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ARTICLE

Ethane Oxidative Dehydrogenation with CO₂ on thiogallatesVera Bikbaeva,^a Olivier Perez,^b Nikolay Nesterenko,^{*c} and Valentin Valtchev^aReceived 00th January 20xx,
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The CO₂-assisted oxidative dehydrogenation of ethane (ODH-CO₂) attracts a lot of research interest since it combines greenhouse gas utilization with the production of valuable chemicals. The present study demonstrates the potential of the novel non-classic catalysts, alkali thiogallates, in this reaction. The contribution also reports a novel solvothermal synthesis method to prepare crystalline KGaS₂ thiogallate materials. Despite the low surface area of the bulk KGaS₂ system, the material shows substantial activity in CO₂ to CO transformation with conversions in the range of 22–36% at 700–800 °C. The catalyst allows utilization of the co-produced hydrogen from ethane thermal cracking for CO₂ hydrogenation without substantially impacting ethylene yield even at 800°C at the conversion level of ethane close to 70%. The catalyst demonstrates stable performance with insignificant coke formation. The structure of the KGaS₂ thiogallate material is fully conserved after the reaction. These results open a promising opportunity for the thiogallate materials as catalysts with moderate hydrogenation function, which are highly tolerant to the CO and highly reactive hydrocarbons environments.

Introduction

Expansion in chemicals is one of the upcoming trends in the transformation of the petrochemical industry, and ethane transformation is an important part of the downstream evolution. A significant portion of the recent investments in olefins was in gas-based petrochemistry, either in ethane steam cracking (ethylene production) or in propane dehydrogenation (propylene production). The transition is a part of the efforts to transform “a fuel refinery” into the “refinery of the future”.¹ However, the CO₂ emissions of a refinery of future per ton of olefins are significantly higher than traditional petrochemical production because the feedstock is produced on purpose via several hydrotreatment steps. Thus, an increase in the amount of chemicals production at a refinery from 10% to 25–40% may almost double the carbon footprint (CO₂/ton) from 1–1.5 to 2.4–2.6.² Consequently, high carbon footprint is not acceptable given the zero-carbon emission target in the industry. In addition, the technologies to produce fossil products are less and less attractive for investors unless the production is low carbon. Thus, the downstream sector needs to rethink how olefins will be produced in the future. Among the options to decarbonize the production of chemicals, a combination of olefins production with CO₂ utilization is an important topic for the next decades in the quest for the downstream industry transformation. This approach may even lead to a carbon-

negative technology for olefins production from the fossil feedstock.

The idea is to directly use the hydrogen produced as a by-product by the processes or benefit from the heat of the process with a low carbon/green H₂ co-feeding. This perspective requires the development of a new catalyst, which could selectively hydrogenate CO₂ in the presence of hydrocarbons. Metal sulfides are known for CO₂ hydrogenation to high-value products, such as methanol, dimethyl ether, CH₄, light alkenes, jet fuel, or CO. The MoS₂-based catalyst showed promising results in CO₂ methanation and methanol synthesis. For example, Hu et al.³ investigated the CO₂ transformation over MoS₂ at 50 atm, 300 °C; this system resulted in MeOH with 94.3% selectivity. Primo et al.⁴ applied oriented MoS₂ nanoplatelets at 10 atm at 300–600 °C for the CO₂ methanation with the 100% key product selectivity. ZnS was used for the direct non-oxidative dehydrogenation of ethane at 550 °C, showing only about 10% of conversion.⁵ The thermal stability of this materials was not sufficiently at higher temperatures, where ethane conversion could reach more significant level. Thus, up to now, there is not any report on the utilization of metal sulfides for ODH-CO₂ of ethane.

Catalytic behavior of sulfur-free gallium-containing systems in ethane dehydrogenation and CO₂-assisted oxidative ethane dehydrogenation was also studied.^{6,7} A significant influence of the nature of the substrate on the deactivation of Ga-containing catalysts in the ODH-CO₂ has been reported.⁸ The samples exhibited low tolerance to coke formation. Most of the studies of ethane dehydrogenation on Ga-containing materials demonstrated the selectivity to ethene >90% with the low amount of the aromatic fraction.⁹ Zeolites (HZSM-5,⁶ HSSZ-13⁹) and oxides (TiO₂,¹⁰ Al₂O₃^{11,12}) were used as carriers of the Ga-containing active phase. However, for CO₂-assisted reactions on these catalytic systems, only the results at low conversion

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were reported. The conversion was about 10% over Ga/TiO₂¹⁰ at 700 °C, and only 3.2% over FeGa@ZSM-5¹³ at 600 °C. The performance of unsupported Ga-containing materials is still seldom reported in the literature.

