# **Inorganic Chemistry**

# MAu<sub>2</sub>GeS<sub>4</sub>-Chalcogel (M = Co, Ni): Heterogeneous Intra- and Intermolecular Hydroamination Catalysts

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### **S** Supporting Information

**ABSTRACT:** High surface area macroporous chalcogenide aerogels (chalcogels) MAu<sub>2</sub>GeS<sub>4</sub> (M = Co, Ni) were prepared from K<sub>2</sub>Au<sub>2</sub>GeS<sub>4</sub> precursor and Co(OAc)<sub>2</sub> or NiCl<sub>2</sub> by one-pot sol-gel metathesis reactions in aqueous media. The MAu<sub>2</sub>GeS<sub>4</sub>-chalcogels were screened for catalytic intramolecular hydroamination of 4-pentyn-1-amine substrate at different temperatures. 87% and 58% conversion was achieved at 100 °C, using CoAu<sub>2</sub>GeS<sub>4</sub>- and NiAu<sub>2</sub>GeS<sub>4</sub>-chalcogels respectively, and the reaction kinetics follows the first order. It was established that the catalytic performance of the aerogels is associated with the  $M^{2+}$  centers present in the structure. Intermolecular hydroamination of aniline with 1-R-4-ethynylbenzene (R = -H,  $-OCH_{3}$ , -Br, -F) was carried out at 100 °C using CoAu<sub>2</sub>GeS<sub>4</sub>-chalcogel catalyst, due to its promising



catalytic performance. The  $CoAu_2GeS_4$ -chalcogel regioselectively converted the pair of substrates to respective Markovnikov products, (*E*)-1-(4-R-phenyl)-*N*-phenylethan-1-imine, with 38% to 60% conversion.

# INTRODUCTION

Metal chalcogenides are able to form aerogels that are also called chalcogels. These are predominantly mesoporous materials constructed from inorganic building blocks to yield a three-dimensional covalent network comprising high surface area, surface polarizability, and chemical selectivity.<sup>1-</sup> Chalcogenide-based aerogels are easily accessible using onepot sol-gel metathesis reactions.<sup>1-3,6</sup> Based on the unique electronic properties (tunable bandgaps and high surface polarizability) of the chalcogels, several potential applications have been proposed and reported including gas separation,<sup>1,2,8,9</sup> heavy metal and radioactive element adsorption,<sup>10,11</sup> energy storage materials,<sup>12,13</sup> and solar cell.<sup>14</sup> Apart from these, due to its large surface area and porosity chalcogenide based aerogels are expected and shown to have promising catalytic performance.<sup>5–7,15</sup> The Co-Mo-S-chalcogels were twice as active as the conventional sulfided Co-Mo/Al<sub>2</sub>O<sub>3</sub> catalyst for the hydrodesulfurization of thiophene.<sup>5</sup> Solid chalcogels containing FeMoS clusters are capable of photochemical conversion of nitrogen to ammonia under ambient conditions in aqueous media.<sup>6</sup> Other examples include low-cost pH universal CoMoS<sub>x</sub> chalcogel for electrocatalytic hydrogen production<sup>7</sup> and chalcogel supported Pt nanoparticles for catalytic reduction of 4-nitrophenol.<sup>15</sup> Chalcogenide aerogels containing late transition metals are believed to result in further interesting applications of this class of materials, and the focus here is on heterogeneous catalytic hydroamination.

An atom efficient route for the synthesis of amines, enamines, and imines is the hydroamination reaction, addition of amine N-H bonds across unsaturated carbon-carbon bonds.<sup>16,17</sup> N-Heterocycles are of particular importance to the pharmaceutical, agrochemical, and dye industries.<sup>16</sup> The interand intramolecular hydroamination of hydrocarbons can be efficiently and selectively achieved through metal catalysis.<sup>18</sup> Good progress has been made by using metal complex catalysts under homogeneous conditions. $^{19-25}$  However, there are few reports on heterogeneous hydroamination catalysis, such as zeolites,<sup>26,27</sup> metal-cation exchanged zeolites,<sup>28</sup> carbon black<sup>29</sup> and glassy carbon supported Rh(I) complexes,<sup>30</sup> mesoporous silica encapsulated Rh complex,<sup>31</sup> tungstophosphoric acid (TPA)<sup>32</sup> and silver-exchanged tungstophosphoric acid (AgTPA),<sup>33</sup> nitrogen-rich mesoporous carbon,<sup>34</sup> SiO<sub>2</sub><sup>35</sup> and TiO<sub>2</sub> supported Au nanoparticles,<sup>36</sup> ion-exchanged montmorillonite, oxide supported Pd<sup>37</sup> and Au<sup>38</sup> complexes, Al<sub>2</sub>O<sub>3</sub> supported Ni particles,<sup>39</sup> sol-gel immobilized Rh complex,<sup>4</sup> supported ionic-liquid phase catalysts,<sup>41</sup> Cu-exchanged SiO<sub>2</sub>/ Al<sub>2</sub>O<sub>3</sub>,<sup>42</sup> polymer supported organo–lanthanide complexes,<sup>4</sup> Zn–Co double metal cyanides,<sup>44</sup> metal complexes supported in

