Chemical properties of intermetallic compounds

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Intermetallic compounds (IMCs) with their ordered crystal structure and well-defined chemical bonding open huge opportunities to be applied as catalysts for various chemical processes. Being of scarce knowledge, their chemical properties (e.g. oxidation behaviour) support the understanding of their catalytic properties, enrich our knowledge about active species and reaction mechanism as well as give ideas concerning the design of new and more efficient and economically favourable catalysts.

The direct epoxidation of ethylene using molecular oxygen and supported, promoted Ag catalyst is exploited worldwide for the production of ethylene oxide. Ethylene oxide (EO) is a thermodynamically unfavourable product compared to CO_2 and H_2O, making the selectivity (S) towards ethylene oxide the main target for the process. Since IMCs are useful model systems for understanding the catalysts' behaviour under reaction conditions, selected Ca-Ag compounds were studied under ethylene epoxidation conditions.

The binary compound $CaAg_2$ was successfully synthesized as single-phase (Fig. 1A) and exposed to ethylene epoxidation conditions [1].

The conversion of ethylene and selectivity towards ethylene oxide increase during the induction period and remain stable afterwards for several hundreds of hours (S = 60-65 %, conversion – 1.5-2.5 %, Fig. 2).

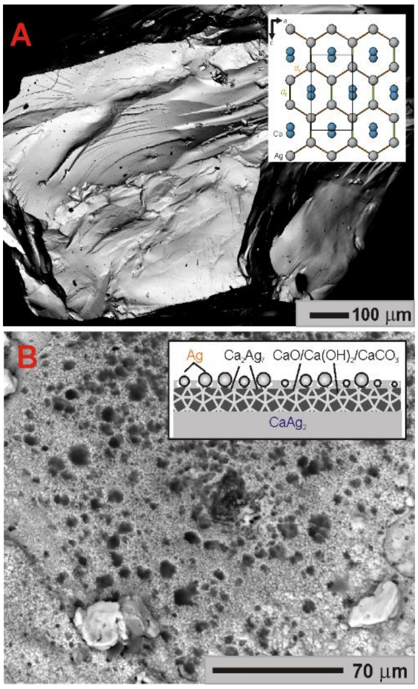


Fig.-1: Morphology of $CaAg_2$ particles: as-prepared (A) and after catalytic test (B). Insets: (A) projection of $CaAg_2$ crystal structure along [010]; (B) schematic representation of particle cross section after ethylene epoxidation test.

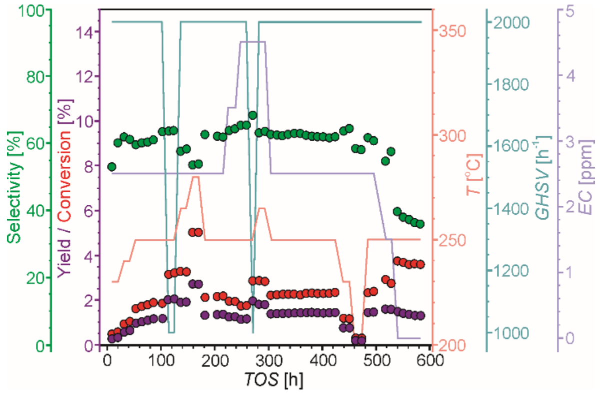
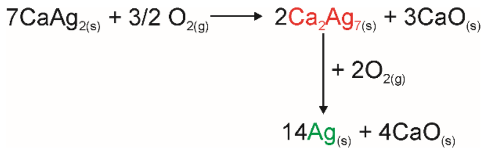


Fig.-2: Ethylene epoxidation on $CaAg_2$: conversion of ethylene (red), yield of EO (violet) and selectivity towards EO (green) as a function of time on stream (TOS).

The presence of more electronegative oxygen in the atmosphere (gas stream) and the high affinity of calcium to oxygen lead to the formation of calcium oxide and a significant segregation of silver towards the surface (PXRD and SEM, Fig. 1B). The oxidation of $CaAg_2$ can be described as:



$$7CaAg_{2(s)} + 3/2\ O_{2(g)} \longrightarrow 2Ca_2Ag_{7(s)} + 3CaO_{(s)} \xrightarrow{+\ 2O_{2(g)}} 14Ag_{(s)} + 4CaO_{(s)}$$

In addition, the presence of carbon dioxide and water vapour from the unwanted total combustion leads to a variety of possible Ca-related products of $CaAg_2$ oxidation, e.g. CaO, $Ca(OH)_2$ and $CaCO_3$.

