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STUDY OF STRUCTURE-PROPERTY RELATIONSHIP IN THE VERSATILE COPPER MOLYBDATE

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Smart materials have properties that can be affected in a controlled manner by external stimuli. For instance, they can respond to light, temperature, pressure, pH, electric and magnetic fields. Due to their pronounced functional properties, smart materials find applications in various technologies including coatings for glasses and windows, security markers, sensors to control environmental conditions, etc. Molybdates and tungstates with a general chemical formula ABO_4 ($A = Co, Ni, Cu, Zn$, etc. and $B = Mo, W$) belong to a wide class of functional materials with interesting and potentially useful properties. Among them, copper molybdate ($CuMoO_4$) and its solid solutions are some of the most fascinating multi-

functional materials that exhibit thermochromic (temperature-induced colour change) [1], piezochromic (pressure-induced colour change) [2], halochromic (pH-induced changes in colour) [3], thermosalient [4], catalytic [5] and antibacterial [6] properties (Fig. 1). The physical properties of $CuMoO_4$ depend on temperature and/or pressure and can be also affected by modifying its chemical composition and morphology. In particular, considerable attention has been paid in the past to colour-related properties of $CuMoO_4$ in the context of sensing applications. Possible chromic applications of $CuMoO_4$ -based materials extend from user-friendly temperature

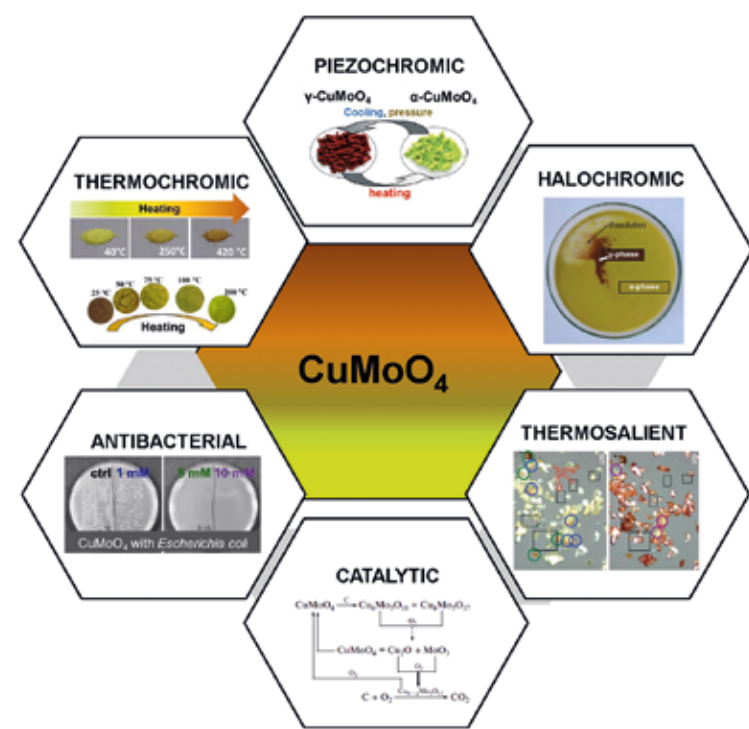


Fig. 1
A schematic representation of $CuMoO_4$ functional properties reported in literature: thermochromic (adapted from [1]), piezochromic (adapted from [2]), halochromic (adapted from [3]), thermosalient (adapted from [4]), catalytic [adapted from [5] and antibacterial (adapted from [6])

