Innovation, Sciences et Développement économique Canada
Office de la Propriété Intellectuelle du Canada

Innovation, Science and Economic Development Canada
Canadian Intellectual Property Office

CA 3030838 A1 2018/01/18

(21) 3 030 838

(12) DEMANDE DE BREVET CANADIEN CANADIAN PATENT APPLICATION

(13) **A1**

(86) **Date de dépôt PCT/PCT Filing Date:** 2017/06/07
(87) **Date publication PCT/PCT Publication Date:** 2018/01/18
(85) **Entrée phase nationale/National Entry:** 2019/01/14
(86) **N° demande PCT/PCT Application No.:** US 2017/036297
(87) **N° publication PCT/PCT Publication No.:** 2018/013263
(30) **Priorités/Priorities:** 2016/07/15 (US62/362,716); 2016/09/14 (US62/394,341)

(51) **Cl.Int./Int.Cl.** *B01J 23/28* (2006.01), *B01J 23/04* (2006.01), *B01J 37/03* (2006.01), *B01J 37/08* (2006.01), *C01B 32/40* (2017.01)

(71) **Demandeur/Applicant:**
THE GOVERNMENT OF THE UNITED STATES OF AMERICA, AS REPRESENTED BY THE SECRETARY OF THE NAVY, US

(72) **Inventeurs/Inventors:**
POROSOFF, MARC, US;
WILLAUER, HEATHER D., US

(74) **Agent:** MBM INTELLECTUAL PROPERTY LAW LLP

(54) Titre : CARBURE DE MOLYBDENE DOPE AVEC UN METAL ALCALIN SUPPORTE SUR DE L'ALUMINE GAMMA POUR L'HYDROGENATION SELECTIVE DE CO2 EN CO

(54) Title: ALKALI METAL DOPED MOLYBDENUM CARBIDE SUPPORTED ON GAMMA-ALUMINA FOR SELECTIVE CO_2 HYDROGENATION INTO CO

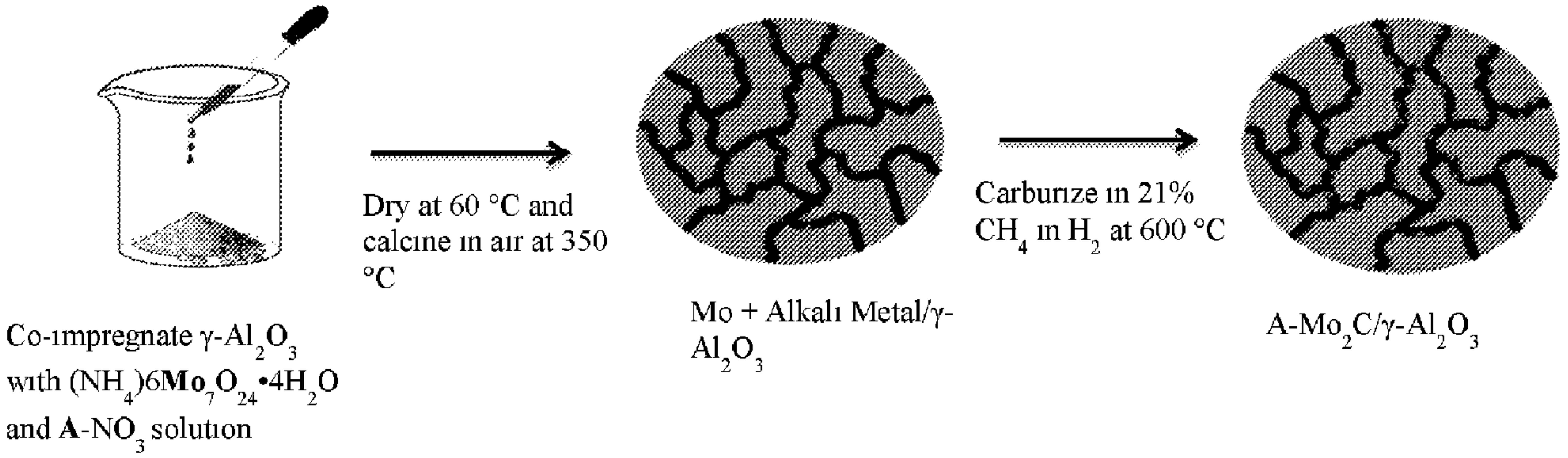

FIG. 1

(57) Abrégé/Abstract:
A class of catalysts for CO_2 hydrogenation via the reverse water-gas shift (RWGS) reaction to selectively produce CO for down-stream hydrocarbon synthesis. Alkali metal-doped molybdenum carbide, supported on gamma alumina (A-Mo_2C/γ-Al_2O_3, A = K, Na, Li), is synthesized by co-impregnation of molybdemun and alkali metal precursors onto a γ-Al_2O_3 support. The A-Mo/γ-Al_2O_3 catalyst is then carburized to form the A-Mo_2C/γ-Al_2O_3 Also disclosed is the related method for CO_2 hydrogenation via the RWGS reaction using the A-Mo_2C/γ-Al_2O_3 catalyst.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) **World Intellectual Property Organization**
International Bureau

