

CGA H-15—2020

**SAFE CATALYST HANDLING
IN HYCO PLANTS**

FIRST EDITION

PREFACE

As part of a program of harmonization of industry standards, the Compressed Gas Association (CGA) has published CGA H-15, *Safe Catalyst Handling in HYCO Plants*, jointly produced by members of the International Harmonization Council.

This publication is intended as an international harmonized standard for the worldwide use and application of all members of the Asia Industrial Gases Association (AIGA), Compressed Gas Association (CGA), European Industrial Gases Association (EIGA), and Japan Industrial and Medical Gases Association (JIMGA). Each association's technical content is identical, except for regional regulatory requirements and minor changes in formatting and spelling.

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1 Introduction

HYCO plants utilize a number of catalyst types and catalytic technologies to produce hydrogen, carbon monoxide, or mixtures thereof. These catalysts are comprised of various chemical compounds across a number of support materials and structures, and reaction occurs in tubular, fixed bed, or modular reactors. Most of these catalysts are replaced periodically.

There are safety hazards involved in the storage, loading, unloading, and disposal of these catalysts. These hazards include the handling of self-heating or potentially pyrophoric materials and the presence of toxic metals (e.g., nickel, chromium, etc.), toxic metal carbonyls, and hexavalent chromium. There are also hazards associated with verification of uniformity of catalyst installation, including managing the differential pressure measurements taken during loading of reformer tubes. Development and implementation of safety procedures appropriate to the hazards associated with catalyst handling is required to maintain the exemplary safety experienced of large scale HYCO production facilities worldwide.

2 Scope

This publication applies to HYCO plants that produce hydrogen, carbon monoxide, or mixtures thereof, with a nominal production capacity greater than 9 MMSCFD hydrogen or carbon monoxide/syngas (approximately 10 000 Nm³/hr). Many of the concepts and issues discussed may also apply to smaller HYCO plants depending on the technology used.

This publication covers the safety aspects of all catalysts and chemisorbents such as zinc oxide used in HYCO facilities. Non-catalytic material such as physical adsorbents, for example, those used for pressure swing adsorbers; activated carbon, ion exchange resins, and inert solids (e.g., sand) are excluded from the publication. The publication scope is limited to catalyst and chemisorbent handling, loading, preparation for operation, unloading, and disposal. The publication scope excludes periods when the reactor is in operation (including startup and shutdown). Catalyst-specific instructions related to startup with new catalyst and shutdown prior to catalyst removal are included in the catalyst manufacturer's documentation, which should be consulted. This publication is not intended to replace catalyst manufacturers' operating manuals, handling manuals, or safety data sheets (SDS).

3 Definitions

For the purpose of this publication, the following definitions apply.

3.1 Publication terminology

3.1.1 Shall

Indicates that the procedure is mandatory. It is used wherever the criterion for conformance to specific recommendations allows no deviation.

3.1.2 Should

Indicates that a procedure is recommended.

3.1.3 May

Indicates that the procedure is optional.

3.1.4 Will

Is used only to indicate the future, not a degree of requirement.

3.1.5 Can

Indicates a possibility or ability.

3.2 Technical definitions

3.2.1 Bulk container

Industrial-grade container, often cubic in form, designed for the transport and storage of free-flowing dry cargo.

NOTE—The container may be single use or reusable, depending on the material of construction.

3.2.2 Bulk loading process

Catalyst loading technique for fixed vessels that relies on human intervention to distribute the catalyst evenly throughout the reactor.

NOTE—The methodology typically involves an individual directing catalyst addition via a fabric sleeve that is attached to the bottom of a hopper vessel or bulk container.

3.2.3 Catalyst handling service company

Specialized company that deals with the loading or unloading of reactor vessels. Qualified catalyst handling service companies typically have experience in vessel entry, including entry into an atmosphere that is Immediately Dangerous to Life and Health (IDLH), and may offer dense loading techniques/equipment.

3.2.4 Catalyst tube (reformer catalyst tube)

Metallic alloy cylinder used to contain the catalyst in the reformer furnace. Catalyst tubes typically measure 3 in to 5 in (8 cm to 13 cm) across the inside diameter with a vertical orientation and a length spanning the height of the reformer furnace.

