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REVIEW

Achieving Ultralow Friction and Wear by Tribocatalysis: Enabled by *In-Operando* Formation of Nanocarbon Films

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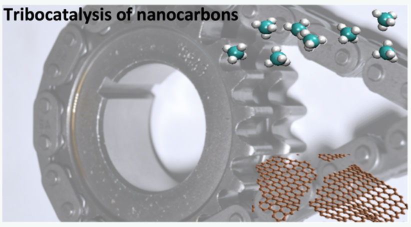

ABSTRACT: Under the high-contact-pressure and shear conditions of tribological interfaces lubricated by gaseous, liquid, and solid forms of carbon precursors, a variety of highly favorable tribocatalytic processes may take place and result in the *in situ* formation of nanocarbon-based tribofilms providing ultralow friction and wear even under extreme test conditions. Structurally, these tribofilms are rather complex and may consist of all known forms of nanocarbon including amorphous or disordered carbon, graphite, graphene, nano-onion, nanotube, *etc.* Tribologically, they shear readily to provide ultralow friction and protection against wear. In this paper, we review some of the latest developments in catalyst-enabled tribochemical films resulting from gaseous, liquid, and solid sources of carbon. Particular focus is given to the nature and lubrication mechanisms of such *in situ* derived tribofilms with the hope that future tribological surfaces can be designed in such a way to exploit the beneficial impact of catalysis in friction and wear control.

KEYWORDS: *tribocatalysis, superlubricity, nanocarbon materials, wear, coatings, in situ film formation, graphene, hydrocarbon environment, graphene*

Surface and interface-specific degradations (i.e., wear, corrosion, deformation, fracture, fatigue, erosion, *etc.*) account for more than 70% of the main causes of eventual failures in all machine components or moving mechanical assemblies.[1−3] Out of this, nearly 50% is attributed to mechanically induced deformation and wear of materials (including scuffing, abrasion, erosion, fretting, and rolling-contact fatigue).[4,5] To alleviate such degradations, surfaces are often subjected to a thermal diffusion treatment (such as case-carburizing, nitriding, *etc.*)[6] or protected with the application of a hard ceramic coating, such as CrN, TiN, TiC, *etc.*[7−9] Such engineered surface layers, however, eventually wear out due to limited thickness, and their repair or replenishment becomes a great challenge since additional treatments or redeposition of protective coatings is not feasible, especially for large components as in wind turbines and combustion engines.[10,11]

The creations of high contact pressure and shear forces on asperity tips is very common in most sliding interfaces, and they can give rise to high flash heating at least at the asperity levels, often reaching several hundred degrees Celsius.[12] Such a combination of high contact pressure, shear, and flash heating can often increase the extent of tribochemical, mechanochemical, and/or catalytic activities at sliding interfaces.[13−16] In the case of lubricated sliding contacts, these conditions may, for example, trigger rigorous tribochemical reactions between sliding surfaces and certain additives leading to the formation of a highly protective boundary film or tribofilm right at the contact interface, hence minimizing the progression of wear damage.[14,17,18] Such tribochemically derived boundary films mostly consist of the reaction products of the additives in oils, the surrounding atmosphere, and the specific tribomaterials being used. However, in the case of the catalytically active tribomaterials or surface layers, the chemical activity at the sliding interface may be dominated by tribocatalysis favoring the formation of carbon-based tribofilms.[19]

Catalysis is a very robust and versatile process by which reaction kinetics and thermodynamics can be manipulated or altered in a very favorable way to selectively enhance the chemical and/or catalytic activity of surfaces and interfaces.[20] It is typically achieved with the use of the right kinds of catalysts which themselves most often remain unaffected or not consumed by the catalytic action; hence, they are often available

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for repeated or continuous use in catalytic activity. Well-known catalysts include a wide range of transition metals but most notably the noble metals such as Pt, Pd, Au, Ir, Rh, *etc.* which can be used in very small amounts (most often at ppm levels or a few atomic layers) to trigger a favorable catalytic action or a catalytically mediated reaction.[21]

In the case when very favorable conditions for tribological contact coating (*i.e.*, high frictional heating, contact pressures, and shear forces) already exist, one would expect favorable tribochemical and/or mechanochemical events to take place. In the presence of a catalyst metal within the contact zone, these events may occur more readily and provide the opportunity to selectively create more robust, durable, and potentially very desirable tribofilms as recently demonstrated in a few model experiments involving gaseous, liquid, and solid forms of carbon precursors.[22−24] These nanocarbon-based tribofilms may, in turn, provide superior protection against wear. In the following sections, we will review some of these cases and discuss the specific fundamental mechanisms that were largely responsible for the formation of such nanocarbon-based tribofilms from gaseous, liquid, and solid sources providing ultralow friction and wear as schematically illustrated in Figure 1.

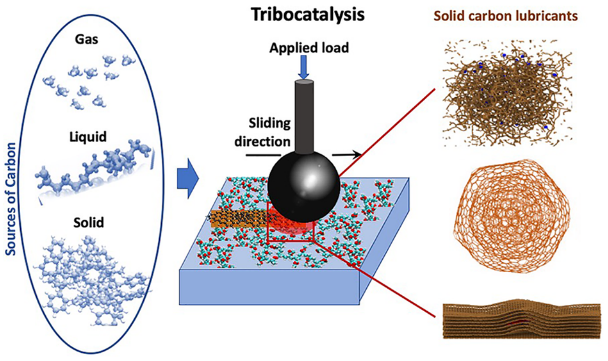

Figure 1. Summary of tribocatalytic nanocarbon film generation concept for ultralow friction and wear.

CARBON MATERIALS AND THEIR TRIBOLOGICAL PROPERTIES

Among the many materials available, carbon-based coatings, nanostructures, and solid nanocarbon-based lubricants have attracted a great deal of attention over the years from a tribological perspective. Thin-film coatings of various carbon forms such as diamond and diamond-like carbons, carbon nitride, graphene, *etc.* are widely used in traditional mechanical systems to enhance their friction and wear properties (Table 1). Most of these carbon coatings are hard and self-lubricating; hence, they can provide excellent antifriction and -wear properties even under dry sliding conditions.[25−27] Among all carbon coatings, diamond-like carbon (DLC) films perhaps attracted the most attention and have been some of the most widely used carbon forms in numerous industrial systems as protective coatings for friction and wear control for more than two decades.[28,29] Alternatively, polycrystalline diamond coatings, as the most abrasive but wear-resistant materials, found their niche in protecting cutting and drilling machinery.[30] Mechanically driven embedding of nanodiamonds from the diamond-containing solution resulting in the formation of diamond-based coatings has also helped to significantly decrease the friction and wear of metal and polymeric surfaces used in artificial joints.[31,32]

Graphitic (sp^2-bonded) carbon has also been used for years in powder form or as a sprayed coating for friction reduction in bike chains and locks operating in an ambient environment[34] as well as as an antifriction and wear additive in lubricating oils and greases for the lubrication of gears and bearing components.[40] Prior studies have demonstrated that the tribological characteristics of graphitic carbon coatings can be further improved by replacing the powder graphite form with layers of two-dimensional (2D) materials, such as graphene[25,26,41,42] and MoS_2.[43−45] Easy shear of 2D layers provides a set of characteristics needed for lubrication and suppressing damage in mechanical contacts.[46−51] Specifically, in the case of graphene, a 4−5 times reduction in friction and an as much as 4 orders of magnitude reduction in wear have been observed in steels.[41,42] This improved performance was interchangeable when transitioning between humid and dry environments.[25] Graphene alone was beneficial in lowering the friction and wear

