# Facile synthesis of polyoxometalate-intercalated layered double hydroxide as efficient catalyst for benzyl alcohol oxidation

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Selective alcohol oxidation is a fundamental transformation in organic chemistry, facilitating the production of carbonyl compounds that act as essential intermediates in a myriad of chemical syntheses. In particular, aerobic oxidation of benzyl alcohol (BA) to benzaldehyde is highly valuable for applications within the chemical industry, pharmaceutical chemistry, and the synthesis of functional polymers. However, despite the availability of conventional oxidation methodologies, attaining high selectivity and yield for benzaldehyde remains a significant challenge. Polyoxometalates (POMs), a widely used inorganic anionic transition metal oxides, have demonstrated considerable potential as catalysts for BA oxidation. Nonetheless, their practical application is often restricted by issues, including low surface area and poor recyclability. To overcome these obstacles, immobilizing POMs onto layered double hydroxides (LDHs)-which possess modular architectures that enhance catalytic activity and selectivity-has emerged as a promising approach. Here, we present a novel "one-pot" anion-exchange technique to incorporate the [P<sub>2</sub>W<sub>17</sub>ZnO<sub>61</sub>]<sup>8-</sup> cluster into tris(hydroxymethyl)aminomethane modified LDHs (Tris-LDHs). The synthesized material, Tris-LDHs-P<sub>2</sub>W<sub>17</sub>Zn, achieved complete conversion of BA with a selectivity of 92.46% for benzaldehyde using  $H_2O_2$  as the oxidant, thereby offering a practical solution for selective oxidation of BA.

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## 1. Introduction

The selective oxidation of alcohols remains a fundamental transformation in chemical industry, underpinning both industrial applications and academic research due to the pivotal role of carbonyl compounds as intermediates in diverse chemical syntheses.<sup>[1]</sup> Among these oxidation

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processes, the aerobic conversion of benzyl alcohol (BA) to benzaldehyde is particularly significant, serving essential functions in chemical industry, pharmaceutical chemistry, and the production of functional polymers, etc.<sup>[2, 3]</sup> Nevertheless, despite the availability of traditional oxidation methodologies, achieving high selectivity and yield for benzaldehyde continues to pose substantial challenges. This highlights the critical need for development of efficient catalysts tailored for selective oxidation of BA.

In recent years, a diverse array of catalysts has been explored for the aerobic oxidation of BA to benzaldehyde.<sup>[1]</sup> Polyoxometalates (POMs), a versatile style of inorganic anion transition metal oxides at the nanoscale, have garnered considerable attention owing to their structural adaptability, robust redox properties, and compositional versatility.<sup>[4]</sup> Although POMs exhibit strong catalytic activity in BA oxidation,<sup>[2, 3, 5, 6]</sup> their practical application is often constrained by limitations such as low surface area and poor recyclability, primarily due to high solubility in solvents. To address these challenges, immobilizing POMs on high-surface-area supports has emerged as a promising strategy to enhance catalytic efficiency, facilitate recovery, and enable recyclability.

Layered double hydroxides (LDHs), consisting of positively main layers intercalated with negative anions and water molecules, are particularly well-suited as supports for POMs due to their tunable and modular architecture.<sup>[7, 8]</sup> LDHs not only prevent POM anion leaching but also improve catalytic selectivity by confining POM clusters within their interlayer galleries.<sup>[7, 9, 10]</sup> For instance, Song et al. successfully incorporated POMs into modified LDHs, achieving enhanced catalytic performance in reactions such as sulfide oxidation and olefin epoxidation.<sup>[11, 12]</sup> Specifically, they developed Mg<sub>3</sub>Al-LDHs modified with ionic liquids, integrating various POM anions for effective sulfide peroxidation and olefin epoxidation.<sup>[13]</sup> Additionally, they introduced an innovative one-pot method for intercalating POM anions into tris(hydroxymethyl)aminomethane (Tris) covalently modified LDHs (Tris-LDHs) under environmental conditions, thereby eliminating the need for CO<sub>2</sub> degassing.<sup>[14, 15]</sup>