The porous 3D microstructure of intermediates and Ca-containing oxidation products (Fig. 1B) is remarkably stable and prevents further sintering of the silver particles. The comparison of *in situ* formed Ag catalyst (using $CaAg_2$ as precursor) with a Ag@CaO catalyst (prepared using a classical impregnation method) reveals the unique catalytic behaviour of the Ag-based catalyst obtained during $CaAg_2$ oxidation.

For a better understanding of $CaAg_2$ oxidation behaviour, electronic structure calculations, real-space study of chemical bonding and surface energy calculations were performed (see report Wagner). The formation of covalently bonded puckered anionic silver layers perpendicular to [010] with calcium cations embedded in-between was revealed. Surface energy calculations (for low-index planes) show almost identical values for different terminations, implying the equivalent ability to cleave in all directions. In view of the epoxidation reaction, a number of fully relaxed oxygen adsorption configurations were considered, showing extremely large adsorption energies for all of them, providing a sizable driving force for the transformation of the intermetallic compound to silver and CaO. The corrosion process can proceed unhindered as the resulting structures are quite open and allow an easy access of the gas phase to the subsurface regions in order to oxidize deeper-lying calcium atoms, followed by expulsion of silver towards the surface. These results are in perfect agreement with experimental observations (Fig. 1B). Therefore, one may consider the intermetallic compound $CaAg_2$ under epoxidation conditions as a model precursor for Ag-based catalysts.

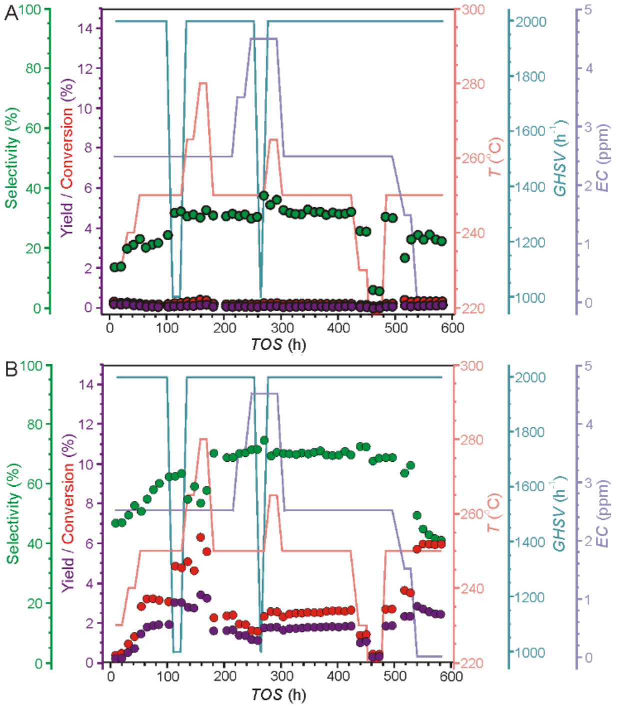


Fig.-3: Ethylene epoxidation on as-synthesized (A) and pre-treated in air (B) CaAg: conversion of ethylene (red circles), yield of EO (violet circles) and selectivity towards EO (green circles) as a function of time on stream (TOS).

Aiming to elucidate if the oxidation behaviour of Ca-Ag compounds under epoxidation conditions depends upon crystal structure and chemical bonding or whether it is mainly dictated by the high oxygen affinity of Ca, the equiatomic compound CaAg was also investigated under ethylene epoxidation conditions [2]. In this case, a different chemical behaviour under air and ethylene epoxidation conditions was observed. Therefore, the catalytic performance of as-prepared material was compared with the one after CaAg pre-oxidation in air (Fig. 3). Significantly enhanced selectivity values (~ 70 %) and improved conversion up to 5 % were observed for the sample after air pre-treatment. Under standard ethylene epoxidation conditions, CaAg remains stable for more than 600 h and the partial oxidation happens exclusively at damaged regions, whereas after sample exposure to air complete oxidation of bulk CaAg takes place (Fig. 4).