Table 1. Summary of the Tribological Characteristics of Different Carbon Allotropes

Carbon lubricant films	*Thickness (μm)*	*Typical COF*	*Wear rates* (mm^3/m N)	*Wear/friction mechanism*
Graphite[33,34]	0.2−5	Dry: 0.5−0.6 Humid: 0.1−0.2	Dry: 10^{-4} Humid: 10^{-7}	Interlayer shear and water intercalation
Diamond-like carbon/ H-DLC[28,35]	1−3	Dry: 0.001−0.05 Humid: 0.2−0.3	Dry: ~10^{-6}−10^{-7} Humid: 10^{-5}	Tribochemically induced surface reaction and termination of top carbon atoms/high chemical inertness and repulsive forces due to hydrogen termination
Polycrystalline diamond (UNCD, NCD, MCD)[36,37]	0.5−1.5	Dry: 0.05−0.13 Humid: 0.007−0.1	$<10^{-8}$	Tribochemically induced reaction with H, O, or OH
Graphene/graphene oxide[25,26]	0.001−0.01	Dry: 0.15−0.2 Humid: 0.15−0.2	$<10^{-9}$	Interlayer shear and prevention of tribocorrosion
Onion-like carbons (OLC)[38,39]	0.01−1	Dry: 0.01−0.15 Humid: 0.15−0.2	$<10^{-8}$	Reduced contact area, ball-bearing mechanism

of a wide range of metal substrates, but when combined with another form of carbon, such as nanodiamonds, it further enabled the mechanically most desirable state of near-zero friction or superlubricity with no wear damage on sliding contact surfaces (Figure 2).[52] In addition to this and other studies demonstrating ultralow friction and wear of 2D materials,[53,54] researchers have also achieved very favorable tribological performance using various other carbon forms including nanotube, nano-onions, and nanodiamonds as additives in lubricating oils and other liquids.[31,32,38,39] In fact, such studies have gained high momentum in recent months with the hope that they can soon be reduced to some industrial products.[55−58]

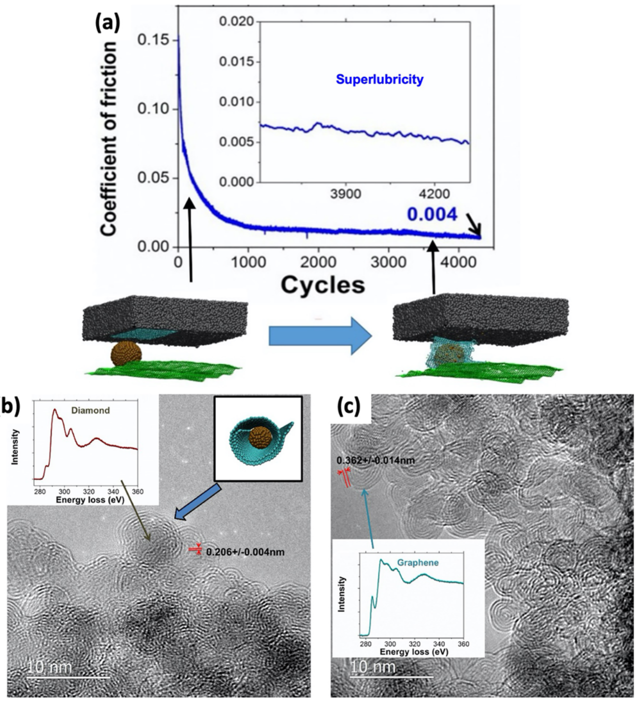

Figure 2. (a) Superlubricity (COF < 0.01) demonstration using graphene and diamond films indicating recombining of carbons in the wear track. Transmission electron microscopy (TEM) images confirm the presence of (b) diamond cores wrapped in (c) graphene layers. Adapted with permission from ref 52. Copyright (2015) AAAS.

All those mentioned carbon-based nanomaterials or structures indeed demonstrated the possibility of great tribological performance and, hence, applications in a broad range of moving mechanical systems.[59] However, in most of the previous studies, protective carbon films applied on the surfaces had a finite thickness (most often only a few micrometers thick) and required specific processing steps for long durability, usually involving high temperatures and/or plasma assistance. As a result, such add-on type protective films are very difficult if not impossible to repair once worn-out, damaged, cracked, or delaminated.

TRADITIONAL APPROACHES FOR THE SYNTHESIS OF LUBRICATING CARBON FILMS

Synthesis of carbon-based nanostructures (Table 1)[60,61] is often assisted by the high-temperature and -pressure conditions, as in the manufacturing of synthetic diamond, or is enabled by extraction from hydrocarbon gases through the use of catalyst metals, as in the synthesis of carbon nanotube, graphene, C_{60}, *etc.* in a chemical vapor deposition (CVD) reactor, which act as templates for solid carbon nucleation and growth.[62,63] For example, the synthesis of ultrananocrystalline diamond (UNCD) is most conveniently performed in a methane + hydrogen environment with the assistance of microwave plasma at temperatures above 600 °C.[36,64,65] DLC films can be produced at temperatures ranging from room temperature up to 400 °C by using plasma or ion-beam-based physical vapor deposition and CVD methods.[28,66] Meanwhile, graphitic structures such as graphene or carbon nanotubes usually require ∼800 °C processing conditions and such catalyst metals as copper and nickel.[67−69] In the past, researchers have also successfully demonstrated the synthesis of graphene layers from different gaseous, liquid, or solid carbon sources.[70] Again, the use of a specific substrate material or catalytic metals, such as, for example, copper or nickel, remains a key to the extraction of carbon from the mentioned hydrocarbon sources and in the nucleation and growth of different forms of carbon-based structures as summarized in Table 2.

It is important to note that after their initial deposition, some of the nanocarbon films may contain highly disordered or amorphous structures.[71] However, under the influence of high contact pressures and shear forces, amorphous structures often undergo a structural transformation, especially when exposed to higher temperatures of sliding contacts. For example, it was demonstrated that DLC films have a tendency to reform into layered graphitic structures or form carbon nano-onions under the influence of frictional heating during sliding,[72] while nanodiamonds may convert into onion-like carbon during annealing or exposure to an electron beam.[73] Additionally, using controllable exposure to nickel catalysts during the rapid thermal annealing process, it was possible to convert the very top layer of an ultrananocrystalline diamond (UNCD) film into graphene shielding a UNCD underneath.[74]

From the foregoing, it is very clear that the processes of carbon film formation at a sliding interface and transformation from one form to another are often enabled by the availability of three

Table 2. Traditional Approaches for CVD Synthesis of Carbon Materials[60] with Beneficial Tribological Characteristics

Forms of carbon materials	*Carbon source*	*Catalyst/substrate*	*Energy source*
Graphene	Methane, ethane	Cu, Ni, Pt, Co, Ir, Ru, Mo, Fe	Heating
Diamond-like carbon (DLC) and amorphous carbon	Methane, acetylene	Si, steel	Heating, RF plasma, direct current (DC) discharge, Penning ionization gauge (PIG)
Polycrystalline Diamond (UNCD, NCD, MCD)	Methane,	Si, Ti, W with diamond seeding	Heating, microwave plasma, hot filament
Carbon Nanotubes	Methane, ethylene, propylene, acetylene	Fe, Mo, Co, Ni, ferrocene, and iron pentacarbonyl	Heating, plasma, arc discharge, laser ablation
Onion-like carbons (OLC)	Acetylene, diamond NPs, phenolic resin	Fe/NaCl, Si	Heating, pulsed laser

major components: (i) access to the catalytically active surfaces, (ii) availability of a carbon form or a source, and (iii) a temperature increase to provide sufficient activation energy for carbon precursor dissociation and redeposition on the catalytically active substrates.[75,76] All three components mentioned above are often available in many tribological systems, and thus, they can be exploited as a process to manipulate tribofilm formation *in situ* and on-demand during sliding due to tribocatalysis.