(43) **International Publication Date**
18 January 2018 (18.01.2018)

WIPO | PCT

(10) **International Publication Number**
WO 2018/013263 A1

(51) **International Patent Classification:**
B01J 23/28 (2006.01) ***B01J 37/08*** (2006.01)
B01J 23/04 (2006.01) ***C01B 32/40*** (2017.01)
B01J 37/03 (2006.01)

(21) **International Application Number:**
PCT/US2017/036297

(22) **International Filing Date:**
07 June 2017 (07.06.2017)

(25) **Filing Language:** English

(26) **Publication Language:** English

(30) **Priority Data:**
62/362,716 15 July 2016 (15.07.2016) US
62/394,341 14 September 2016 (14.09.2016) US

(71) **Applicant: THE GOVERNMENT OF THE UNITED STATES OF AMERICA, AS REPRESENTED BY THE SECRETARY OF THE NAVY** [US/US]; Naval Research Laboratory, 875 North Randolph Street, Suite 1425, Arlington, VA 22203 (US).

(72) **Inventors: POROSOFF, Marc**; 2130 P Street NW, Washington, DC 20037 (US). **WILLAUER, Heather D.**; 8306 Holy Haven Lane, Fairfax Station, VA 22039 (US).

(74) **Agent: BROOME, Kerry L.**; US Naval Research Laboratory, 4555 Overlook Ave, SW, Code 1008.2, Washington, DC 20375 (US).

(81) **Designated States** *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) **Designated States** *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report (Art. 21(3))*

(54) **Title:** ALKALI METAL DOPED MOLYBDENUM CARBIDE SUPPORTED ON GAMMA-ALUMINA FOR SELECTIVE CO_2 HYDROGENATION INTO CO

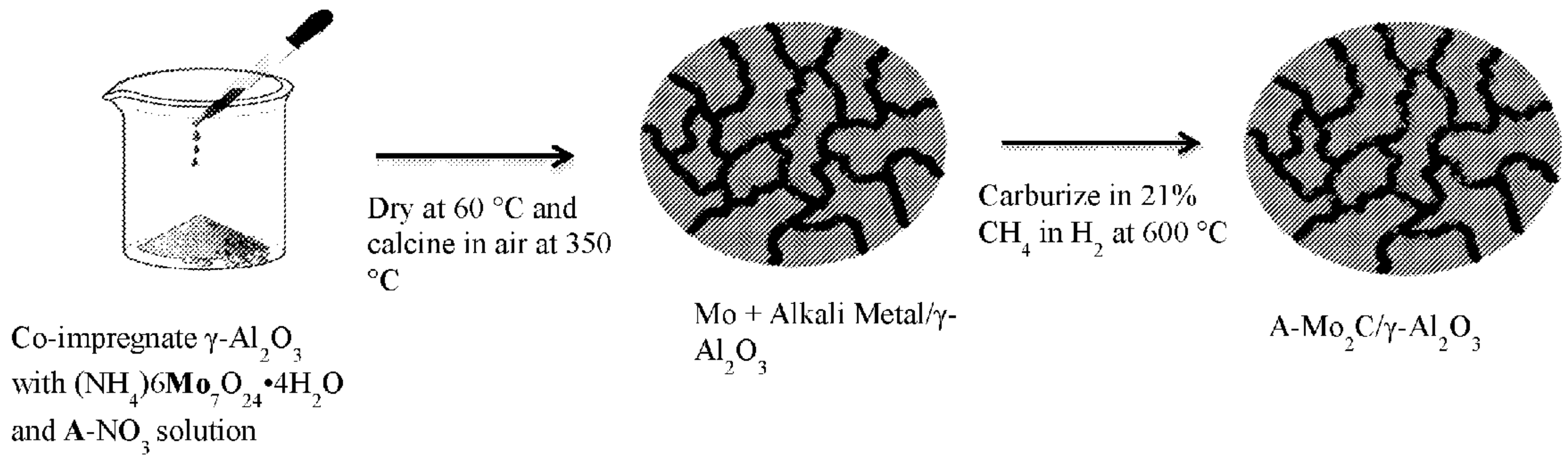

FIG. 1

(57) **Abstract:** A class of catalysts for CO_2 hydrogenation via the reverse water-gas shift (RWGS) reaction to selectively produce CO for down-stream hydrocarbon synthesis. Alkali metal-doped molybdenum carbide, supported on gamma alumina (A-Mo_2C/γ-Al_2O_3, A = K, Na, Li), is synthesized by co-impregnation of molybdemun and alkali metal precursors onto a γ-Al_2O_3 support. The A-Mo/γ-Al_2O_3 catalyst is then carburized to form the A-Mo_2C/γ-Al_2O_3 Also disclosed is the related method for CO_2 hydrogenation via the RWGS reaction using the A-Mo_2C/γ-Al_2O_3 catalyst.