3.2.5 Chemisorbent

Solid material that removes an impurity from a process stream by chemically reacting with the impurity.

3.2.6 Dense loading

Catalyst loading technique that relies on a mechanical means to distribute the catalyst evenly throughout the reactor. Dense loading techniques are available for fixed reactor vessels as well as for reformer catalyst tubes.

3.2.7 Flue gas duct

Portion of the reformer, downstream of the furnace, where flue gas passes over heat exchangers and heat transfer occurs via radiation and convection.

NOTE—Also referred to as convection section.

3.2.8 Furnace

Portion of the reformer where the combustion process takes place.

3.2.9 Pyrophoric

Material that will ignite spontaneously when exposed to air. The reaction is sufficiently exothermic such that the material quickly reaches combustion temperature and then incandescence. The material does not rely on insufficient loss of heat to promote the reaction, so any particle size will ignite on exposure to air.

3.2.10 Safety data sheet (SDS)

Written or printed information concerning a hazardous material (properties, precautions, etc.) following globally harmonized standards.

3.2.11 Self-heating

Material that reacts with air resulting in an increase in temperature. When a sufficient amount of the material is piled in one place, the heat cannot escape fast enough and the center of the mass will develop an uncontrolled exothermic reaction. The heating will bring the center of the mass to combustion temperature and then incandescence.

3.2.12 Steam reformer (or reformer)

Processing unit where steam is reacted with hydrocarbons over a catalyst at high temperatures to produce hydrogen and carbon oxides. The reformer includes a furnace/radiant section and a convection section.

3.2.13 Tube hanger

Mechanism that supports the reformer tubes as they move due to thermal expansion or contraction. This may be weights and pulleys, a variable load spring hanger, or a constant load spring hanger.

4 General safety considerations

The catalysts and chemisorbents used in a HYCO facility are potentially hazardous, and all activities involving the materials shall be assessed to identify the potential risks and the necessary safeguards. Some of the hazards involved in catalyst handling are specific to the catalyst composition (e.g., reactivity and toxicity of the material), while other hazards are specific to the catalyst handling activity (e.g., lifting, confined space entry, working at heights). The hazards associated with catalyst and catalyst handling activities shall be addressed through the various elements of a HYCO facility's safety program including training, procedures, personal protective equipment (PPE), work permits, contractor safety, and hazard communication.

4.1 Catalyst composition hazards (SDS considerations)

When developing a safety plan associated with catalyst handling, the relevant SDSs shall be consulted. The SDS includes information on potential short- and long-term health effects due to exposure as well as recommended precautions for safe handling. Many of the catalysts are toxic if inhaled (e.g., catalyst dust of nickel-containing catalysts) or can cause damage to organs through prolonged or repeated exposure. Some catalysts (e.g., zinc oxide) are very toxic to aquatic life, with long-lasting effects.

It should be noted that SDSs apply only to new catalyst. After use, the catalyst can have different chemical and physical properties, which can also vary with the reactor feed and operating conditions. The catalyst supplier should be consulted for the SDS or other information associated with the used catalyst. Laboratory analyses might be necessary to characterize the hazards of used catalyst.

4.2 Pyrophoric and self-heating hazards

Any catalyst in a reduced state can be self-heating. Pre-reduced and stabilized catalyst has an oxide layer on the surface to minimize the potential for self-heating.

Within the scope of this publication, there are no unused catalysts that are pyrophoric. There are materials that can be deposited on and around used catalyst (e.g., on top of the bed) that are pyrophoric (e.g., iron sulphides) or flammable (e.g., coke/carbon). Under certain conditions there is a risk of producing high temperatures and combustion. Because of this risk, some suppliers will refer to self-heating catalyst as pyrophoric.

To mitigate the risks, the catalyst should be cooled to ambient temperature (less than 120 °F [50 °C]) before being put in contact with air. Also, exposure to air/oxygen should be controlled while handling used catalyst and the associated contaminants. Oxygen exposure is controlled by minimizing exposure time to air. The primary method of cooling is flushing the catalyst with cold nitrogen while it is still in the production unit.