Among the major components mentioned for the synthesis of lubricating nanocarbon films on sliding surfaces, high contact pressure, shear, and temperature are always present at least at the asperity tips leading to the onset of chemical reactions. It is well-documented that the dissipation of frictional energy generated during sliding can give rise to a significant increase in bulk and flash heating or asperity temperatures,[77] thus facilitating tribocatalytic decomposition of carbonaceous molecules and subsequent deposition on rubbing surfaces as a solid tribofilm. Previous studies[78−80] have indeed shown that under high contact pressure and shear, local asperity temperatures during sliding can reach up to 1773 K (Figure 3). Further, even in the cases of the lubricated sliding contacts, high contact pressures of the boundary lubrication regime squeeze out nearly all of the lubricant molecules outside the sliding interface and thus may trigger similarly high-temperature increases.

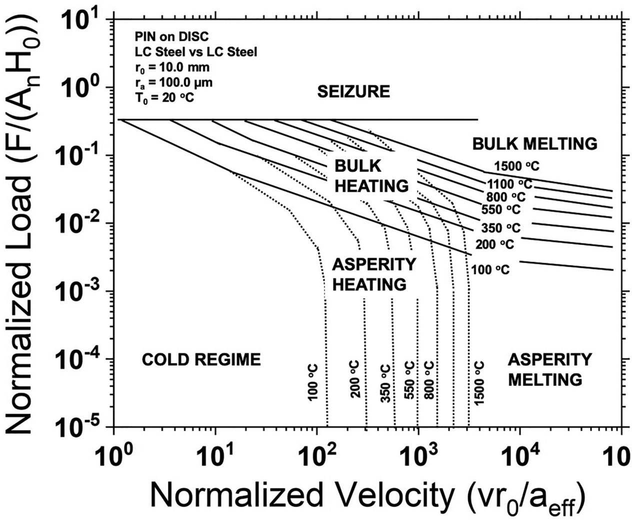

Figure 3. Temperature map for a low carbon steel pin sliding on a disk of the same material. *F* is applied load, A_n is the apparent contact area, H_0 is the hardness, *v* is the sliding velocity, r_0 is the radius of nominal contact, and a_{eff} is the mean diffusivity of the materials in contact. Adapted with permission from ref 78. Copyright 1991 Taylor & Francis.

BASICS OF TRIBOCATALYSIS AS AN *IN SITU* AND CONTINUOUS CARBON SYNTHESIS APPROACH

The concept of generation of the protective tribofilms during sliding has been previously explored for lubricated contacts. Among the most used models, major attention has been given to the Eyring model and the stress-assisted thermal activation (SATA) model or the Arrhenius model.

In the case of the Eyring model,[81−83] which applies to describing the mechanism of tribofilm formation from liquid lubricants, the amount of energy required for the sliding motion of lubricated contacts is explained by a thermally activated cage model. The sliding is enabled when enough activation energy is provided to overcome the cage-like potential barrier present due to the interactions of the surface molecules involved in sliding with those neighboring stationary molecules. The model, however, is limited in terms of providing quantitative analysis of such tribofilms' formation.

The Arrhenius model, meanwhile, has been employed for understanding the mechanochemistry of the sliding contacts. It aims to estimate the growth rate Γ for the tribofilm formation as a function of temperature and stress conditions:[84,85]

$$\Gamma = \Gamma_0 \exp(-(\Delta U_{act} - \sigma \Delta V_{act})/k_B T) \tag{1}$$

where Γ_0 depends on the effective attempt frequency and the molar volume of the growth species (23), ΔU_{act} is the internal activation energy (*i.e.*, the energy barrier in the absence of stress), σ is the mean value of the stress component affecting the activation barrier (assumed to be the compressive contact pressure), ΔV_{act} is the activation volume, k_B is Boltzmann's constant, and T is the absolute temperature.

Specifically, for initiating the growth of the tribofilm, the system should gain a certain activation energy to overcome the energy barrier. This activation energy is easier to provide by applying shear stresses rather than normal stresses. The model has been successfully employed for zinc dialkyldithiophosphate (ZDDP) film growth both in nanoscale and macroscale experiments.[85,86]

For a tribocatalytically mediated tribofilm formation process, some very specific theoretical hypotheses were proposed in the past, including the one claiming that the chemical reactions at the sliding interfaces are primarily triggered when precursor molecules are supplied with the energy high enough to overcome the energy of breaking the precursor bonds.[87] This needed energy to overcome the barrier for bond breakage can be provided by the specific tribocatalyst used and the high contact pressures generated during sliding. It was suggested that the energy required for the precursor molecules to go into a transition state decreases under the shear forces, thus decreasing the energy required to initiate the tribocatalytic reactions.[87] In this case, the energy introduced during sliding as mechanical work done on the solid material surfaces is accumulated in the vicinity of the contact spot and then emitted to the reaction zone (*i.e.*, asperity tips) for the catalyst reaction to proceed at temperatures much lower than for static contact or traditional catalytic systems. Tribocatalytic and tribochemical reactions, unlike the electronic excitation-driven typical chemical reactions, greatly depend on the energy accumulation at the mechanically modified interfaces.[88] The possibility of such energy accumulation that can take place in the layers adjacent to the top surface due to cyclic microplastic deformations[89] is thus important for triggering tribocatalysis. It is usually presented by structural defects, broken chemical bonds, or mechanical vibrations which altogether give rise to the formation of a highly chemically reactive state.[90]

Gershman *et al.*[91] characterized the possibility for the tribocatalytic effect from the nonequilibrium thermodynamics and the theory of self-organization of materials during rubbing. The authors confirmed that the higher concentration of the catalyst at the contact interface lowers the energy needed for activation of nonspontaneous physiochemical processes leading to carbon deposition from the carbon dioxide atmosphere and thus decreasing the wear rate of materials.[91]

The major idea behind the tribocatalysis of nanocarbon films is based on two major processes taking place near the catalytic

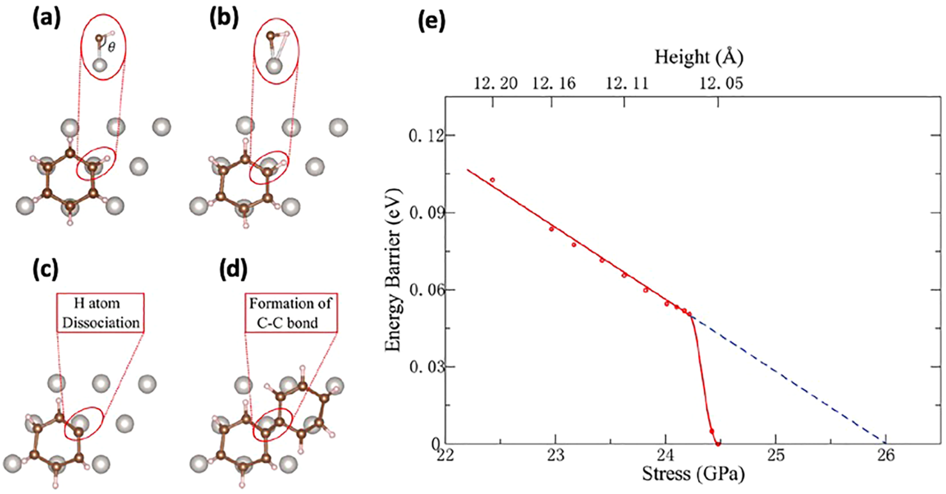

Figure 4. (a−d) Stages of the benzene molecule reconstruction on the Pt surface. (e) Lowering in energy barrier for benzene reconstruction into the tribopolymer upon stress and the presence of Pt catalyst. Reprinted with permission from ref 93. Copyright 2016 American Chemical Society.

