heterobimetallic nanostructured material by pyrolysis of silver chromate (Ag_2CrO_4) highly dispersed on the readily available bio-waste polymer chitosan. We show that the resulting material, which comprises a heterogeneous composition of metal species, efficiently catalyzes the dehydrogenative coupling of hydrosilanes with alcohols under aerobic and mild conditions (even at 0 ºC) with excellent selectivity toward the formation of silyl ethers and molecular hydrogen. On the bases of a comparative catalytic study, we demonstrate that catalytic activity mainly arises from the Ag particles and that their activity is boosted by the presence of Cr-derived species. Furthermore, *in-situ* Raman spectroscopic studies have allowed the explanation of the enhanced catalytic activity, which is directly related with the oxygen activation ability of the catalyst.

RESULTS AND DISCUSSION

Preparation and catalytic performance of catalysts AgCr@CN

We started our study by preparing a series of silver and chromium bimetallic catalysts according to the procedure depicted in Scheme 1. A mixture of chitosan and Ag_2CrO_4 was homogeneously dispersed in ethanol by sonication. After solvent evaporation under atmospheric pressure and continuous stirring conditions, the resultant powder was pyrolyzed at different temperatures in the range from 400 to 900 °C under a nitrogen flow to yield the heterobimetallic materials AgCr@CN-X, where X stands for the pyrolysis temperature (see the Experimental Section for more preparation details). The metal content in the as-prepared materials was determined by inductively coupled plasma mass spectrometry (ICP-MS) analysis. The obtained results revealed an increase of the metal amount (Ag + Cr) from 13.7 to 18.0 wt% with the pyrolysis temperature because of increasing weight loss in chitosan decomposition (Table S1). Interestingly, the Ag/Cr ratio is maintained constant independently of the pyrolysis temperature.



Scheme 1. Synthesis of heterobimetallic materials AgCr@CN-X (X = 400-900 °C) used as catalysts.

With these materials in hand, we evaluated their catalytic performance for the dehydrogenative coupling of hydrosilanes with alcohols using as a benchmark system the reaction between dimethyl(phenyl)silane (**1a**) and methanol (**2a**) at 60 °C under aerobic conditions. As shown in Figure 1a, all prepared heterobimetallic materials displayed catalytic activity with excellent selectivity toward the formation of methoxydimethyl(phenyl)silane (**3aa**) (see also Figure S1). A control experiment revealed that no reaction took place in the presence of a metal-free catalyst (M-free@CN-800) prepared by pyrolysis of chitosan at 800 °C in the absence of Ag_2CrO_4, thus indicating that the catalytically active species are metal-based. The most active catalyst, determined by comparison of the initial reaction rates normalized to the mass of metal weights (Figure 1b), resulted to be the heterobimetallic material pyrolyzed at 800 °C (AgCr@CN-800). Other heterobimetallic catalysts containing silver and a second transition metal different to chromium (W or V), which were also prepared following the same preparation methodology shown in Scheme 1, displayed lower activity for the investigated reaction (Figure S2).

In the presence of the most active catalyst AgCr@CN-800 (15 mg; 2.75 mol% of metal with respect to **1a**), full conversion of **1a** was achieved in 20 min, affording **3aa** in 97 % yield with only residual amounts (< 3 %) and traces (< 1 %) of the corresponding silanol (**4a**) and disiloxane (**5a**) compounds as by-products, respectively (Figure 1c). Moreover, H_2 release was also detected during the reaction between **1a** and **2a.** This dehydrogenative coupling reaction also proceeds well when using lower amounts of catalyst AgCr@CN-800 (5 mg; 0.91 mol% of metal with respect to **1a**), corresponding to a turnover number (TON) of 111. Interestingly, the reaction could also be conducted at lower temperature, 30 °C and even 0 °C, achieving full conversion of **1a** with excellent selectivity to **3aa** in 1 and 2 h, respectively (Figure S3), together with the formation of equimolecular amounts of H_2 (see the Supporting Information). It is worth mentioning that compared to previously reported Ag-based heterogeneous systems, the catalyst AgCr@CN-800 catalyzes this reaction at significant lower temperatures (0 ºC).[135, 172, 182-185]

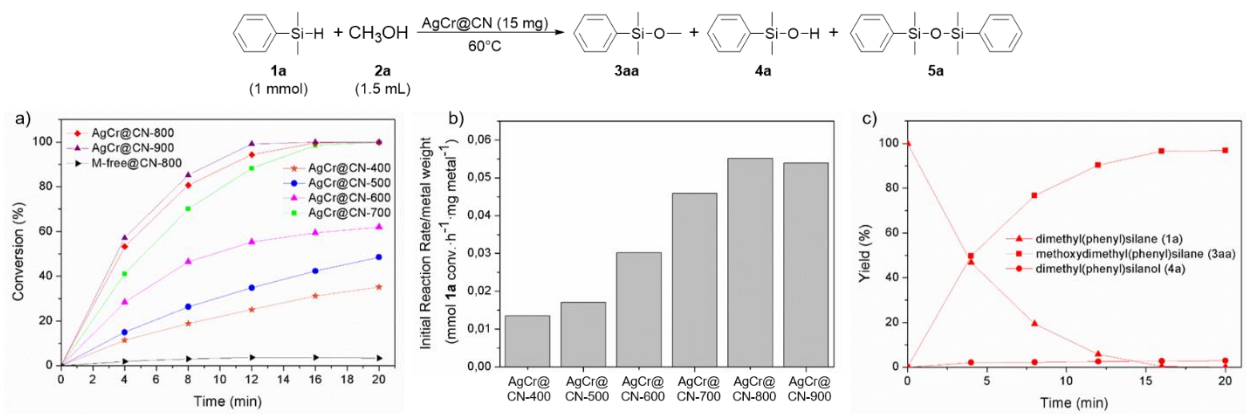


Figure 1. (a) Catalytic performances of catalysts AgCr@CN-X (X = 400-900) and M-free@CN-800 for the dehydrogenative coupling reaction of **1a** with methanol. (b) Comparison of the metal mass activity. (c) Concentration/time diagram for catalyst AgCr@CN-800.

Interestingly, the reaction rate was significantly increased when pure O_2 was bubbled into the reaction solution providing a 98 % yield of **3aa** within 20 min at 30 ºC (TOF = 327 h^{-1}). In contrast, almost no reaction took place when the reaction was carried out under Ar atmosphere, thus revealing that the presence of the catalyst AgCr@CN-800 in combination with O_2 is essential to achieve the dehydrogenative coupling reaction of **1a** with methanol (Figure S3).

Characterization of catalyst AgCr@CN-800

The best heterobimetallic material AgCr@CN-800 in terms of catalytic activity was characterized in detail. The XRD pattern (Figure 2) is dominated by the presence of diffraction peaks associated with the face-centered cubic (*fcc*) structure of Ag^0 in agreement with the JCPDS database (PDF Card 1-1164). Since these peaks are very sharp, it is expected that this phase is present in the form of large particles. Moreover, a broad shoulder peak in the range of 20–30° (2θ) associated with reflections of the (002) of graphitic carbon could also be inferred.[186] However, no additional peaks corresponding to chromium species were detected.