Surface energy calculations carried out for all possible terminations in low-index crystallographic directions find the (010)-c plane as the most stable one (Fig. 5). This result is in perfect agreement with the expectations based on the chemical bonding analysis (see report Wagner), the experimental SEM

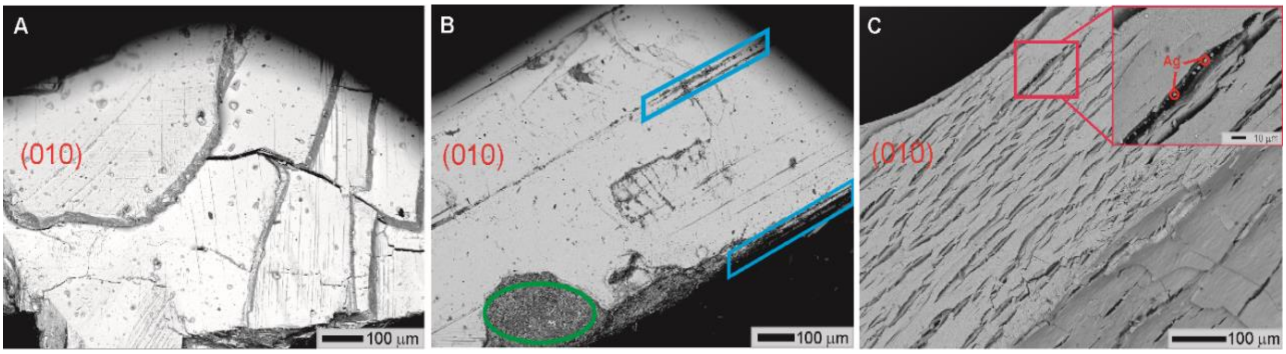


Fig.-4: CaAg particles:(A) as-synthesized, (B) after ethylene epoxidation experiment, and (C) after exposure to air followed by catalytic test. The preferential cleavage plane is (010). Steps (blue) and damaged regions (green) of CaAg undergo oxidation.

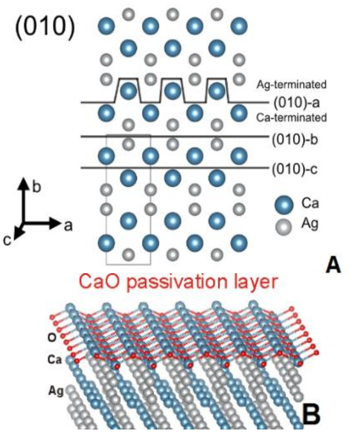


Fig.-5: (A) Possible terminations perpendicular to the [010] direction; (B) CaO@CaAg surface with protective properties.

observations of plate-like particles after grinding (Fig. 4) and EBSD analysis which identifies the cleavage plane as (010).

The stability of CaAg under reaction conditions leads to the assumption that an oxide layer with protective functionality forms on the surface of CaAg and hinders the further oxidation of bulk CaAg by oxygen present in the gas stream. To pursue this assumption, different scenarios of oxygen-covered (010) surfaces with respect to the absolute surface adsorption energies with increasing oxygen pressure have been considered. As result, the surface with protective properties CaO@CaAg possessing (010)-a termination (relating to the underlying pristine surface) was found. The path from the most stable pristine surface towards the most favourable oxidized CaO-overlayer variant requires the removal of one atomic layer of Ca and two atomic layers of Ag. The so-formed Ag particles may be the cause of the observed low catalytic activity (Fig. 3A). Furthermore, the CaO@CaAg surface does not appear to be a well-suited system for the ethylene epoxidation reaction due to the strong binding energies of the competing reaction product acetaldehyde as well as the combustion products.

On the one hand, CaAg possesses an outstanding stability during long-term ethylene epoxidation experiment (600 h) due to the formation of a highly ordered, stable and dense CaO passivation layer with a small amount of embedded Ag atoms on the (010) surface.

On the other hand, it oxidizes quickly during exposure to air forming $CaAg_2$, Ca_2Ag_7, Ag, and Ca-containing products (e.g. CaO, $Ca(OH)_2$, $CaCO_3$). Most probably, water vapour (in significantly higher amount in air compared to the ethylene epoxidation conditions) causes the reconstruction of a CaO-overlayer with the formation of hydroxyl groups. The latter leads to the oxidation of CaAg towards elemental silver.