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a thin film of ionic liquid,<sup>45</sup> silica supported Co catalysts,<sup>46</sup> transition metal exchanged clays,<sup>47</sup> and polymer bound oxidovanadium complexes.<sup>48</sup> However, no work has been reported on heterogeneous catalytic hydroamination using chalcogenide based aerogels (chalcogels).

This work is aimed at the preparation of high surface area porous chalcogels containing catalytically active transition metal sites confined inside the 3D covalent framework. These types of chalcogels are expected to have desirable electronic properties, Lewis acidic, toward the attachment of the substrate molecules. Herein, (i) the synthesis and characterization of novel quaternary  $K_2Au_2GeS_4$ , (ii) preparation and characterization of the  $MAu_2GeS_4$ -chalcogels (M = Co, Ni) from  $K_2Au_2GeS_4$ precursor, and (iii) catalytic performance of the  $MAu_2GeS_4$ chalcogel heterogeneous catalysts for intra- and intermolecular hydroamination reactions are presented.

#### EXPERIMENTAL SECTION

**Synthesis of K<sub>2</sub>Au<sub>2</sub>GeS<sub>4</sub>.** The samples were handled in a nitrogen-filled (99.999%) glovebox due to the air and moisture sensitivity of the starting materials. Elemental gold (Alfa Aesar 99.5%), germanium(II) sulfide (Sigma-Aldrich 99.99%), and sulfur (Alfa Aesar 99.99%) were used as received. X-ray single phase K<sub>2</sub>S was prepared in liquid ammonia according to a published procedure.<sup>49</sup> K<sub>2</sub>Au<sub>2</sub>GeS<sub>4</sub> was synthesized from a stoichiometric mixture of elemental Au (2 mmol), GeS (1 mmol), S (2 mmol), and K<sub>2</sub>S (1 mmol) by direct combination reaction. The starting materials were weighed and mixed inside the glovebox and sealed in fused silica ampules. The sample was heated at 650 °C for 3 days and cooled down to room temperature within 5 days. Phase-pure K<sub>2</sub>Au<sub>2</sub>GeS<sub>4</sub> was obtained after washing the reaction products with dimethylformamide (Sigma-Aldrich 99.9%) and diethyl ether (Sigma-Aldrich 99.9%). The yield was ~80% based on supplied Au.

Chalcogel Preparation. K<sub>2</sub>Au<sub>2</sub>GeS<sub>4</sub> dissolves in water forming a light yellow clear solution. The removal of water from the  $K_2Au_2GeS_{4(aq)}$  solution, by slow evaporation inside the glovebox, resulted in the formation of the following solid products: K<sub>3</sub>[GeS<sub>3</sub>(OH)]·H<sub>2</sub>O, KHS, GeS<sub>2</sub>, and Au<sub>2</sub>S (Figure S1). This fact clearly indicates that the  $[Au_2GeS_4]^{2-}$  anion is only stable in the liquid phase (Figure 4) and does not recrystallize from the solution. The hydrolysis of  $[Au_2GeS_4]^{2-}$  cannot be ruled out completely and might take place slowly with time. Therefore, the  $M^{2+}$  (M = Co, Ni) linker has to be added straight away after the dissolution of K2Au2GeS4 in water, to avoid the hydrolysis of [Au2GeS4]2- anion. All divalent third row transition metals were screened for the gel formation, and only Co(II) and Ni(II) formed rigid gels. 0.146 mmol of K2Au2GeS4 precursor was dissolved in 7 mL of deionized and degassed water, inside the glovebox. One equimolar  $Co(OAc)_{2(aq)}$  or  $NiCl_{2(aq)}$  was immediately added dropwise under continuous stirring, which resulted in the formation of dark brownish clear solutions. The black chalcogels were formed after 7 days by heating the solutions at 40 °C (Figure 1). The water-soluble products were removed together with the water by washing the gels with absolute ethanol more than 10 times. The gels were dried using the CO<sub>2</sub> critical point drier to remove the ethanol and retain the porous nature of the materials.

