

Elastomer-Steel Laminate Armor

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Introduction: The final countermeasure against bombs and bullets is mitigation of the effects of the blast or ballistic impact. The rise of terrorism has led to increased efforts to develop better armor, including lighter materials to expand the range of applications, for example to civilian infrastructure. Elastomeric coatings applied to building foundations minimize fragmentation from a bomb blast. This helps the building retain its structural integrity and also minimizes collateral damage (flying debris is the second leading cause of injury to occupants of a bombed building). Elastomers also increase the resistance to ballistic penetration when applied to hard substrates. This approach was an early method of “up-armor” Marine Corps Humvees during Operation Iraqi Freedom. The initial coatings were elastomeric polyurea, which is easy to process and generally regarded as a mechanically “tough” material. However, since the operating mechanism of the coatings was unknown, the material could not be optimized.

The physics of ballistic penetration is complex, with the nature of the interaction and its effects dependent on the properties of both target and projectile. Moreover, rubber is viscoelastic, so that its mechanical behavior varies with deformation frequency.¹ This rate dependence can drastically alter the response — from liquid-like, to rubbery, to a glassy state — as the perturbation frequency increases. Since elastomers are also highly nonlinear (their properties depend on the magnitude of the strain), analysis of impact penetration can be difficult, requiring deconvolution of these effects.

Damage mitigation from elastomeric coatings likely relies on a variety of mechanisms. We have identified one important factor, in turn enabling critical aspects of the performance to be identified. The result has been the discovery of new and improved elastomeric coatings. Teaming with the Naval Surface Warfare Center, Indian Head Division (NSWC-IH), this led to the development of a laminate design that provides superior resistance to ballistic penetration, in combination with lower weight.

Ballistic Impact Response: The average strain rate for ballistic impact is the ratio of the projectile speed to the coating thickness, typically about 10^5 s^{-1} . The rate of motion of the segments (repeat units) of the chain molecules comprising the elastomer depends on temperature. For common elastomers, such as those

in tires, at room temperature these segmental motions occur at GHz and higher frequencies. However, for certain elastomers (including polyurea) they can be much slower. If this rate is on the order of the strain rate imposed by the impacting projectile, the polymer response will change from rubbery to glassy behavior (Fig. 1).² This impact-induced viscoelastic transition of the rubber is crucial for impact mitigation because the greatest energy dissipation occurs when segmental motion of the molecules occurs on the time scale of the external perturbation, causing the kinetic energy of the bullet to be converted to heat within the coating. Our tests showed that elastomers meeting this criterion had significantly higher penetration velocities (V_{50} , also known as the ballistic limit) for blunt projectiles.

Laminate Structures: Armor is always a compromise between performance and weight, and thinner elastomer coatings have lower V_{50} . However, there is a threshold around 3 mm, above which the performance changes weakly with thickness (Fig. 2). This means that the surface of the coating is dissipating a disproportionate amount of the impact energy. The near invariance of V_{50} to thickness can be exploited with a multilaminate structure. Various combinations of elastomer-steel layers were incorporated into armor structures; multiple layers always outperform single bilayers (Table 1).³

This approach was extended by making the coating itself a laminate of rubber and aluminum. With negligible increase in weight, this increases V_{50} by over 60% (Table 1). Using conventional “Rolled Homogeneous Armor,” more than twice the thickness would be required to achieve equivalent performance. A laminate construction forces a longer path-length for the incoming shock wave, due to impedance mismatching between the elastomer and metal. The multiple reflections break up the wave into a series of lower-amplitude waves. This is seen in the profuse, fragmented damage of the target (Fig. 3).

Summary: Elastomeric coatings can enhance the resistance of steel armor to high-speed projectiles. The requisite property is that the impact frequency be within the range of rates of segmental motion of the polymer molecules. Multiple bilayers further increase the ballistic limit by breakup and attenuation of the pressure wave due to impedance mismatching. Reduced weight, facile installation, use of commercially available materials, and multihit capability are among the advantages of the elastomeric coating, whose applications extend beyond military armor to include such uses as railway car and tanker protection, explosion barriers, and fragmentation protection panels.