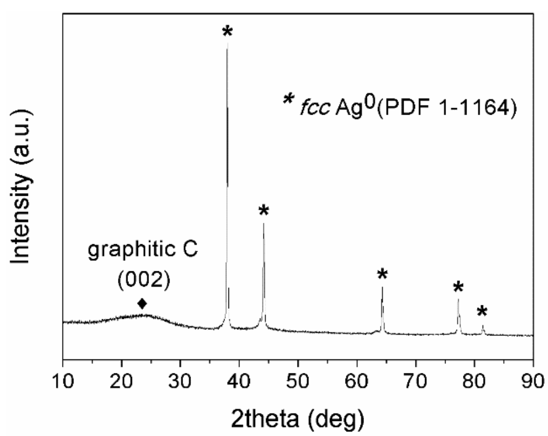


Figure 2. XRD pattern for catalyst AgCr@CN-800.

Transmission electron microscopy (TEM) images show aggregates of metal particles with non-homogeneous sizes of tens to hundreds of nanometers. This broad site distribution is likely generated by partial metal agglomeration during the pyrolysis treatment because of the high metal content (Figures 3a and Figure S4). The high-resolution TEM (HRTEM) images show two types of metal particles of different nature, both coated by few layers of a (defect/N-doped) graphitic carbon shell (Figure 3b-c). The well-resolved lattice spacing of 0.237 nm consistent with the (111) plane of the cubic Ag phase was clearly identified in some of these particles. Besides, an additional phase of chromium nitride (CrN) that displays the characteristic lattice spacing of 0.239 nm associated with its (111) plane was also detected in the HRTEM images. Moreover, the nature of these particles was undoubtedly confirmed by a fast Fourier transform (FFT) analysis, which revealed other characteristic lattice fringe spaces of 0.211 and 0.128 nm associated with the (200) and (311) planes of CrN, respectively (Figure 3c, inset).

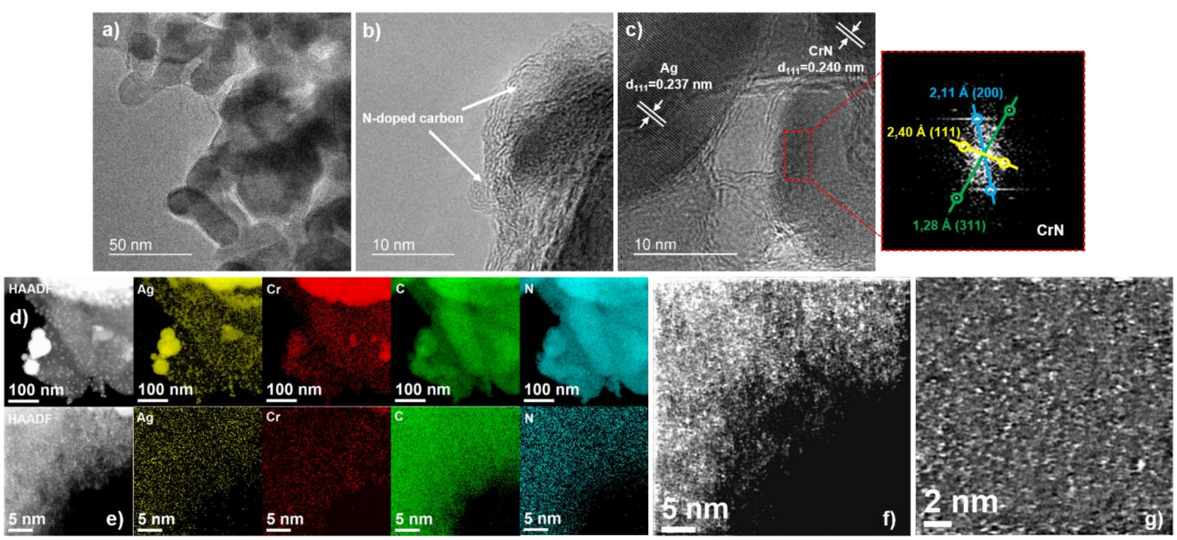


Figure 3. Electron microscopy characterization of catalyst AgCr@CN-800. TEM (a) and HRTEM (b-c) micrographs. The inset shows the FFT from the square region in image c). (d-e) HAADF-

STEM images and EDS elemental mapping of Ag, Cr, C, and N. (f-g) High-magnification images for the Cs-corrected HAADF-STEM analysis.

Spherical aberration (Cs)-corrected scanning transmission electron microscopy (STEM) using a high-angle annular dark-field (HAADF) detector coupled with spectroscopic analysis by means of energy dispersive X-ray spectroscopy (EDS) was employed to investigate the structure of catalyst AgCr@CN-800 in a further extent. These studies revealed that Ag, Cr, N, and C elements overlap in spatial locations on each other around the entire sample, including particles (Figure 3d and Figure S5) as well as sites where no particles were visualized (Figure 3e and Figure S5), thus suggesting that metal species may be atomically distributed along the N-doped graphitic material. Interestingly, a closer look at these regions revealed a high density of monodispersed bright dots, likely associated with highly dispersed metal atoms of both Ag and Cr, according to the EDS elemental mapping analysis results (Figure 3f-g and Figure S6-S7).

For further characterization of the catalyst surface, X-ray photoelectron spectroscopy (XPS) measurements were performed. The high-resolution Ag 3d core level spectrum displays two peaks at ~ 368 and 374 eV associated with the characteristic spin–orbit splitting of Ag $3d_{5/2}$ and Ag $3d_{3/2}$ orbitals, respectively, each of them being possible to be fitted into two separated components denoting the presence of two distinct chemical Ag species (Figure 4a). More specifically, the components at 368.1 and 374.1 eV correspond to Ag^+ species, whereas the ones at 369.3 and 375.3 eV are related to metallic Ag.[187-191] The higher contribution of the component associated with Ag^+ species suggests that, in spite of the shielding effect of thick N-doped graphitic carbon layers encapsulating the Ag particles, these could be constituted by a metallic core and a partially oxidized surface. In addition, it should be considered that the XPS-detectable Ag^+ species could also arise from highly dispersed Ag^+ species inserted in the graphitic sheets coordinated to N atoms, that is, as AgN_x sites. Comparison of the obtained electron binding energy of Ag $3d_{5/2}$ (368.1 eV) in catalyst AgCr@CN-800 with that one for previously reported molecular-defined complexes that contain Ag-N bonds within a related structure (368.4 eV),[192] revealed a prominent increase of the electron density of the Ag^+ species in the graphitized structure, in good agreement with previous studies.[150]