**Hydroamination Catalysis.** The 4-pentyn-1-amine (95%, Sigma-Aldrich), phenylacetylene (98%, Sigma-Aldrich), aniline (99.5%, Sigma-Aldrich), 1-ethynyl-4-methoxybenzene (97%, Sigma-Aldrich), 1-bromo-4-ethynylbenzene (97%, Sigma-Aldrich), and 1-fluoro-4ethynylbenzene (99%, Sigma-Aldrich) were used as received. The chalcogel catalyzed intra- and intermolecular hydroamination reactions were carried out, on a small scale, in a NMR tube fitted with Young's concentric Teflon valve, at three different temperatures, 60, 80, and 100 °C. All sample preparation and handling was done in a N<sub>2</sub>-filled glove box. 0.03 mmol (5 mol % to the substrate) of the catalyst, 0.6 mmol of respective substrates, and 0.7 mL of trichlorobenzene (TCB) were loaded into a NMR tube. For the intermolecular hydroamination reactions, the substrates were taken in 1:1 mol ratio. The progress of



**Figure 1.** Photographic illustration of the gel formation by metathesis reaction. The light yellow aqueous solution of  $K_2Au_2GeS_4$  was reacted with Co(OAc)<sub>2</sub> yielding dark brownish solution. CoAu<sub>2</sub>GeS<sub>4</sub>-chalcogel was formed after heating the dark brownish solution at 40 °C for 7 days.

the hydroamination reaction was monitored by acquiring <sup>1</sup>H NMR spectra in situ.<sup>50,51</sup> Blank measurements were carried out to record the NMR spectrum of the pure substrates to evaluate the characteristic peaks of the substrates as well as the purity of the material. The weak resonance peaks associated with the impurities were identified and taken into account for further evaluation of the results (Figures S2–S6).

The recoverability of the catalyst was demonstrated on the example of intramolecular hydroamination of 4-pentyn-1-amine substrate using  $CoAu_2GeS_4$  catalyst, at 100 °C. The duration of a catalytic cycle was 48 h. After every cycle, the reaction mixture was cooled down to room temperature and the liquid phase was decanted. The catalyst was washed five times with 1,2,4-trichlorobenzene (TCB) to completely remove the reaction products from the catalyst surface. The conversion rate was determined by measuring <sup>1</sup>H NMR after each catalytic cycle.

X-ray Diffraction. The powder diffraction patterns were recorded on a STOE STADI MP X-ray diffractometer, equipped with a DECTRIS MYTHEN 1 K microstrip solid-state detector, using monochromatic Cu K $\alpha_1$  ( $\lambda$  = 1.5406 Å) radiation. The samples were measured in transmission mode using  $(2\theta + \omega)$  scan type, in the 2° <  $2\theta$  < 80° range. The observed and calculated powder diffraction patterns of K<sub>2</sub>Au<sub>2</sub>GeS<sub>4</sub> are shown in Figure S7. The colorless needleshaped crystals of K<sub>2</sub>Au<sub>2</sub>GeS<sub>4</sub> were measured on a STOE IPDS2 single crystal X-ray diffractometer with graphite monochromatized Mo K $\alpha$  ( $\lambda$ = 0.71073 Å) radiation at 200 K. The programs X-Area<sup>52</sup> and X-Shape<sup>53</sup> were used for data collection, determination, and refinement of the lattice parameters as well as for data reduction including LP correction. The crystal structure was solved by direct methods and refined using SHELX2014<sup>54</sup> in the WinGX program package.<sup>55</sup> The graphical images of the crystal structure were produced using CrystalMaker.