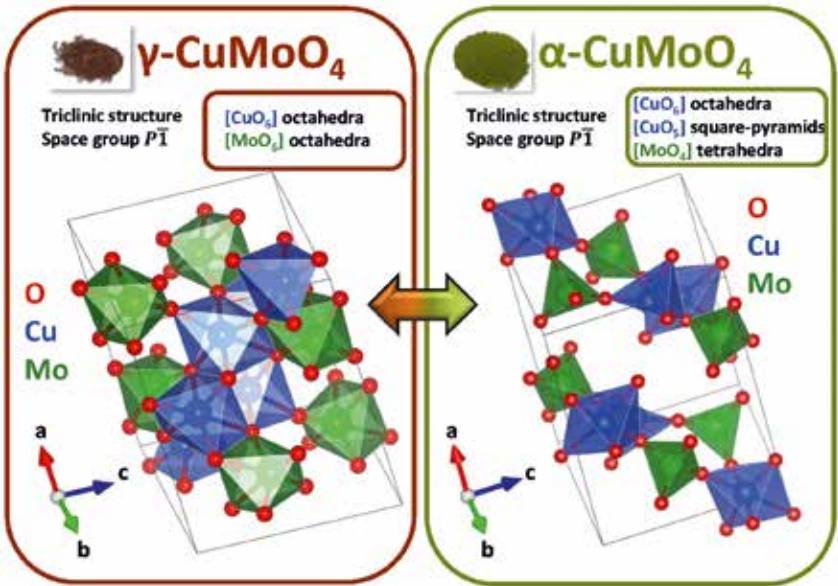


Fig. 2
The unit cell of the low-temperature γ -phase and high-temperature α -phase of $CuMoO_4$. The polyhedra forming the structure are indicated. Photographs of corresponding powder samples are also shown

and pressure indicators to cost-effective “smart” inorganic pigments, light filters and sensors [2, 3, 7–9]. Pure $CuMoO_4$ possesses thermochromic properties both at low (100–300 K) and high (400–700 K) temperature ranges but the origin of the colour change is different. At low temperatures, $CuMoO_4$ exhibits a reversible structural phase transition between α and γ phases with a hysteretic behaviour, which is accompanied by a drastic colour change between greenish and brownish (Fig. 2). At high temperatures, the molybdate also changes its colour from greenish to brown, but no phase transition is observed. The thermochromic properties of $CuMoO_4$ and related materials are closely connected to the local atomic structure of the constituting metal ions. Therefore, the knowledge of their structure is crucial for understanding and optimising their properties, which ultimately determines their practical applications. X-ray absorption spectroscopy (XAS) is a powerful technique providing valuable information on the local atomic and electronic structure as well as the local lattice dynamics in the material of interest. When combined with a bright synchrotron radiation source, it becomes an ideal tool for studying crystalline and disordered solids, liquids, and gases [10, 11]. In complex materials, XAS allows one to ex-

plore the local environment around particular chemical elements at both high and low concentrations. Furthermore, materials can be studied by XAS at different environmental conditions, i.e. different temperatures, pressures, electric and magnetic fields [10]. Operando and time-dependent XAS experiments are also possible [11]. The structural information in XAS spectra is encoded in tiny fluctuations of the X-ray absorption coefficient, known as the extended X-ray absorption fine structure (EXAFS). The interpretation of the experimental EXAFS spectra is based on the multiple-scattering theory [12] and might be challenging [13], especially for low-symmetry materials as tungstates and molybdates. This analysis often involves high-performance computing due to the huge amount of computations that must be performed. Further, we summarise the main findings of the systematic study of $CuMoO_4$ that allowed us to elucidate its structure-chromic property relationship. First, we describe the phase transition below room temperature. Then the possibility to affect the phase transition temperature by chemical doping is discussed. Finally, the evolution of the structure upon heating above room temperature up to 973 K is analysed. Both high (α) and low (γ) temperature phases of $CuMoO_4$ have a complex triclinic structure.