In this study, we present a novel "one-pot" anion-exchange technique to incorporate the  $[P_2W_{17}ZnO_{61}]^{8-}$  cluster into Tris-LDHs under ambient conditions. This streamlined approach obviates the CO<sub>2</sub> degassing step, facilitating the efficient synthesis of the intercalated material. Comprehensive characterization confirms the successful incorporation of  $[P_2W_{17}ZnO_{61}]^{8-}$  anions within the LDH structure. The resultant material, Tris-LDHs-P<sub>2</sub>W<sub>17</sub>Zn, exhibits exceptional catalytic performance in BA oxidation, achieving complete conversion with a selectivity of 92.46% for benzaldehyde using H<sub>2</sub>O<sub>2</sub> as the oxidant. This advancement offers a practical solution for the selective oxidation of BA.

## 2. Experimental

## 2.1. Chemicals

MgCl<sub>2</sub>·6H<sub>2</sub>O, AlCl<sub>3</sub>·6H<sub>2</sub>O, Na<sub>2</sub>CO<sub>3</sub>, Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, acetic acid (CH<sub>3</sub>COOH, AcOH), lithium acetate (CH<sub>3</sub>COOLi, AcOLi), potassium chloride (KCl), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, 30 wt%), tris(hydroxymethyl)aminomethane (Tris), benzyl alcohol (BA), acetonitrile (MeCN), and diethyl ether were procured from Sigma Aldrich Co., Ltd. All chemicals were utilized in the experiments without further purification.

#### 2.2. Characterizations

Powder X-ray diffraction (XRD) patterns of materials were acquired on a Rigaku XRD-600 diffractometer (Cu-K $\alpha$  radiation,  $\lambda = 0.15405$  nm) and scanned at 10°/min in the 2 $\theta$  range of 3° to 70°. Fourier transform infrared (FT-IR) spectra were obtained by KBr pellets method on a Bruker Vector 22 spectrometer. Thermogravimetric-differential thermal analysis (TG-DTA) was studied on a Mettler Toledo TGA/DSC 1/1100 SF instrument under a N<sub>2</sub> atmosphere heated at 10 °C/min from 40 °C to 1000 °C. Solid-state nuclear magnetic resonance (NMR) spectroscopy of <sup>13</sup>C and <sup>31</sup>P was performed on a Bruker Avance 300 MHz spectrometer with a 5 mm MAS NMR probe at 75.6 MHz and 121.0 MHz. The N<sub>2</sub> adsorption-desorption isotherms at liquid N<sub>2</sub> temperature were taken on the Quantachrome Autosorb-1 system. Scanning electron microscopy (SEM) images were captured using a Zeiss Supra 55 SEM equipped with energy dispersive X-ray spectroscopy (EDX) for elements analysis.

## 2.3. Synthesis of K-P<sub>2</sub>W<sub>17</sub>Zn, Tris-LDH-CO<sub>3</sub>, and Tris-LDH-P<sub>2</sub>W<sub>17</sub>Zn

The K<sub>8</sub>[ $\alpha_1$ -P<sub>2</sub>W<sub>17</sub>ZnO<sub>61</sub>]·16H<sub>2</sub>O sample (denoted as K-P<sub>2</sub>W<sub>17</sub>Zn) was synthesized following the established method.<sup>[16]</sup> Specifically, 10.0 g of K<sub>9</sub>Li[ $\alpha_1$ -P<sub>2</sub>W<sub>17</sub>O<sub>61</sub>]·18H<sub>2</sub>O was dissolved in 100 mL of an AcOH/AcOLi buffer (0.5 M, pH=4.7). Subsequently, 3.0 mL of a 1.0 M Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O solution was added under continuous stirring. The mixture was then filtered using a pleated filter and allowed to stand. The supernatant (70 mL) was collected, followed by addition of 7.0 g of KCl. The precipitate material was filtered, washed thoroughly with ethanol and diethyl ether, and air-dried to yield K-P<sub>2</sub>W<sub>17</sub>Zn powder.