metal surface: (i) dissociation of C−H bonds and random scission of backbone C−C bonds to form shorter hydrocarbon and carbon fragments and (ii) reconstruction of released carbon to form tribologically beneficial, mostly graphitic in nature, films.[92] As was shown by Li *et al.*,[93] both stress and the presence of the catalyst help to lower the energy barrier for such reconstruction (Figure 4). Specifically, the authors used the DFT model to show the linear dependence of the energy barrier on the applied stress due to the stress-increased energy of the system being added to the adsorbates on the surface that promotes their reactivity.[93] At a certain separation of the surfaces, the catalyst presence starts to affect the energy barrier, resulting in its sudden drop to zero values and thus enabling the carbon release.

It should be noted that the quantitative evaluation of the trbocatalytically induced film growth is challenging, as the process is self-limiting. The accessibility of the catalytically active surfaces is an important attribute for the tribocatalysis to facilitate the continuous growth of the carbon films. Therefore, the growth rate is expected to slow down with the increased thickness of the formed tribofilm and the reduced access to the catalytically active centers. Once the formed carbon film is worn during sliding, thus exposing the original surfaces, the tribocatalysis is reactivated.

TRIBOCATALYTIC EXTRACTION OF LUBRICIOUS CARBON FILMS FROM GASEOUS, LIQUID, AND SOLID CARBON PRECURSORS

Gaseous Sources. Several studies have recently focused on exploring the possibility of *in situ* extraction of lubricating carbon films from hydrocarbon gases or vapors facilitated by the use of different catalytic materials at sliding contact interfaces. Under static conditions, platinum has been used ubiquitously as a common catalyst for converting hydrocarbon gases into other carbon forms through dehydrogenation,[94] isomerization,[95] and oxidation.[96] Previous theoretical studies on ethylene for example indicated that with the temperature rising to 900 K, the adsorbed hydrocarbon species on Pt(111) are completely dehydrogenated and converted to graphene and/or graphite.[97,98] In the cases of dynamic sliding, the high contact loads and shear forces further assisted in the cracking of hydrocarbons into smaller reactive species and thus helped to enhance the propensity for tribochemical events.[93]

Under certain sliding conditions or regimes, the compressed isopropanol molecules trapped at the sliding contact interfaces and exposed to the catalytic platinum surfaces were shown to undergo scission and dehydrogenation processes followed by deposition of released carbon onto platinum in the form of lubricating solid films.[99] The researchers in this study claimed that the catalysis process occurred in two sequential steps: first, the dissociation of C−H bonds[100] near the sliding surface leading to the release of hydrogen and, then, the rapturing of C−C bonds. Though breaking the C−C bond (bond-dissociation energy of ∼347 kJ mol^{-1}) is, in general, easier than the C−H bond (bond-dissociation ∼414 kJ mol^{-1}), platinum, as a metal catalyst, assists in the dehydrogenation process *via* forming a three-centered transition state, in which metal−H and metal−C bonds form. The released free hydrogen is expected to be either forming H_2 molecules or adsorbing on the metal surface. Meanwhile, ruptured and dehydrogenated hydrocarbons recombine and form a diamond-like carbon film. Previous studies performed in a dry environment with traces of hydrocarbons at concentrations of 20−100 ng/L indicated the potential of Pt−Au films to initiate the formation of carbon-rich tribofilms, that in its turn results in ultralow friction (the coefficient of friction decreased to 0.01) and wear results (Figure 5).[99] Additionally, the formation of DLC films on platinum−aluminum alloys was observed in a dry sliding environment with the controlled introduction of organic vapors, such as isopropyl alcohol and hexane, in the testing chamber.[99] The observed reduction of friction to superlubricity values has been directly attributed to the tribocatalytic activity of the surfaces.

The formation of carbon-based tribofilms was observed not only from the partial pressures of organics but also from the atmospheric pressures of methane.[101] Methane is one of the major sources of carbon traditionally used in chemical vapor deposition of carbon materials, such as graphene,[102,103] polycrystalline diamond,[104,105] or diamond-like carbon.[106,107] In traditional CVD synthesis, the methane dissociation energy is provided by thermal or plasma assistance.[108] By exposing Ni-, Cu-, and CuNi-containing vanadium nitride coatings on steel substrates to sliding in a methane atmosphere, Ramirez *et al.*[101] demonstrated the formation of graphene, nano-onions, and

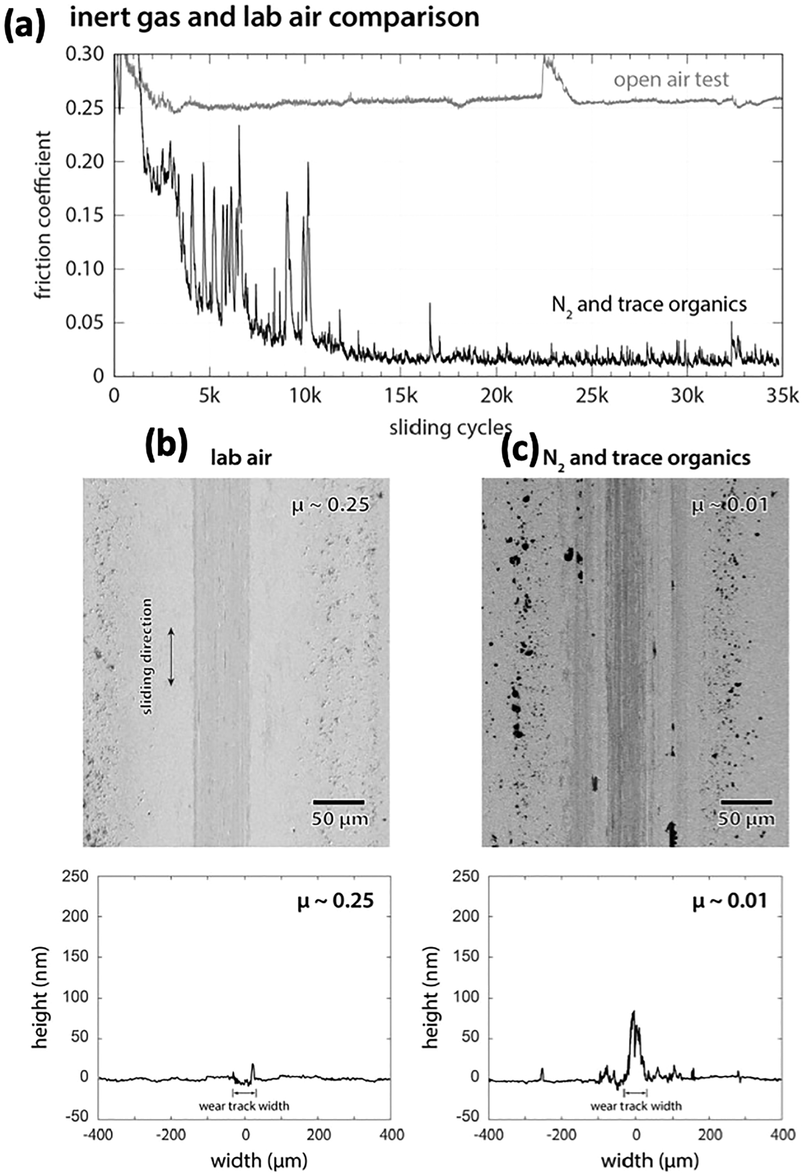

Figure 5. (a) Friction reduction to superlubricity values for a sapphire sphere sliding on a Pt−Au surface in open air and dry nitrogen with traces of organic environments. Comparison of the wear tracks formed in (b) open air and (c) dry nitrogen with traces of organic environments suggests formation of a carbon-based tribofilm responsible for the observed beneficial tribological performance. Reprinted with permission from ref 99. Copyright 2018 Elsevier.