Scanning Electron Microscopy/Energy Dispersive X-ray Spectroscopy (SEM/EDS). The semiquantitative chemical analyses were conducted on an Energy Dispersive X-ray (EDX)-equipped SEM (FEI Quanta 200).

**Raman Spectroscopy.** Raman spectra were recorded on a HORIBA JobinYvon ARAMIS Raman spectrometer, using a He–Ne laser (473 nm) with a resolution of 50 cm<sup>-1</sup>. The spectra acquisition time was 10 s. For the liquid sample, ten consecutive spectra were recorded and averaged to get better signal-to-noise ratio.

UV-Visible Spectroscopy. UV-vis diffuse reflectance spectra were recorded at room temperature on a Cary 5000 UV-vis-NIR double-beam, double monochromator spectrophotometer using the Praying Mantis accessory for solid samples. The measurements were done in the range 200-800 nm with a scan rate of 200 nm per minute.

**Thermal Analysis.** The thermal stabilities of the substances were examined up to 600 °C by a Netzsch STA 449 F3 Jupiter using Al crucibles (25  $\mu$ L) with punched lids under nitrogen flow (20 mL·min<sup>-1</sup>) with a heating and cooling rate of 10 K·min<sup>-1</sup>.

**Supercritical Drying.** Drying of the MAu<sub>2</sub>GeS<sub>4</sub>-chalcogels (M = Co, Ni) was carried out on a Tousimis Autosamdri-815B instrument. The sample was placed on a small particle holder with 2  $\mu$ m

preinstalled particulate screen (mesh) and transferred to the critical point drier in a sealed container. The chalcogel was soaked and flushed with liquid  $CO_2$  below 10 °C to remove the ethanol completely. Finally, chalcogenide aerogels were obtained after supercritical drying at 35 °C.

Adsorption Measurements. The specific surface area of the aerogels (~80 mg) was measured on a Micromeritics ASAP 2020 HD instrument with Kalrez modification. Nitrogen adsorption and desorption isotherms were recorded at 77 K. The samples were degassed at 348 K under vacuum ( $<10^{-4}$  mbar) overnight before the analysis. Low-pressure incremental dosing of 0.1338 mmol/g (STP) and 30 s equilibration were applied as analysis conditions. BET transform plots were obtained in the 0.05 to 0.35 relative pressure ( $P/P_o$ ) region, and the correlation coefficient of 0.999 was obtained in all of the cases, while the pore size distribution was calculated using the Barrett–Joyner–Halenda (BJH) model.

<sup>1</sup>**H NMR.** The NMR spectra were acquired at 60, 80, and 100 °C using Bruker 600 AVANCE III spectrometer (Bruker BioSpin, Rheinstetten, Germany) equipped with Bruker 5 mm broadband observe (BBO) multinuclear probe. The <sup>1</sup>H NMR spectra were recorded by collecting 32 scans using a standard 1D 90 deg pulse sequence and (zg) program from Bruker pulse library. For quantitative analysis, the recycle delay time was set to at least 10 s. Chemical shifts were adjusted using tetramethylsilane (TMS) as internal chemical shifts reference. Exponential line broadening of 1 Hz was applied before Fourier transformation. All spectra were then visually phased, and the chemical shifts were adjusted manually to the TMS peak where necessary. Bruker TopSpin 2.1 software (Bruker BioSpin, Rheinstetten, Germany) was used in all NMR experiments to collect and analyze the data.

# RESULTS AND DISCUSSION

**Crystal Chemistry of K<sub>2</sub>Au<sub>2</sub>GeS<sub>4</sub>.** K<sub>2</sub>Au<sub>2</sub>GeS<sub>4</sub> crystallizes in the monoclinic space group C2/c (15) and is isostructural to previously reported K<sub>2</sub>Ag<sub>2</sub>GeS<sub>4</sub>.<sup>57</sup> The crystal structure contains two K, one Au, one Ge, and two S sites in the asymmetric unit. The Ge atom is 4-fold coordinated by S atoms to form slightly distorted GeS<sub>4</sub> tetrahedra (Figure 2). These tetrahedra are bidentate to Au atoms and form helical chains, which are charge balanced by the K cations. The K atoms are surrounded by 6 sulfur atoms. The interatomic distances (Ge–



**Figure 2.** Crystal structure of  $K_2Au_2GeS_4$  showing the 1D polyanionic chains separated by  $K^+$  ions. The CIF file can be obtained from CSD database quoting the CSD number 429757.