After unloading, dividing catalyst among multiple smaller containers prior to exposure to air will limit the overheating risk, as this division provides sufficient surface area to remove the generated heat. The larger the mass of catalyst that is exposed to air, the more likely there will be insufficient cooling. If the rate of heat generation exceeds the rate of cooling, then the temperature will rise and could reach a point that would melt the catalyst and/or damage the container or vessel.

4.3 Nickel/iron carbonyl hazards and safeguards

Nickel carbonyl is highly toxic and formed by the reaction of carbon monoxide with nickel. Nickel carbonyl formation is a potential hazard in HYCO plants containing nickel catalyst. Similarly, iron carbonyl is a toxic compound that can form by the reaction of carbon monoxide with iron from iron-containing catalyst.

Nickel carbonyl is considered to be one of the most toxic chemicals found in industry. The U.S. Occupational Safety and Health Administration (OSHA) Time-Weighted Average–Permissible Exposure Limit (TWA–PEL) for nickel carbonyl is 0.001 ppmv. The TWA–PEL for iron carbonyl is 0.1 ppmv. Regulatory exposure limits can vary by jurisdiction, and the appropriate guidance documents should be consulted [1, 2].¹

¹ References are shown by bracketed numbers and are listed in order of appearance in the reference section.

The formation of nickel carbonyl occurs when carbon monoxide is in the presence of nickel catalyst in the temperature range of 120 °F to 400 °F (50 °C to 204 °C). Its formation is prevented by removal of carbon monoxide by purging equipment prior to reaching the upper formation limit of 400 °F (204 °C). Iron carbonyl is formed when carbon monoxide is in the presence of iron catalyst and is similarly avoided by purging equipment of carbon monoxide prior to reaching a temperature of 400 °F (204 °C). This purging requirement applies to nickel catalysts (e.g., prereformer, reformer and methanation) and iron catalysts (e.g., high temperature shift [HTS]).

If carbon monoxide is not purged prior to reaching 400 °F (204 °C) and there is a possibility that nickel or iron carbonyl has formed, purging at low temperature will not remove it. Reheating the vessel to a temperature greater than 400 °F (204 °C) will cause the carbonyls to decompose.

4.4 Work permits, system isolation, and work planning

All catalyst handling operations shall be conducted under the plant work permit system. Safe loading or unloading operations also require that the system be isolated properly, which is ensured through the plant lockout/tagout program. Things that should be considered when developing the work permit include:

- influence of health and environmental hazards of catalyst on neighboring activities (e.g., dust);
- simultaneous maintenance activities;
- system isolation requirements; and
- purging activities.

When conducting catalyst handling activities, close coordination and communication with the catalyst handling service company is required to prevent conflicts between different maintenance tasks that take place in the same plant area, which often occurs if the catalyst activity will take place during a plant maintenance outage. When loading or unloading reformer catalyst, for example, the loading/unloading activity may occur at the top of the reformer, while at the same time it could be desirable to conduct maintenance activities beneath the reformer. Further, it might not be possible to isolate a reactor from all systems to which the reactor is connected. This is often the case for reformer catalyst tubes, which connect to multiple downstream systems without isolation. If two or more systems cannot be isolated from each other, it might not be possible to work on the systems simultaneously.

In some cases, the plant is configured with two reactors in series or parallel with sufficient isolation valves such that one reactor can be taken off-line and the catalyst replaced while the plant continues to operate. When working on a reactor that is connected to a “live” system, care shall be taken to ensure that the reactor is isolated and deenergized in accordance with company procedure prior to conducting work.

4.5 Personal protective equipment

The catalyst SDS (new or used catalyst) shall be consulted to determine the PPE required for those individuals involved in the direct handling of any catalyst (e.g., loading, unloading, screening, housekeeping, etc.). Additional information and recommendations could be included in the catalyst supplier's documentation. In general, eye protection, gloves and boots are required. Hearing protection, or even double hearing protection, could be required depending on the handling activity. Disposable protective overalls could be required, in particular for individuals handling catalyst within a confined space. Respiratory protection shall be utilized if required to control the inhalation of catalyst dust to a level below the allowable exposure limit. Respiratory protection generally is required for tasks that involve the direct handling of catalyst but might not be required for all tasks. The level of respiratory protection required should be defined for each specific task (e.g., drum handling, hopper loading, screening, vessel entry, catalyst unloading).