The Tris modified LDH (denoted as Tris-LDH-CO<sub>3</sub>) was synthesized according to established protocols.<sup>[17]</sup> Initially, a 100 mL 2.0 M Tris solution was mixed with an equal volume of a mixed solution containing MgCl<sub>2</sub>·6H<sub>2</sub>O (13.1 mM) and AlCl<sub>3</sub>·6H<sub>2</sub>O (6.9 mM). The mixture was aged for 12 hours in a Teflon-lined autoclave at 80 °C. The resulting LDH gel was separated via high-speed centrifugation, re-dispersed in 100 mL 0.5 M Na<sub>2</sub>CO<sub>3</sub> solution, and then reacted for 1 hour. Finally, the precipitate material was washed with deionized (DI) water and dried at 60 °C to yield the Tris-LDH-CO<sub>3</sub> sample.

The K-P<sub>2</sub>W<sub>17</sub>Zn-intercalated Tris-LDHs-CO<sub>3</sub> (denoted as Tris-LDH-P<sub>2</sub>W<sub>17</sub>Zn) was synthesized through a straightforward ion-exchange method under conditions where CO<sub>2</sub> was present, as previously described.<sup>[15]</sup> Specifically, Tris-LDHs-CO<sub>3</sub> (2 mg/mL) was dispersed at room temperature in a solution of 0.1 M K-P<sub>2</sub>W<sub>17</sub>Zn. The resulting precipitate was filtered, thoroughly cleaned with DI water and acetone, and oven-dried at 70 °C for 10 hours to yield the final Tris-LDH-P<sub>2</sub>W<sub>17</sub>Zn product.

## 2.4. Catalytic oxidation of benzyl alcohol

The catalytic activity was evaluated through a one-pot oxidation of BA. The catalytic reaction was carried out in a 25 mL glass reactor containing the solid catalyst (50.0 mg), BA (1.0 mmol), 30 wt% aqueous H<sub>2</sub>O<sub>2</sub> solution (612  $\mu$ L), acetonitrile (2.0 mL), where the mixture was agitated vigorously at 80 °C for 6 hours. Subsequently, the reaction was quenched by adding 1.5 mL of water and 6.0 mL of diethyl ether. The product yields were analyzed using gas chromatography (GC) with a flame ionization detector (FID). The GC conditions were set as inlet temperature at 340 °C, detector temperature at 340 °C, oven temperature at 70 °C, carrier gas was ultrapure nitrogen and sample size was 1  $\mu$ L.

### 3. Results and discussion

The XRD patterns of Tris-LDH-CO<sub>3</sub> (Figure 1) display peaks at  $2\theta = 11.7^{\circ}$ ,  $23.7^{\circ}$ ,  $34.9^{\circ}$ ,  $61.3^{\circ}$ , and  $62.4^{\circ}$ , corresponding to the characteristic reflections of the (003), (006), (012), (110), and (113) planes of typical LDHs, respectively, thereby confirming the successful synthesis of Tris-LDH-CO<sub>3</sub>.<sup>[17]</sup> Following the ion-exchange process, the characteristic reflections of (003) and (006) for Tris-LDH-P<sub>2</sub>W<sub>17</sub>Zn shift to lower angles ( $2\theta = 7.7^{\circ}$  and  $13.7^{\circ}$ , respectively), indicating the successful intercalation of [P<sub>2</sub>W<sub>17</sub>ZnO<sub>61</sub>]<sup>8–</sup> ions into the interlayered spaces of Tris-LDH-CO<sub>3</sub>.<sup>[14, 15]</sup>