S, 2.225(3) Å and 2.213(2) Å; Au–S, 2.302(2) Å and 2.312(2) Å; and K–S, 3.169(3)–3.284(4) Å) are comparable to the respective distances observed in  $K_4GeS_4$ , <sup>58</sup>  $K_2Au_2Ge_2S_6$ , <sup>59</sup>  $K_2Ag_2GeS_4$ , <sup>57</sup>  $K_6Ge_2S_6$ , <sup>60</sup> and  $K_4Ag_2Ge_3S_9$ ·H<sub>2</sub>O.<sup>61</sup> Detailed crystallographic data is listed in Tables S1–S4. The semiquantitative analyses of selected crystals show the presence of all four elements in the atomic ratio K:Au:Ge:S = 1.7:1.8:1:4.7 (Figure S8), which is in agreement with crystal structure refinement results.

**Characterization of K**<sub>2</sub>**Au**<sub>2</sub>**GeS**<sub>4</sub>. The solid-state UV-vis spectrum of the K<sub>2</sub>Au<sub>2</sub>GeS<sub>4</sub> powder was measured in diffuse reflectance mode and plotted using the Kubelka–Munk function F(R) (Figure 3).<sup>62</sup> The bandgap was determined as



Figure 3. UV-vis spectrum of  $K_2Au_2GeS_4$  measured in diffuse reflectance mode and plotted using the Kubelka-Munk function.

the intersection point between the energy axis and the line extrapolated from the linear portion of the absorption edge in an F(S) vs E plot. The compound exhibits semiconducting behavior with a band gap of around 2.9 eV.

The Raman spectrum of  $K_2Au_2GeS_4$  possesses several Ge–S and Au–S characteristic vibrational modes in the 200–500 cm<sup>-1</sup> range. Figure 4 (black line) shows the Raman spectrum of polycrystalline  $K_2Au_2GeS_4$  powder. The modes above 350 cm<sup>-1</sup> can be assigned to the Ge–S stretching modes; the peaks at 389 and 414 cm<sup>-1</sup> are very close to the vibrational modes observed in Na<sub>4</sub>GeS<sub>4</sub><sup>63</sup> and Na<sub>6</sub>Ge<sub>2</sub>S<sub>6</sub>,<sup>64</sup> while the bands at 366 and 445 cm<sup>-1</sup> are comparable to the terminal Ge–S stretching vibrations found in Na<sub>2</sub>GeS<sub>3</sub> and Na<sub>4</sub>Ge<sub>3</sub>S<sub>10</sub>.<sup>65</sup> Bulk Au<sub>2</sub>S



Figure 4. Raman spectra of  $K_2Au_2GeS_4$  powder (black line) and  $K_2Au_2GeS_4$  aqueous solution (blue line).

shows a broad Raman band centered at 332 cm<sup>-1</sup>, which can be deconvoluted to 265, 302, and 336 cm<sup>-1</sup>.<sup>66,67</sup> Formation of the Au–S covalent bond, with Raman mode at 287 cm<sup>-1</sup>, was observed on the Au-electrode surface by electrochemical oxidation using different electrolytes such as tetrathionate (Na<sub>2</sub>S<sub>4</sub>O<sub>6</sub>), trithionate (Na<sub>2</sub>S<sub>3</sub>O<sub>6</sub>), [Au(S<sub>2</sub>O<sub>3</sub>)<sub>2</sub>]<sup>3-</sup> complex,<sup>66</sup> and thiosulfate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>).<sup>66–68</sup> Therefore, the bands at 290 and 337 cm<sup>-1</sup> can be assigned to the Au–S vibrational modes.

**Stability of K<sub>2</sub>Au<sub>2</sub>GeS<sub>4</sub>.** The thermal stability of K<sub>2</sub>Au<sub>2</sub>GeS<sub>4</sub> was examined up to 600 °C. No weight loss was observed based on the TG results, while the DSC curve has a strong single endothermic effect with onset point of 490 °C (Figure S9). X-ray phase analysis of the sample after the DSC shows the presence of GeS<sub>2</sub>, Au, and K<sub>2</sub>Au<sub>2</sub>GeS<sub>4</sub>. Therefore, incongruent melting behavior was supposed for K<sub>2</sub>Au<sub>2</sub>GeS<sub>4</sub>. The comparison of the powder XRD patterns before and after DSC is depicted in Figure S10.