WO 2018/013263 A1

ALKALI METAL DOPED MOLYBDENUM CARBIDE SUPPORTED ON GAMMA-ALUMINA FOR SELECTIVE CO_2 HYDROGENATION INTO CO

TECHNICAL FIELD

The present invention relates to catalysts for CO_2 hydrogenation reactions to selectively produce CO via the reverse water-gas shift (RWGS) reaction for down-stream hydrocarbon synthesis.

BACKGROUND ART

The high concentration of CO_2 in seawater, ca. 100 mg L^{-1}, represents a significant opportunity to extract and use this CO_2 as a C_1 feedstock for synthetic fuels. Through an existing process patented by the U.S. Navy (US Patent 9,303,323), CO_2 and H_2 can be concurrently extracted from seawater and used as reactants for direct Fischer-Tropsch from CO_2 (CO_2-FT) to produce valuable oxygenates, specialty chemicals and intermediate hydrocarbons (C_2-C_6) for synthetic fuel. (Wang et al., Chem. Soc. Rev. 40, 3703-3727 (2011) and Centi et al., Today, 148, 191-205 (2009)). If the energy input is nuclear or renewable, the entire process can be considered CO_2-neutral. (Willauer et al., J. Renew. and Sustain. Energ., 4, 033111 (2012)).

The most commonly used catalysts for CO_2-FT are slight variations of Fe and Co-based Fischer-Tropsch (FT) catalysts, which show promise, but are not specifically designed for the CO_2 reactant. (Kaiser et al., Chem-Ing-Tech, 85, 489-499 (2013), Chakrabarti et al., Ind. Eng. Chem. Res., 54, 1189-1196 (2015), and Dorner et al., Energ. Environ. Sci., 3, 884-890 (2010)). The current optimal catalyst, K-Mn-Fe/Al_2O_3, achieves a CO_2 conversion of 41.4% and a selectivity towards C_2-C_5+ hydrocarbons of 62.4% at a gas hourly space velocity (GHSV) of 0.0015 L g^{-1} s^{-1}, but the mechanism is poorly understood, making catalyst improvements challenging. (Dorner et al., Appl. Catal. A-Gen., 373, 112-121 (2010)). There is some consensus that an Fe carbide formed during the reaction is the catalytically active phase (Lee et al., J. Mol. Catal. A-Chem., 301, 98-105 (2009)); however, reports also state that Fe catalysts are poisoned by water, an unavoidable byproduct, negatively influencing catalytic activity and product selectivity. (Riedel et al., Appl. Catal. A-Gen., 186, 201-213 (1999) and Willauer et al., J. CO2 Util., 3–4, 56-64 (2013)). Conversely, Co-based catalysts are water tolerant (Schulz et al., in Studies in Surface Science and Catalysis, Vol. 107 (Eds.: dePontes et al.), Elsevier, pp. 193-200 (1997)) and modifying an Fe catalyst with Co improves catalytic performance and selectivity towards C_2+ hydrocarbon products. (Satthawong et al., Catal. Today, 251, 34-40 (2015) and Satthawong et al., Top. Catal., 57, 588-594 (2014)). Improvements have also been made to Fe-based catalysts by adding Cu, which enhances CO_2-FT activity and selectivity. (Satthawong et al., Top. Catal., 57, 588-594 (2014)).

Although there are promising catalysts for CO_2-FT, the structure-property relationships that control activity and selectivity to intermediate hydrocarbons are not well studied. (Porosoff et al., Energ. Environ. Sci., 9, 62-73 (2016)). Furthermore, because of the complexity of CO_2-FT, the alternative route of feeding CO produced from reverse water-gas shift (RWGS) into a FT reactor must also be considered. For industrial RWGS, operating temperatures are very high, typically at or above 600 °C at 2.8 MPa, over ZnO/Al_2O_3 and ZnO/Cr_2O_3 catalysts. Because methane (CH_4) is thermodynamically favored below 600 °C, these catalysts require high temperatures to selectively produce CO, which also results in substantial deactivation. (Joo et al., Ind. Eng. Chem. Res., 38, 1808-1812 (1999) and Park et al., Journal of Chemical Engineering, 17, 719-722 (2000)). To make fuel synthesis from CO_2 viable, a low-cost and stable RWGS catalyst is first required, which can achieve high selectivity to CO over a wide range of conversion and operating temperatures.

