



Industry  
Canada Industrie  
Canada

Canada

strategis.gc.ca

Strategis Index:  
[Home](#) [Advanced Search](#) [Help](#)

CIPO  OPIC



## Canadian Patents Database

12/20/2001 - 16:09:56  
 (11) CA 540828

(12) Patent:

(54) CATALYST FOR CARBON MONOXIDE-STEAM REACTION

(54) CATALYSEUR POUR REACTION D'OXYDE DE CARBONE ET DE VAPEUR

(72) Inventor (Country):	KENNETH D. ASHLEY (Not Available) WILLIAM B. INNES (Not Available)
(73) Assignor (Country):	AMERICAN CYANAMID COMPANY (United States)
(71) Applicant (Country):	
(74) Agent:	
(45) Filing Date:	May 14, 1957
(22) Filing Office:	
(43) Filing Date (national phase):	
(52) International Class. (IPC):	252/74
(51) International Class. (IPC):	N/A

(70) Priority (IPC): No

(30) Application priority (IPC): None

(70) Priority (national phase): N/A  
 (70) Priority (national phase): Unknown

Patent Information Summary

\*\*\* Note: Data on abstracts and claims is shown in the official language in which it was submitted.

View or Download Images :

- Cover Page Image
- Abstract Image
- Claims Image
- Disclosures Image
-

1           This invention relates to a method for the production of  
2 catalysts of improved activity for the reaction of carbon monoxide with  
3 steam to produce carbon dioxide and hydrogen, and to an improved type  
4 of catalyst composition.

5           Catalysts composed of iron oxide and magnesium oxide, pro-  
6 moted by the addition of a small quantity of potassium bichromate, have  
7 been used for carrying out the so-called water gas reaction for many  
8 years. These catalysts are usually prepared by mixing the iron oxide  
9 and magnesium oxide with a water solution of potassium bichromate to  
10 form a paste which is dried to a powder of about 5% water content by  
11 heating at 100-140° C. and then formed into pellets by compacting in an  
12 automatic tablet-forming machine to produce an autogenous bond. The  
13 tablets so obtained have a physical strength corresponding to an  
14 average crushing weight of about 20 lbs. for tablets of 3/8" diameter.  
15 This strength increases slightly during the initial period of use of  
16 the catalyst.

17           It is a principal object of the present invention to provide  
18 an improved method of manufacturing catalysts of the above type, which  
19 method will produce pelleted catalysts combining the advantages of  
20 high activity and greater mechanical strength. A further important ad-  
21 vantage is the production of catalysts which have a long effective  
22 life, even when used with gases that contain impurities that would re-  
23 duce the activity of the prior art catalysts described above.  
24  
25  
26  
27  
28  
29  
30  
31  
32

1           The catalysts of our invention, like those that have pre-  
2 viously been used, contain iron oxide together with about 10% - 100%  
3 of its weight of magnesia as their principal constituents. The present  
4 invention, however, employs an adsorbent type of magnesium oxide known  
5 commercially as "active magnesia." By employing this type of magnesia,  
6 and by modifying the manufacturing procedure as will subsequently be  
7 described, we have obtained catalysts combining improved activity with  
8 greater mechanical strength.

9           The active magnesia which we employ is obtained by calcining  
10 precipitated magnesium hydroxide at a relatively low temperature or,  
11 if higher calcination temperatures are used, for a relatively short  
12 time. Ordinarily the precipitated magnesium hydroxide is calcined on  
13 a temperature-time schedule varying from 300-400° C. for 4 hours to  
14 625-750° C. for 0.5 hour. The resulting products are most readily  
15 identified by the fact that they possess definite iodine numbers, in-  
16 dicative of their ability to adsorb iodine from a carbon tetrachloride  
17 solution thereof. These iodine values will vary from about 25, in the  
18 case of a magnesia calcined for 4 hours at 300-400° C., to 150 or more  
19 when a calcination at 750° C. for 0.5 hour is used. The iodine value  
20 is determined in the usual manner by shaking a weighed sample of the  
21 calcined magnesia with an 0.1 N solution of iodine in carbon tetra-  
22 chloride, transferring an aliquot portion of the supernatant iodine  
23 solution to a measured quantity of 0.03 N potassium iodide in ethanol  
24 and titrating with standard 0.05 N sodium thiosulfate. The iodine  
25 number is calculated by subtracting the amount of thiosulfate used  
26 from the amount required for an equal quantity of the original iodine  
27 solution and multiplying the result by 250 times the normality of the  
28 sodium thiosulfate.