The K<sub>2</sub>Au<sub>2</sub>GeS<sub>4</sub> is readily soluble in water forming a light yellow clear solution. The Raman spectrum of the solution is illustrated in Figure 4 (blue line). The Raman spectra of K<sub>2</sub>Au<sub>2</sub>GeS<sub>4</sub> both in the solid state and in aqueous solution show practically identical shapes, and the location of the peaks indicates intactness of the polyanionic chain during the dissolution and its stability in the solution. Small shifts and peak broadening might be associated with hydrolysis of the parent compound, which might be slowly taking place with time to form thio-hydroxogermanate ions. K<sub>2</sub>Au<sub>2</sub>GeS<sub>4</sub> is air sensitive and not soluble in organic solvents such as DMF, DMSO, ethanol, methanol, THF, and acetone. The synthesized K<sub>2</sub>Au<sub>2</sub>GeS<sub>4</sub> was used as a precursor material for MAu<sub>2</sub>GeS<sub>4</sub>chalcogel (M = Co, Ni) preparation.

 $MAu_2GeS_4$ -Chalcogel (M = Co, Ni). The  $MAu_2GeS_4$ chalcogels were synthesized by one-pot sol-gel metathesis reaction between equimolar  $K_2Au_2GeS_4$  and  $Co(OAc)_2$  or NiCl<sub>2</sub> aqueous solutions. The  $Co(OAc)_{2(aq)}$  or NiCl<sub>2(aq)</sub> was added dropwise right after dissolving the  $K_2Au_2GeS_4$  in water to avoid the hydrolysis of  $K_2Au_2GeS_4$ . The  $MAu_2GeS_4$ -chalcogels were obtained by  $CO_2$  critical point drying of the wet chalcogels. The BET results and BHJ pore size distribution analysis reveal that the  $MAu_2GeS_4$ -chalcogels are mainly macroporous materials with specific surface area of 344 m<sup>2</sup>/g and 217 m<sup>2</sup>/g for  $CoAu_2GeS_4$  (Co-gel) and NiAu\_2GeS\_4 (Nigel), respectively, containing covalently bonded  $Au_2GeS_4$ building blocks connected through  $M^{2+}$  ions. Figure 5 shows the BET isotherm curve together with the SEM image of the Co-gel in the inset (see Figure S11 for Ni-gel).

The pore size distribution curve is depicted in Figure S12a,b. The MAu<sub>2</sub>GeS<sub>4</sub>-chalcogels are amorphous in nature and relatively stable at ambient conditions (Figure S12e,f). EDS analyses of the MAu<sub>2</sub>GeS<sub>4</sub>-chalcogels show the presence of M/Au/Ge/S with compositional ratio of 1.1:2.0:1:5.3, averaged from 10 different measurement points, which agrees well with the nominal composition (Figure S13). The MAu<sub>2</sub>GeS<sub>4</sub>-chalcogels are both thermally stable up to 150 °C and decompose at elevated temperatures forming Au, MS<sub>2</sub> (M = Co, Ni), and germanium sulfides (Figure S12c-f). The MAu<sub>2</sub>GeS<sub>4</sub>-chalcogels were further explored for their catalytic performance in hydroamination reactions.

**Intramolecular Hydroamination.** The Co-gel has higher surface area compared to the Ni-gel. Therefore, the intramolecular catalytic hydroamination reaction of 4-pentyn-1amine substrate to 2-methylpyrroline was first carried out using the Co-gel as a catalyst at 60, 80, and 100 °C (Scheme 1). The



Figure 5.  $N_2$  adsorption and desorption isotherms of CoAu<sub>2</sub>GeS<sub>4</sub>chalcogel. The SEM image of the chalcogel is shown in the inset.