Recently, Pt-based catalysts have been investigated for RWGS (Kattel et al., Angew. Chem. Int. Edit., 128, 8100-8105 (2016) and Porosoff et al., J. Catal., 301, 30-37 (2013)), but they are expensive, and thus, unviable for an industrial scale CO_2 conversion process. As an alternative, transition metal carbides (TMCs) are low-cost, with similar electronic properties to precious metals. (Levy et al., Science, 181, 547-549 (1973) and Porosoff et al., Chem. Comm., 51, 6988-6991 (2015)). Density functional theory (DFT) calculations over the TMC, molybdenum carbide (Mo_2C) demonstrate that Mo-terminated Mo_2C has many properties similar to transition metals including Ru, Fe, Co and Ni catalysts, all of which are active for CO_2 conversion. (Medford et al., J. Catal., 290, 108-117 (2012)). DFT calculations by Shi et al. further illustrate that CO_2 dissociation ($CO_2 \rightarrow CO + O$) is more favorable than CO_2 hydrogenation ($CO_2 + H \rightarrow HCOO$ or $COOH$) over Mo_2C, suggesting high CO selectivity. (Shi et al., Appl. Catal. A-Gen., 524, 223-236 (2016)). Reactor experiments over unsupported-Mo_2C powder catalysts for RWGS at 300 °C and 0.1 MPa show 8.7% conversion and 93.9% selectivity towards CO (Porosoff et al., Angew. Chem. Int. Edit., 53, 6705-6709 (2014)), confirming the DFT calculations. Another study over Mo_2C nanowires also reports high activity and CO selectivity at 600 °C. (Gao et al., Catal. Comm., 84, 147-150 (2016)). The high intrinsic activity of Mo_2C originates from CO_2 binding in a bent configuration, leading to spontaneous breakage of a C=O bond, leaving CO and O bound to the surface. (Posada-Perez et al., Phys. Chem. Chem. Phys., 16, 14912-14921 (2014)). The CO can desorb from the surface, while the oxy-carbide (O-Mo_2C) is restored to the active carbide through hydrogenation. (Porosoff et al., Angew. Chem. Int. Edit., 53, 6705-6709 (2014)).

Mo_2C can also be modified with metal nanoparticles (Cu, Co, Ni), which influence the product selectivity, leading to MeOH with Cu (Posada-Perez et al., Catal. Sci. Technol., 6, 6766-6777 (2016)), C_2+ hydrocarbons with Co and CH_4 with Ni. (Griboval-Constant et al., Appl. Catal. A-Gen., 260, 35-45 (2004) and Xu et al., Catal. Lett., 145, 1365-1373 (2015)). Because modifying Mo_2C with a metal promoter can further tune the selectivity between MeOH, C_2+ hydrocarbons or CH_4, it may be possible to modify Mo_2C to selectively produce even more CO across a wide range of conversions and temperatures. Experimental and theoretical studies suggest that potassium (K) promoters increase the binding energy, and therefore, reactivity of CO_2, thereby promoting C=O bond scission and formation of CO. (Solymosi et al., Catal. Lett., 66, 227-230 (2000) and Pistonesi et al., Catal. Today, 181, 102-107 (2012)).

Molybdenum carbide has been employed as a catalyst for CO_2 hydrogenation as a pure material, supported on γ-Al_2O_3 and when modified with various metals (Co, Ni, Fe). It has been used as an alternative to precious metals for many catalytic reactions, and more recently has been applied to CO_2 hydrogenation. CO_2 hydrogenation over these previous catalysts is comparable to the current invention; however, the selectivity and yield to CO is significantly lower.

DISCLOSURE OF INVENTION

The present invention provides a class of catalysts for CO_2 hydrogenation via the RWGS reaction to selectively produce CO for down-stream hydrocarbon synthesis. Alkali metal-doped molybdenum carbide, supported on gamma alumina (A-Mo_2C/γ-Al_2O_3, A = K, Na, Li), is synthesized by co-impregnation of $(NH_4)6Mo_7O_{24}{\bullet}4H_2O$ and A-NO_3 precursors (A = K, Na, Li) onto a γ-Al_2O_3 support. The A-Mo/γ-Al_2O_3 catalyst is then carburized to form the A-Mo_2C/γ-Al_2O_3.

Alkali metal-promoted molybdenum carbide supported on gamma alumina is a low-cost, stable and highly selective catalyst for RWGS over a wide range of conversion. These findings are supported by X-ray diffraction (XRD), scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDS), X-ray photoelectron spectroscopy (XPS) and density functional theory (DFT) calculations.

These and other features and advantages of the invention, as well as the invention itself, will become better understood by reference to the following detailed description, appended claims, and accompanying drawings.

BRIEF DESCRIPTION OF DRAWINGS

FIG. 1 shows the synthesis procedure for alkali metal doped molybdenum carbide supported on gamma alumina.

FIG. 2A is a low magnification scanning electron microscopy (SEM) image of K-Mo_2C/γ-Al_2O_3. FIG. 2B is a high magnification SEM image of K-Mo_2C/γ-Al_2O_3.

FIG. 3 is a schematic of a reactor set-up for CO_2 hydrogenation.

FIG. 4A is a plot of CO_2 conversion versus time for the Mo_2C and A-Mo_2C (A = K, Na, Li) supported on γ-Al_2O_3. FIG. 4B is a plot of production of CO and CH_4 versus time for Na-Mo_2C/γ-Al_2O_3, Li-Mo_2C/γ-Al_2O_3 and Mo_2C/γ-Al_2O_3.