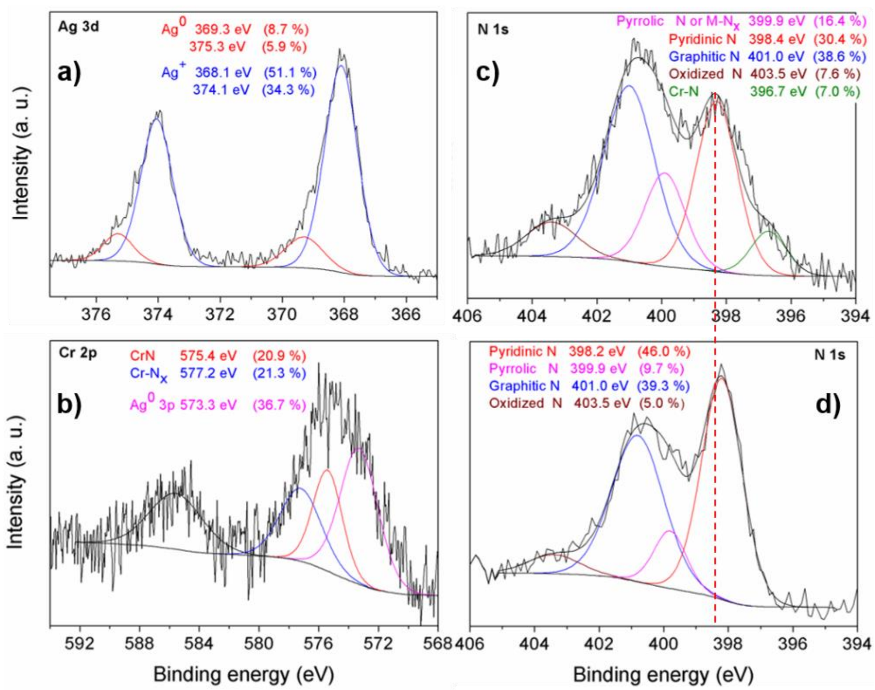


Figure 4. XPS spectra of Ag 3d (a), Cr 2p (b) and N 1s (c) core levels of catalyst AgCr@CN-800. (d) N 1s XPS spectrum of catalyst M-free@CN-800.

Determination of Cr oxidation states in heterobimetallic materials containing Ag is challenging because in the Cr 2p region of the XPS spectrum some Cr species have similar electron binding energy values than that of the Ag 3p peak (~ 573.6 eV) associated with metallic Ag. The Cr 2p XPS spectrum (Figure 4b) for catalyst AgCr@CN-800 shows a broad peak, which could be fitted into three different components after deconvolution. The major peak at 573.3 eV can be ascribed to metallic Ag, whereas, according to the literature, the other two peaks at 575.4 and 577.2 eV denote the presence of CrN[193] and atomically dispersed Cr-N_x sites embedded in the graphitic sheets,[194] respectively.

The signal deconvolution in the high-resolution N 1s energy-level spectrum (Figure 4c) suggests that catalyst AgCr@CN-800 contains different nitrogen species, at least including pyridinic N-oxide (403.5 eV), graphitic-N (401.0 eV), pyrrolic-N (399.9 eV) and pyridinic-N (398.4 eV). Furthermore, an additional component (at 396.7 eV) attributed to CrN could also be inferred, which is absent in the XPS spectrum of the metal-free catalyst M-free@CN-800 (Figure 4d). Importantly, further comparison of both spectra (Figure 4c and 4d) revealed that while the relative content of graphitic-N and pyridinic N-oxide species is almost the same, an increase of the ratio of pyrrolic-N to pyridinic-N species is observed in catalyst AgCr@CN-800. This increase could be associated with the presence of highly dispersed species attached to pyridinic-N that results in the formation of M-N_x (M = Ag, Cr) sites, whose binding energies fall in the same range as the pyrrolic-N function binding energy. Moreover, an energy shift of over 0.2 eV was detected in the pyridinic-N component of catalyst AgCr@CN-800, thus verifying the existence of metal-N interactions.[150, 152, 195]

Acid-leaching and characterization of catalyst AgCr@CN-800-Acid

Catalyst AgCr@CN-800 was leached with acid (see details in the Experimental Section) and further characterized. The Ag and Cr content, determined by ICP-MS analysis, in the leached catalyst (denoted as AgCr@CN-800-Acid) were reduced from 12.74 to 0.12 wt% and from 3.74 to 2.29 wt%, respectively. In consequence, no diffraction peaks associated with metallic Ag species were detected in the XRD pattern of the acid-leached catalyst AgCr@CN-800-Acid (Figure 5a). However, besides the broad diffraction peaks of graphitic carbon (at 2θ values of 25.3

and 43.6°), other peaks located at 37.5, 43.6, 63.4 and 76.1°, that could be indexed to the (111), (200), (220) and (311) planes, respectively, of the cubic phase of CrN (PDF Card 65-2899), became known in catalyst AgCr@CN-800-acid. This confirms that the acid-leaching treatment fully removed the Ag particles, while keeping almost intact the CrN phase, which is known to display an excellent chemical stability to acids.[196-197]

The diffraction peaks associated with CrN are also present in the XRD pattern measured after the acid treatment of a catalyst (AgCr@CN-800-Ar) pyrolyzed under Ar atmosphere instead of using N_2 (see Figure S8). This result, besides the fact that only a slight decrease of the N content (determined by combustion elemental analysis) was detected in catalyst AgCr@CN-800-Ar (7.6 wt %) when comparing with catalyst AgCr@CN-800 (7.8 wt %), proves that the CrN phase is preferentially formed during the pyrolysis treatment by extracting N atoms from chitosan rather than by activation of N_2 gas molecules. Moreover, both catalysts AgCr@CN-800 and AgCr@CN-800-Ar displayed similar catalytic performance for the investigated dehydrogenative coupling reaction between dimethylphenylsilane (**1a**) and methanol (see Figure S8).

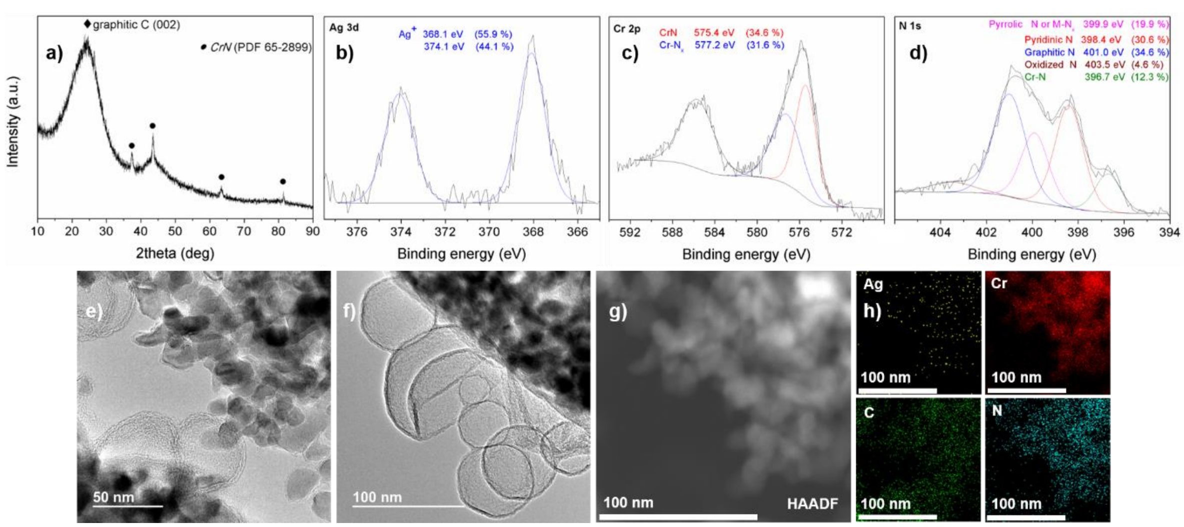


Figure 5. Characterization of catalyst AgCr@CN-800-Acid. (a) XRD spectrum. Ag 3d (b), Cr 2p (c) and N 1s (d) core level XPS spectra. TEM (e, f) and HAADF-STEM (g) images. (h) EDS elemental mapping of Ag, Cr, C, and N.