Scheme 1. Catalytic Conversion of the 4-Pentyn-1-amine Substrate to 2-Methylpyrroline over MAu<sub>2</sub>GeS<sub>4</sub>-Chalcogel Catalysts



progress of the hydroamination reaction was monitored by acquiring <sup>1</sup>H NMR spectra in situ. The sample was heated and kept within the magnet during the whole reaction time. Thus, the first spectrum was measured as soon as after the sample had been heated to the target temperature. The moment of this first acquisition was taken to be time zero. Conversion of starting material to the product was determined by integration of the product resonances relative to the substrate resonances. The turnover frequency (TOF) was calculated as the [conversion × (mole of substrate/mol of catalyst × time)] and was determined at 50% conversion. The conversion rate at room temperature was negligible even after 72 h. Figure S14 shows the in situ NMR spectra of the hydroamination reaction at 80 °C using Co-gel catalyst.

The catalytic hydroamination of 4-pentyn-1-amine substrate using Co-gel catalyst with 5 mol % loading was convincing, but kinetically rather slow, at 60 °C. The conversion of the substrate reached only 56% after 120 h. As expected, the reaction rate increased with temperature, and the conversion reached 66% at 80 °C after 47 h and 87% at 100 °C after 48 h (Table 1). Figure 6 depicts the conversion rate vs reaction time

Table 1. Kinetic Results of the  $MAu_2GeS_4$ -Chalcogel (M = Co, Ni) Catalyzed Hydroamination Reaction

gel	$T(^{\circ}C)$	time (h)	convn (%)	$\mathrm{TOF}^{a}(\mathrm{h}^{-1})$
Co	60	120	56	0.12
	80	47	66	0.44
	100	48	87	1.25
Ni	100	48	58	0.30
<sup>a</sup> TOF was	s calculated a	t 50% convers	ion.	

plot at different reaction temperatures. The initial kinetic studies suggest that the reaction is first order with respect to the substrate concentration (Figure S15). Presumably, the rate-determining step of the reaction is the attachment of the substrate to a high surface area, polarizable chalcogel surface containing Lewis acidic catalytically active sites. The reaction



Figure 6. Kinetic data for the  $CoAu_2GeS_4$ -chalcogel catalyzed conversion of the 4-pentyn-1-amine substrate to 2-methylpyrroline at 60, 80, and 100 °C.

mechanism might follow the oxidative addition of the amine to the metal center followed by insertion of the C–C unsaturated moiety into the metal–nitrogen bond,<sup>69,70</sup> or the  $M^{2+}$   $\pi$ -acid catalysis route.<sup>71,72</sup>

The catalytic activity of Ni-gel was measured only at 100  $^{\circ}$ C, under the same conditions used for Co-gel. About 58% of the 4-pentyn-1-amine substrate was converted to 2-methylpyrroline after 48 h, which is rather slow in comparison with Co-gel, 87% at 100  $^{\circ}$ C.

Both Co- and Ni-gel contain a combination of metals, Co/ Au and Ni/Au, which are known to be active for catalytic hydroamination reactions. In order to confirm which metal in the aerogels is responsible for the catalytic activity, the following measurements were carried out.  $Co(OAc)_2$  was catalytically inactive for the hydroamination process at room temperature (Figure S2a). However, at higher temperatures,  $Co(OAc)_2$  started to react with the substrate molecule, which was evidenced by the color change of the solution as well as by NMR (Figure S2a). The K<sub>2</sub>Au<sub>2</sub>GeS<sub>4</sub> precursor did not show any catalytic performance even at elevated temperature, 100 °C after 24 h (Figure S2b). Therefore, based on the catalytic activity results of the Co- and Ni-gels, the catalytic performance of the MAu2GeS4-chalcogels is believed to be associated with the M(II) species present in the aerogels. The TOF of the MAu2GeS4-chalcogel catalysts were calculated at the 50% conversion and tabulated in Table 1.

The activity of the MAu<sub>2</sub>GeS<sub>4</sub>-chalcogel catalysts is comparable with the other homogeneous and heterogeneous catalysts studied for intramolecular hydroamination of 4pentyn-1-amine substrate. [{CH(PPh<sub>2</sub>NSiMe<sub>3</sub>)<sub>2</sub>}SmCl<sub>2</sub>]<sub>2</sub><sup>51</sup> shows TOF of 1.54 for cyclication of 4-pentyn-1-amine, and [Ir(bim)CO<sub>2</sub>][BPh<sub>4</sub>] complex has TOF of 5,<sup>73</sup> while cis-[PtCl<sub>2</sub>(PTA)<sub>2</sub>]<sup>74</sup> is less active with TOF of 0.35. Rh(PyP)-(CO)(OSO<sub>2</sub>CF<sub>3</sub>) and Rh(PyP)(CO)Cl complexes show TOF of 3.5 and 2.7, respectively.<sup>75</sup> Glassy carbon supported [Rh(bmp)(CO)<sub>2</sub>] heterogeneous catalyst shows 50% conversion after 72 h at 60 °C.<sup>30</sup>