Alkali ternary thiogallates are one of the varieties of the unsupported Ga-containing materials. They exist in several structure types. The most known and the most well-studied is AGaS₂ (A=Na,¹⁴ Cs,¹⁵ Ag^{16–18}) family of materials. Several novel members in this family, Na₆Ga₂S₆¹⁹ and A₅GaS₄ (A=Li, Na),²⁰ were recently discovered.

A standard protocol for synthesizing the various ternary A_xGaS_y materials involves heating to 650–800 °C for several hours in the sealed quartz ampoule.^{14,20} A few studies report the low-temperature synthesis route to alkali-containing ternary thiogallates, which is more advantageous for industrialization. For instance, AgGaS₂¹⁸ was obtained at 300 °C under the N₂ atmosphere in the presence of oleates. The first solvothermal synthesis of AgGaS₂ was reported by J. Hu et al.¹⁷ Tetragonal crystals (a = 5.7538 Å, c = 10.3026 Å) with the size of 5–12 nm were prepared using ethylenediamine as solvent and template at the same time at 180–230 °C for 10 h. Nanoflowers with similar composition (AgGaS₂) and the tetragonal unit cell (I-42d space group, a=5.76 Å and c=10.3 Å) were described by Yuan et al.²¹ The nanocrystalline tetragonal phase (a = 5.523 Å, c = 11.141 Å) CuGaS₂ was also synthesized by a solvothermal approach by Lu et al.²² In contrast, the literature is silent about a solvothermal crystallization of AGaS₂ (A=K, Na, Cs) in monoclinic configuration. Up to now, the monoclinic structure of KGaS₂,^{23,24} NaGaS₂,¹⁴ CsGaS₂ as well as Cs₂Ga₂S₅²⁵ were obtained only by solid-state reaction at 600–900 °C.

The alkali thiogallates, e.g., AgGaS₂, are known for their photocatalytic activities.^{26,27} For instance, Lee and al. studied the photocatalytic activity of AgGaS₂ nanoparticles in H₂S splitting reaction to produce hydrogen.²⁶ The same group also reported the utilization of AgGaS₂-type photocatalyst for H₂ production from water.²⁸ Besides the photocatalytic activity, a distinctive feature of the alkali thiogallates is their exceptional thermal stability (800–900 °C) which is not very common for Ga-containing materials. Another advantage of these compounds is their potentially high coking resistance thanks to the sulfur present in the structure and their moderate hydrogenation activity. Hence, we considered these materials as potentially a promising catalytic system for the ethane ODH-CO₂ reaction.

For many metals, such as Mo and Fe, a transformation to the carbide phase occurs over 700 °C under a hydrocarbon environment.^{29,30} In contrast, gallium carbide would not be formed under these conditions, which is also one more reason to focus on the alkali thiogallates. The alkali ternary thiogallates will remain in their initial state while preventing the reduction of gallium to the individual metal. These systems as catalysts for ethane oxidative dehydrogenation with CO₂ have never been reported.

The present study reports the synthesis of monoclinic potassium ternary thiogallate (KGaS₂) and its application in ODH-CO₂ of ethane.

Experimental

Catalyst preparation

The crystals of KGaS₂ were obtained via a solvothermal synthesis using Ga₂O₃ (99.99%, 50 mesh powder, Alfa Aesar), Sulfur (≥ 99.5%, Sigma-Aldrich), and KNO₃ (≥ 99.0%, Sigma-Aldrich) as reagents. Ethylenediamine (EDA) (≥ 99.5%, Fluka Analytical) and 1-2-(aminoethyl) piperazine (AEP) (98%, Alfa Aesar) were used as the solvent and the template, respectively. The solids were loaded in a molar ratio Ga₂O₃/S/KNO₃=1/25.5/2.3, followed by the addition of template (EDA or AEP) to the mixture. The resulting mixture was stirred at room temperature for 30 min. Then the suspension was transferred to a stainless-steel autoclave with Teflon liner and kept at 190 °C for 1–7 days under static conditions. The solid was recovered by filtration, washed with ethanol, and, eventually, dried at 50 °C for 1 h in an air atmosphere.