Morphological characterization of the acid-etched catalyst AgCr@CN-800-Acid by TEM showed the presence of coated nanoparticles (~ 30 nm) as well as hollow-centered (defect/N-doped) graphitic carbon layers (Figure 5e-f). These empty carbonaceous spheres result from the leaching of Ag particles, further confirming the core-shell structure of this heterobimetallic material. The elemental distribution of catalyst AgCr@CN-800-Acid was investigated by EDS elemental mapping (Figure 5g-h), and confirms that, as in the case of catalyst AgCr@CN-800, Cr, C and N elements overlap well in spatial locations, while monodispersed Ag is present in a considerably lower amount, in good agreement with the ICP-MS analysis.

Interestingly, the Ag 3d core level XPS spectrum of catalyst AgCr@CN-800-acid discloses the only presence of Ag^{+} ionic species (i.e. AgN_x sites) represented as two peaks with electron-binding energy values of 368.1 and 374.1 eV after deconvolution and fitting (Figure 5b). It should be noted that the component associated with the Ag 3p peak (~ 573.6 eV) of metallic Ag completely disappeared from the Cr 2p core level XPS spectrum (Figure 5c), being possible to fit the observed peak into two only components corresponding to CrN (575.4 eV) and to atomically dispersed Cr-N_x sites embedded in the graphitic carbon (577.2 eV). On the contrary, no relevant changes are observed in the high-resolution N 1s energy-level spectrum after the acid leaching treatment (Figure 5d).

Based on all characterization results before and after the acid-leaching treatment, we can conclude that catalyst AgCr@CN-800 is a heterobimetallic N-doped carbonaceous material, in which different metal species coexist. More specifically, catalyst AgCr@CN-800 comprises Ag and CrN aggregated particles covered by few layers of defect N-doped graphitic carbon containing highly dispersed Ag-N_x and Cr-N_x species as well.

Probing into the metal active species

To unveil which of these species is catalytically active for the investigated dehydrogenative coupling reaction between dimethylphenylsilane (**1a**) and methanol (**2a**) to afford methoxydimethyl(phenyl)silane (**3aa**), the titled reaction was carried out in the presence of different catalysts (see the Experimental Section and the Supporting Information for preparation and characterization details, respectively). As shown in Figure 6a, a significant decrease of the initial reaction rate (normalized to the mass of metal weights) was achieved by using the acid-etched catalyst AgCr@CN-800-Acid. Nevertheless, it is worth mentioning that reaction proceeded with excellent selectivity after longer reaction times (Figure 6b). Since Ag particles are the species removed with the acid-leaching treatment, this result denotes that they are required for the high activity of catalyst AgCr@CN-800, while the remaining species (i.e. CrN particles and highly dispersed CrN_x and AgN_x sites) contribute in a considerable lower extent to the overall catalytic activity.

In the presence of a monometallic Ag-based catalyst (Ag@CN-800), which is constituted by core-shell metallic nanoparticles with a narrow size distribution (5-20 nm) and by highly dispersed AgN_x species (see Figure S9 and accompanying discussion), good activity toward the formation of product **3aa** was achieved (Figure 6a) as well. However, in spite of the smaller particle size (and therefore higher specific surface area to interact with the reactants), catalyst Ag@CN-800 is less active than the heterobimetallic one AgCr@CN-800 for the investigated reaction. This result unambiguously corroborates that the presence of chromium-derived species in catalyst AgCr@CN-800 boosts its catalytic activity.

When the monometallic catalyst Ag@CN-800 was leached with acid to remove the metallic Ag nanoparticles, and the resulting material (Ag@CN-800-Acid) only containing highly dispersed Ag-N_x sites (see Figure S10 and accompanying discussion) was used as a catalyst under otherwise the same conditions, a decrease of the selectivity toward the coupling product **3aa** was observed as the conversion increases (Figure 6c). Similarly, the use of catalyst Cr@CN-800-Acid, which is constituted by the same Cr species (i.e. CrN and highly dispersed Cr-N_x sites) than catalyst AgCr@CN-800-Acid but in the absence of Ag-N_x species (see Figure S11 and accompanying discussion), led to the same loss of selectivity as well (Figure 6d).

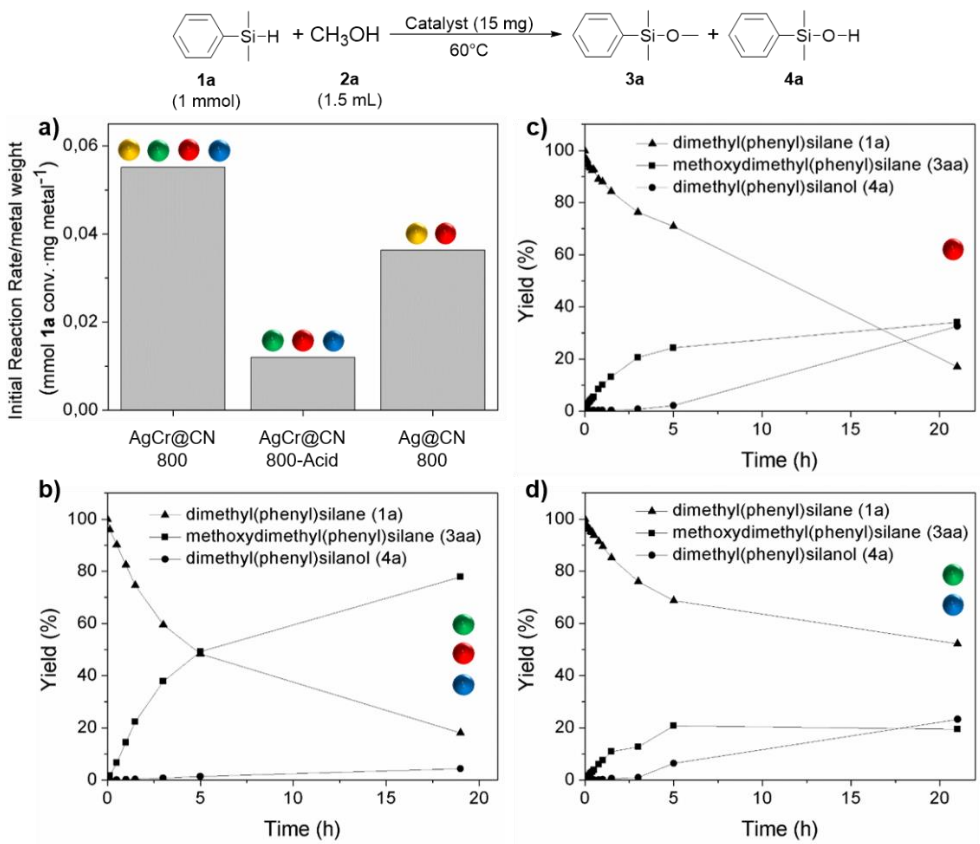


Figure 6. (a) Comparison of the metal mass activity for catalysts AgCr@CN-800, AgCr@CN-800-Acid and Ag@CN-800 in the dehydrogenative coupling reaction of **1a** with methanol (**2a**). Concentration/time diagram for catalyst AgCr@CN-800-Acid (b), Ag@CN-800-Acid (c), and

Cr@CN-800-Acid (d). Reaction conditions: **1a** (1 mmol), **2a** (1.5 mL), catalyst (15 mg), 60 °C. Colored dots represent which active species are present in the catalyst used: Ag particles (yellow), CrN particles (green), AgN_x sites (red), and CrN_x sites (blue).