The CoAu<sub>2</sub>GeS<sub>4</sub> catalyst demonstrated excellent recoverability after multiple catalytic intramolecular hydroamination cycles. The conversion of the 4-pentyn-1-amine substrate was ~87%, ~86.7%, and ~86.8% after the first, second, and third catalytic cycles, respectively (Figure S16).

Intermolecular Hydroamination. Catalytic intermolecular hydroamination reactions were carried out using the more promising cobalt aerogel catalyst at 100 °C (Scheme 2). Intermolecular hydroamination reactions of aniline with (A)

# Scheme 2. Intermolecular Hydroamination Reactions Using Co-Gel Catalyst



phenylacetylene, (B) 1-ethynyl-4-methoxybenzene, (C) 1bromo-4-ethynylbenzene, and (D) 1-fluoro-4-ethynylbenzene were screened for 60 h, 60 h, 57 h, and 60 h, respectively. Table 2 summarizes kinetic data of intermolecular hydroamination

Table 2. Kinetic Results of the CoAu<sub>2</sub>GeS<sub>4</sub>-Chalcogel Catalyzed Intermolecular Hydroamination Reactions at 100 °C

reaction code	R	time (h)	convn (%)	$TOF^{a}$ (h <sup>-1</sup> )
А	-H	60	38	
В	-OCH <sub>3</sub>	60	60	0.45
С	-Br	57	55	0.24
D	-F	60	40	
<sup><i>a</i></sup> TOF was calc	ulated at 50%	conversion.		

reactions that have been examined. All four intermolecular hydroamination reactions regioselectively converted to the respective Markovnikov products, which was confirmed by <sup>1</sup>H NMR and HR-MS (Figures S3-S6). The substituted ethynylbenzene derivatives show higher conversion rate compared to the phenylacetylene. However, the reaction kinetics was slower compared to the cyclization of 4-pentyn-1-amine. The conversions of the educts are comparable to the other heterogeneous catalysts used for the same reactions. For instance, the TiO<sub>2</sub> supported Au-NP's showed 79%, 56%, and 80% conversion for reactions A, B, and C, respectively, at 40 °C after 25 h.<sup>36</sup> Several catalysts were screened for intermolecular hydroamination of aniline with phenylacetylene: Cu-exchanged K-10 zeolite yielded 93% product after 10 h at 110 °C,<sup>47</sup> and Co/K-10 catalyst was less active with only 7% conversion at 111 °C,45 while 79% yield was achieved using Zn-Co double metal cyanide catalysts at 150 °C after 24 h.44 Nevertheless, CoAu2GeS4-chalcogel is catalytically active for both intra- and intermolecular hydroamination reactions.

# CONCLUSION

High surface area porous  $MAu_2GeS_4$ -chalcogel (M = Co, Ni) heterogeneous catalysts were prepared from [Au<sub>2</sub>GeS<sub>4</sub>]<sup>2-</sup> helical chain precursor and screened for the intra- and intermolecular hydroamination of various substrates. The MAu<sub>2</sub>GeS<sub>4</sub>-chalcogels were catalytically active for both intraand intermolecular hydroamination and showed excellent recoverability and regioselectivity toward the Markovnikov products. It was established that the catalytic active site of the materials is the Lewis acidic M<sup>2+</sup> centers. The chalcogenidebased aerogels are a potentially interesting class of materials that can find application in the synthesis of industrially important heterocycles through heterogeneous catalytic hydroamination. Preparation of new chalcogels with different catalytic active centers and higher catalytic performance, as well as expanding the library of screened substrates, is the subject of the future studies.

#### **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.7b01099.

Crystallographic tables, EDS/SEM, TGA/DSC, powder diffraction patterns, BET surface area, pore size distribution, linear fit, <sup>1</sup>H NMR spectra, and HR-MS (PDF)

# **Accession Codes**

CCDC 1546598 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif, or by emailing data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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#### Notes

The authors declare no competing financial interest.

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