MODES FOR CARRYING OUT THE INVENTION

The present invention provides for a supported heterogeneous catalyst material for catalyzing the RWGS reaction for the selective formation of CO. The catalyst has a support material of γ-Al_2O_3 and an active material of alkali-metal doped molybdenum carbide. The alkali-metal component of the active material may comprise one or more alkali-metal precursors in elemental form or in the form of oxides, with the metals being K, Na, Li, or any combination thereof. The molybdenum component of the active material may comprise one or more molybdenum precursors in the form of carbides, oxycarbides, oxides, elemental molybdenum, or any combination thereof.

FIG. 1 shows the synthesis procedure for alkali metal doped molybdenum carbide supported on gamma alumina. Alkali metal-doped molybdenum carbide, supported on gamma alumina (A-Mo2C/γ-Al2O3, A = K, Na, Li) was synthesized by co-impregnation of $(NH_4)6Mo_7O_{24}\cdot 4H_2O$ and A-NO_3 precursors (A = K, Na, Li) onto a γ-Al_2O_3 support by the evaporation deposition method. In brief, the precursors were dissolved in deionized water at the concentrations required to obtain molar ratios of 1/4/15 A/Mo/γ-Al_2O_3, which translates to 2% potassium (K), 1.2% sodium (Na), 0.4% lithium (Li) and 20.8% Mo loading on the γ-Al_2O_3 support. Aqueous solutions of the metal precursors were added to a beaker of γ-Al_2O_3 and dried overnight under stirring at 60 °C, then calcined in air overnight at 350 °C.

The A-Mo/γ-Al_2O_3 catalyst was then carburized in a 21% CH_4 in H_2 mixture at 600 °C for 2.5 hours to form the A-Mo_2C/γ-Al_2O_3. After the first 1.5 hour, the CH_4 was shut off and the carbide was cooled to room temperature in H_2. At room temperature, the catalyst was passivated in 1% O_2 in N_2 for several hours. FIG. 2A shows a low magnification scanning electron microscopy (SEM) image of K-Mo_2C/γ-Al_2O_3, and FIG. 2B shows a high magnification SEM image of K-Mo_2C/γ-Al_2O_3.

CO_2 hydrogenation via the RWGS reaction is performed while flowing carbon dioxide, hydrogen gas, or any combination thereof over the A-Mo_2C/γ-Al_2O_3 catalyst material. FIG. 3 shows a schematic of a reactor set-up for CO_2 hydrogenation. In the CO_2 hydrogenation experiment, 500 mg of A-Mo_2C/γ-Al_2O_3 was loaded into a ¼ in stainless steel reactor and reduced under 50 sccm H_2 at 50 psig for 2.5 h at 300 °C. After reduction, the reactor was isolated and the bypass pressurized to 290 psig with 6.3 sccm CO_2, 18.9 sccm H_2 and 5.0 sccm N_2, for a H_2:CO_2 ratio of 3:1. At 290 psig, concentration of the reactants in the bypass was recorded as a baseline and gases were flowed into the reactor. Reactions were run for 22 h at 300 °C and concentrations of reactants and products were measured by an inline gas chromatograph.

Table 1 shows a summary of performance of Mo_2C and A-Mo_2C (A = K, Na, Li) supported on γ-Al_2O_3 for CO_2 hydrogenation. FIG. 4A shows a plot of CO_2 conversion versus time for the Mo_2C and A-Mo_2C (A = K, Na, Li) supported on γ-Al_2O_3, and FIG. 4B shows a plot of production of CO and CH_4 versus time for Na-Mo_2C/γ-Al_2O_3, Li-Mo_2C/γ-Al_2O_3 and Mo_2C/γ-Al_2O_3. The CO_2 hydrogenation via the RWGS reaction can achieve a CO yield of 12% or greater and a CO selectivity of 90% or greater.

Table 1

Catalyst	Conversion / %	CO Selectivity / %	CO Yield / %
Mo_2C/γ-Al_2O_3	19.9	73.5	14.6
K-Mo_2C/γ-Al_2O_3	17.2	95.9	16.5
Na-Mo_2C/γ-Al_2O_3	19.6	86.3	16.9
Li-Mo_2C/γ-Al_2O_3	19.8	62.1	12.3

The increased CO yield from doping a Mo_2C/γ-Al_2O_3 catalyst with alkali metals offers an improved route for CO production from CO_2. The best currently available catalysts can only achieve a CO yield and selectivity of 14.6% and 75% at 300 °C, respectively, while K-Mo_2C/γ-Al_2O_3 reaches a CO yield and selectivity of 16.5% and 96%, respectively. Selectively producing CO from CO_2 enables a facile route to synthesize synthetic hydrocarbons from CO_2 through down-stream Fischer-Tropsch.

