Journal of CO_2 Utilization 26 (2018) 314–322

Contents lists available at ScienceDirect

Journal of CO_2 Utilization

journal homepage: www.elsevier.com/locate/jcou

Recent applications of polyoxometalates in CO_2 capture and transformation

Bing Yu[a,b,*], Bo Zou[a], Chang-Wen Hu[a,*]

[a] Key Laboratory of Cluster Science of Ministry of Education, Beijing Key Laboratory of Photoelectronic/Electrophotonic, School of Chemistry and Chemical Engineering, Beijing Institute of Technology, Beijing 100081, PR China

[b] College of Chemistry and Molecular Engineering, Zhengzhou University, Zhengzhou 450001, Henan Province, PR China

ARTICLE INFO

Keywords:
Polyoxometalates
Carbon dioxide fixation
Carbon dioxide capture

ABSTRACT

CO_2 chemistry has drawn considerable attention as abundant, low cost, and renewable carbon source in the past decades. The natural stability of CO_2 made its utilization a daunting challenge under mild conditions. Recently, there has been significant progress of CO_2 fixation by using cheap and abundant functionalized polyoxometalate (POM) catalysts. In this review, the POM catalytic system for transformation of CO_2 into valuable compounds such as urea, cyclic carbonate, quinazoline-2,4(1*H*,3*H*)-diones, α-methylene cyclic carbonate, oxazolidinones etc. were discussed. The future of POM catalysis for sustainable chemistry lies in the synthesis of highly functionalized task-specific POM catalysts, and rational design of novel reactions which would eventually pave the pathway for the establishment of green, effective, inexpensive and sustainable technologies.

1. Introduction

Over the last few decades, carbon dioxide (CO_2) as a natural gas has gained worldwide attention due to its steadily increasing concentration in the atmosphere, which may cause climate changes and global warming [1]. In the recent decades, tremendous efforts have been devoted to reducing CO_2 emission and conversion of CO_2 into value-added fine chemicals or fuels [[2]]. To a great extent, CO_2 will be one of the most abundant carbon sources in the future, because the fossil sources are limited [3]. Besides CO_2 capture and storage/sequestration (CCS) [2a,2b,4], an alternative strategy for reducing CO_2 emission is chemical fixation of CO_2, delivering organic carbonates [5], polycarbonates [6], carbamates [7], ureas [7,8], carboxylic acids [9], valuable heterocycles [10], and MeOH [11], etc. as products (Scheme 1). Although the chemical fixation of CO_2 is not efficient as CCS strategy for reducing CO_2 emission in a short period, the utilization of CO_2 as a renewable and nontoxic C_1 resource for the construction of value-added fine chemicals is significantly attractive.

Molecular metal oxide clusters, so-called polyoxoanions or polyoxometalates (POMs), are commonly referred to a class of compounds based on early transition metal (group 5 and 6) oxide building blocks with a general formula of $(MO_x)_n$, where M = Mo, W, V, Nb, Ta etc [12]. When the POMs exclusively contain one type of metal and oxygen, the clusters are called as isopolymetalates, such as the Lindqvist type anion $[M_6O_{19}]^{2-}$. When additional elements (e.g. P, Si, As, S, rare earth element, etc.) are coordinated in POMs, they are known as heteropoly complexes, such as the Keggin and Wells-Dawson type anions.

In the past decades, capture and transformation of CO_2 has been widely explored. Particularly, a plethora of POM-based compounds have been reported as efficient catalysts or promoters for CO_2 fixation processes. Although the basic science of the synthesis, modification and application of POM-based materials are well documented [12b,13], few of them have specialized in the application of POMs in this sustainable field previously [14]. The goal of this review is to provide a comprehensive summary of current developments for CO_2 fixation using POM related systems. The combination of environmentally benign POMs and sustainable CO_2 chemistry will open new avenues in the field of POM catalysis.