Overall, the above comparative catalytic study reveals that Ag particles are the most active species and that their activity is boosted by the presence of Cr-derived species. In the absence of Ag particles, the rest of metal species (i.e. CrN particles as well as highly dispersed Ag-N_x and Cr-N_x sites) cooperatively catalyze this reaction with a slower reaction rate but with high selectivity. However, a considerably loss of selectivity is achieved when the catalyst only comprises either Ag-N_x sites or Cr-derived species (i.e. CrN particles and Cr-N_x sites), further supporting the synergistic role of Ag- and Cr-derived species in catalyst AgCr@CN-800.

Kinetic and *in-situ* Raman spectroscopy investigations

To get insights into the reaction pathway for the dehydrogenative coupling of silanes with alcohols in the presence of catalyst AgCr@CN-800, kinetic experiments at 30 ºC under air conditions were performed by measuring initial reaction rates at variable concentrations of the silane **1a** or methanol (**2a**) while keeping constant the other reactant. The initial reaction rate for the generation of **3aa** was proportional to the concentration of methanol, but a decrease was observed when increasing the amount of the silane (Figure S12). According to Hougen−Watson/Langmuir−Hinshelwood principles, developed for describing reaction mechanisms occurring on the surface of heterogeneous catalysts, these observations suggest that the alcohol activation is the rate-determining step, and that both reactants, i.e. the silane and the alcohol, compete by the same active sites.[198-201] Furthermore, a kinetic isotope effect (k_H/k_D = 2.45) was observed when using O-deuterated methanol (CH_3OD) as reactant, further confirming that the activation of the O-H bond is involved in the slowest reaction step.

As commented above, the presence of O_2 is crucial to accomplish the dehydrogenative coupling reaction and higher catalytic activity was obtained in the presence of catalyst AgCr@CN-800 in comparison with the Cr-free catalyst (Ag@CN-800). Thus, with the aim of getting more clues into the reaction mechanism, we first performed Raman studies of oxygen activation, revealing that catalyst AgCr@CN-800 displays a higher ability to activate oxygen than catalyst Ag@CN-800 (Figure 7a). Apart from the G- (1570 cm^{-1}), D- (1350 cm^{-1}) and 2D- (2500-2800 cm^{-1}) bands (Figure S13), characteristic of the formation of graphitic carbon with some degree of defect sites, the recorded spectra for both catalysts display different Raman bands as consequence of a markedly different reactivity toward O_2 activation. The Raman spectrum of catalyst AgCr@CN-800 exhibits intense bands at 613 cm^{-1} corresponding to subsurface atomic oxygen species (labelled as O_β), and at 801 and 350 cm^{-1} associated with the stretching and bending vibration of chemisorbed surface atomic oxygen species (denoted as $O\gamma$).[202-204] In the opposite, in catalyst Ag@CN-800 weakly activated molecular O_2 is predominately observed (Raman bands at 911 and 1012 cm^{-1})[203, 205] together with weakly adsorbed atomic oxygen species at 479 cm^{-1} (denoted as $O\alpha$). According to previous studies on Ag-based catalysts, the different reactivity toward oxygen activation observed between both catalysts could arise from structural defects and/or electronic properties modification in the Ag particles likely provoked in catalyst AgCr@CN-800 by the presence of Cr species, which are in intimate contact with the Ag particles, as revealed by electron microscopy characterization.

In order to unravel the role of the surface oxygen species on the reaction mechanism, "*in-situ*" Raman experiments in the presence of catalyst AgCr@CN-800 were undertaken. After dosing methanol on a pre-oxidized catalyst, new Raman bands associated to hydroxyl (575 cm^{-1}) and alkoxy (ν(C-O) at 1013 cm^{-1}) species emerged concomitant with the depletion of the bands at 801 cm^{-1} associated with the surface Oγ species (Figure 7b). A similar depletion behaviour of these species was also observed after silane dosing on the pre-oxidized catalyst in the absence of methanol (Figure S14a), further confirming that both reactants, i.e. the silane and the alcohol, compete by the same active sites, as revealed the kinetic study. It should be mentioned that the reactivity observed for the surface Oγ species is in line with other studies in the literature where they have been reported as active centres for silane[206-209] and methanol[204] oxidation reactions. Interestingly, no O-H bond activation of methanol was observed in a non-oxidized catalyst surface (Figure S14b). This result agrees not only with the fact that no reaction took place under an inert atmosphere, but also with the higher reaction rate observed by bubbling pure O_2 gas into the reaction, which agrees with the kinetic findings where methanol activation was found to be the rate-limiting step.

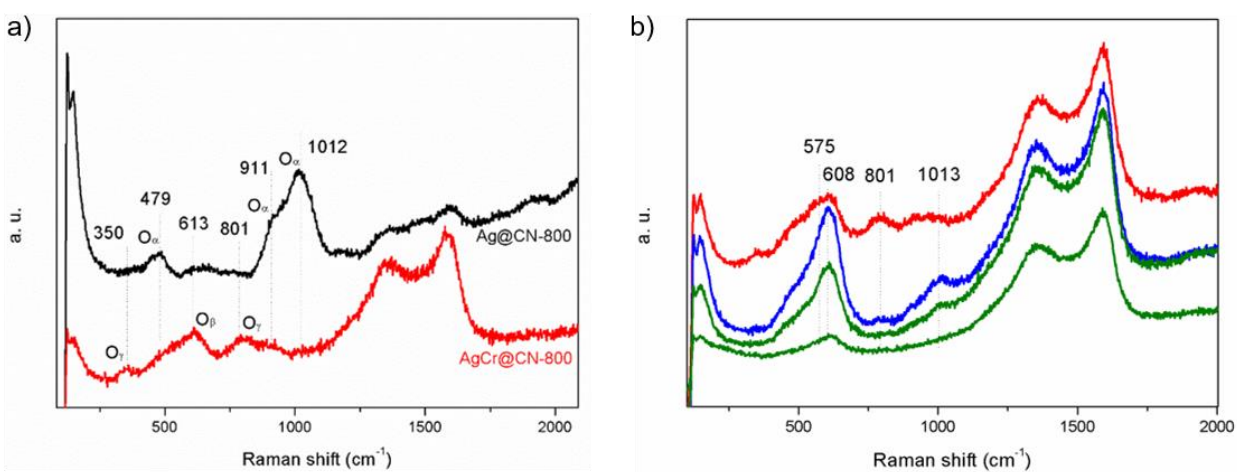
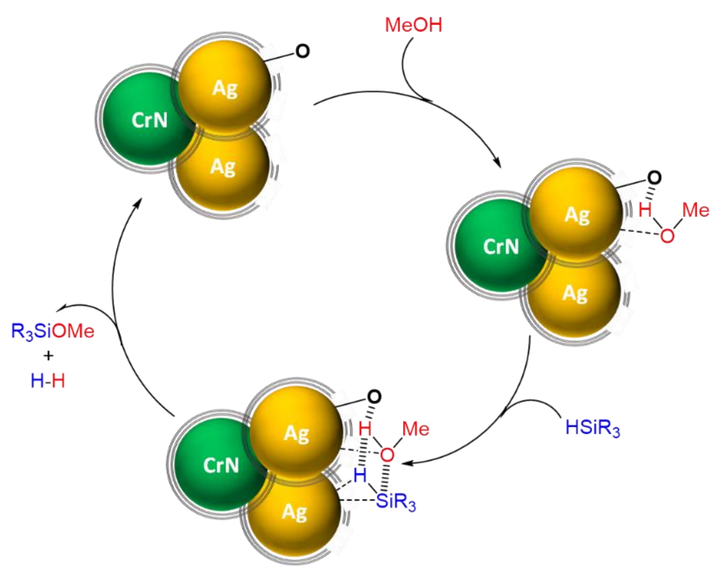