Material characterization

The powder X-ray diffraction (PXRD) analysis of the samples was performed with a PANalytical X'Pert Pro diffractometer using Cu Kα radiation (λ = 1.5418 Å).

Measurements of nitrogen sorption isotherms at -196 °C were carried out on Micromeritics ASAP 2020 surface area analyzer. The pretreated samples in nitrogen were analyzed after degassing at 300 °C. The microporous volume (V_{mic}, cm³·g⁻¹) and the specific surface area (S_{ext}, m²·g⁻¹) was obtained by the t-plot method. The crystal size and the morphology were studied by a field-emission scanning electron microscope (SEM, MIRA-LMH TESCAN) equipped with an energy-dispersive X-ray spectroscopy (EDS) analyzer. The EDS analyses were obtained with SDD detector.

Ultraviolet-visible (UV-Vis) spectra of the samples were recorded with Cary 4000 spectrometer from Varian. The spectrum acquisition was done between 800–200 nm with a speed of 300 nm/min.

Catalyst evaluation

300 mg of a catalyst (fraction 100–400 μm) was loaded to a fixed bed downflow quartz reactor. Prior to the reaction, all the catalysts were dried in the reactor at 350 °C under N₂ flow for 2 hours. Afterward, the catalyst was heated up from room temperature to the reaction temperature under the reactants flow with a 10 °C/min ramp rate. The test was terminated by stopping the flow of the reactants, switching to N₂ flow, and cooling down the set-up to the room temperature under N₂ flow.

The reaction effluent was analyzed online with a gas chromatograph (Interscience Compact GC) equipped with two TCDs and one FID. A molecular sieve 5A, Rt-QBond, Rtx-1 columns were used to separate light gases mixtures (H₂, N₂, CO, CO₂), light hydrocarbons mixture (CH₄, C₂H₄, C₂H₆) and aromatic hydrocarbons (from benzene till naphthalene), respectively. In all the experiments, N₂ was used as the internal standard to calculate the conversion and to closure the material balance.

The tests were performed with a C₂H₆/CO₂/N₂=/49.5/36.5/14 (vol.%) mixture (C₂H₆/CO₂ – 1/0.74 v/v) in the temperature

range 700-800 °C, at atmospheric pressure, WHSV (C₂H₆) = 5.9 h⁻¹.

The conversion and selectivities were obtained as follows:

$$\text{Conversion}(a) = \frac{C_{\text{inlet}}(a) - C_{\text{outlet}}(a)}{C_{\text{inlet}}(a)} \cdot 100\% \quad (1)$$

$$\text{Carbon selectivity}(i) = \frac{F(i)}{\sum F(i)} \cdot 100\% \quad (2)$$

where $F(i)$ – mol of the C in the product compound

Results and discussion

Synthesis and characterization of the catalysts

In the presence of amines, the crystallization of gallium sulfides may occur in different pathways. The synthesis usually results in octahedral clusters, e.g., Na₅(Ga₄S)(GaS₄)₃·6H₂O,³¹ anionic layers, e.g. [Ga₄S₇(en)₂]³² with gallium atoms trigonal-pyramidally coordinated by Sulfur, or [GaS₂]⁻ layers, e.g., NaGaS₂.¹⁴ In this contribution, we focused on a solvothermal synthesis of thiogallates with ethylenediamine and 1-2-(aminoethyl)piperazine. In the absence of the potassium cation, the preparation resulted in the amorphous phase with the AEP template and the non-defined low crystalline phase of gallium sulfide with the EDA template (Fig.S1). Representative SEM images of obtained solids are shown in Fig. S2. The presence of inorganic cations, e.g., potassium, plays the role of a structural directing agent and drives the formation of a well-crystallized material (Fig.S1). The resulted thiogallate, synthesized with potassium and EDA, was determined as KGaS₂.