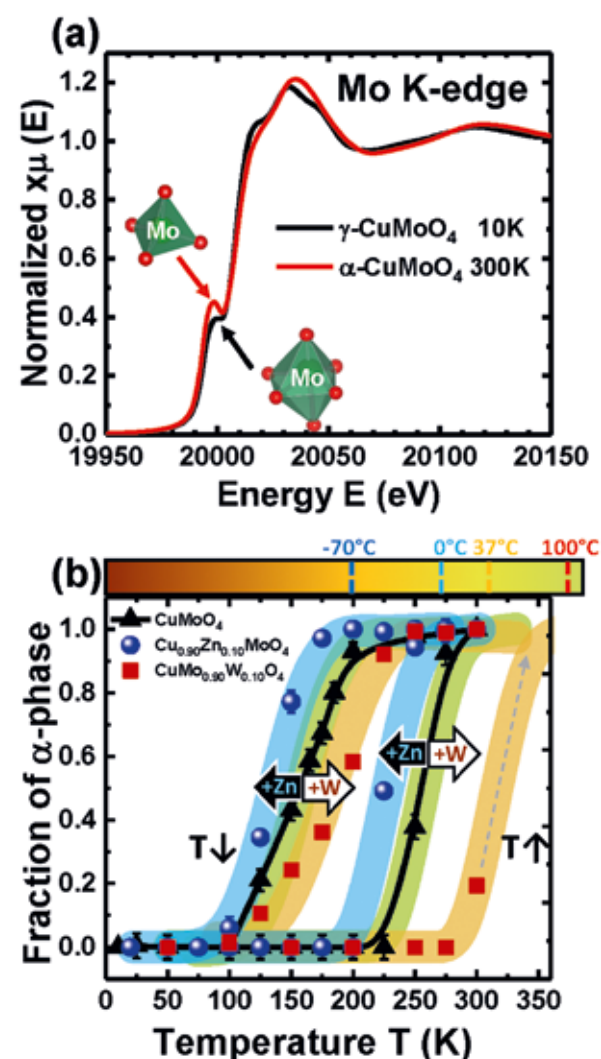


Fig. 3
(a) The Mo K-edge X-ray absorption spectra of α -CuMoO₄ and γ -CuMoO₄ with tetrahedral and octahedral coordination of molybdenum atoms, respectively. (b) The fraction of α -phase as a function of temperature for CuMoO₄, Cu_{0.90}W_{0.10}O₄ and Cu_{0.90}Zn_{0.10}MoO₄. The hysteresis loops of the α -to- γ phase transition are highlighted. The hysteresis shift to higher or lower temperatures for solid solutions is indicated with arrows. The gradual colour change between greenish and brownish is illustrated on the top of the graph

is built up of distorted CuO₆ octahedra, CuO₅ square pyramids and MoO₄ tetrahedra, while γ -phase consists of distorted CuO₆ octahedra and MoO₆ octahedra. The unit cells of both structural phases are illustrated in Figure 2.

Temperature-dependent XAS study of pure CuMoO₄ in the low-temperature range (10–300 K) [14, 15] revealed changes in the local structure around metal atoms during the structural phase transition between α and γ phases. The Mo K-edge X-ray absorp-

tion spectra are strongly sensitive to the coordination of molybdenum atoms (Fig. 3 (a)). The analysis of the experimental data allowed us to reconstruct the hysteresis of the α -to- γ phase transition in CuMoO₄ (Fig. 3 (b)). Molybdenum atoms change their coordination from tetrahedral (in α -phase) to octahedral (in γ -phase) at ~143 K upon cooling and back to the tetrahedral environment when heated above ~255 K. We found that, in the low-temperature range, static changes of the local environment around Mo atoms are responsible for chromic properties, while the influence of thermal effects is weak.

While the α -to- γ phase transition in CuMoO₄ is well pronounced, the temperature range of its hysteresis is potentially interesting only for the limited number of practical applications. Fortunately, the properties of pure copper molybdate can be adjusted, for instance, by chemical doping [7]. Close ionic radii of Mo⁶⁺ and W⁶⁺ ions [16] facilitate the formation of CuMo_{1-x}W_xO₄ solid solutions. It is also possible to substitute Cu²⁺ ions with other divalent ions, for instance, Zn²⁺, Co²⁺ and Mg²⁺.

Composition-dependent XAS experiments were performed to study the influence of W⁶⁺ and Zn²⁺ ions on the thermochromic properties of polycrystalline CuMo_{1-x}W_xO₄ and Cu_{1-x}Zn_xMoO₄ solid solutions in [17, 18]. We observed that the addition of 10 mol% of tungsten to CuMoO₄ promotes local distortions and stabilises the low-temperature γ -phase, leading to an increase of the phase transition temperature by ~50–100 K (Fig. 3 (b)). As a result, the α -to- γ phase transition takes place at ~190 K while γ -to- α phase transition occurs at ~340 K. It should be noted that it is also possible to stabilise the γ -phase of CuMo_{1-x}W_xO₄ with a low tungsten content ($x < 0.15$) at ambient conditions by cryogenic quenching (for example, treatment with liquid nitrogen) [1]. The possibility to obtain a material that changes its colour, for instance, close to the water boiling point may find applications in daily life.