Figure 7. (a) Evolution of the bands in the Raman spectra on catalysts AgCr@CN-800 (red line) and Ag@CN-800 (black line) in a 20% O_2/Ar flow at room temperature. (b) Evolution of the bands

in the Raman spectra on catalyst AgCr@CN-800 after sequentially dosing at room temperature a 20% O_2/Ar flow (red line), a methanol/Ar flow (blue line), and a silane **1a**/Ar flow (green lines).

Next, the reactivity of the pre-formed methoxy (-OCH_3) and hydroxyl (-OH) species was investigated after silane feeding. As shown in Figure 7b, the methoxy species (1012 cm^{-1}) rapidly disappeared in the presence of the silane together with a decrease in the intensity of the band associated to hydroxyl and subsurface oxygen species (575-613 cm^{-1}), thus indicating that reaction between activated methanol and the silane to form the silyl ether **3aa** and H_2 was accomplished. The fact that the silanol (**4a**) and disiloxane (**5a**) compounds were detected as by-products in the macro-kinetic studies agrees with the herein observed progressive depletion of the Raman bands at 613 and 801 cm^{-1} associated with subsurface O_β and surface $O\gamma$ species, respectively, by further reaction of these species with the silane.



Scheme 2. Proposed mechanism for the oxygen-assisted dehydrogenative coupling reaction of silanes with alcohols in the presence of catalyst AgCr@CN-800.

Based on these results, a plausible mechanism for the dehydrogenative coupling of silanes with alcohols in the presence of catalyst AgCr@CN-800 is proposed (Scheme 2). Oxygen activated Ag surface species act as Brønsted base sites producing hydroxyl and alkoxy species by reaction with the alcohol. No direct evidence on the silane activation on the catalyst surface were obtained likely because of it is a fast step of the overall catalytic reaction. However, considering the well-stablished reactivity of silanes with metals, the activation could take place through the formation of a silyl-metal hydride intermediate by Si-H bond insertion into the Ag surface.[206] Subsequently, the nucleophilic attack of the alkoxy species derived from the alcohol to the electrophilic Si atom of the silyl-metal hydride intermediate would generate the corresponding silyl ether and molecular H_2 as well as the recovering of the oxygen activated Ag surface species. It should be noted that, accordingly to the work of Belkova, Shubina and co-workers,[210] the silane activation could also be accounted by coordination of the previously formed alkoxide ionic species yielding hypervalent pentacoordinate silicon complexes,[211-213] which enable the formation of dihydrogen bonded $(MeO)R_3SiH\cdots HOMe$ species making straightforward the proton-hydride transfer and H_2 formation.

Reusability of catalyst AgCr@CN-800

In order to investigate the recyclability of catalyst AgCr@CN-800, the model reaction between the silane **1a** and methanol was scaled-up by the factor of seven for practical reasons. After each catalytic run, the catalyst was separated from the reaction mixture, washed with ethyl acetate and diethyl ether, and reused without any reactivation treatment. ICP-MS analysis of the reaction filtrate after each run revealed that the metal (Ag and Cr) content was below the detection limit, thus confirming that no significant metal leaching occurred. Moreover, when the catalyst was removed from the reaction mixture by filtration at 51 % yield of **3aa** the reaction did not proceed any further (Figure S15).

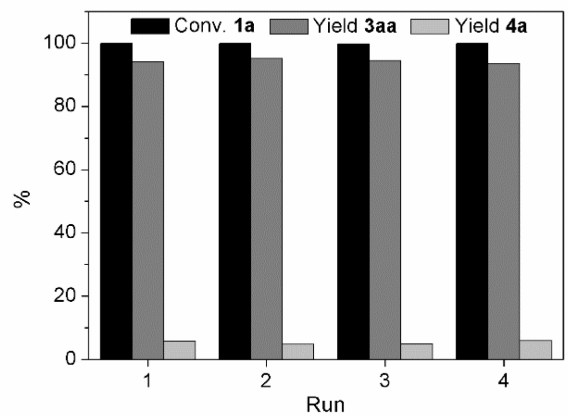


Figure 8. Recycling of catalyst AgCr@CN-800 for the dehydrogenative coupling reaction of **1a** with methanol. Reaction conditions: **1a** (7 mmol), **2a** (10.5 mL), catalyst AgCr@CN-800 (105 mg), 30 ºC, 75 min (run 1), 90 min (run 2) 135 min (run 3) or 180 min (run 4). Conversions and yields determined by GC using anisole as an internal standard (380 µL, 3.5 mmol).

After the fourth run, the morphology of the catalyst was investigated by TEM and EDS elemental mapping (Figure S16). Metal particles were still covered by a few layers of N-doped graphitic carbon shell and good dispersion of all elements (C, N, Ag and Cr) overlapping to each other in spatial locations could also be observed. Furthermore, no significant changes were detected by XRD and XPS analysis (Figure S17). The stability of catalyst AgCr@CN-800, suggested by the characterization results, was further confirmed by the excellent yields of the silyl product **3aa** obtained after each catalytic run with only a slight decrease of the reaction rate, which could be overcome by prolonging the reaction time (Figure 8).

Reaction scope of catalyst AgCr@CN-800

The catalytic performance of catalyst AgCr@CN-800 was further explored for the dehydrogenative coupling of various silanes with different alcohols. As shown in Table 1, excellent selectivity to the corresponding alkoxysilane products (**3ab-ag**) was achieved in the reaction between dimethylphenylsilane (**1a**) and alcohols (**2b-g**) with longer alkyl chain length, including linear and branched ones. (Table 1, entries 1-7). Comparing to methanol, longer reaction times were needed for full (or high) conversions, most likely because of steric effects. Benzyl alcohol (**2h**) also reacted efficiently at higher temperature (100 ºC) with silane **1a** affording the desired silyl ether product (**3ah**) in 91 % selectivity (Table 1, entry 8). Interestingly, when the reaction was performed in the presence of ethylene glycol, the silyloxy(ethan-1-ol) product (**3ai**) was afforded with high selectivity (Table 1, entry 9). Besides silane **1a**, triphenyl- (**1b**), diphenyl- (**1c**), and phenylsilane (**1d**) were also excellent candidates to accomplish the dehydrogenative coupling reaction with different alcohols in the presence of catalyst AgCr@CN-800 to the corresponding mono- (**3ba**), di- (**3ca**, **3cc**, **3cd**), and trialkoxysilane (**3da**) products with good to excellent selectivity (Table 1, entries 10-14). In general, the discrete loss of selectivity is associated with the formation of the corresponding silanol, disiloxane and/or siloxane oligomer products by reaction of silanes with oxygen activated Ag surface species and/or with ubiquitous water present in alcohols.