The powder X-ray diffraction (PXRD) patterns of the obtained product powders showed patterns similar to NaGaS₂ and to K_{0.56}Na_{0.44}GaS₂.¹⁴ The ICSD structure of KGaS₂ published in the Inorganic Crystal Structure Database (ICSD collection code 107928) refers to Delgado's study,³³ the object of which is the analysis of the compound TlGaSe₂. So, the assignment in the database was done for a compound of a different to KGaS₂ composition and remains questionable. To make a proper analysis of our PXRD patterns, the profile matching has been performed on the basis of two previously reported structural analysis of KGaS₂. A first structure solution of KGaS₂ using single crystal data resulted in the non-centrosymmetric space group Aa³⁴ (a=14.721(5) Å, b=10.425(3) Å, c=10.424(2) Å, γ=100.16 (2)°). By analogy with compounds TlGaSe₂ and NaGaS₂ compounds, a PXRD study proposes a new description in the centrosymmetric monoclinic space group C2/c (a=10.4136(2) Å, b=10.4143(2) Å, c=14.7866(2) Å, β = 100.165(2)°).²³ The result of the pattern matching analyses performed using Jana2006,³⁵ using these two references clearly indicates the purity and the quality of the different synthesized KGaS₂ samples (refined cell parameters: a=10.417(3) Å, b=10.399(3) Å, c=14.788(4) Å, β =100.129(3)°) (Fig. S3).

The synthesis of KGaS₂ with EDA crystals resulted in the crystals of 1-2 μm with a plate-like rectangular morphology (Fig.1a). The EDS analysis of the EDA-synthesized KGaS₂ crystals showed a uniform distribution of all the elements (Fig.2). According to the

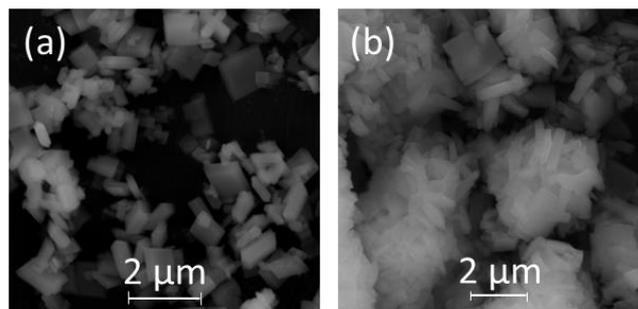


Fig.1 SEM images of KGaS₂ synthesized with EDA (a) and AEP (b).

EDS analysis, the molar ratio K:Ga:S was 1:1:1.9 (Fig.S4). The similar Ga/S ratio was reported in earlier studies for the alkali-containing thiogallates obtained by solid-state high-temperature synthesis.^{14,36}

The collected UV-Vis spectra of KGaS₂ were identical to the NaGaS₂ spectra reported by V. Klepov et al.¹⁴ (Fig. S5). The recorded spectrum showed a curve with the characteristic intense peak at 280 nm and the two weak peaks in the region of 330-470 nm. The specific surface area of the EDA-synthesized KGaS₂ determined by N₂ physisorption was 12 cm²g⁻¹, which is a typical value for the non-porous material with a size of about 1 μm.

The physicochemical analysis of solvothermally synthesized K-thiogallates confirmed that they are structurally identical to the KGaS₂ obtained by solid-state high-temperature synthesis.

Synthesis optimization

The influence of the sulfur content on the crystallization results was studied. The products obtained with the molar ratio Ga/S/K=1/5.7/2.3, still showed the presence of some amorphous phase. At the same time, an excess of the sulfur in the mixture (molar ratio Ga/S/K=1/25.5/2.3) resulted in a solid of much higher crystallinity (Fig.3).

The crystallization time was varied from 1 to 7 days. After 1 day (Fig. S6), the product already contained a crystalline phase. The SEM analysis showed the presence of a mixture of crystallites of 200-300 nm and of 1-3 μm (Fig. S7). With further prolongation of the crystallization time to 4 days, the nanosized crystals disappeared, and the particle size distribution has become uniform. The changes in the crystal size were also coupled with an increase in X-ray crystallinity.

Further extension of the synthesis time to 7 days did not result in any further changes in morphology and crystallinity.

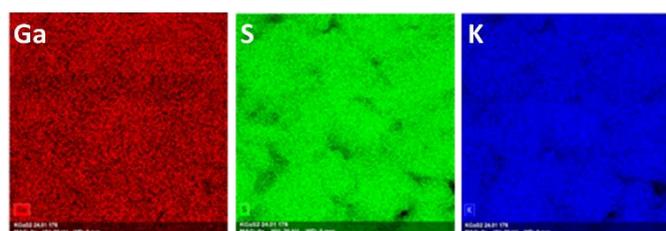


Fig.2 EDS elemental distribution in KGaS₂ (EDA, 4d, 190 °C).