The role of tungsten ions on the structure and thermochromic properties of CuMoO₄ was studied in detail by multi-edge (W L₃-edge and Cu/Mo K-edges) X-ray absorption spectroscopy [15] and resonant X-ray emission spectroscopy (RXES) [19]. It was demonstrated that the analysis of the RXES plane provides valuable information on the coordination of

tungsten atoms in the material due to the high energy resolution of the method. It was found that tungsten ions in CuMo_{1-x}W_xO₄ solid solutions have always octahedral coordination in samples with $x > 0.15$. At the same time, for $x < 0.15$, tungsten ions co-exist in the octahedral and tetrahedral environment at room temperature but their coordination changes to octahedral upon cooling. Preference of tungsten ions to form the octahedral environment, as compared to molybdenum ions, was evident. A change in the tungsten coordination from tetrahedral to octahedral affects the optical properties of the material. The band gap is smaller (and material is darker) in the case of octahedral coordination of tungsten, i.e. at higher tungsten content or lower temperature.

The substitution of Cu²⁺ ions by Zn²⁺ ions [18], in turn, stabilises the α -phase, which is natural for α -ZnMoO₄. The substitution modifies the electronic structure of the Cu_{1-x}Zn_xMoO₄ solid solutions due to the first-order Jahn-Teller effect for Cu²⁺(3d⁹) ions and its absence for Zn²⁺(3d¹⁰) ions. In Cu_{0.90}Zn_{0.10}MoO₄, the α -to- γ phase transition takes place at ~134 K and γ -to- α phase transition at ~226 K. Note that only α -phase exists at room temperature, thus once the material reaches room temperature it becomes greenish, and it must be cooled down significantly (below ~200 K) to change its phase and colour. Such a material with an irreversible colour change in a certain temperature range could serve as a time-temperature indicator, warning if at some point in time the temperature has exceeded the limit.

In the low-temperature range, the considerable optical contrast between the two polymorphic phases and the possibility to tune the thermochromic properties of CuMoO₄ to a more desired and accessible temperature ranges by doping may be the key for the material to serve as a robust indicator for monitoring storage or processing conditions of temperature-sensitive products (food, drugs, vaccines, chemicals, biological materials, etc.). At the same time, such inorganic materials with a thermochromism at high temperatures (above 400 K) attract much attention because of their potential applications for temperature sensing in the ranges where the majority of commonly used thermochromic organic compounds and liquid crystals are unstable.

In the high-temperature range (above room temperature), in contrast to low temperatures, the heating has a stronger effect on the local environment of copper atoms than molybdenum atoms, while the colour also changes from greenish to brownish. The evolution of α -CuMoO₄ structure upon heating was investigated by analysing the Cu and Mo K-edges X-ray absorption spectra using the reverse Monte-Carlo method with an evolutionary algorithm approach (RMC/EA) [20]. This approach made it possible to obtain three-dimensional models of the structure, including the effects of the thermal disorder. We found [21] that the local environment of copper atoms is more susceptible to thermal disorder than the environment of molybdenum atoms. The heating decreases the correlation in the motion between copper and nearest axial oxygen atoms in CuO₆ octahedra, whereas MoO₄ tetrahedra behave as rigid structural units. This dynamic effect is, apparently, the main reason for the temperature-induced changes in the O²⁻→Cu²⁺ charge transfer processes and, thus, underlies the thermochromic properties of α -CuMoO₄ when heated above room temperature.

To summarise, the impact of the local atomic structure and lattice dynamics on the thermochromic properties of copper molybdate and its solid solutions was studied using synchrotron-based X-ray absorption spectroscopy. The thermochromic effect below room temperature is caused by the α -to- γ structural phase transition whereas above room temperature the α -phase remains unchanged but thermal disorder plays an important role. The control of the α -to- γ phase transition temperature was achieved by chemical doping and the formation of CuMo_{1-x}W_xO₄ and Cu_{1-x}Zn_xMoO₄ solid solutions. Hysteretic type of the transition together with its tunability could be useful for an application of the material as a cheap and robust indicator for monitoring storage or processing conditions of temperature-sensitive products, however, in the future, more knowledge about the cyclability and the possibilities of achieving higher temperature resolution will be required. CuMoO₄ has surprised the scientific community with its versatile properties, and we believe that one day it will find its place in some smart systems for daily applications.