Table 1 Dehydrogenative coupling of silanes and alcohols catalyzed by AgCr@CN-800[a]

Entry	Silane	Alcohol	Time [min]	Conversion[b] [%]	Selectivity to **3**[b] [%]
1[c]	Me_2PhSiH (**1a**)	MeOH (**2a**)	20	>99	97 (89)[d]
2	Me_2PhSiH (**1a**)	EtOH (**2b**)	60	>99	93
3[c]	Me_2PhSiH (**1a**)	*n*-PrOH (**2c**)	60	>99	94
4[e]	Me_2PhSiH (**1a**)	*n*-BuOH (**2d**)	180	96	96
5[c, e]	Me_2PhSiH (**1a**)	*n*-HexOH (**2e**)	60	97	96

6[e]	Me_2PhSiH (**1a**)	*i*-PrOH (**2f**)	60	99	85
7	Me_2PhSiH (**1a**)	*sec*-BuOH (**2g**)	360	99	89
8[e, f]	Me_2PhSiH (**1a**)	BzOH (**2h**)	120	95	95
9	Me_2PhSiH (**1a**)	HOEtOH (**2i**)	60	>99	(79)
10[c]	Ph_3SiH (**1b**)	MeOH (**2a**)	60	95	(93)
11[c]	Ph_2SiH_2 (**1c**)	MeOH (**2a**)	45	99	89
12	Ph_2SiH_2 (**1c**)	*n*-PrOH (**2c**)	45	99	(92)
13	Ph_2SiH_2 (**1c**)	*n*-BuOH (**2d**)	60	99	(80)
14[c, g]	$PhSiH_3$ (**1d**)	MeOH (**2a**)	20	99	89

[a]Reaction conditions: silane (1 mmol), alcohol (1.5 mL), AgCr@CN-800 (15 mg), 60 ºC. [b]Determined by GC using anisole (54 μL, 0.5 mmol) as an internal standard. Yield of isolated products in parentheses. [c]Anhydrous alcohol as reactant. [d]Isolated yield on a gram-scale reaction: **1a** (1 g), MeOH (11 mL), AgCr@CN-800 (110 mg), 30 ºC, 75 min. [e]AgCr@CN-800 (30 mg). [f]100 ºC. [g]AgCr@CN-800 (5 mg).

CONCLUSIONS

We have developed a series of N-doped carbonaceous heterobimetallic nanostructured materials prepared by pyrolysis of chitosan at different temperatures in the presence of highly dispersed Ag_2CrO_4. Their catalytic potential has been investigated for the dehydrogenative coupling reaction of various silanes with different alcohols. The most active catalyst AgCr@CN-800 catalyzes this reaction under aerobic and mild conditions, even at 0 °C, affording the corresponding silyl ether products with excellent selectivity. Furthermore, the catalyst displays good stability and recyclability.

Characterization results revealed that catalyst AgCr@CN-800 comprises Ag and CrN aggregated particles, as well as highly dispersed Ag-N_x and Cr-N_x sites embedded in N-doped graphitic structures. The rational design of structure-related catalysts in combination with acid-leaching treatments allowed for carrying out catalytic control experiments, which revealed that the most active species are the Ag particles and that their activity is boosted by the presence of Cr-derived species. It has been demonstrated by *in-situ* Raman spectroscopy that this boosting effect is related with a higher ability for the generation of oxygen activated surface species, which has resulted to play a crucial role as Brønsted base sites for the dissociative activation of the alcohol that is the rate-determining step of the whole process.

This work not only provides solid evidences of a catalyst involving surface oxygen activated species as key active sites for environmentally benign reactions for green organic synthesis, but also offers insights for disentangling the heterogeneous composition of chitosan-derived annealed materials containing metals.

EXPERIMENTAL SECTION

Reagents

Ag_2CrO_4 was synthesized according to the co-precipitation method previously reported in the literature.[214] α-Ag_2WO_4 and α-$AgVO_3$ were prepared according to literature methods as well.[215-216] Chitosan, silanes and alcohols, including anhydrous methanol, were obtained from commercial sources (Sigma Aldrich) and were used as received, while *n*-propanol and *n*-hexanol were dried over molecular sieves prior to be used.

Synthesis of catalysts AgCr@CN

In a 250 mL beaker, Ag_2CrO_4 (0.074 g) and chitosan (0.926 g) were dispersed by sonication in 30 mL of ethanol for 20 min. Then, the solvent was evaporated under atmospheric pressure and stirring conditions at 70 °C, and the residue was dried overnight at this temperature under high vacuum. The dried sample was transferred into a quartz tube, and pyrolyzed at temperatures between 400-900 °C for 2 h in a vertical tubular oven with a ramp rate of 10 ºC/min while flushing

N_2 through the tube constantly until the oven was cooled down to room temperature. The resulting material was ground in an agate mortar and stored in an Eppendorf under air. Catalyst M-free@CN was prepared by directly pyrolyzing chitosan (1 g) under the same annealing treatment, followed by grinding in an agate mortar.

Synthesis of AgW@CN-800 and AgV@CN-800

The preparation of catalysts AgW@CN-800 and AgV@CN-800 was carried following the same procedure to the one described for AgCr@CN materials. 0.070 g of α-Ag_2WO_4 or 0.078 g of α-$AgVO_3$, and 0.930 g or 0.922 g of chitosan, respectively, were used as precursors. The other experimental procedures were the same, and the pyrolysis temperature was 800 ºC.

Preparation of catalyst AgCr@CN-800-Acid

AgCr@CN-800-Acid was prepared by acid leaching of AgCr@CN-800. In a 100 mL beaker, 200 mg of catalyst AgCr@CN-800 were dispersed in a 0.5 mol/L H_2SO_4 aqueous solution (50 mL) under stirring conditions and heated at 75 °C for 6 h. After that, the resulting material was recovered by centrifugation, washed twice with water, twice with ethanol and dried at 60 ºC overnight.

Synthesis of Ag@CN-800

Chitosan (0.924 g) was dispersed by sonication for 20 min in an ethanol solution of $AgNO_3$ (0.076 g in 30 mL). The other experimental procedures were the same the ones described for AgCr@CN materials, and the pyrolysis temperature was 800 ºC.