1           In carrying out the process of our invention we first prepare  
2 a uniform dry mixture of the powdered active magnesia with an iron  
3 oxide ( $\text{Fe}_2\text{O}_3$ ) which is preferably of pigment grade having an average  
4 particle size of less than one micron diameter. Into this mixture we  
5 incorporate uniformly about 3-40% of magnesium chromate. This may be  
6 done by adding an aqueous solution of chromic acid containing about  
7 2-50% of  $\text{CrO}_3$ , based on the weight of the magnesia, which reacts  
8 readily with a portion of the active magnesia present in the dry mix-  
9 ture. Alternatively an equivalent amount of a separately prepared  
10 magnesium chromate solution may be added; in this case, the amount of  
11 dry magnesia mixed with the iron oxide is reduced accordingly. In  
12 either case an amount of water is added, usually within the range of  
13 about 50-100% on the weight of the magnesia, which is sufficient to  
14 hydrate all of the magnesia and, in addition, to provide a free mois-  
15 ture content of about 3-10% in the finished mixture. This excess  
16 moisture accelerates the hydration of the magnesia, prevents dust  
17 formation and aids in producing a granular powder that is easily  
18 pelleted on an automatic pelleting machine.

19           Some of the free moisture of the composition reacts with the  
20 magnesia before pelleting; the degree of hydration of the magnesia at  
21 this point is usually about 20-35%. The material is then a free-  
22 flowing powder, and in this condition it is pressed into pellets in a  
23 tableting machine which is preferably of the automatic type.  
24  
25  
26  
27  
28  
29  
30  
31  
32

1           The catalyst pellets from the tableting machine are aged or  
2 conditioned in a closed container in order to complete the reaction be-  
3 tween their water content and the magnesium oxide and magnesium chro-  
4 mate with the formation of a set hydraulic cement. This increases  
5 their mechanical strength by a factor of two to five or more and pro-  
6 duces a bond that is not materially weakened during the subsequent cal-  
7 cination. The aging or conditioning may be carried out at room tem-  
8 perature during about 5-24 hours or longer, depending on the degree of  
9 mechanical strength desired, or for a correspondingly reduced time at  
10 elevated temperatures up to 100° C., at which temperature only about  
11 30 minutes is required. After aging the pellets are dehydrated by cal-  
12 cining them at 500-650° C. preferably at 575-625° C. for about 1 hour,  
13 which increases still further the activity of the magnesia and improves  
14 the porosity and activity of the catalyst as a whole.

15           We have also found that the heat stability of the catalyst  
16 can be improved if desired by incorporating therein a small amount of  
17 alumina. This is accomplished by adding to the original ferrous oxide-  
18 magnesia mixture about 0.5% to 2%, based on the weight of the iron  
19 oxide, of an active form of alumina such as bauxite, alumina gel and  
20 the like. A gel of freshly precipitated hydrated alumina may also be  
21 used in like amounts, as it is converted into active alumina during  
22 the final calcination of the catalyst.

23

24

25

26

27

28

29

30

31

32

1 As is noted above, the formation of magnesium chromate may be  
2 carried out either by adding a portion of the magnesia to an aqueous  
3 chromic acid solution or simply by dissolving the desired amount of  
4  $\text{CrO}_3$  in water and adding the solution to a uniform mixture of the iron  
5 oxide and magnesium oxide, whereby magnesium chromate is formed in situ.  
6 These methods of preparation present the important additional advantage  
7 that the introduction of alkali metal compounds such as potassium or  
8 sodium into the catalyst is avoided, which is an important factor in  
9 increasing the effective life of the catalyst. Our experiments have  
10 shown that even small amounts of potassium, for example, will cause the  
11 catalyst to lose most of its activity after a few days of use unless  
12 the carbon monoxide gases have been carefully purified. We believe  
13 that this loss of activity is caused by the formation of an alkali  
14 metal sulfate coating, which is brought about by reaction of sodium or  
15 potassium in the catalyst with sulfur compounds in the carbon monoxide  
16 gas. This is indicated by the fact that a prior art catalyst of the  
17 type described above, prepared by mixing potassium bichromate solution  
18 with iron oxide and magnesium oxide, poisoned very rapidly in a steam-  
19 carbon monoxide gas containing 1000 parts per million of hydrogen sul-  
20 fide; the poisoned catalyst was found to be encrusted with a coating  
21 consisting mainly of potassium sulfate.

22 The catalysts of our invention can be operated at tempera-  
23 tures of about  $450^\circ\text{C}$ . to  $600^\circ\text{C}$ . at space velocities on the order of  
24 1800-2200, using an inlet gas containing about 35% of carbon monoxide  
25 and a steam:CO ratio of about 2.5. Under these conditions the exit gas  
26 contains from about 2.2 to about 5.5% of carbon monoxide.

