Generation of Fuel and Value-Added Chemicals from Carbon Dioxide

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Abstract

Despite its life-threatening long term effects, the continuous increase of carbon dioxide (CO_2) in the environment requires immediate actions to control the accelerating climate change. An appealing solution to this problem is to utilize CO_2 as feedstock to generate useful chemicals, e.g., fuel, hydrocarbons, and valuable chemicals. The chemical inertness of CO_2 needs considerably large energy for its conversion into useful chemicals. Therefore, CO_2 reduction reaction requires an effective catalyst for its conversion into fuel (methanol, methane) and industrial chemicals (syngas, formic acid). Recently, two-dimensional layers of early transition metal carbides and nitrides, called MXene, have shown potential for catalysis due to its exposed transition metal sites, and mechanical and chemical stability at high temperatures. Herein, the author presents the MXene as a potential heterogeneous catalyst for the CO_2 reduction reaction (CRR), and the future scope in this currently developing field.

Keywords: CO_2 reduction, Fuel generation, MXene.

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Introduction

To fulfill the energy demands of society, fossil fuels are burned from ages. Excessive consumption of fossil fuel, e.g., coal, petroleum, and natural gases, not only exhausts the limited fossil fuel sources available, but also results in the continuous increase of greenhouse gas.[1,2] Around 60% of the greenhouse gases comprise CO_2. Therefore, it is of paramount importance to find a substitute for fossil fuel, which can help us to deal with the increasing energy requirement of today's society, which can control the emission of greenhouse gases. Energy sources, e.g., wind energy,[3] water energy, or hydrogen energy,[4] can be utilized; however, the implementation of wind or water energy is difficult. The development of hydrogen energy resources is still in the research stage and needs time for its practical implementation. An attractive solution to this problem is to convert the CO_2 into useful chemicals,[5-9] e.g., formic acid, and fuel, e.g., methanol.

Owing to the negative adiabatic electron affinity and large ionization potential, it is energy extensive to convert CO_2 into useful chemicals, thus, making the use of catalyst inevitable. Variety of catalytic materials, e.g., titanium based semiconductor (TiO_2),[10] transition metal (Cu and Ni) based composites,[11,12] and noble metal (Pt, Pd, Ru, Rh, and Ir) based material,[13,14] have been tested, and their performances were optimized to maximize the yield. The noble metal catalyst, often supported on oxides, shows the best activity and selectivity. However, scarcity and high cost

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hinder their use in practical purposes. Non-metallic catalyst, e.g., nitrogen-doped carbon nanotubes[15] or In_2O_3[16] provide a cheaper option; however, suffers from low stability and weak adsorbent binding. Transition metals (TM) based catalysts,[14,17] although do overcome the former two challenges; however, low yield, poor selectivity, and undesired by-products are a big problem with TM based catalysts. Furthermore, under extreme reaction conditions, they tend to distort and form agglomeration of TM nanoparticles. Many other materials proposed for the conversion of CO_2 into useful chemicals and fuels, but after several decades of research, it is still challenging to find highly efficient, stable, and cheap catalysts for the conversion of CO_2.

Recently, two-dimensional materials[18] have drawn the attention of the scientific community for the catalysis of the

CRR.[19,20] Graphene based materials, e.g., reduced graphene oxide, have shown their potential for the catalysis of the CO$_2$ reduction reaction. Two-dimensional layers of early transition carbide, called MXene,[21,22] possess the properties of metal, as well as, of ceramic, therefore, highly conducting and can withstand extreme reaction conditions for CRR. High specific area and two-dimensional (2D) morphology with plenty of exposed TM sites make MXene potentially attractive for catalysis of CRR. Recent studies reveal the activations of the CO$_2$ molecule, and its conversion to methanol on the surface of MXenes. Herein, the author has discussed the theoretical exploration of MXenes as a highly efficient and economic catalyst for the conversion of CO$_2$ into methanol and methane.

TWO-DIMENSIONAL (2D) MXENE

The advent of graphene initiated an extensive search of other 2D materials. In this search, various other 2D materials were synthesized in laboratories. This continually growing family of 2D dimensional materials now contains, insulators, e.g., hexagonal boron nitride, semiconductors, e.g., transition metal dichalcogenides, phosphorene, metals, e.g., early transition metal carbides (MXene), and superconductors, e.g., NbSe$_2$.[18,23] Due to the confinement of electrons in 2D, these 2D materials display technologically appealing properties, not observed in their bulk counterparts. The 2D nature provides a high specific surface area to volume ratio for their use as support. Potentials of these materials for various functionalities, e.g., batteries, supercapacitors, field-effect transistors (FETs), solar cells, and catalysis, are scrutinized. Indeed in many cases, 2D materials outperform their 3D counterparts.

The 2D layers of transition metal carbides/ nitrides and carbonitrides, called MXene, are successfully synthesized from the ceramic material MAX (M$_{n+1}$AX$_n$) phase, using hydrofloric acid (HF) as an etchant.[21,22] Here, M stands for the early transition metal (Sc, Ti, Nb, etc.), A represents a group 13 or 14 elements, usually "Al," and X can be C and/or N, and n can take a value between 1 to 3. Clearly, depending upon the chosen M, A, and X, MXene with various chemical compositions can exist in 3, 5, or 7 atomic (sub) layers for n = 1, 2, or 3, (Figure 1) respectively.