Another pronounced example of correlation between electronic structure and the catalytic properties is addressed by applying unsupported intermetallic materials from the solid solution $Ga_{1-x}Sn_xPd_2$ ($0 \leq x \leq 1$) in the semi-hydrogenation of acetylene [3]. The semi-hydrogenation of acetylene is applied industrially to reduce the acetylene levels in the ethylene stream used for the production of polyethylene (80×10^6 t/a[8]) and ethylene oxide (15×10^6 t/a[9]) to a low ppm level. The ideal catalyst for this process has to be very active and at the same time possess an excellent selectivity. The latter is beneficially influenced by isolated active sites, which are offered by well-ordered, largely covalently bonded intermetallic compounds like Ga_7Pd_3, GaPd and $GaPd_2$ [4, 5]. Among these, $GaPd_2$ shows the best catalytic properties which is also displayed in its kinetic parameters [6, 7].

Replacing gallium by tin in $GaPd_2$ leads to disorder on the gallium site only, leaving the palladium atoms

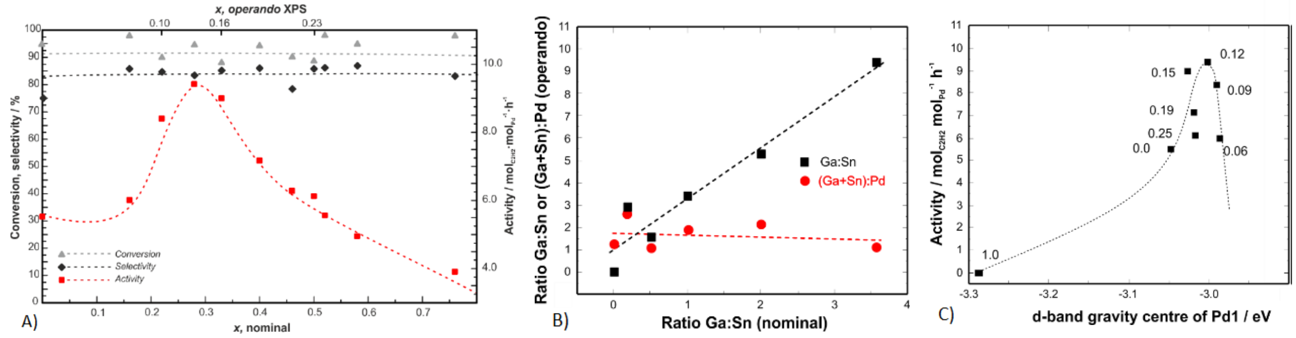


Fig.-6: (A) Catalytic properties of $Ga_{1-x}Sn_xPd_2$ in the semi-hydrogenation of acetylene; (B) Composition of $Ga_{1-x}Sn_xPd_2$ according to the results of operando XPS measurements. Ratios (Ga+Sn):Pd from XPS vs nominal (red) and Ga:Sn from XPS vs nominal (black) are shown. (C) Catalytic activity of $Ga_{1-x}Sn_xPd_2$ vs the position of the d-band centre of gravity for Pd1.

arranged as in the end-members of the substitutional series. With this, $Ga_{1-x}Sn_xPd_2$ falls within the active-site isolation concept, but at the same time the filling level of the electronic structure can finely be altered. Due to the merely marginal changes in the crystal structure, the whole series shows excellent selectivity to ethylene (~ 85%) comparable with the binary $GaPd_2$. Moreover, the incremental addition of one electron per formula unit reveals a maximum in the specific catalytic activity at the nominal composition $x = 0.28$ corresponding to 4.0 at. % tin in the near-surface region as revealed by *operando* XPS measurements (Fig. 6A).

Under *operando* conditions, the near-surface region in all samples is depleted of palladium and enriched in gallium in comparison to the nominal Ga:Sn ratio. Nevertheless, a linear correlation between the nominal and *operando* Ga:Sn ratio is observed (Fig. 6B). Plotting the specific activity of the materials against the centre of gravity of the *d*-band of the Pd1 atoms, a very sharp maximum was revealed (Fig. 6C). The same behaviour is observed for Pd2 with a maximum at -2.88 eV instead of -3.03 eV for Pd1. The correlation in the form of a volcano plot reveals an optimum of the electronic structure. These results reveal the strong influence of the electronic structure on the catalytic properties.