REFERENCES

- Joseph N., Varghese J., Teirikangas M., Jantunen H. A temperature-responsive copper molybdate polymorph mixture near to water boiling point by a simple cryogenic quenching route. *ACS Appl. Mater. Interfaces*, 2020, Vol. 12, pp. 1046–1053.
- Gaudon M., Deniard P., Demourgues A., Thiry A. E., Carbonera C., Le Nestour A., Létard J.-F., Jobic S. Unprecedented “one-finger-push”-induced phase transition with a drastic color change in an inorganic material. *Adv. Mater.*, 2007, Vol. 19, pp. 3517–3519.
- Gaudon M., Riml C., Turpain A., Labrugère C., Delville M. H. Investigation of the chromic phase transition of CuMo_{0.9}W_{0.1}O₄ induced by surface protonation. *Chem. Mater.*, 2010, Vol. 22, pp. 5905–5911.
- Robertson L., Penin N., Blanco-Gutierrez V., Sheptyakov D., Demourgues A., Gaudon M. CuMo_{0.9}W_{0.1}O₄ phase transition with thermochromic, piezochromic, and thermosalient effects. *J. Mater. Chem. C*, 2015, Vol. 3, pp. 2918–2924.
- Chigrin P. G., Lebukhova N. V., Ustinov A. Y. Structural transformations of CuMoO₄ in the catalytic oxidation of carbon. *Kinet. Catal.*, 2013, Vol. 54, pp. 76–80.
- Tanasic D., Rathner A., Kollender J. P., Rathner P., Müller N., Zelenka K. C., Hassel A. W., Mardare C. C. Silver-, calcium-, and copper molybdate compounds: preparation, antibacterial activity, and mechanisms. *Bioinorganic*, 2017, Vol. 12, 05G607.
- Gaudon M., Carbonera C., Thiry A. E., Demourgues A., Deniard P., Payen C., Létard J.-F., Jobic S. Adaptable thermochromism in the CuMo_{1-x}W_xO₄ Series (0 ≤ x < 0.1): a behavior related to a first-order phase transition with a transition temperature depending on x. *Inorg. Chem.*, 2007, Vol. 46, pp. 10200–10207.
- Thiry A.-E., Gaudon M., Payen C., Daro N., Létard J.-F., Gorsse S., Deniard P., Rocquefelte X., Demourgues A., Whangbo M.-H., Jobic S. On the cyclability of the thermochromism in CuMoO₄ and its tungsten derivatives CuMo_{1-x}W_xO₄ (x < 0.12). *Chem. Mater.*, 2008, Vol. 20, 2075.
- Yanase I., Mizuno T., Kobayashi H. Structural phase transition and thermochromic behavior of synthesized W-substituted CuMoO₄. *Ceram. Int.*, 2013, Vol. 39, pp. 2059–2064.
- Van Oversteeg C. H. M., Doan H. Q., de Groot F. M. F., Cuk T. In situ X-ray absorption spectroscopy of transition metal based water oxidation catalysts. *Chem. Soc. Rev.*, 2017, Vol. 46, pp. 102–125.
- Mino L., Borfecchia E., Segura-Ruiz J., Giannini C., Martinez-Criado G., Lamberti C. Materials characterization by synchrotron X-ray microprobes and nanoprobe. *Rev. Mod. Phys.*, 2018, Vol. 90, 025007.
- Rehr J. J., Albers R. C. Theoretical approaches to X-ray absorption fine structure. *Rev. Mod. Phys.*, 2000, Vol. 72, pp. 621–654.
- Kuzmin A., Timoshenko J., Kalinko A., Jonane I., Anspoks A. Treatment of disorder effects in X-ray absorption spectra beyond the conventional approach. *Rad. Phys. Chem.*, 2020, Vol. 175, 108112.
- Jonane I., Cintins A., Kalinko A., Chernikov R., Kuzmin A. X-ray absorption near edge spectroscopy of thermochromic phase transition in CuMoO₄. *Low Temp. Phys.*, 2018, Vol. 44, pp. 568–572.
- Jonane I., Cintins A., Kalinko A., Chernikov R., Kuzmin A. Probing the thermochromic phase transition in CuMoO₄ by EXAFS spectroscopy. *Phys. Status Solidi B*, 2018, Vol. 255, 1800074.
- Shannon R. D. Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Cryst.*, 1976, Vol. A32, pp. 751–767.
- Jonane I., Cintins A., Kalinko A., Chernikov R., Kuzmin A. Low temperature X-ray absorption spectroscopy study of CuMoO₄ and CuMo_{0.9}W_{0.1}O₄ using reverse Monte-Carlo method. *Rad. Phys. Chem.*, 2020, Vol. 175, 108112.
- Pudza I., Anspoks A., Cintins A., Kalinko A., Welter E., Kuzmin A. The influence of Zn²⁺ ions on the local structure and thermochromic properties of Cu_{1-x}Zn_xMoO₄ solid solutions. *Mater. Today Commun.*, 2021, Vol. 28, 102607.
- Pudza I., Kalinko A., Cintins A., Kuzmin A. Study of the thermochromic phase transition in CuMo_{1-x}W_xO₄ solid solutions at the W L₃-edge by resonant X-ray emission spectroscopy. *Acta Mater.*, 2021, Vol. 205, 116581.
- Timoshenko J., Kuzmin A., Purans J. EXAFS study of hydrogen intercalation into ReO₃ using the evolutionary algorithm. *J. Phys. Condens. Matter.*, 2014, Vol. 26, 055401.
- Jonane I., Anspoks A., Aquilanti G., Kuzmin A. High-temperature X-ray absorption spectroscopy study of thermochromic copper molybdate. *Acta Mater.*, 2019, Vol. 179, pp. 26–35.