4.6 Vessel entry and purging

When loading or unloading catalyst from a vessel, entry into the vessel could be required. Standard confined space entry procedures shall be followed, taking into account the presence of the catalyst and any components that could be present on the catalyst such as contaminants from the process gas or reaction by-products.

If the vessel will be entered under a nitrogen purge, the preferred location for nitrogen introduction is such that the nitrogen flow path is through all or a portion of the catalyst inside the vessel. This reduces the risk for pockets of catalyst to come into contact with air versus a blanketing method supplying nitrogen from the vessel top. When introducing nitrogen with flow through some or all of the catalyst, a test assuring there is not a dangerous pressure differential across the bed of material should be conducted. This test ensures that there is no pocket of high pressure gas that when reached could cause a pressure release that could expel catalyst or personnel. The test, sometimes called a Grubbs' Test, involves flowing nitrogen through the catalyst at the maximum rate that will be used during the confined space entry, then quickly stopping the nitrogen flow and confirming that the pressure at the nitrogen introduction point decreases to atmospheric pressure within 5-10 seconds. If the pressure does not decrease in this time frame, it indicates that there could be blockage within the catalyst bed. In this scenario, consider alternative purge points to avoid the flow blockage, reduce the maximum nitrogen flow needed during entry and retest, or vacuum out the catalyst or blockage without entry into the vessel.

Some of the other confined space hazard mitigations associated with loading or unloading including:

- Catalyst can present an engulfment hazard either due to differences in height or bridging, which can be addressed by using a safety line and by keeping the bed surface relatively flat while vacuuming and never allowing a difference in elevation across the bed of greater than waist-high;
- Appropriate respiratory protection based upon the hazards of the task shall be utilized (dust mask, supplied air, or IDLH-appropriate supplied air);
- Confined space conditions shall be monitored continually because conditions can change due to the reaction of the catalyst with air, which will cause a depletion of oxygen, resulting in asphyxiation risk and temperature increase;
- Due to the reactivity hazards of catalyst, purging with nitrogen can be required throughout the loading or unloading process. Loss of the nitrogen purge can cause a sudden increase in temperature within the vessel;
- If entering the vessel under a nitrogen purge (due to reactivity concerns), then confined space entry protocols applicable to IDLH atmospheres shall be implemented. IDLH entry is an extremely hazardous activity that shall be planned and managed rigorously;
- If there is a potential for the asphyxiating atmosphere to extend beyond the vessel, this shall be taken into account when defining the safety precautions associated with all vessel vent points (e.g., downwind exposure) and with work going on near any of the vessel vent points (e.g., blinding, nozzle disassembly and assembly); and
- If a vessel is purged after catalyst loading is complete (e.g., to prevent moisture ingress or to maintain an inert atmosphere) an area around the vessel outlet sufficient to prevent exposure to an asphyxiating atmosphere shall be roped off or otherwise barricaded.

4.7 Working at heights

Catalyst loading or unloading is typically done from the top of the reactor. In most cases, this means that work is conducted at a significant elevation relative to grade. If permanent platforms are not available, access is often provided by means of temporary scaffolding. Whether working from a platform or a scaffold, precautions should be taken to prevent objects from falling to grade.

The platform or scaffold shall be rated for the maximum combined weight of the equipment, catalyst, and personnel that might be on the platform/scaffold at any one time. Heavy-duty scaffolds typically are required. Permanent platforms should be evaluated depending on the load that they will be required to handle.

4.8 Equipment-related precautions

The equipment used during catalyst loading or unloading shall be considered when identifying the safety protocols required for a particular catalyst handling task such as the following:

- When utilizing vacuum trucks for catalyst unloading, double hearing protection (ear muffs with ear plugs) may be required for individuals working near the vacuum truck. In addition, vacuum trucks should be equipped with a means to instantaneously break or reduce the vacuum in the event that the vacuum either