Na-Mo_2C/γ-Al_2O_3 reaches a similar CO yield to K-Mo_2C/γ-Al_2O_3, while Li-Mo_2C/γ-Al_2O_3 shows a lower selectivity to CO than Mo_2C/γ-Al_2O_3. Maintaining the same A:Mo weight ratio in Li-Mo_2C/γ-Al_2O_3 results in a significantly lower weight fraction of Li because of the lower atomic weight of Li relative to Na and K. It is possible this lower amount of dopant results in the lower CO selectivity for Li-Mo_2C/γ-Al_2O_3. The Li:Mo and Na:Mo ratios can be further optimized.

The addition of K to catalysts as a promoter has not yet been recorded with a Mo_2C-based catalyst for CO_2 hydrogenation. Furthermore, doping Mo_2C-based catalysts with Li and Na has not been attempted in literature for CO_2 hydrogenation. By doping Mo_2C/γ-Al_2O_3 with alkali metals, CO selectivity substantially increases for K and Na, which is likely caused by attenuation of the electronic properties of the Mo_2C phase. These electronic effects are only present when Mo_2C is doped with a small amount of alkali metal, thereby attenuating the CO binding energy and preventing further hydrogenation into CH_4 or other hydrocarbons.

A-Mo_2C/γ-Al_2O_3 (A = K, Na, Li) was also tested at other temperatures (250 – 1000 °C), other alkali metal loadings (0.1 – 15%), other Mo loadings (1 – 70%), carburization temperatures (400 – 1000 °C) on other supports (SiO_2, TiO_2, ZrO_2), gas compositions (CO_2:H_2 = 1:1, 1:2, 1:3) and pressures (0 – 350 psig). Higher temperature improves conversion for K-Mo_2C/γ-Al_2O_3 to 28.6%, without the expense of CO selectivity (94.8%). Increasing K loading to 5% increases CO selectivity to 99.4% at the expense of conversion (3.8%). Higher Mo loading lowers conversion to 6.6% and raises selectivity slightly to 97.8%.

The exact optimal metal loading and A:Mo (A = K, Na, Li) ratio on the γ-Al_2O_3 support can be further optimized based on this finding of such high CO selectivity, especially over Na-Mo_2C/γ-Al_2O_3 and K-Mo_2C/γ-Al_2O_3.

Example

In this example, kinetic experiments and characterization tools were combined with DFT calculations to probe the catalytic properties of K-promoted Mo_2C and understand the reaction mechanisms of CO_2 dissociation. Flow reactor results indicate that K-Mo_2C/γ-Al_2O_3 is a highly active and stable RWGS catalyst exhibiting high selectivity towards CO over a range of operating conditions, with the presence of K promoting CO_2 dissociation to CO. These findings were supported by X-ray diffraction (XRD), scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDS), X-ray photoelectron spectroscopy (XPS) measurements and DFT calculations.

To experimentally determine the effect of K addition on Mo_2C-based supported catalysts, K-Mo_2C/γ-Al_2O_3 and the corresponding Mo_2C, Mo and K-Mo control catalysts, all supported on γ-Al_2O_3, were synthesized through an evaporation-deposition procedure. XRD measurements over the reduced catalysts indicate that each of the syntheized catalysts contain a combination of MoO_2, β-Mo_2C and metallic Mo. Each of these phases was assigned to the synthesized catalysts by comparing the XRD spectra with the standard database for specific bulk Mo phases. XRD measurements of the Mo-based catalysts indicated that Mo_2C/γ-Al_2O_3 and 2 wt% K-Mo_2C/γ-Al_2O_3 contained a mixture of β-Mo_2C and MoO_2 supported on γ-Al_2O_3. All supported Mo-based catalysts exhibited large peaks at 45.8° and 66.6°, from the γ-Al_2O_3 support, and no identifiable peaks for MoO_3 were present in any of the samples. Closer inspection of the XRD spectra revealed the presence of a phase assigned to metallic Mo at 40.5°, 58.7° and 73.7° on the K-Mo_2C/γ-Al_2O_3 and K-Mo/γ-Al_2O_3 catalysts. These peaks were not present in Mo_2C/γ-Al_2O_3, suggesting that the addition of K promotes the formation of a metallic Mo phase.

SEM images with EDS mapping of the reduced catalysts were used to better identify the structure of K-Mo_2C/γ-Al_2O_3. Overall, the morphology and particle size of the catalysts appeared to be similar, with the SEM image of Mo_2C/γ-Al_2O_3 found in the SI. The EDS maps, however, showed that the distribution of Mo over each catalyst was notably different. The EDS map of the Mo_2C/γ-Al_2O_3 catalyst, found in the SI, indicated that molybdenum was evenly distributed over the γ-Al_2O_3 support. On K-Mo_2C/γ-Al_2O_3, there was both (1) a large degree of segregation between Mo and Al-rich areas and (2) K being preferentially found in the Mo-rich areas, which suggests K directly affects the electronic properties of the active Mo_2C phase.