The FT-IR spectra of K-P<sub>2</sub>W<sub>17</sub>Zn, Tris-LDH-P<sub>2</sub>W<sub>17</sub>Zn, and Tris-LDH-CO<sub>3</sub> are depicted in Figure 1b. For Tris-LDH-CO<sub>3</sub>, absorption bands at 449, 1085, and 1136 cm<sup>-1</sup> are corresponding to the tensile vibrations of O-M-O, M-O-C, and C-C-O.<sup>[17]</sup> For K-P<sub>2</sub>W<sub>17</sub>Zn, absorption bands at 938, 912, and 711 cm<sup>-1</sup> correspond to the vibrations of W-Ot, W-Oc-W, and W-Oe-W (where t, c, e denote terminal-, corner-, and edge-shared).<sup>[16]</sup> As for Tris-LDH-P<sub>2</sub>W<sub>17</sub>Zn, these W-O vibrations exhibit slight shifts to 938, 903, and 733 cm<sup>-1</sup>, which can be assigned to the hydrogen bond interactions between hydroxyl groups in the LDH and the O atoms from POMs.<sup>[15]</sup> Additionally, the peak at 1052 cm<sup>-1</sup>, corresponding to the P-O bond vibration, shifts marginally to 1049 cm<sup>-1</sup> in Tris-LDH-P<sub>2</sub>W<sub>17</sub>Zn. These observations confirm that the  $[P_2W_{17}ZnO_{61}]^{8-}$  ions retain their Dawson structure post-intercalation.



Fig. 1. (a) XRD patterns of Tris-LDH-CO<sub>3</sub> and Tris-LDH-P<sub>2</sub>W<sub>17</sub>Zn; (b) FT-IR spectra of K-P<sub>2</sub>W<sub>17</sub>Zn, Tris-LDH-P<sub>2</sub>W<sub>17</sub>Zn, and Tris-LDHs-CO<sub>3</sub>; TG-DTA curves of (c) K-P<sub>2</sub>W<sub>17</sub>Zn and (d) Tris-LDH-P<sub>2</sub>W<sub>17</sub>Zn.

Thermogravimetric-differential thermal analysis (TG-DTA) was conducted for K-P<sub>2</sub>W<sub>17</sub>Zn and Tris-LDH-P<sub>2</sub>W<sub>17</sub>Zn. The Tris-LDH-P<sub>2</sub>W<sub>17</sub>Zn has two distinct weight-loss stages as increasing the temperature from 30 °C to 800 °C (Figure 1c). Between 40 °C and 258 °C, the initial weight loss rate was 11.51% due to the desorption of surface-absorbed H<sub>2</sub>O molecules and within the interlayered space of Tris-LDH-P<sub>2</sub>W<sub>17</sub>Zn (Figure 1d). The second weight loss, amounting to 9.49%, occurs between 258 °C and 800 °C, corresponding to the Tris molecules decomposition followed by the collapse of LDH layered structure.<sup>[14, 15]</sup> Furthermore, the DTA curves revealed two endothermic peaks between 200 °C and 368 °C, suggesting phase transitions associated with these decomposition processes.

Solid-state <sup>13</sup>C CPMAS NMR studies of Tris-LDH-CO<sub>3</sub> and Tris-LDH-P<sub>2</sub>W<sub>17</sub>Zn (Figure 2a) further validate the successful exchange of CO<sub>3</sub><sup>2–</sup> anions. The prominent signal at  $\delta$  = 171.3 ppm in the <sup>13</sup>C CPMAS NMR spectrum of Tris-LDH-CO<sub>3</sub> is ascribed to the interlayered CO<sub>3</sub><sup>2–</sup> anions. In contrast, the intensity of this peak is significantly reduced in the spectra of Tris-LDH-P<sub>2</sub>W<sub>17</sub>Zn, indicating that CO<sub>3</sub><sup>2–</sup> has been replaced by [P<sub>2</sub>W<sub>17</sub>ZnO<sub>61</sub>]<sup>8–</sup> anions during the ion-exchange process.<sup>[15, 17]</sup> Additionally, the <sup>31</sup>P CPMAS NMR spectra of K-P<sub>2</sub>W<sub>17</sub>Zn and Tris-LDH-P<sub>2</sub>W<sub>17</sub>Zn exhibit two signals at  $\delta$  = -8.3 and -13.9 ppm, confirming the successful intercalation of POM anions into the CO<sub>3</sub><sup>2–</sup> sites (Figure 2b).<sup>[16]</sup> Other peaks observed at 0.5, -2.1, and -3.5 ppm are likely due to the formation of different polytungstate to phosphate species during the ion-exchange reaction.<sup>[16]</sup>