27

28

29

30

31

32

1           The invention will be further illustrated by the following  
2 specific example:

3           A pigment grade  $\text{Fe}_2\text{O}_3$  having an average particle size of  
4 about 0.5 micron was used. A mixture of 200 lbs. of this iron oxide  
5 with 50 lbs. of active magnesia was prepared, the magnesia being a pre-  
6 cipitated magnesium hydroxide that had been calcined at  $300\text{-}400^\circ\text{C}$ . for  
7 about 4 hours.

8           A solution of 12 lbs. of  $\text{CrO}_3$  in 36 lbs. of water was pre-  
9 pared and was added to the magnesia-iron oxide mixture by spraying  
10 slowly with continuous agitation. Five pounds of powdered graphite  
11 were then added.

12           In the resulting material all of the visible moisture had  
13 disappeared and a dry and free-flowing powder was obtained. No heating  
14 was necessary, as the active magnesia reacted easily with the chromic  
15 acid solution to form a mixture of partially hydrated magnesia and  
16 magnesium chromate. The material was then passed through a ten mesh  
17 screen and was formed into pellets of  $7/16$  inch diameter on a rotary  
18 pelleting machine. The setting on the punches was such as to give an  
19 initial crushing strength of 5-10 lbs.

20           The pelleted material was placed in a closed container and  
21 allowed to age for about 24 hours. Experience has shown that this  
22 aging step is very important when catalyst pellets of high mechanical  
23 strength are desired, as it helps the hydration of the magnesia and  
24 aids in forming a uniform hydraulic cement bond in the catalyst. The  
25 aged pellets were then calcined at  $550\text{-}650^\circ\text{C}$ . for about 1-3 hours by  
26 contact with hot products of combustion in a rotary kiln. After cool-  
27 ing, the catalyst was ready for use.

28  
29  
30  
31  
32

1 Tests made on the pelleted catalysts after conditioning for  
2 24 hours but prior to calcination showed an average crushing strength  
3 of 55 lbs. After calcination the average crushing strength of the  
4 pellets was 50 lbs.

5 The catalyst was tested with a carbon monoxide gas having  
6 the following composition:

7	CO	37%
	CO <sub>2</sub>	6%
8	O <sub>2</sub>	0.5%
	H <sub>2</sub>	36%
9	CH <sub>3</sub>	0.5%
10	N <sub>2</sub>	20%
	H <sub>2</sub> S	1000 p.p.m.
11	Organic sulfides and 12 tarry materials, about	500 p.p.m.

13 The steam to carbon monoxide ratio was 2.5:1, and tempera-  
14 tures of 485-500° C. and a space velocity of about 2000 were main-  
15 tained during the first week. The catalyst was then maintained at  
16 545-555° C. during a run of four months, using the same steam to gas  
17 ratio and the same space velocity. The average conversion during this  
18 run was 86.4%; on the last day of the run the conversion was 86.1%,  
19 showing that the catalyst had retained its activity throughout the  
20 entire test.

21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32



8 540828

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A method of producing an iron oxide-magnesia catalyst of high activity and improved mechanical strength which comprises preparing a mixture of  $\text{Fe}_2\text{O}_3$ , active magnesia, magnesium chromate and sufficient water to hydrate all of the magnesia, compressing said mixture into pellets, aging the pellets while retaining their water content to form therein a set hydraulic cement, and subsequently dehydrating the pellets by calcining them at 500-650°C.
2. A method of producing an iron oxide-magnesia catalyst of high activity and improved mechanical strength which comprises preparing a mixture of  $\text{Fe}_2\text{O}_3$ , about 10-100% of active magnesia based on the weight of the iron oxide and about 3-40% of magnesium chromate and about 50-100% of water based on the weight of said magnesia, compressing the mixture into pellets while retaining therein sufficient water to hydrate all of the magnesia, aging the pellets while retaining their water content to form therein a set hydraulic cement, and subsequently dehydrating the pellets by calcining them at 500-650°C.
3. A method according to claim 2 in which about 0.5% to 2% of active alumina, based on the weight of the iron oxide, is incorporated into the mixture prior to pelleting.
4. A chromium oxide-activated iron oxide-magnesia catalyst in the form of pellets of high activity and improved mechanical strength, said pellets consisting essentially of finely divided  $\text{Fe}_2\text{O}_3$  and a set hydraulic cement formed by mixing said  $\text{Fe}_2\text{O}_3$  uniformly with about 10-100% of its weight of active magnesia and about 3-40% of its weight of magnesium chromate together with about

EA

A

50-100% of water based on the weight of said magnesia, compressing the mixture into pellets while retaining therein sufficient water to hydrate all of the magnesia, aging the pellets while retaining their water content to form therein said set hydraulic cement, and then dehydrating the pellets by calcining them at 500-650°C.

**A**

EA