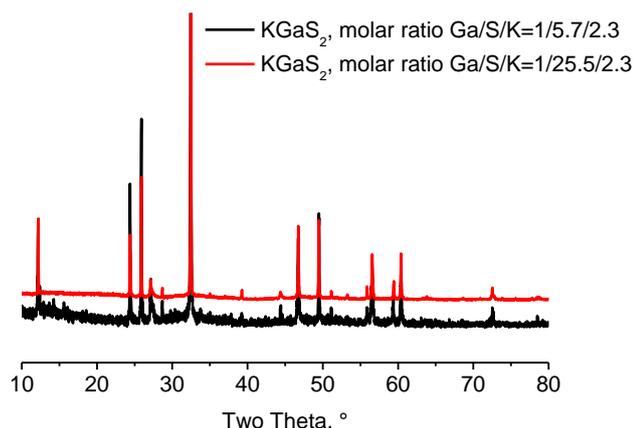


Fig.3 Powder XRD patterns of as-prepared KGaS_2 with two different Ga/S/K ratios (EDA, 7d, 190 °C).

The impact of ethanol and water on the formation of KGaS_2 was also investigated. Ethanol-water mixture was used as co-solvents in combination of the EDA template. The addition of ethanol led to a decrease in product crystallinity keeping the same crystallization time (Fig. S8 and S9). The SEM images revealed a significant presence of small nanoparticles with random morphology that are most probably amorphous (Fig.4). The obtained XRD patterns were similar to the simulated structure Shim et al.²³(Fig. S9).

Catalytic performances

KGaS_2 thermal stability

At 600 °C, the measured conversion of thiogallate-based materials in CO_2 hydrogenation and ethane transformation was very limited, in the range of 1-2% of conversion. A noticeable increase in catalytic activity was observed with the temperature rise to 700 °C or higher. The most relevant range for, the ODH- CO_2 tests of ethane was found between 700-800 °C. Before using the novel material in high temperature reaction, it was necessary to confirm its thermal stability. In order to do so, a sample for KGaS_2 was subjected to 800 °C for 1 hour in N_2 flow, which was the highest temperature set point used in the catalytic experiments. The XRD analysis confirmed the retention of crystallinity (Fig. S10) and that the treatment did not result in

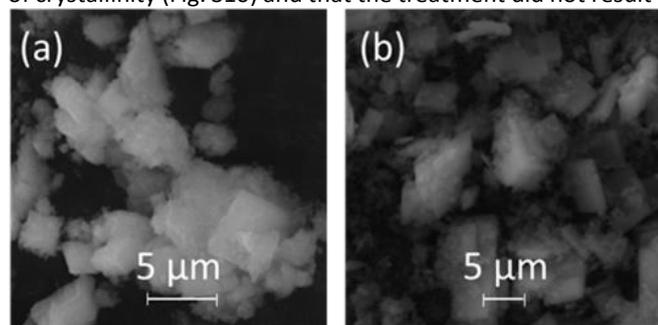


Fig.4 SEM micrographs of KGaS_2 prepared in (a) solvent system EDA-EtOH (2:1, volume ratio), and (b) EDA-EtOH- H_2O (2:1:1, volume ratio).

morphological changes (Fig. S11).

Blank test

In order to reveal the catalytic impact of the thiogallate-based materials on the reaction yield, a blank test without any catalyst was performed under the same operating conditions (same linear velocity, same temperature, same total and partial pressure of the reagents). In the blank test C2 (ethane), N_2 , and CO_2 were co-fed in the same ratio as in the catalytic reaction ($\text{C}_2\text{H}_6/\text{CO}_2/\text{N}_2=49.5/36.5/14$ v/v/v). The blank test without ag catalyst is referred to in the text as a thermal process (“C2 thermal”).

Performance in ODH- CO_2 of ethane

The presence of the thiogallate-based material in the reactor showed substantial difference in performances already at 700 °C (the lowest reaction temperature); the conversions of CO_2 increased from 2% to 22% (Fig. 5). Interestingly, the ethane conversion on thiogallate even exceeded the thermal value at 700 °C (Fig. 5). So, the material not only showed a substantial hydrogenation activity for CO_2 , but also were able to hydrogenate CO_2 without destroying ethylene yield from ethane. The activity of the catalyst was stable for the tested time-on-stream of 225 min (Fig.S12).