Regardless of the differences in catalyst particle size and morphology, there was no significant difference in catalytic activity between the two samples. The conversion of Mo_2C/γ-Al_2O_3 and K-Mo_2C/γ-Al_2O_3 was similar. Although the activity of the two catalysts was comparable, the addition of 2 wt% K to Mo_2C/γ-Al_2O_3 significantly improved the selectivity towards CO. There was a strong promotional effect from the addition of K, which led to high CO selectivity (~95%) from 6 to 23% conversion, the thermodynamic maximum for RWGS at 300 °C with a 3:1 H_2:CO_2 mixture. Furthermore, the addition of the K promoter decreased the deactivation percentage from 11.7% to 7.3% after 68 h on stream, an improvement in catalytic stability.

The K loading was varied from 1 – 3 wt% to determine the effect of K on catalytic performance. The 1 wt% K-Mo_2C/γ-Al_2O_3 had a slightly higher CO yield than 2 wt% K-Mo_2C/γ-Al_2O_3, but with increased methane production, which wastes valuable H_2 and requires a separation step before FT. Furthermore, as K loading increased, there was a drop in catalytic activity, likely from the blocking of active sites. This relationship between K loading and CO yield was not linearly dependant on temperature. At the higher temperature, the 3 wt% K-Mo_2C/γ-Al_2O_3 achieved 40.5% conversion and 98.2% CO selectivity, which outperformed the 2 wt% K-Mo_2C/γ-Al_2O_3 and industrial ZnO/Al_2O_3 and ZnO/Cr_2O_3 catalysts. (Joo et al., Ind. Eng. Chem. Res., 38, 1808-1812 (1999)).

Uncarburized Mo/γ-Al_2O_3 and 2 wt% K-Mo/γ-Al_2O_3 catalysts were tested to clarify the role of metallic Mo identified in K-Mo_2C/γ-Al_2O_3 in the XRD measurements. The Mo/γ-Al_2O_3 and K-Mo/γ-Al_2O_3 control catalysts were reduced *ex situ* in pure H_2 at 600 °C prior to reaction to form metallic Mo. The pre-reduction step ensured the high activity and CO selectivity of the Mo_2C-based catalysts originated from the Mo carbide phase, and not metallic Mo. The Mo carbides, synthesized with CH_4, were more active than the corresponding uncarburized catalysts, indicating that the carburization step was necessary for high catalytic activity and that the metallic Mo phase in K-Mo_2C/γ-Al_2O_3 was not solely responsible for the high performance.

By modifying Mo_2C/γ-Al_2O_3 with a K promoter, the CO selectivity and yield increased significantly, and approached the maximum thermodynamic yield for RWGS, under the appropriate reaction conditions. Addition of K also improved the catalyst stability, with only 7.3% deactivation after 68 h on stream. Catalyst characterization by SEM with EDS clearly showed that K is preferably found in Mo-rich regions, while Mo is more evenly distributed in Mo_2C/γ-Al_2O_3. Furthermore, K-Mo_2C/γ-Al_2O_3 maintained the Mo in a reduced and active state as evidenced by XPS measurements. These experimental results are supported by DFT calculations, which showed enhanced CO_2 adsorption and reduced CO_2 dissociation barriers on the K-promoted, compared to the pristine, Mo-terminated β-$Mo_2C(001)$ surfaces. Notably, the DFT calculations predicted a 2.8 kcal mol^{-1} lower activation barrier for CO formation upon K addition, which is in excellent agreement with the experimentally measured difference of 2.6 kcal mol^{-1}. These findings show that K-Mo_2C/γ-Al_2O_3 is a highly selective catalyst for producing CO from CO_2 and has the potential to be used as a commercial RWGS catalyst.

The above descriptions are those of the preferred embodiments of the invention. Various modifications and variations are possible in light of the above teachings without departing from the spirit and broader aspects of the invention. It is therefore to be understood that the claimed invention may be practiced otherwise than as specifically described. Any references to claim elements in the singular, for example, using the articles “a,” “an,” “the,” or “said,” is not to be construed as limiting the element to the singular.

CLAIMS

What is claimed as new and desired to be protected by Letters Patent of the United States is:

1. A supported heterogeneous catalyst material for catalyzing the reverse water-gas shift (RWGS) reaction for the selective formation of CO, comprising:

a support material comprising γ-Al_2O_3; and

an active material comprising alkali-metal doped molybdenum carbide.

2. The catalyst material of claim 1, wherein the alkali-metal component of the active material comprises one or more alkali-metal precursors in elemental form or in the form of oxides, said metals being selected from the group consisting of K, Na, Li, or any combination thereof.

3. The catalyst material of claim 1, wherein the molybdenum component of the active material comprises one or more molybdenum precursors in the form of carbides, oxycarbides, oxides, elemental molybdenum, or any combination thereof.

4. A method for making a catalyst for use in carbon dioxide hydrogenation via the reverse water-gas shift (RWGS) reaction for the selective formation of CO, comprising:

co-impregnating molybdenum and alkali-metal precursors onto a γ-Al_2O_3 support, wherein the alkali metal is K, Na, or Li;

drying and calcining impregnated γ-Al_2O_3 support; and

carburizing the dried and calcined γ-Al_2O_3 support to form A-Mo_2C/γ-Al_2O_3, where A is K, Na, or Li.