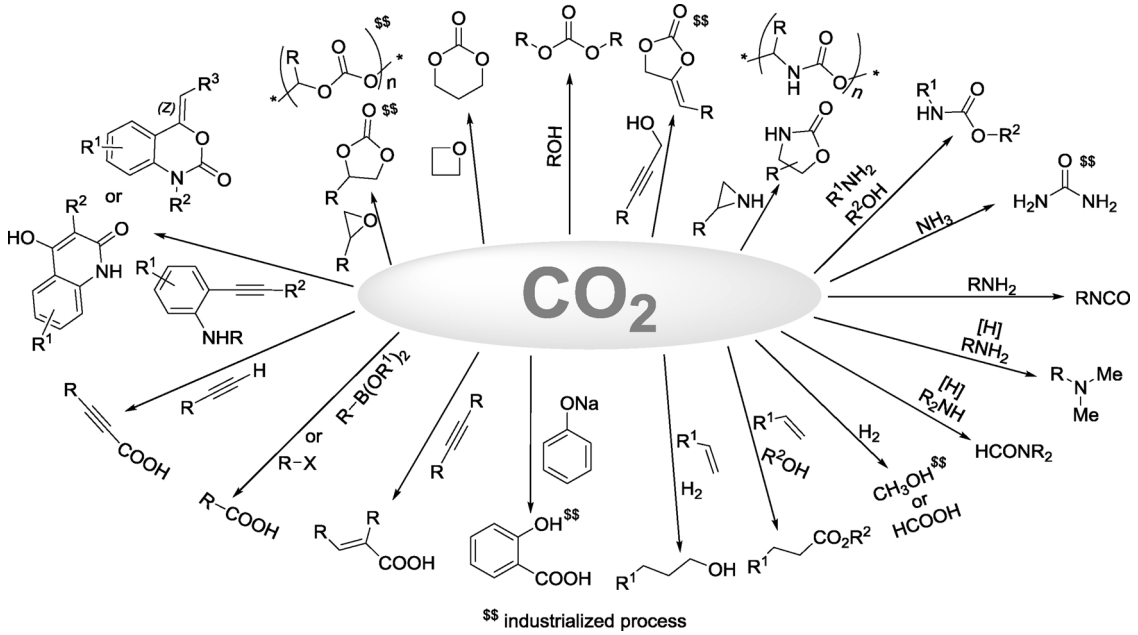
2. CO_2 binding and capture with POMs

CO_2 capture and separation is an important research area from the viewpoints of environmental protection and industrial processes [15]. Organic and inorganic bases have been widely used in CO_2 capture, while they are usually toxic, corrosive and difficult to regeneration [16]. Alternatively, a new class of porous materials have been investigated, such as zeolites and metal-organic frameworks (MOFs). Recently, POMs were reported to show great potential in terms of CO_2 capture and separation, based on their flexible binding modes to small molecular.

In 1998, Kozik et al reported that tetraheptylammonium salts of Co (II), Ni(II), Mn(II)-substituted α-Keggin ($[SiW_{11}O_{39}M]^{n-}$ and $[GeW_{11}O_{39}M]^{n-}$), α_2-Wells-Dawson ($[P_2W_{17}O_{61}M]^{m-}$) could react with CO_2 in nonpolar solvents. The CO_2 adducts were characterized by

* Corresponding authors.
E-mail addresses: bingyu@zzu.edu.cn (B. Yu), cwhu@bit.edu.cn (C.-W. Hu).

https://doi.org/10.1016/j.jcou.2018.05.021
Received 10 March 2018; Received in revised form 9 May 2018; Accepted 20 May 2018



Scheme 1. Chemical fixation of CO_2.