However, upon further increase of the temperature to 750 °C, the thiogallate-based materials also started partially hydrogenate ethylene. The CO_2 conversion increased but the rise was relatively modest. Thus, due to the hydrogenation back of ethylene to ethane, the apparent ethane conversion decreased by 8% compared to the thermal one (Fig. 5).

Further temperature increases to 800 °C, resulted in a significant growth of both CO_2 and ethane conversions in the presence of the catalyst (Fig. 5). Although the catalyst still showed some ethylene hydrogenation, the difference with the thermal process decreased in comparison the one observed at 750 °C. In contrast, the CO_2 conversion reached the level of 36% at 800 °C, which was 12% higher relative to the one at 750 °C and roughly 13% lower than the thermodynamic equilibrium conversion (Fig. S13). The ethane conversion at 800 °C reached almost 70% what was relatively close to the thermodynamic value (Fig. S13).

Thus, the thiogallate-based material shows about 36% of CO_2 hydrogenation at 800 °C with only a minor impact on the ethylene yield and selectivity relatively to the thermal process (Fig.6).

One can also see that at 700 °C, the ODH- CO_2 of ethane on the thiogallate-based material results in the almost equivalent conversion of ethane and CO_2 . That means that the produced hydrogen in ethane transformation to ethylene is almost fully utilized for CO_2 hydrogenating (Fig.5). In contrast, at 750 °C and 800 °C the conversion of CO_2 is roughly two times lower in comparison with the ethane conversion. This means that only half of the produced hydrogen was consumed for CO_2 hydrogenation.

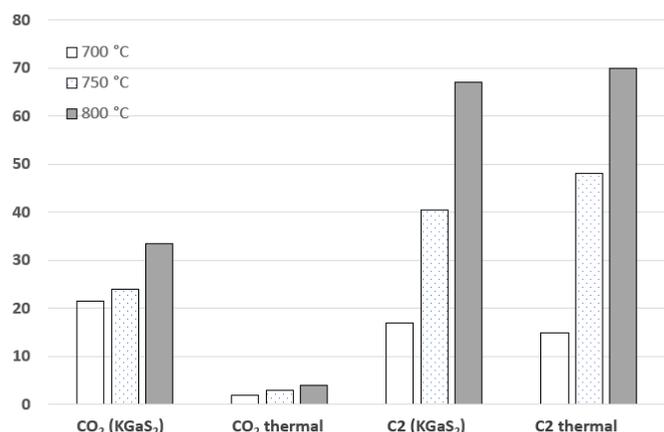


Fig. 5 Comparison of C₂H₆ and CO₂ conversions on KGaS₂-based catalysts with the thermal one (P = 1 atm, C₂H₆/CO₂ = 1/0.74, WHSV = 5.9 h⁻¹).

One can see that the presented thiogallate-based materials have demonstrated a promising CO₂ hydrogenation activity that is comparable with the reported in literature for gallium oxide-based samples.^{10,37}

The selectivity to the by-products (to heavies) on the alkali thiogallate catalyst is slightly higher than in the transformation without catalyst. The absolute values vary with the increase of the temperature due to a change in the predominant transformation pathways of ethylene but the impact on selectivity remains minor (Fig. 6).

Logically, the rise of the temperature from 700 to 800 °C resulted in higher methane production with the selectivity increase from 1 to 7%. However, the selectivities to methane remained comparable between the catalytic and the thermal processes.

One can see that the experimentally observed conversion level of ethane at 700 °C and 750 °C in both catalytic and non-catalytic tests remain at about 50% relative to the thermodynamic equilibrium conversion (Fig. S13). The latter shows only a limited impact of the catalyst on the ethane activation in the studied temperature range. The value

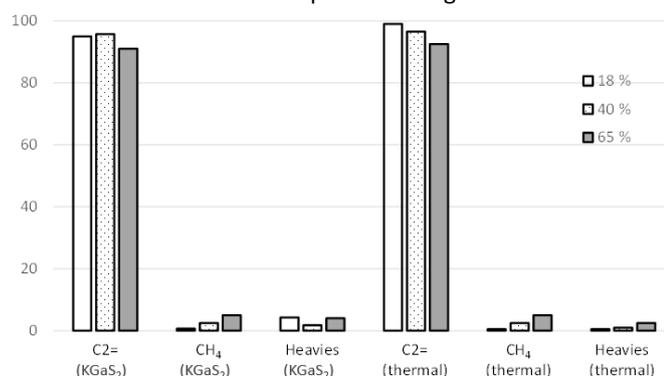


Fig. 6 Comparison of carbon molar selectivities on coke-free basis at the same conversion level of ethane (18%, 40%, 65%) for the thermal and the catalytic (over KGaS₂) routes (T = 700–800 °C, P = 1 atm, C₂H₆/CO₂ = 1/0.74, WHSV = 5.9 h⁻¹).

becomes much closer, almost reaching the thermodynamic level only at 800 °C.