Due to the similarity of the electronic density of states of the ternary phase $Ga_{2+x+y}Sn_{4-x}Pd_9$ ($x = 0.72$, $y = 0.06$) to the DOS of the catalytically active binary compounds GaPd and $GaPd_2$, it was also investigated as a possible catalyst in the semi-hydrogenation of acetylene [8]. Being relatively selective to ethylene, $Ga_{2+x+y}Sn_{4-x}Pd_9$ does not show significant catalytic activity in the reaction of acetylene semi-hydrogenation in ethylene-rich streams. This catalytic behaviour can be understood applying the chemical bonding analysis. The electron localizability indicator reveals a system of heteroatomic electron-deficient two-centre Pd–Ga and Pd–Sn interactions, well in analogy to GaPd (see report Wagner). In contrast to the latter, the heteroatomic interactions are isotropically organized in the position space, which may prevent the systematic cleavage and formation of isolated active Pd sites on the surface. This leads to low catalytic performance.

Above-mentioned results reveal the importance of the crystal and electronic structures which determine the adsorption and, thus, the catalytic properties of a heterogeneous catalyst and are decisive for possible side reactions, the surface coverage with reactants as well as the (re)activity. Furthermore, the sufficient amount of information about the catalyst in its initial state helps to understand its behaviour (in case of stability) and/or changes (if the catalyst undergoes any chemical changes, e.g. oxidation) under reaction conditions.

Outlook

The chemical properties of intermetallic compounds link their structural and electronic nature with the catalytic performance for different types of chemical processes. In case of oxidative reactions, the chemical behaviour becomes even more complicated due to the dynamic change of the catalyst under reaction conditions. More detailed studies of the surface species as well as detailed microstructure analysis under different oxidative conditions will provide new insights into the catalytic performance of stable catalysts as well as *in situ* formed supported ones. Furthermore, the chemistry of Ag-based catalysts can be extended towards other *AE*-Ag (*AE* = Ba, Sr) systems as well as possible ternary Ag-based compounds.

External Cooperation Partners

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References

[1] *Chemical behaviour of $CaAg_2$ under ethylene epoxidation conditions, I. Antonyshyn, O. Sichevych, K. Rasim, A. Ormeci, U. Burkhardt, S. Titlbach, S. A. Schunk, M. Armbrüster and Y. Grin, Eur. J. Inorg. Chem.* ***35*** *(2018) 3933, DOI: 10.1002/ejic.201800710.*

[2] *Anisotropic reactivity of CaAg under ethylene epoxidation conditions, I. Antonyshyn, O. Sichevych, K. Rasim, A. Ormeci, U. Burkhardt, S. Titlbach, S. A. Schunk, M. Armbrüster and Yu. Grin, Inorg. Chem.* ***57*** *(2018) 10821, DOI 10.1021/acs.inorgchem.8b01449.*

[3] *Revealing electronic influences in the semi-hydrogenation of acetylene, O. Matselko, R. R. Zimmermann, A. Ormeci, U. Burkhardt, R. Gladyshevskii and M. Armbrüster, J. Phys. Chem. C* ***122****(38) (2018) 21891.*

[4] *Pd-Ga intermetallic compounds as highly selective semi-hydrogenation catalysts, M. Armbrüster, K. Kovnir, M. Behrens, D. Teschner, Y. Grin and R. Schlögl, J. Am. Chem. Soc.* ***132*** *(2010) 12745.*

[5] *Atomic interactions in the intermetallic catalyst GaPd, Yu. Grin, M. Armbrüster, A. I. Baranov, K. Finzel, M. Kohout, A. Ormeci and F. R. Wagner, Molec. Phys.* ***114*** *(2016) 1250.*

[6] *Synthesis and catalytic properties of nanoparticulate intermetallic Ga-Pd compounds, M. Armbrüster,*

G. Wowsnick, M. Friedrich, M. Heggen and R. Cardoso-Gil, J. Am. Chem. Soc. ***133*** *(2011) 9112.*

[7] *Kinetic parameters for the selective hydrogenation of acetylene on* $GaPd_2$ *and GaPd, R. R. Zimmermann, T. Hahn, W. Reschetilowski and M. Armbrüster, ChemPhysChem* ***18*** *(2017) 2517.*

[8] *The first ternary phase in the Ga-Sn-Pd system: synthesis, crystal structure, and catalytic properties of* $Ga_{2+x+y}Sn_{4--}Pd_9$*, O. Matselko, U. Burkhardt, Y. Prots, R. R. Zimmermann, M. Armbrüster, R. Gladyshevskii and Y. Grin, Eur. J. Inorg. Chem.* ***29*** *(2017) 3542.*

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