Fig. 2. (a) <sup>13</sup>C CPMAS NMR spectra, (c) N<sub>2</sub> adsorption-desorption isotherms and (d) the pore size distribution of Tris-LDH-CO<sub>3</sub> and Tris-LDH-P<sub>2</sub>W<sub>17</sub>Zn; (b) <sup>31</sup>P CPMAS NMR spectra of K-P<sub>2</sub>W<sub>17</sub>Zn and Tris-LDH-P<sub>2</sub>W<sub>17</sub>Zn.

Nitrogen adsorption-desorption isotherms were measured to elucidate the structural properties of Tris-LDH-CO<sub>3</sub> and Tris-LDH-P<sub>2</sub>W<sub>17</sub>Zn samples (Figure 2c). The Tris-LDH-CO<sub>3</sub> sample exhibited a type IV adsorption isothermal lines with an H3 hysteretic loop and lack of platform in the high-pressure area (P/P<sub>0</sub> > 0.5), which suggests the existence of slit-shaped pores due to the aggregation of the layers. In contrast, Tris-LDH-P<sub>2</sub>W<sub>17</sub>Zn also appeared a type IV adsorption isothermal lines but with an H2 hysteretic loop and a sharp increase at higher relative pressures (P/P<sub>0</sub> > 0.5), indicative of mesoporous materials.<sup>[15]</sup> This transformation is likely a result of POM anion intercalation, which disrupts the regular stacking of LDH layers. Pore size distribution curves confirmed the mesoporous nature of Tris-LDH-CO<sub>3</sub> and Tris-LDH-P<sub>2</sub>W<sub>17</sub>Zn (Figure 2d). Table 1 shows the surface area and pore volume, as well as average pore size of the two samples, derived from the analysis of N<sub>2</sub> adsorption-desorption isotherms. Notably, the specific surface area of Tris-LDH-P<sub>2</sub>W<sub>17</sub>Zn increased significantly to 200.37 m<sup>2</sup>/g from 51.76 m<sup>2</sup>/g for Tris-LDH-CO<sub>3</sub>, the pore volume expanded from 0.16 cm<sup>3</sup>/g to 0.43 cm<sup>3</sup>/g, and the average pore size increased from 19.31 nm to 27.85 nm, indicating a substantial enhancement in porosity upon POM intercalation.

Table 1. Comparison of physicochemical parameters of Tris-LDH-CO<sub>3</sub> and Tris-LDH-P<sub>2</sub>W<sub>17</sub>Zn.

Samples	Surface area $(m^2/g)$	Pore volume (cm <sup>3</sup> /g)	Average pore diameter (nm)
Tris-LDH-CO <sub>3</sub>	51.76	0.16	19.31
Tris-LDH-P2W17Zn	200.37	0.43	27.85



*Fig. 3. (a)* SEM image, (b) EDX spectrum and (c) elements (C, Mg, Al, Zn, W, and P) mapping images of Tris-LDH-P<sub>2</sub>W<sub>17</sub>Zn.

SEM images (Figure 3a) reveal that Tris-LDH-P<sub>2</sub>W<sub>17</sub>Zn exhibits an irregular nanoparticle morphology. The EDX spectrum and elemental mapping (Figures 3b and 3c) confirm the presence of all constituent elements from both the LDHs and the POM anions in Tris-LDH-P<sub>2</sub>W<sub>17</sub>Zn. This provides unequivocal evidence of the successful intercalation of [P<sub>2</sub>W<sub>17</sub>ZnO<sub>61</sub>]<sup>8–</sup> anions within the interlayered spaces of Tris-LDH-CO<sub>3</sub>, with a uniform dispersion throughout the entire sample.