MXene combines the metallic conductivity of TM carbide/ nitride with the ceramic properties of MAX phase, e.g., high melting point, low electrical resistivity, high anticorrosivity, and hardness. The exfoliation process leaves the broken bond sites exposed, therefore, MXene surfaces get functionalized by F, OH, and O groups. Graphene is hydrophobic, therefore, at places where 2D morphology is needed with metallicity and hydrophilicity, the MXene surface can be used. Moreover, these functional groups are dispersed over the MXene surfaces, making it attractive for various functionalities. MXenes have already shown their promises for energy storage and other applications, including Li-ion batteries,[24] electrochemical capacitors,[25] sensors,[26] as water purification systems,[27] and as support for catalysts.[28]

MXene as CRR Catalysts

Recently, these 2D layers with exposed TM sites have shown to possess good catalytic activity for CRR. Few experimental works checked the feasibility of catalytic reduction of CO$_2$ over hybrid MXene. Platinum atoms embedded at Ti-vacancies in Ti$_3$C$_2$T$_X$[29] can act as a strong catalyst for the reduction of CO$_2$ molecules. This Pt/Ti$_3$C$_2$T$_X$ provides an efficient way to utilize CO$_2$ gas for the formylation of amines. Density functional calculations showed that Pt/Ti$_3$C$_2$T$_X$ show catalytic activity for CRR better than that of Pt-nanoparticle due to the dispersion of Pt atoms. In a study, TiO$_2$ nanoparticles are grown over the conducting sheets of MXene Ti$_3$C$_2$T$_X$, study reveals that TiO$_2$/ Ti$_3$C$_2$ composite[30] show far better photocatalytic activity for CO$_2$ conversion to CH$_4$ compared to the commercially available TiO$_2$ catalyst. In another experimental study, Bi$_2$WO$_6$ nanosheets are grown over the metallic nanosheets of Ti$_3$C$_2$T$_X$.[31] Conducting MXene sheets increases the bulk to surface charge transfer and promotes the CO$_2$ reduction to fuels: CH$_4$ and CH$_3$OH over the hybrid heterostructures of MXene/Bi$_2$WO$_6$ nanosheets.[31]

Various theoretical studies have also focussed on the catalytic activity of MXene for the CRR. Due to the open TM sites, the unfunctionalized MXene M$_2$C (M is early TM)[32] shows better absorption and activation of CO$_2$. In another study, unfunctionalized M$_3$C MXene surfaces are shown to selectively convert CO$_2$ to methane.[33] Although, these studies show promises of unfunctionalized or pristine MXene for catalysis of CRR; however, both, experiments[21,22] and theoretical[34] studies confirm the spontaneous functionalization of MXene layers during the exfoliation process. The unavailability of pristine MXene makes the CRR catalysis using MXene unachievable. Functional groups are always present on the surface of MXene. They affect the properties of MXene drastically. Therefore, the presence of these functional groups cannot be avoided. Very recently, a study explored the
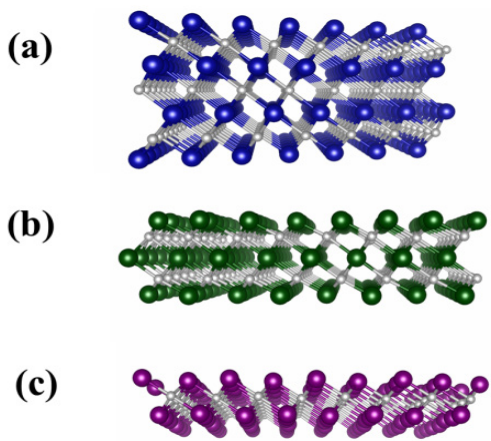

Figure 1: MXene with varying M and n; (**a**) n = 3; (**b**) n = 2; (**c**) n = 1; grey balls are representing C and/or N; blue, green, and magenta balls are representing different TM atoms

OH-functionalized M$_2$C type MXene for CRR, and scandium based OH-functionalized MXene was predicted as the best catalyst for CRR among all OH-functionalized M$_2$C MXene.[35] Another study performed on O-functionalized Ti$_2$C MXene predicts that the O-vacancies in MXene can act as a center for photocatalytic reduction of CO$_2$ and result in CH$_3$OH or CH$_2$ generation.[36]

FUTURE DIRECTIONS

Undoubtedly, MXene possesses properties, e.g., metalicity, strong charge transfer effects, high specific area, open TM sites, due to which it is suitable for the catalysis of CRR. However, rational thinking is strongly required before designing a suitable MXene based catalyst for the CRR. Here, I discuss a few aspects which should be taken into consideration.

- As the MXene surfaces are always decorated with various functional groups, one has to check the possibility of CRR in functionalized instead of pristine MXene.
- MXene family is quite extended, with more than 70 MXenes with varying M, A, and X are possible. Suitable MXene can be found by checking the adsorption energy of CO$_2$ on various MXene.
- The functional group, O/F/OH, can also be selected based on the binding of CO$_2$ on functionalized MXenes.

Most of the efforts invested in understanding the thermo-dynamics CRR over the MXene sheets. Studies performed to understand the CRR on MXene surfaces have checked the adsorption of CO$_2$ and possible intermediates; however, understanding of kinetics, e.g., rate of the reaction, efficiency, yield, etc., of the CRR is also very important. Selectivity is another criterion that needs special attention.

CRR can effectively control the level of CO$_2$ in air, and at the same time, can provide value-added chemicals. Finding an effective catalyst, which is cheap, highly selective, and gives a good yield, is the key to the successful conversion of CO$_2$. MXenes family undoubtedly has great potential for the catalysis of CRR. At least theoretical studies predict, however, more experimental studies are required to establish the effectiveness of MXene as a CRR catalyst.

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