disordered carbons directly inside the wear tracks. The carbon film formation led to a substantial reduction in wear of the sliding surfaces, *i.e.*, 2−3 orders of magnitude, in comparison to bare steel surfaces (Figure 6).

Detailed analysis of the wear debris collected from the wear tracks confirmed the very complex nature of the carbon tribofilms consisting of graphitic layers, amorphous carbon, graphene, and onion-like carbon clusters (Figure 7). The *ab initio* calculations for methane molecules on the Ni(111) and VN(100) surfaces indicated that the energies needed for the methane dissociation into carbon and hydrogen are 0.02 and 0.89 eV, correspondingly, which is not favorable under static conditions.[101] However, the mechanical stresses and local heating provided during sliding, as suggested by the MD simulations, could promote the dissociation processes, thus enabling the formation of carbon nanostructures at the sliding interfaces.

Tribofilm formation from the gas sources has also been shown to benefit the tribological performance of predeposited low-friction DLC coatings.[109,110] Specifically, the introduction of the partial pressures of ethanol to the main flow of hydrogen used as a tribotesting environment for the DLC sliding against a zirconia surface resulted in the stable friction fade-out to noise-level values (COF drop to 0.0001).[109] This observation has been attributed to the catalytically mediated hydrocarbon polymer film formation on the zirconia surface.

Liquid Sources. While the tribocatalytic formation of the carbon-rich lubricating films from the gaseous environment is a recent concept, the formation of the protective coatings from liquid lubricants has been an area of interest for decades.

Wear protective tribofilm formation is a common practice in oil lubrication. For this, additive packages that work for application-defined surfaces and sliding parameters are usually created. One of the most used additives is zinc dialkyldithio-

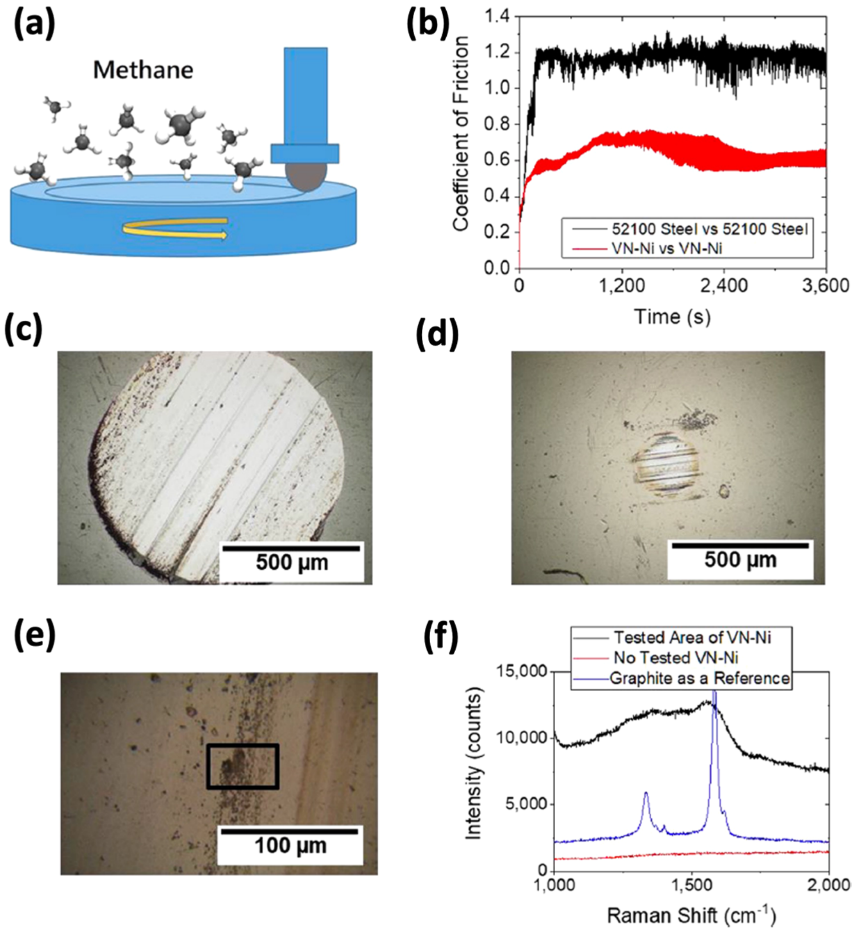

Figure 6. Friction and wear reduction initiated by the formation of carbon-based films during sliding in a methane environment. (a) Schematic of the test, (b) friction results, and the corresponding wear results for (c) a bare steel ball and (d) a VN-Ni-coated ball. (e) Formation of the blackish wear debris inside the VN-Ni wear track suggests tribocatalytic formation of carbon-based films as confirmed by Raman (f). Reprinted with permission from ref 101. Copyright 2020 American Chemical Society.

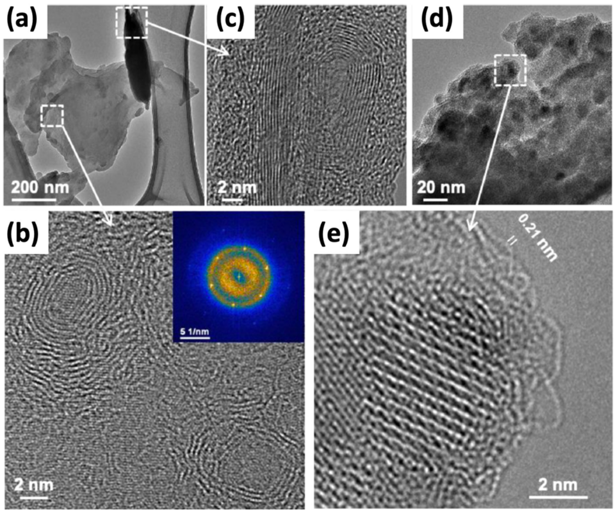

Figure 7. TEM images of the wear debris demonstrating the formation of (a) carbon-based tribofilms of different nature, (b) OLC, and (c) graphitic and (d and e) amorphous carbon, inside the wear track. Reprinted with permission from ref 101. Copyright 2020 American Chemical Society.

phosphate or ZDDP. Extensive macroscopic[111,112] and microscopic studies[85] have demonstrated that when introduced onto oil-lubricated sliding steel and/or cast iron surfaces, ZDDP molecules decompose readily during rubbing action and form a tribochemical, or tribo, film that minimizes direct metal-to-metal contacts and thus reduces wear. These tribofilms consist of rough and patchy islands of pyro- or orthophosphate glasses bonded to the metal surface by zinc polyphosphates. First-principles atomistic simulation suggested that the formation of such tribofilms primarily results from contact pressure-induced cross-linking of zinc phosphate molecules.[113] Gosvami *et al.*[85] further demonstrated that the growth rate increases exponentially with applied compressive stresses or temperature increases (Figure 8). Interestingly, the films can grow regardless of the iron presence or availability at the contact interface.[85,114] In those cases, though, the tribofilms are mostly phosphorus based and do not undergo a tribocatalytic decomposition or conversion into the solid lubricant films.