The catalytic activity of the Tris-LDH-P<sub>2</sub>W<sub>17</sub>Zn composite was evaluated as an active heterogeneous catalyst in the oxidation of BA to benzaldehyde. Initially, the influence of various solvents on the BA oxidation process was investigated (Figure 4a). It was observed that, except for toluene and dimethyl sulfoxide (DMSO), most solvents had minimal impact on BA conversion. Considering the solubility of BA, acetonitrile (MeCN) was selected as the solvent. As depicted in Figure 4b, the effect of varying the volume of MeCN between 1.0 and 3.0 mL on BA conversion and benzaldehyde selectivity was assessed. The results indicated that as the MeCN volume increased from 1.0 to 3.0 mL, BA conversion decreased from 96.51% to 88.89% and 82.40%, while benzaldehyde selectivity increased from 49.09% to 99.34% and 100%. Based on both BA conversion and benzaldehyde selectivity, a MeCN volume of 2.0 mL was deemed optimal. The influence of reaction time on conversion of BA and selectivity of benzaldehyde on the Tris-LDH-P<sub>2</sub>W<sub>17</sub>Zn composite was evaluated at 4, 6, and 8 hours (Figure 4c).



Fig. 4. (a) Effect of solvent on BA oxidation: solvent volume = 2 mL;  $H_2O_2 = 612 \ \mu$ L; t = 6 h. (b) Influence of solvent volume on BA oxidation:  $H_2O_2 = 612 \ \mu$ L; t = 6 h. (c) Influence of reaction time on BA oxidation: MeCN = 2 mL;  $H_2O_2 = 612 \ \mu$ L. (d) Effect of  $H_2O_2/alcohol$  molar ratio on BA oxidation: MeCN = 2 mL; t = 6 h. Experimental conditions: Tris-LDH- $P_2W_{17}Zn = 50 mg$ ; BA = 1.0 mmol;  $T = 80 \circ$ C.

Extending the reaction time from 4 to 8 hours resulted in an increase in BA conversion from 73.04% to 88.89% and 89.59%, while benzaldehyde selectivity remained relatively constant. Additionally, the impact of the H<sub>2</sub>O<sub>2</sub>/BA molar ratio on the catalytic efficiency was explored by adjusting the ratio within the range of 5 to 7 (Figure 4d). The results revealed that BA conversion increased from 78.86% to 88.89% and 100%, while benzaldehyde selectivity increased from 72.55% to 99.34% before decreasing to 92.46%. Based on these findings, the optimal H<sub>2</sub>O<sub>2</sub>/BA molar ratio was determined to be 6.

#### 4. Conclusion

In summary, the immobilization of polyoxometalates (POMs) on layered double hydroxides (LDHs) presents an effective strategy to overcome limitations related to low surface area and poor recyclability, thereby enhancing both catalytic performance and selectivity. In this study, we successfully employed an innovative "one-pot" anion-exchange technique to intercalate the  $[P_2W_{17}ZnO_{61}]^{8-}$  cluster into Tris-LDH-CO<sub>3</sub> under ambient conditions. The resulting Tris-LDHs- $P_2W_{17}Zn$  catalyst exhibited exceptional catalytic efficiency, achieving complete conversion of BA and a benzaldehyde selectivity of 92.46% in the existence of H<sub>2</sub>O<sub>2</sub>. These results provide a promising approach for the design of effective catalysts in the selective alcohols oxidation.