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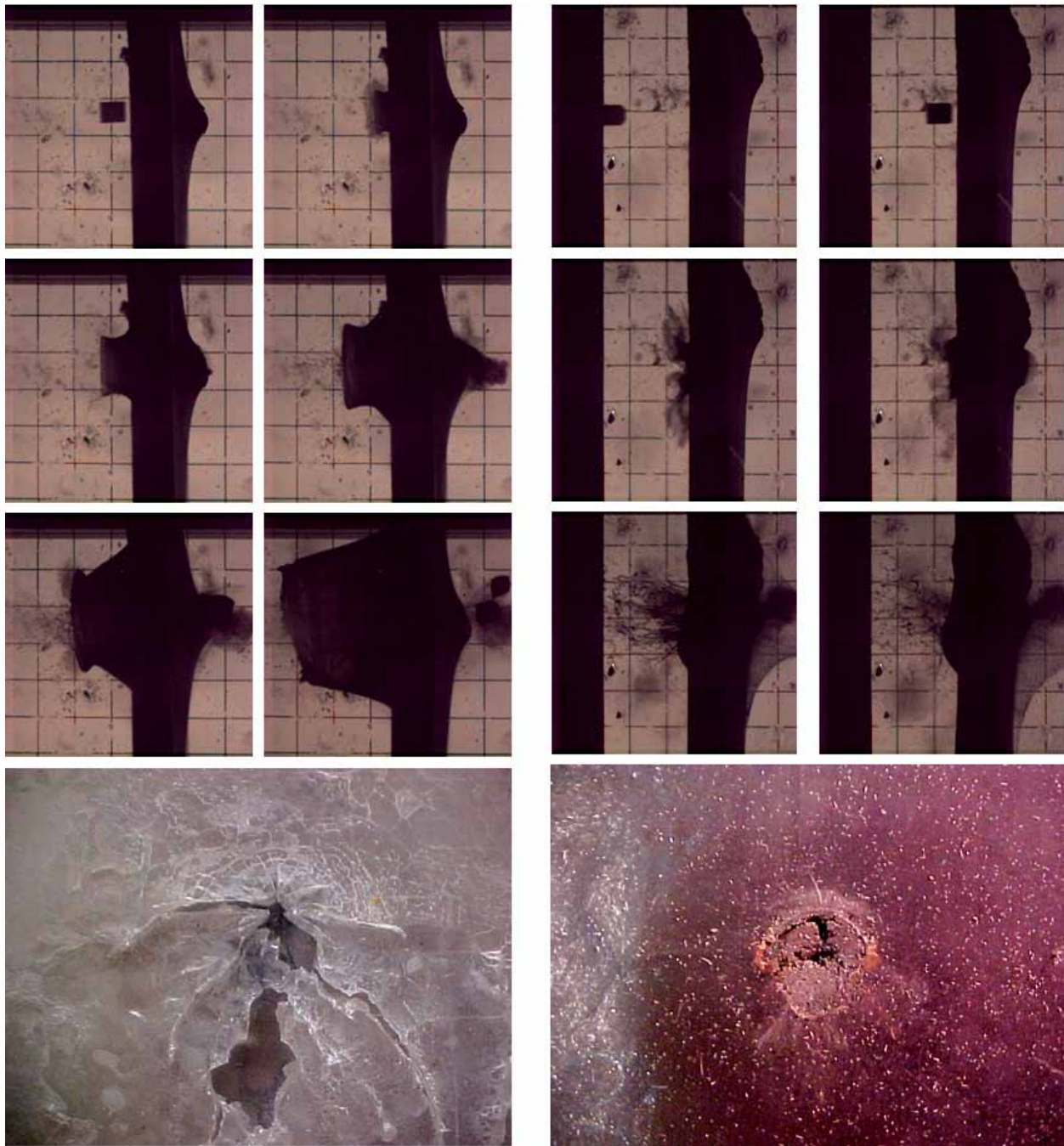


FIGURE 1

Left: Six high-speed photographs (top) of the impact response of a conventional elastomer responding in rubbery fashion with (bottom) substantial cracking. Right: The photographs (top) show the elastomer undergoing an impact-induced viscoelastic transition with (bottom) failure via shear-dominated separation of a cylindrical section of material having a cross section matching that of the blunt projectile. The projectile arrives from the left with a speed of ~ 900 m/s. The grid lines are spaced 25 mm apart.