In another effort, the formation of carbon-rich tribofilms was achieved from lubricating oils containing nanocolloids of magnesium silicate hydroxide (MSH).[23] MSH is one of the main components of serpentine minerals with its tribological properties mainly being dependent on the release of Si−O, Mg−O, and −OH active groups that can form a tribochemical layer during the friction process.[115] Cross-sectional transmission electron microscopy (TEM) analysis of these layers which formed during sliding in MSH-containing synthetic oil unraveled the presence of the DLC-like structures in them

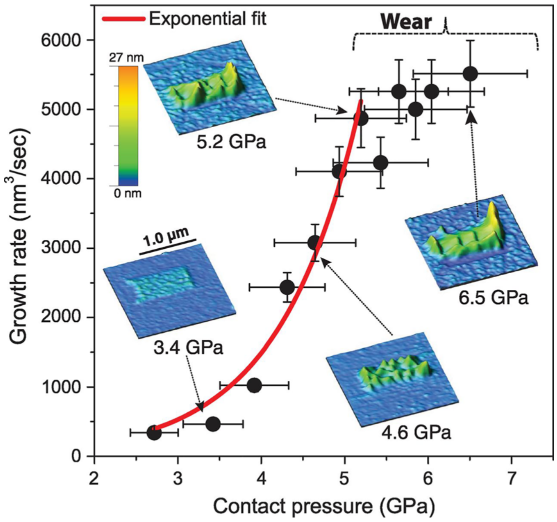

Figure 8. Tribofilm formation rate as a function of applied contact pressure. The analysis of the tribofilm formation on the iron oxide surfaces was performed for the DLC-coated silicon AFM tip immersed in ZDDP-containing base oil. Reprinted with permission from ref 85. Copyright 2015 AAAS.

(Figure 9). The Raman analysis revealed that these DLC-like structures were composed of a mixture of both crystalline and amorphous carbon phases. Replacement of the MSH additives with nano black phosphorus (BP) additives enabled further lowering of the friction to the macroscale superlubricity regime.[116]

Recently, the targeted or controlled formation of carbon-based materials has been considered an effective practice for enhancing the tribological performance of moving mechanical systems in several studies. Erdemir *et al.*[92] have confirmed the formation of DLC-based boundary films within the wear track of the catalytically active nanocomposite coatings during sliding in base oils. For this, a thin film of a metal oxide (MeN), MoN_x, matrix with incorporated clusters of catalytically active Cu has been sputtered on steel surfaces. During sliding in poly alpha-olefin oil (PAO), tribocatalytic processes facilitated the decomposition of oil molecules into dimers and trimers and subsequent redeposition of them as a carbon-rich tribofilm inside the wear tracks and scars of such coated disks and balls. Analysis of the tribofilm supported by the molecular dynamic (MD) simulations further substantiated the DLC-based chemical nature of such tribofilms. These catalytically driven DLC films significantly reduced the wear of the sliding interfaces. Figure 10 provides the representative summary of the process of tribocatalysis on the MoNx-Cu surfaces from olefin molecules resulting in the formation of the DLC films.[92]

Xu *et al.*[117] tried replacing the catalytically active copper in the MoN matrix with Pt and observed a similar formation of amorphous carbon inside the wear track during sliding of the film against the silicon nitride ball in the PAO10 synthetic oil. Analysis of the wear track suggested that during sliding under the high Hertzian contact pressure of 1.7 GPa, the PAO10 oil underwent dehydrogenation and a carbon chain scission process leading to the formation of an amorphous carbon film in the wear track. Notably, not only has the resulting wear rate of the materials been substantially reduced (to 1.08×10^{-8} mm^3 (N m)$^{-1}$), but the coefficient of friction also decreased from ~0.15

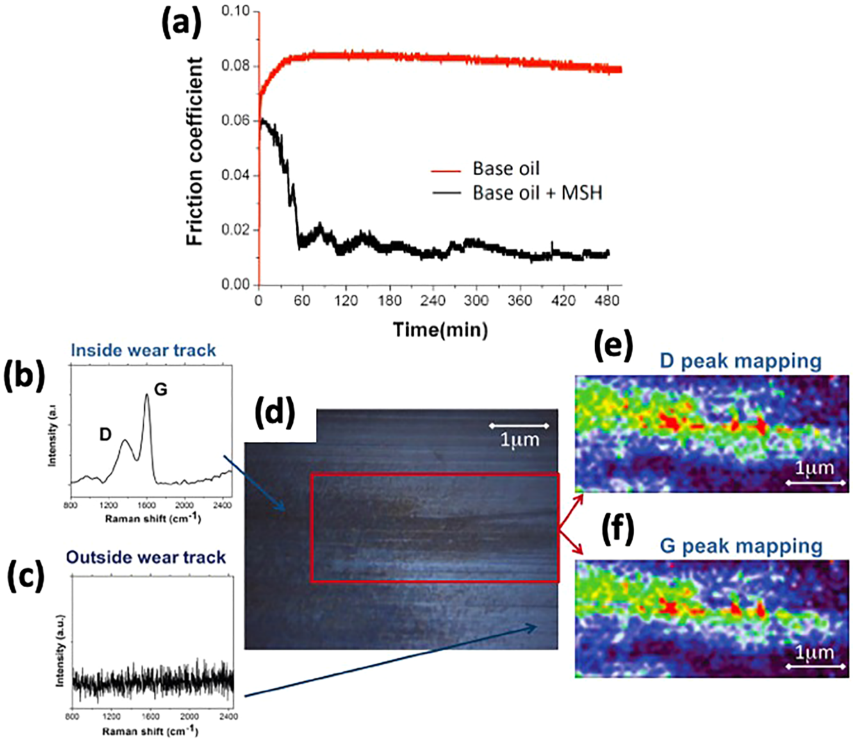

Figure 9. Formation of lubricating DLC-like films facilitated by MSH in oil. (a) COF results indicating a decrease in friction values when MSH is added to the oil. Raman spectra (b) inside the wear track and (c) outside the wear track formed during sliding (d). Raman 2D mapping of the carbon (e) D peak (at ~1340 cm^{-1}) and (f) G peak (at ~1560 cm^{-1}) confirms the DLC nature of the formed tribofilm. Reprinted with permission from ref 23. Copyright (2016) Elsevier.