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COBALT-CATALYSED C-H BOND FUNCTIONALISATION OF AMINO ACID AND AMINO ALCOHOL DERIVATIVES

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Chemistry is a science of molecules and transformations between them. Some reactions proceed in a blink of an eye, whereas sometimes a reaction rate may vary from one week to ten years. To increase the reaction rate, scientists have developed different rate-increasing chemical compounds – catalysts. The main advantage of using catalysts is that they are not consumed during the reaction and remain unchanged after its completion. This property allows one catalyst molecule to deliver one molecule of the desired product from one molecule of the starting material and then take the second molecule, the third one, and so on, continuing the catalytic cycle until all of the starting material molecules are consumed. As a result, a very small amount of catalyst is required for the reaction to proceed fast and productively.

The term ‘Carbon-Hydrogen (C-H) bond functionalisation’ is often used in the field of organic chemistry to describe a chemical transformation where the carbon-hydrogen bond presented in the molecule is broken to be replaced with another one: carbon-carbon (C-C), carbon-nitrogen (C-N) bonds etc. [1]. In contrast to the classical organic chemistry methodology, C-H bond functionalisation approach allows one to skip long-reaction sequences and obtain the desired product in a considerably faster and cheaper manner (Fig. 1). This approach to synthesise molecules is a relatively new addition to the field of the organic synthe-

sis and nowadays is used both in academia and industry to construct highly valuable products.

Unfortunately, these kinds of transformations may not always be performed due to low reactivity of C-H bonds. To overcome this problem, chemists have invented a new approach towards C-H bond functionalisation reactions, employing metal catalysts. Ruthenium (Ru), rhodium (Rh), or palladium (Pd) are proven to be very efficient at accelerating these types of reactions, making them to be the most used catalysts in the industry. On the other hand, these noble metals sometimes may be toxic and their abundance in Earth's crust is very limited, which makes them very expensive [2]. As a solution to this, the development of methods employing less toxic and more earth-abundant metal catalysts such as nickel (Ni), copper (Cu), or cobalt (Co) is of great desire.

Cobalt is an earth-abundant and non-toxic element with the symbol Co and atomic number 27. It plays an essential role in mammal biological processes in the form of cobalamin (vitamin B12) [3]. Historically, the first organic chemist who used cobalt as a catalyst in the C-H bond functionalisation reaction was Murahashi in 1955 [4]. Since then, over 60 years of study turned this transition metal into one of the most promising catalyst for C-H bond functionalisation reactions.

Our research is dedicated to the development of new methodologies for the amino acid and amino alcohol C-H bond functionalisation, employing Co as a reaction catalyst. Amino acids are a great subject of our research for multiple reasons. First, a large variety of natural amino acids can be easily isolated from natural products, which makes them a relatively cheap starting material that can be transformed into more valuable products. Second, a considerable portion of drug molecules used in pharmaceutical industry contain one or more amino acid fragments; thus a development of novel methodologies where unnatural amino acids can be easily obtained, may potentially

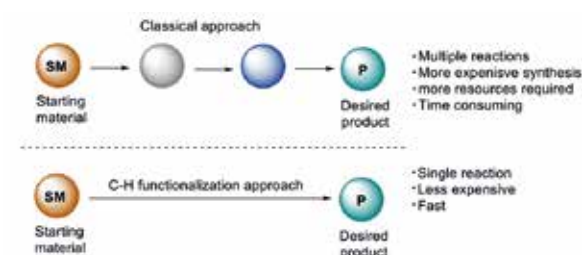


Fig. 1
C-H functionalisation vs classical approach