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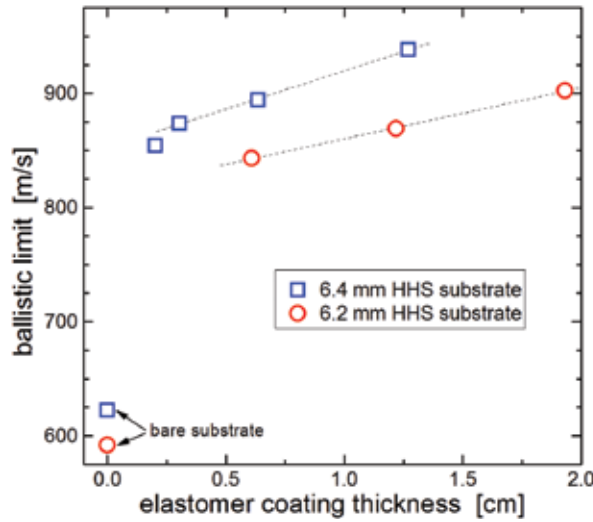


FIGURE 2
Variation in V_{50} for two steel plates as a function of the thickness of the elastomer coating (HHS = High Hard Steel). The dashed lines are the fits to the linear portion of the data, extrapolation of which gives a V_{50} much larger than that measured for the uncoated steel substrate.

TABLE 1—Effect of Front-Surface Elastomer Layers on Ballistic Limit of Steel Plates

construction	steel layers	elastomer layers	areal density [†] (kg/m ²)	V_{50} (m/s) [®]
single layer	one 12.7 mm [†]	none	99	1097 ± 15
single layer	one 12.7 mm [#]	none	99	1184 ± 5
bilayer	one 12.7 mm [#]	one 12.7 mm	113	1483 ± 7
four layers	two 6.4 mm [#]	two 6.4 mm	113	1819 ± 2
eight layers	four 3.2 mm [#]	four 3.2 mm	113	1579 ± 7
bilayer	one 12.7 mm [#]	one 6.4 mm	106	1365 ± 6
four layers	two 5.3 mm [#]	two 3.2 mm	90	1457 ± 1
single layer	one 5.3 mm [#]	none	42	622 ± 7
21 layers	one 5.3 mm [#]	6.1 mm total (21 soft)	48	869 ± 1
21 layers	one 5.3 mm [#]	6.1 mm total (11 soft / 10 hard))	51	1006 ± 5

[†]weight per unit area

[®] MIL-STD-662-F using 0.50 cal fragment simulating projectiles

[†]Rolled Homogeneous Armor

[#]High Hard Steel (MIL-A-46100)



FIGURE 3
Profuse damage accompanying penetration of laminate with 21 alternating elastomer and aluminum layers.