Synthesis of Ag@CN-800-Acid

Ag@CN-800-Acid was prepared by five consecutive acid leaching treatments starting from 240 mg of catalyst Ag@CN-800. After each treatment, the resulting material was recovered by centrifugation, washed twice with water, twice with ethanol, dried at 60 ºC, and used for the next one. The first three acid leaching treatments were carried out in a 100 mL beaker, in which the catalyst was dispersed in a 1, 2 or 4 mol/L H_2SO_4 aqueous solution (50 mL), respectively, under stirring conditions and heated at 75 ºC for 16 h. The last two acid leaching treatments were performed in a 100 mL Teflon vessel containing a stirring bar. Once the materials were dispersed in a 4 mol/L H_2SO_4 aqueous solution (50 mL), the Teflon vessel was sealed and heated at 120 or 140 ºC, respectively, under stirring conditions for 2 h with a heating rate of 5 °C/min in a microwave equipment using an irradiation power of maximum 800 W.

Synthesis of Cr@CN-800-Acid

Chitosan (0.957 g) was dispersed by sonication for 20 min in an ethanol solution of K_2CrO_4 (0.043 g in 30 mL). Afterward, the solvent was evaporated under atmospheric pressure and stirring conditions at 70 ºC, and the residue was dried overnight at this temperature under a high *vacuum*. Then, the dried sample was transferred into a quartz tube, and pyrolyzed at 800 ºC for 2 h in a vertical tubular oven with a ramp rate of 10 ºC/min while flushing N_2 through the tube constantly until the oven was cooled down to room temperature again. The resulting material was ground in an agate mortar and transferred to a 100 mL beaker containing a stirring bar where it was dispersed in a 1 mol/L H_2SO_4 aqueous solution (50 mL) under stirring conditions and heated at 75 ºC for 16 h. This material was recovered by centrifugation, washed twice with water, twice with ethanol, and dried at 60 ºC.

Characterizations

Powder X-ray diffraction (XRD) measurements were performed in a D/MAX-2500 PC diffractometer (Rigaku) with Cu Kα radiation (l = 1.5406 Å). Samples for electron microscopy studies were prepared by sprinkling the material directly onto the holey-carbon-coated nickel or copper grids. Some of the measurements were performed in a JEM 2100F microscope operating at 200 kV both in transmission (TEM) and in scanning-transmission modes (STEM). C_s-corrected Scanning Transmission Electron Microscopy (STEM) measurements were performed in a probe corrector Titan Themis operated at 300 kV. X-ray photoelectron spectra were acquired with a monochromatic Al Kα X-ray source (1486.6 eV) using a pass energy of 20 eV on a Kratos AXIS ultra DLD spectrometer. The C1s peak at 284.6 eV was used to provide a precise energy calibration. The metal content in catalysts was determined by inductively coupled plasma mass spectrometry (ICP-MS) using an ICP-MS Agilent 7500 CX spectrometer. Samples for ICP-MS analysis were previously digested in a microwave equipment (CEM Corp, Matthews, NC) equipped with a temperature controller (MARS6 iWave). A previously weighted amount of material and 10 mL HNO_3 (65 % p/p) were introduced in a 100 mL Teflon vessel, sealed and heated at 210 ºC under static conditions for 25 min with a heating rate of 12 ºC/min by irradiating at a maximum power of 1800 W. After cooling down to room temperature, the resulting solution was transferred to a previously tared 25 mL-volumetric flask and diluted with MiliQ H_2O.

^{1}H-NMR spectra of isolated products were recorded on a Bruker AV 300 spectrometer. All chemical shifts (δ) are reported in parts per million (ppm) and coupling constants (*J*) in Hz. For ^{1}H-NMR and ^{29}Si-NMR chemical shifts are reported relative to tetramethylsilane (δ 0.0 ppm in $CDCl_3$) or *d*-solvent peaks (δ 77.16 ppm $CDCl_3$) for ^{13}C-NMR. GC analyses were obtained on a Shimadzu GC-2010 apparatus equipped with a FID and a Technokroma (TBR-5MS, 30 m x 0.25

mm x 0.25μm) column. GC-Mass characterization was carried out on a GC-Mass Agilent 6890 Network equipped with a capillary column Agilent (HP-5, 30 m×0.32 mm×0.25 μm) and a mass-selective detector. The unambiguously detection of the H_2 evolved from the reaction was carried out using an Agilent 490 MicroGC equipped with two columns (Pore Plot Q and MolSieve 5A) and one thermal conductivity detector (TCD).

Raman spectra were recorded at room temperature using a 514 nm laser excitation on a Renishaw Raman spectrometer ("in via") equipped with a CCD detector. The laser power on the sample was 10-50 mW and a total of 20 acquisitions (10 s exposure time) were taken for each spectrum. Analyses on different positions of the sample were recorded (spectral resolution ~2 μm). Measurements were carried out using a home-made cell, where the catalyst powder was introduced without any previous treatment.

General procedure for the catalytic dehydrogenative coupling of silanes and alcohols

Catalytic experiments were performed under aerobic conditions in a 50 mL round-bottom flask equipped with a reflux condenser and a magnetic stirring bar. Once the catalyst (15 mg) and the alcohol (1.5 mL) were introduced, the reaction flask was heated at 60 °C and let equilibrate for 5 min. Then, the silane (1 mmol) and anisole (54 μL, 0.5 mmol) as an internal standard were added, setting this point as the starting time of the reaction. Yields and conversions were determined by GC analysis taking samples from the reaction mixture at the reported times. No internal standard was added in reactions from which isolated yields were calculated. After reaction completion and dilution with ethyl acetate, the catalyst was separated off by filtration, and the solvent was removed under reduced pressure. Some of the products were purified by flash-column chromatography using *n*-hexane as an eluent phase (see the Supporting Information). For the recycling experiments, the general procedure was scaled up by the factor of 7, and the reaction was performed at 30 °C in an opened 50 ml centrifugation tube. After reaction completion, the reaction mixture was diluted with ethyl acetate, and the catalyst was separated off by centrifugation, cleaned with ethyl acetate, diethyl ether, and dried at 60 °C for 30 min before using for the next run again.

ASSOCIATED CONTENT

The Supporting Information is available free of charge via the Internet at http://pubs.acs.org.

Extended data for the characterization of catalysts, additional catalytic and Raman spectroscopic experiments, and characterization data of isolated products.

Notes

The authors declare no competing financial interest.

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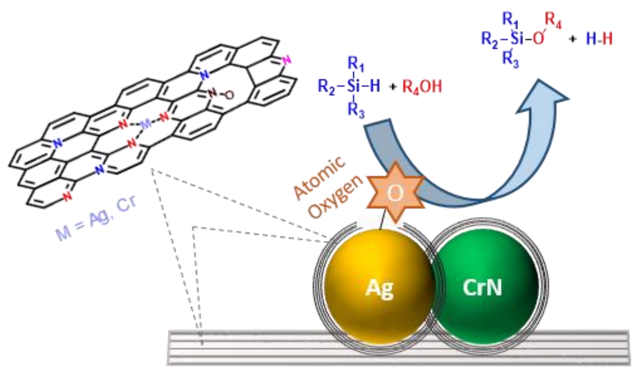
TOC/ABSTRACT GRAPHIC



SYNOPSIS: A silver- and chromium-based heterogeneous catalyst derived from pyrolysis of chitosan displays remarkable activity and selectivity for the synthesis of silyl ethers by oxygen-assisted silane/alcohol dehydrogenative coupling.