In contrast, one can see that in the thermal non-catalytic process, the level of CO₂ conversion remains negligible, below 5% even at 800 °C. This value is more than order of magnitude lower relative to the equilibrium level of conversion. However, the introduction of the catalyst in the reactor allows achieving significantly higher conversion of CO₂, as high as 36% at 800 °C. This value is not that far from the thermolytic equilibrium conversion of CO₂ of about 49% at 800 °C (Fig. S13). So, the catalyst clearly contributes to CO₂ activation and in the utilization of the formed hydrogen from the thermal ethane transformation for CO₂ transformation to CO.

Interestingly, an estimation of the thermodynamic equilibrium in the system containing CO₂ and ethane, H₂, CO, H₂O, and ethylene showed that the preferred reaction should be the dry reforming of CO₂ with ethane to CO and hydrogen with only a very limited selectivity to ethylene (Fig. S14). This reaction is undesirable for the ethylene synthesis from ethane and is not taking place without a specific catalyst. In contrast, the current KGaS₂ material preferentially catalyzes CO₂ hydrogenation in presence of ethylene with the hydrogen produced in-situ from the thermal conversion of ethane and substantially without making any significant production of heavy hydrocarbons and of methane.

The analysis of the spent catalysts after the reaction showed no formation of any amorphous or any other phases. The XRD pattern of the aged sample remained identical to the parent material before loading (Fig. 7). One can see no modifications of crystal morphology as well as no indications of any agglomerations or crystallites decompositions (Fig. 7).

Considering that the material was synthesized according to a new method and hasn't ever been tested before in high temperature applications, the observation is important and shows a perspective in further optimization of the catalytic performances of the alkali thiogallates-type materials.

Conclusions

Crystalline alkali thiogallates were synthesized under solvothermal conditions, which represents a novel alternative route to obtain these materials. The physicochemical properties, including the thermal stability, of thiogallates were studied and revealed that they are sufficiently stable to be used as high-temperature heterogeneous catalysts. The KGaS₂-based material showed promising performance in the ODH-CO₂ of ethane process in the temperature range of 700–800 °C. The process showed close to thermodynamic conversion of ethane at 800 °C with a significant utilization of the produced hydrogen for CO₂ transformation to CO. The conversion of CO₂ to CO was at the level of 22–36%. The catalyst showed insignificant coke formation and allowed obtaining similar levels of the ethane conversion as for the thermal decomposition substantially

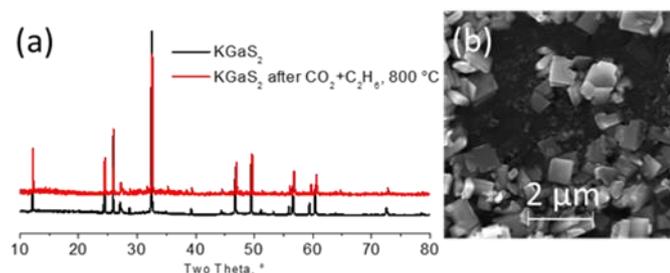


Fig. 7 (a) PXRD patterns of as-prepared KGaS₂ and after ODH-CO₂ test (800 °C, P = 1 atm, C₂H₆/CO₂ = 1/0.74, WHSV = 5.9 h⁻¹); (b) SEM images of KGaS₂ N₂-treated after ODH-CO₂ test (700 °C).

without making any additional production of by-products (heavy hydrocarbons, CH₄). The set of experimental results proves that the thiogallate catalysts could be of interest for the processes where a moderate hydrogenation function is required in the presence of CO and highly reactive hydrocarbons.

Author Contributions

Vera Bikbaeva: Investigation, methodology, and writing-original draft. Olivier Perez: Investigation. Nikolay Nesterenko: Conceptualization, supervision, writing-review and editing. Valentin Valtchev: Conceptualization, supervision, writing-review and editing.

Conflicts of interest

There are no conflicts to declare.

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