Contaminant Monitoring in Ground and Surface Water

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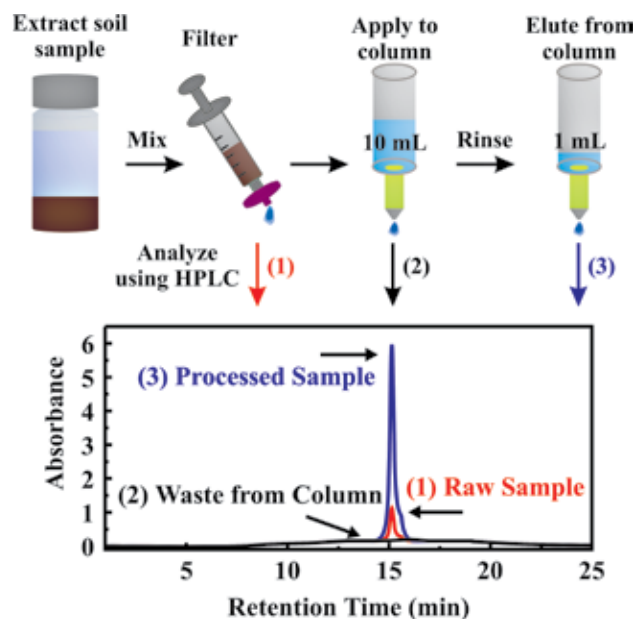
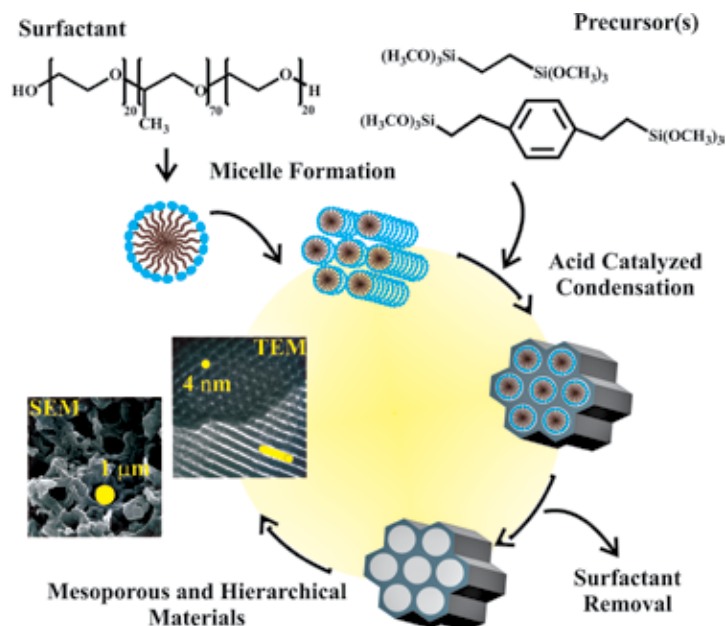
Contamination of Ordnance Ranges: The nitroenergetic compounds RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine), HMX (octahydro-1,3,5,7-tetra-nitro-1,3,5,7-tetrazocine), TNT (2,4,6-trinitrotoluene), DNT (2,4-dinitrotoluene), and nitroglycerin (trinitroglycerin) are used as explosives and propellants in common ordnance. These compounds are present in the soil, ground water, and surface water at many U.S. Department of Defense (DoD) testing and training facilities as a result of the activities, both current and former, at those sites. Many of these compounds are cardioactive as well as suspected or confirmed carcinogens. There is concern regarding the ecological impact and the threat posed to personnel as a result of the persistence and distribution of nitroenergetic compounds.

Methods for monitoring levels of these compounds are needed to provide relevant data on the expansion of contaminated areas and the resulting threat to surrounding populations and wildlife. Monitoring the presence of such contaminants in the environment is challenging due to the rapid diffusion of targets into the surrounding matrix. Preconcentration of targets is often necessary to provide levels that are detectable by currently available technologies. Preconcentration involves processing a large volume of sample in order to provide a high concentration in a smaller volume. It is also often desirable to remove nontarget analytes from samples to prevent their interfering with evaluation of targets.

Novel Materials for Monitoring Contamination Levels: Preconcentration by solid-phase extraction (SPE) involves adsorbing targets onto a solid support. Desorption of target is accomplished either through a thermal process or through elution from the support using a solvent, resulting in more target in a smaller volume. Selective and semiselective adsorption can also help to eliminate nontarget compounds from the

FIGURE 4

Synthesis of porous sorbent materials. Synthesis begins with the formation of surfactant micelles in solution. The siloxane precursors are condensed around the organized micelles, which act as a template for the pore structure. After extraction of the surfactant, an organized system of pores of 2 to 8 nm diameter remains, as shown in the transmission electron microscopy (TEM) image. Coupling this templating process with a phase-separation process during synthesis produces the large pores (~1 μm) shown in the scanning electron microscopy (SEM) image.