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#### References

[1] S. Najafishirtari, K. Friedel Ortega, M. Douthwaite, S. Pattisson, G. J. Hutchings, C. J. Bondue, K. Tschulik, D. Waffel, B. Peng, M. Deitermann, G. W. Busser, M. Muhler, M. Behrens, Chemistry - A European Journal 27(68), 16809-16833(2021); https://doi.org/10.1002/chem.202102868

[2] C. Xu, S. Zhong, L. Yuan, M. Yu, Y. Chen, L. Dai, X. Wang, Chemical Engineering Journal 481, 148767(2024); https://doi.org/10.1016/j.cej.2024.148767

[3] Y. Wang, X. Wang, Y. Dong, M. Peng, L. Guo, M. Cui, Y. He, J. Yi, H. Ma, H. Zhang, H. Fan, Green Chemistry 26(10), 6131-6138(2024); <u>https://doi.org/10.1039/D4GC00554F</u>

[4] J.-X. Liu, X.-B. Zhang, Y.-L. Li, S.-L. Huang, G.-Y. Yang, Coordination Chemistry Reviews 414, 213260(2020); <u>https://doi.org/10.1016/j.ccr.2020.213260</u>

[5] K. Qin, D. Zang, Y. Wei, Chinese Chemical Letters 34(8), 107999(2023); https://doi.org/10.1016/j.cclet.2022.107999

[6] J. Díaz, L. R. Pizzio, G. Pecchi, C. H. Campos, L. Azócar, R. Briones, R. Romero, A.

Henríquez, E. M. Gaigneaux, D. Contreras, Catalysts 12(5), 507(2022); https://doi.org/10.3390/catal12050507

[7] A. Farhan, A. Khalid, N. Maqsood, S. Iftekhar, H. M. A. Sharif, F. Qi, M. Sillanpää, M. B. Asif, Science of The Total Environment 912, 169160(2024);
 <u>https://doi.org/10.1016/j.scitotenv.2023.169160</u>

[8] L. Li, I. Soyhan, E. Warszawik, P. van Rijn, Advanced Science

[9] C. Ning, S. Bai, J. Wang, Z. Li, Z. Han, Y. Zhao, D. O'Hare, Y.-F. Song, Coordination Chemistry Reviews 480, 215008(2023); <u>https://doi.org/10.1016/j.ccr.2022.215008</u>

[10] Y. Xu, H. Liu, Y. Wu, Q. Wu, C. Li, X. Wang, H. Qin, A. Qin, L. Wang, ChemNanoMat 9(12), e202300414(2023); <u>https://doi.org/10.1002/cnma.202300414</u>

[11] Stamate, Pavel, Zavoianu, Marcu, Catalysts 10(1), 57(2020); https://doi.org/10.3390/catal10010057

[12] L. Silaen, M. F. Azmi, N. R. Palapa, R. Mohadi, Elfita, A. Lesbani, IOP Conference Series: Materials Science and Engineering 902(1), 012048(2020); <u>https://doi.org/10.1088/1757-899X/902/1/012048</u>

[13] Y. Xu, W. Xuan, M. Zhang, H. N. Miras, Y. F. Song, Dalton Trans. 45(48), 19511-19518(2016); <u>https://doi.org/10.1039/C6DT03445D</u>

[14] Y. Chen, Z. Yao, H. N. Miras, Y. F. Song, Chem. Eur. J. 21(30), 10812-10820(2015); https://doi.org/10.1002/chem.201501214

[15] K. Liu, Y. Xu, Z. Yao, H. N. Miras, Y.-F. Song, ChemCatChem 8, 929-937(2016); https://doi.org/10.1002/cctc.201501365

[16] R. Contant, M. Richet, Yu W. Lu, B. Keita, L. Nadjo, European Journal of Inorganic Chemistry 2002(10), 2587-2593(2002); <u>https://doi.org/10.1002/1099-</u> 0682(200210)2002:10<2587::AID-EJIC2587>3.0.CO;2-D

[17] Y. Kuroda, Y. Miyamoto, M. Hibino, K. Yamaguchi, N. Mizuno, Chem. Mater. 25(11), 2291-2296(2013); <u>https://doi.org/10.1021/cm400846k</u>