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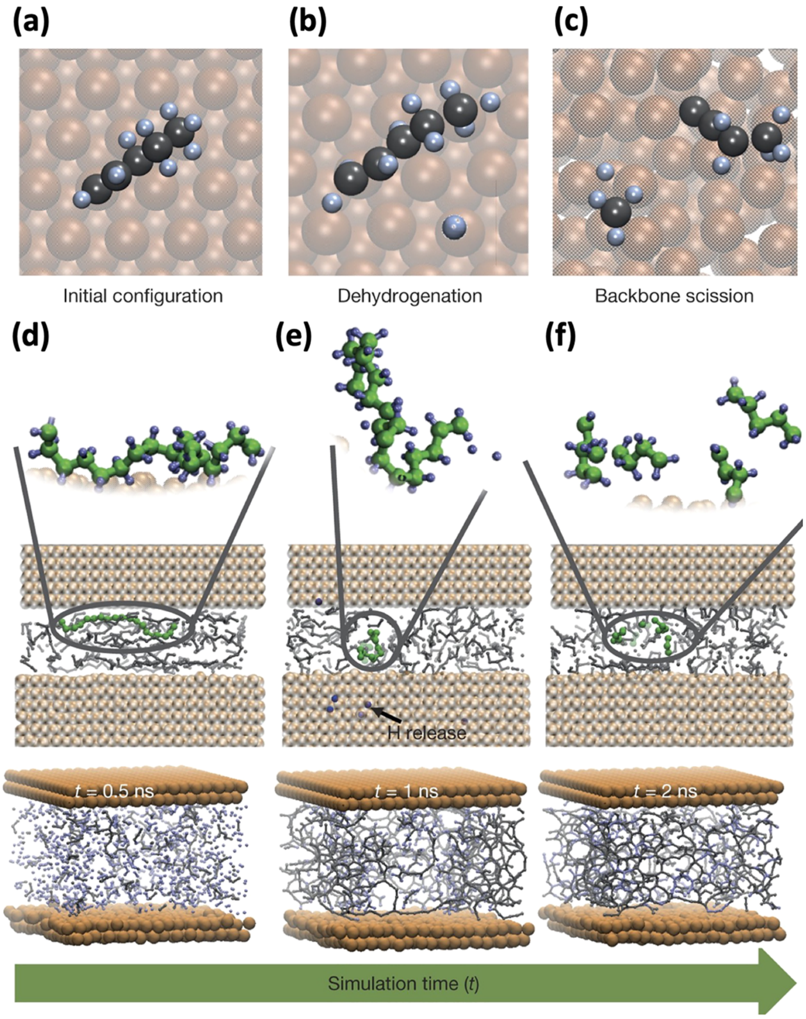

Figure 10. Tribocatalysis mechanism. (a−c) AIMD simulations illustrate the catalytic action of copper, dehydrogenating and breaking linear olefins into shorter-chain hydrocarbons. (d−f) A similar reaction pathway is predicted by the reactive molecular-dynamics simulations. The end result is that dehydrogenated short-chain hydrocarbons recombine to nucleate, and grow into, a compact amorphous carbon tribofilm. Simulations suggest that this tribofilm mechanism is suppressed on surfaces where carbide formation is thermodynamically favored. Reprinted with permission from Springer Nature.[92] Copyright 2016.

for bare steel to ∼0.04 for the coating.[117] Further, a similar mechanism of the carbon-based film formation from oil was reported for MeN coatings with tribocatalytically active silver patches.[118]

Alternatively, the MeN-Cu coatings demonstrated great potential for tribocatalytic activation of the protective tribofilms' formation in different alkane environments with the alkane molecule length and wetting characteristics affecting the effectiveness of the film growth and protection.[119] Alkane-based and alcohol-based environments as hydrocarbon sources have also been reported to facilitate the formation of graphene-like structures on tungsten carbide[120,121] and MoS_2[122] surfaces.

In addition to the common widely used hydrocarbon sources, the formation of graphitic layers has been detected from proteins of the body fluids in metal-on-metal hip replacements that are made of catalytically active metals such as cobalt and molybdenum, triggering carbon film formation.[123] That, in turn, allowed the wear to be suppressed in enclosed artificial joint systems.

Solid Sources. In contrast to liquid and gaseous carbon sources, the formation of the superlubricating tribofilms from solid carbon precursors, while it has also been demonstrated, was proven to be more complex and challenging as the source of the precursor materials is limited to their availability at the sliding interfaces. In this case, the solid carbon precursor can be either dispersed on the surface prior to the tribotest or continuously provided by the carbon-based counterfaces that are subject to wearing-off during sliding.

The concept of precoating the contact interfaces with solid carbon sources, such as polymers, has been initially explored for the lubrication of microelectromechanical systems (MEMS),[124,125] though it is usually considered as a deficiency for the systems' performance leading to an increase in the contact resistance.[126] Hook *et al.* coated the MEMS microdevice with a monolayer of tridecafluorotris(dimethylamino)silane (FOTAS).[127] Upon repetitive normal loading and sliding cycling, though, the tribologically induced modifications of the materials at the contact interface led to negative effects, such as increased adhesion of the surfaces, which was attributed to changes in the chemical (such as surface energy) and physical (such as roughness and real contact area) nature of the contacting surfaces. The formation of the tribopolymer on Pt MEMS contacts has also led to an increase in the electrical contact resistance.[126,128]

Transitioning to a macroscale sliding regime involving larger contact areas, however, enabled the generation of a carbon-rich tribofilm which markedly enhanced the tribological performance of the whole tribosystems. Even more, tribocatalytically induced phase transformation within the contact interfaces resulted in the lowering of the friction and wear to near-zero values or to a superlubric regime. This was achieved by mixing MoS_2 with nanodiamond particles.[24] During sliding, the MoS_2 layers disintegrated and subsequently released sulfur and molybdenum into the sliding contact zone and thus triggered the amorphization of diamond nanoparticles and then their subsequent conversion into onion-like carbon (OLC) structures.[24] The resulting OLC exhibited much superior lubrication capacity with friction coefficients well within a superlubric sliding regime.[24]

In another study (Figure 11),[129] it was also shown that the catalytically induced transformation of carbon to OLC during sliding in a dry environment can lead to significant reductions in friction and wear. Specifically, iron nanoparticles dispersed on the silicon substrate surface during sliding against DLC counterfaces facilitated the reconstruction of DLC into OLC structures.[129] The resulting OLCs of ∼30−50 nm in diameter were capable of supporting the contact load and thus separating the sliding surfaces by acting as ball bearings and thus reducing the coefficient of friction and wear of the whole sliding system. This tribocatalytic conversion was very sensitive to oxygen presence as oxygen seizes the carbon reconstruction and thus leads to high friction and wear during sliding.

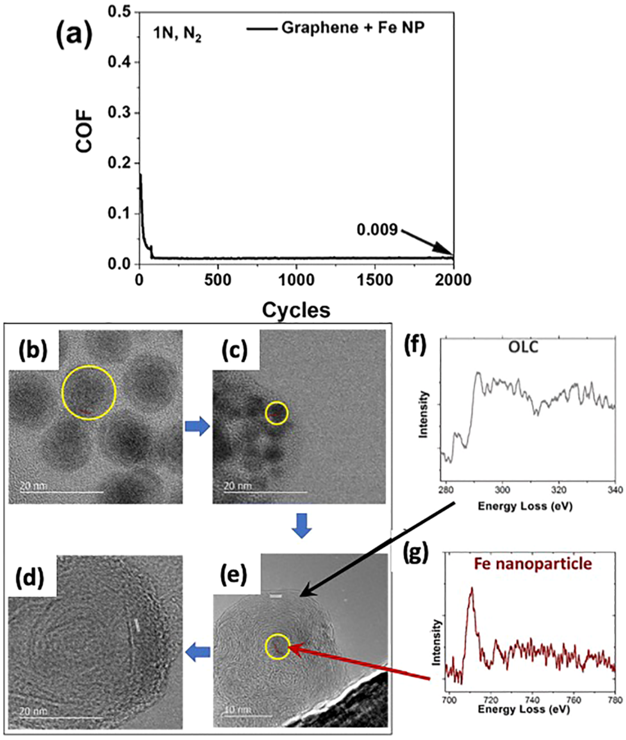

Figure 11. (a) COF evolution of graphene + FeNP sliding against DLC in a dry nitrogen environment. TEM evaluation of wear debris collected from the wear track at different sliding time intervals ((b) initial and (c) after 100, (d) 200, and (e) 500 cycles) and the corresponding electron energy loss spectra for (f) OLC and (g) Fe, demonstrating tribocatalytic iron−carbon transformation. Reproduced with permission from ref 129. Copyright 2019 Wiley-VCH.