**FIGURE 5**

Preconcentration of TNT. The sorbents have been applied to the pre-concentration of TNT from soil extracts for enhanced detection. First, the soil is mixed with water to solubilize the contaminants. The particulate is then removed from the sample using filtration. A large volume of the resulting solution is applied to the sorbent column. Targets are then eluted from the column in a small volume of solvent. HPLC analysis shows the level of TNT to be quite low in the raw soil extract (1). The level of target washing through the column is undetectable (2). The concentration of TNT in the column eluent is significantly enhanced over that in the raw sample (3).

resulting sample. Our efforts in developing SPE materials have focused on periodic mesoporous organosilicas (PMOs), which are materials that combine organic groups with inorganic silica components to produce sorbents with the properties of both.^{1,2} The materials are rugged and stable, withstanding temperatures of up to 200 °C and a wide range of solvents and pH levels. The materials are synthesized as shown in Fig. 4. First, a surfactant is placed into solution at a

concentration high enough to force the formation of organized groups of molecules called micelles. Siloxane precursors, which have alternating organic and silicate groups, are then added to the solution. The conditions for condensation (polymerization) of the siloxanes are controlled through the concentrations of water, alcohol, acid, and additives in the solution. After curing, the surfactant can be washed out of the materials, leaving a porous framework with structure on two

length scales. As shown in Fig. 4, the resulting powders consist of particles that have large (~1 μm) spherical pores. In addition, there are much smaller pores (~5 nm) in the walls of the spherical pores. The small pores provide the desired high concentration of binding sites. The larger pores provide reduced resistance to liquid flow and increased connectivity throughout the structure.

Preconcentration of Contaminants: The powders can be packed into columns to provide a method for target preconcentration. When a volume of solution, ground water, surface water, or soil extract is passed through the column, the sorbent binds targets from the matrix. The column is then rinsed with water to remove any nontarget compounds. Finally, the sample is eluted from the column in a small volume of solvent such as acetonitrile. The result is that the target originally contained in 10 mL of water is now in 1 mL of solvent, an order of magnitude enhancement in concentration. As shown in Fig. 5, target that was undetectable in the raw solution is detected in the processed sample. Here, high performance liquid chromatography (HPLC) has been used for analysis of samples, but the same approach can be applied to in situ detection technologies. For example, the sorbents can be used to preconcentrate targets prior to analysis by portable electrochemical detectors or ion mobility spectrometers.

Applications: This sorbent technology was originally developed with a view toward environmental monitoring in areas on or near DoD sites of potential contamination. The techniques described can, however, be applied to monitoring in other situations, for example in the search for underwater unexploded ordnance (UXO). While the primary targets of interest have been nitroenergetics, the techniques described can also be used to synthesize sorbents applicable to the preconcentration of other targets of interest such as perchlorates, solvents, and organophosphates. The materials and approaches described provide enhanced capability to detection techniques that have traditionally been limited to laboratory applications, offering the potential to put protective detection capabilities on site and in the hands of military personnel.

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Synfuel from Seawater

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Introduction: NRL's Navy Technology Center for Safety and Survivability is developing a novel ocean-based capability that combines carbon dioxide and hydrogen captured from seawater for the synthesis of jet fuel at sea. In-theater, synthetic fuel production is a "game changing" proposition that will offer the Navy significant logistical and operational advantages by reducing dependence on increasingly expensive fossil fuels and by reducing fuel logistic tails and their vulnerabilities. From an environmental perspective, such a process could be considered carbon dioxide neutral since carbon dioxide is removed from the ocean and converted into a liquid hydrocarbon fuel. Upon combustion of the fuel, carbon dioxide is returned to the atmosphere where it re-equilibrates with the ocean to complete the natural carbon cycle. In addition, the synthetic hydrocarbon fuel would replace petroleum-derived fossil fuel to eliminate the emissions (sulfur and nitrogen oxides) that are produced from the combustion of these fuels by the Navy.