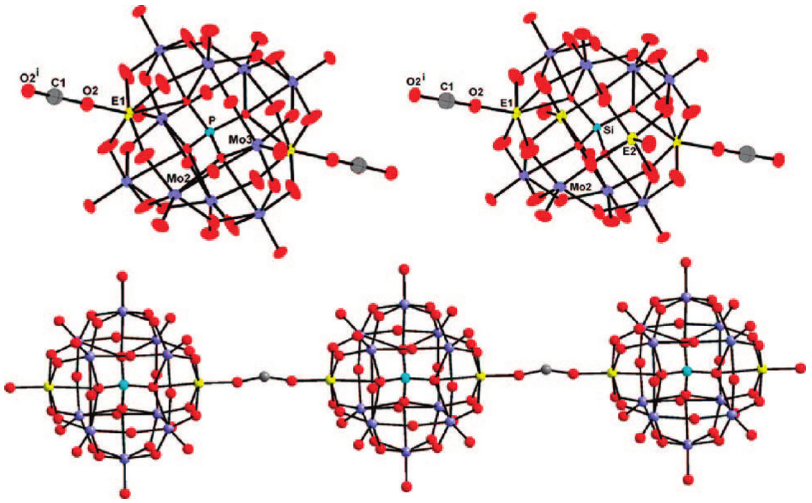


Fig. 1. Thermal ellipsoid plots of polyoxoanions located in **1** (top left) and **2** (top right). Ball-stick representation of polymeric chain structure of complex **1** (bottom). Adapted from Ref. [18] with permission.

UV/vis, IR, and ^{13}C NMR, albeit no crystalline samples were obtained [17]. It was hypothesized that a direct η^1 metal-carbon bond between the transition metal and CO_2 was possible, which could be stabilized by hydrogen bonding utilizing both hydrogen atoms from water.

The combination of POMs and CO_2 was observed in aqueous solution by Xu et al in 2008. Two unusual CO_2-ligated compounds, $(C_3H_5N_2)_3(C_3H_4N_2)[PMo_{11}CoO_{38}(\mathbf{CO_2})]\cdot 4H_2O$ (**1**) and $(C_3H_5N_2)_4[SiMo_{11}CoO_{38}(\mathbf{CO_2})]\cdot 4H_2O$ (**2**) were obtained, which first shown the μ-η^1,η^1-**OCO** linear coordination mode (Fig. 1) [18].

A much larger metal oxide cluster $[\{(Mo^{VI})Mo_5^{VI}O_{21}(H_2O)_6\}_{12}\{Mo_2^{V}O_4(\mathbf{CH_3COO})\}_{30}]^{42-}$ (denot-ed as $\{Mo_{132}\}$) was reported to pick up 30 CO_2 molecules inside the capsule (**3**) (Fig. 2) [19]. With CO_2 bubbled, the acetates in $\{Mo_{132}\}$ are replaced by carbonate ligands individually, and this process is reversible to release CO_2 in acidified solution upon mild heating.

Various POM-based hybrid materials were synthesized for CO_2 separation. For instance, $Na_3[PW_{12}O_{40}]$ contained membrane can remarkably increase the permeability of CO_2, resulting the ratio of permeance of CO_2 over N_2 up to 3200 [20]. Additionally, the strong interaction of $Na_{1.5}H_{11.4}[ZnMo_{12}O_{40}\{Zn_2\}]\cdot 5.5H_2O$, a inorganic 3D frameworks, with CO_2 was observed, which has been successfully utilized for separating CO_2/CH_4 in gas chromatography [15]. Moreover, POM-LDH nanohybrids (LDH = layered double hydroxide) [21] also exhibited a significant improvement on CO_2 absorption (0.74 mmol g^{-1} at 0 °C, 101.325 kPa), compared to Mg-Al-LDH (0.08 mmol g^{-1} under the same condition). Mizuno group [22] reported a flexible organic-inorganic ionic crystals with ordered pores, which can selectively adsorb CO_2 from acetylene. Besides the surface adsorption of pores, the interaction of POMs with CO_2 played important roles in the CO_2 capture process. Particularly, the oxygen-rich surface of the polyanions might enhance the selective adsorption of CO_2 over acetylene.