Similar to the tribocatalysis that reduces or overcomes the high energy barriers for decomposition of longer-chain hydrocarbon molecules of oils, external heating or thermal energy is often needed for the formation of solid carbon tribolayers on sliding surfaces from the solid carbon sources. In fact, the formation of an easy-shearing carbon film from the burnished MSH/C coating has been proven to be facilitated by the elevated temperatures during sliding in an open-air environment, and the resultant tribofilm afforded high-temperature superlubricity (*i.e.*, the COF of 0.008) to such sliding surfaces.[130] It was shown that such tribofilms provided extreme protection against the wear of the sliding surfaces. It should be noted, though, that such burnished solid carbon coatings are often unreliable as they wear out or are removed from the sliding surface more readily, thus only providing very limited benefits of the lubricant.

CONCLUSIONS AND FUTURE PROSPECTS

This review summarized some of the recent research activities dealing with the *in situ* generation and replenishment of highly wear-resistant and lubricious tribofilms resulting from tribocatalysis under the influence of high contact pressures and shear forces. From the published results, it looks as though tribocatalysis can potentially help resolve some of the major shortcomings of the traditional ways of overcoming friction and wear through the formation of phosphorus-rich boundary films from fully formulated oils or through the uses of physical or chemical vapor deposition of protective coatings on tribological surfaces. Table 3 summarizes the major shortcomings of the traditional lubrication approaches and the potential pathway for addressing them with tribocatalysis.

While the use of additive packages in liquid lubricants follows a similar concept of *in situ* tribofilm formation, such an approach, however, is unavailable for a range of operation conditions involving sliding contacts in dry hydrocarbon-based gaseous or solid environments, thus suggesting that tribocatalysis broadens the range of the tribological systems capable of continuous replenishment of the low-shear and highly protective tribofilms. It should be noted, also, that the tribocatalytically formed carbon films demonstrated high robustness during sliding. Highlighted in this review results (*e.g.* Figures 5, 6, and 9) indicate their high durability for the whole long-duration tests performed in different environments over several hours. This is mostly due to the fact that oftentimes only a very small supply of the hydrocarbon source is needed to enable the tribocatalytic replenishment of the protective carbon films. Notably, in contrast to traditional lubrication approaches, the tribocatalysis is the self-regulating approach that continues while the catalytically active surfaces are exposed and diminishes once the sliding surfaces are covered with the tribocatalytically generated carbon films.

Further, we provide specific examples of recent successful efforts in this direction that clearly showed super low friction and wear and will thus potentially extend the tribological performance, efficiency, and reliability of the sliding mechanical systems beyond what is currently feasible with other methods. Specifically, it was shown that the *in situ* formation of carbon films is quite feasible from gaseous, liquid, and solid carbon sources using a wide range of catalytically active tribomaterials. The key differences among the films formed in different environmental conditions, though, need further investigation to identify the major underlying mechanisms responsible for tribocatalysis in various gas/liquid/solid source lubrication cases.

Table 3. Summary of the Lubrication Approaches in Comparison to Tribocatalysis

Approach	*Examples*	*Operation environment*	*Lubrication mechanism*	*Advantages*	*Limitations*
Liquid lubricant	Base oils, biolubricants, water, *etc.*	Lubricated	Wetting surfaces, shearing in between liquid layers	Easy replenishment	Failure upon lubricant starvation regime, not compatible with dry sliding and high temperature
Additives in liquid lubricants	TCP, ZDDP, IL in oils	Lubricated	Tribofilm formation activated from additives	Formed tribofilm provides protection upon lubricant starvation	Designed toward specific surfaces, requires certain activation energy, not compatible with dry sliding
Coatings	Carbide (*e.g.*, WC), nitride (*e.g.*, CrN, AlN), oxide (*e.g.*, Al_2O_3) coatings	Dry and lubricated	Shearing of the planes, high hardness-supported wear reduction	Compatible with various environment and high-temperature regimes	Need replenishment (usually requires certain deposition conditions)
Solid lubricants	Graphene, BN, MoS_2 flakes	Dry and lubricated	Shearing of the planes	Compatible with various environment and high-temperature regimes	Need replenishment (but easier than coatings)
Tribocatalysis	Catalytic elements in coatings or powders (*e.g.*, Mo, Cu, Pt)	Dry and lubricated	*In situ* formation of protective tribofilm	Continuous replenishment of the protective films, compatible with various environment and high-temperature regimes	Source of hydrocarbons (easy to provide in a range of applications)

The review also unravels the promise of tribocatalysis in the realization of ultralow friction and wear properties in future sliding systems across the scales. Broad adaptability of this concept to a wide range of operating environments (*i.e.*, gaseous, liquid, solid), contact pressures, and ambient temperatures further reinforces the notion that tribocatalysis indeed presents a direction for the design of more robust and tribologically efficient mechanical systems than those that were available before. Though still in the early stages of realization, the interest in tribocatalysis from both the fundamental science and application potentials in the industry is expected to bring more attention to this topic in the near future and thus enable more efficient, durable, and environmentally compliant mechanical systems. The continuous and *in situ* repair of sliding surfaces has been a highly desirable goal of all moving mechanical assemblies for many decades, and the concept of tribocatalysis may offer possibilities toward achieving such a goal with more active research and industrial interest in the concept. Moving forward, the major challenges that should still be addressed are the fundamental understanding of the key underlying mechanism of tribocatalysis under high-pressure and -shear conditions and how it can be manipulated to control friction and wear more reliably over a wide range of environmental and/or sliding conditions. So far, the focus of the prior work has been to find the specific conditions that would work for those materials that could readily trigger tribocatalytic effects. For further successes, meanwhile, the concept should be further broadened to identify those more specific material requirements that can more favorably or selectively trigger tribocatalysis when used under specific sets of tests or application conditions. In this respect, the use of emerging computational tools including artificial intelligence/machine learning may further help in the selection of more robust catalyst metals or alloys leading to the formation of more effective tribofilms providing much better tribological performance.

Overall, tribocatalysis offers a perspective on better addressing the friction, wear, and lubrication issues in moving mechanical systems in the future, from macroscale machinery to micro- and nanoelectromechanical devices.

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Notes

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VOCABULARY

Tribocatalysis, Acceleration of a chemical reaction induced by the presence of material exposed to a sliding/rubbing process; Hydrocarbon, Compound containing the elements hydrogen and carbon; Coefficient of friction, Force acting against sliding, friction force, divided by the normal load; Wear, Physical loss of materials due to friction during sliding; Solid lubricants, Solid materials used to reduce friction; Sliding interfaces, Two surfaces that are in physical contact during sliding; Superlubricity, Reduction of coefficient of friction to near-zero values, below 0.01

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