Carbon Capture: The world's oceans contain approximately 100 mg/L of carbon dioxide, of which 2% to 3% of the carbon dioxide is dissolved carbon dioxide gas in the form of carbonic acid, 1% is carbonate, and the remaining 96% to 97% is bound as bicarbonate. On a weight per volume basis, carbon dioxide concentration in the ocean is about 140 times greater than in air, thus making this source of carbon ideal for a synthetic fuel process at sea. However, developing the technologies to capture sufficient quantities of carbon dioxide from seawater fast enough and efficiently is a significant research challenge. NRL researchers have made breakthroughs in the development of an electrochemical cell that is able to extract all the dissolved gas and ionically bound carbon dioxide from seawater. The ion exchange materials incorporated into the cell re-equilibrate carbonate and bicarbonate in the seawater to carbon dioxide gas. The ion exchange materials offer the ability to operate at high flow rates and can be used in a wide variety of salt water compositions, which makes them ideal for this sea-based application.

In addition to carbon dioxide, the cell can produce a portion of the hydrogen needed for the hydrocarbon synthesis process with no additional energy penalty. The process efficiency, the ability to produce a portion of the hydrogen needed for the synthesis process, and the ability to regenerate the ion exchange material without the use of caustic chemicals, have made this technology superior to membrane and anion exchange processes previously developed and tested by NRL for use at sea.

Synfuel Production: The key challenge with using carbon dioxide as a chemical feedstock for production of liquid fuel is its great chemical stability. One of the few avenues open for chemical reaction is that with hydrogen. Carbon dioxide has been thought of as having too high an energy barrier for polymerization, even in the presence of a catalyst. To overcome these challenges, novel approaches in catalyst development by NRL researchers have led to thermodynamic improvements in the heterogeneous catalysis of the carbon dioxide and hydrogen to hydrocarbons. A two-step approach by NRL is shown in Fig. 6. In the first step of the approach, a key breakthrough is the development of an iron-based catalyst. Using this catalyst, we have achieved carbon dioxide conversion levels

up to 42% and have decreased unwanted methane production from 97% to 26% in favor of longer-chain unsaturated hydrocarbons. Further modification of the catalyst support has also led to increases in carbon dioxide conversion levels up to 50%. The second step of the approach, which is the subject of current efforts, involves the oligomerization of the olefins to jet fuel by a second solid acid catalyst such as zeolite.

The Future of Synfuel at Sea: We are now set to begin experiments to transition the carbon capture electrochemical cell from the laboratory to a littoral environment where carbon dioxide and hydrogen can be produced in quantities far above those achieved at the laboratory scale. There are many challenges to scaling this technology, including design, ion exchange material regeneration, process efficiency, water fouling, and power requirements. We are also facing great challenges in the effort to oligomerize olefins to a jet fuel fraction by solid acid zeolite catalysts. By modifying the pore size and acidity of the catalyst surface, we envision control over the liquid fuel fraction and yield.

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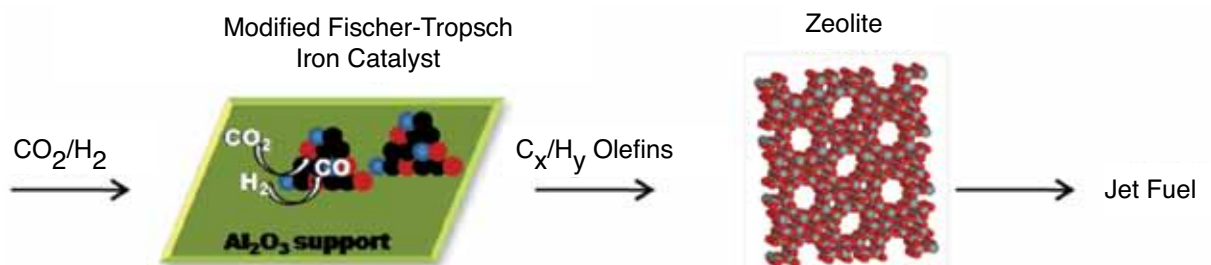


FIGURE 6
Carbon dioxide and hydrogen conversion over a modified Fischer-Tropsch iron catalyst.