5. The method of claim 4, wherein the loading of Mo is in the range of 1 to 70%.

6. The method of claim 4, wherein the loading of the alkali metal is in the range of 0.1 to 15%.

7. The method of claim 4, wherein the carburization is performed at a temperature in the range of 400 to 1000 °C.

8. A method for CO_2 hydrogenation via the reverse water-gas shift (RWGS) reaction for the selective formation of CO, comprising:

co-impregnating molybdenum and alkali-metal precursors onto a γ-Al_2O_3 support, wherein the alkali metal is K, Na, or Li;

drying and calcining impregnated γ-Al_2O_3 support;

carburizing the dried and calcined γ-Al_2O_3 support to form A-Mo_2C/γ-Al_2O_3, wherein A is K, Na, or Li; and

reacting the A-Mo_2C/γ-Al_2O_3 with CO_2 and H_2 to form CO.

9. The method of claim 8, wherein the loading of Mo is in the range of 1 to 70%.

10. The method of claim 8, wherein the loading of the alkali metal is in the range of 0.1 to 15%.

11. The method of claim 8, wherein the carburization is performed at a temperature in the range of 400 to 1000 °C.

12. The method of claim 8, wherein the reaction is performed while applying external heat.

13. The method of claim 8, wherein the reaction is performed at a temperature in the range of 250 to 1000 °C

14. The method of claim 8, wherein the reaction is performed at a pressure between 0 and 350 psig.

15. The method of claim 8, wherein the reaction is performed while flowing carbon dioxide, hydrogen gas, or any combination thereof, over the A-Mo_2C/γ-Al_2O_3 catalyst material.

16. The method of claim 8, wherein the reaction is performed while applying external heat and flowing carbon dioxide, hydrogen gas, or any combination thereof, over the A-Mo_2C/γ-Al_2O_3 catalyst material.

17. The method of claim 8, wherein the CO_2 hydrogenation via the RWGS reaction achieves a CO yield of 12% or greater.

18. The method of claim 8, wherein the CO_2 hydrogenation via the RWGS reaction achieves a CO selectivity of 90% or greater.

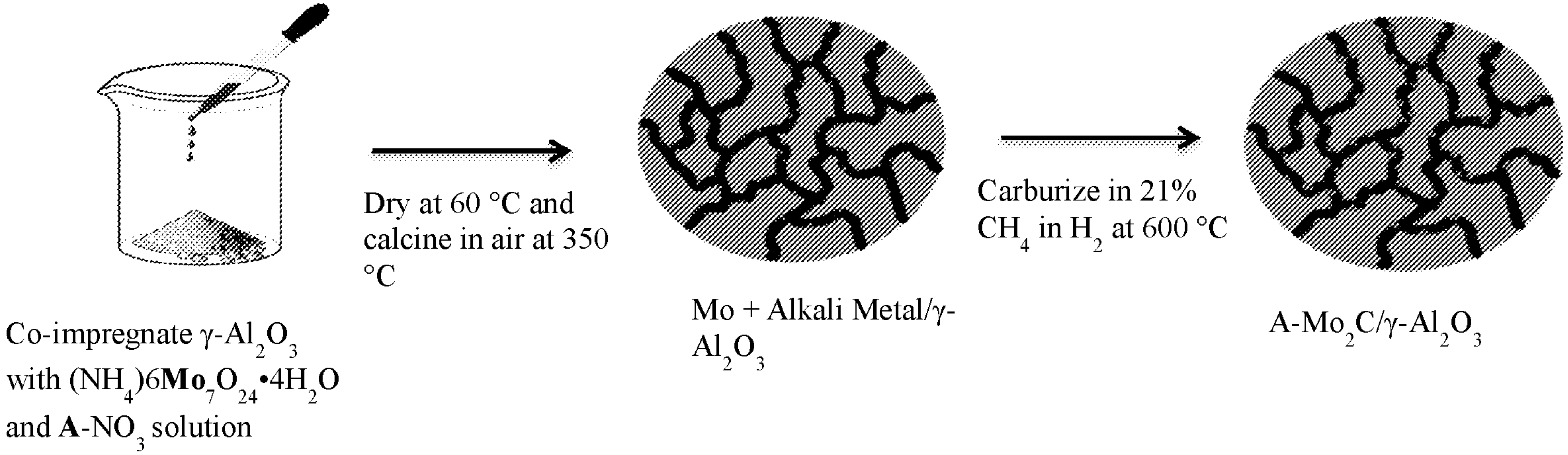
Co-impregnate γ-Al_2O_3 with $(NH_4)6\mathbf{Mo}_7O_{24}{\bullet}4H_2O$ and **A**-NO_3 solution
Dry at 60 °C and calcine in air at 350 °C
Mo + Alkali Metal/γ-Al_2O_3
Carburize in 21% CH_4 in H_2 at 600 °C
A-Mo_2C/γ-Al_2O_3

FIG. 1

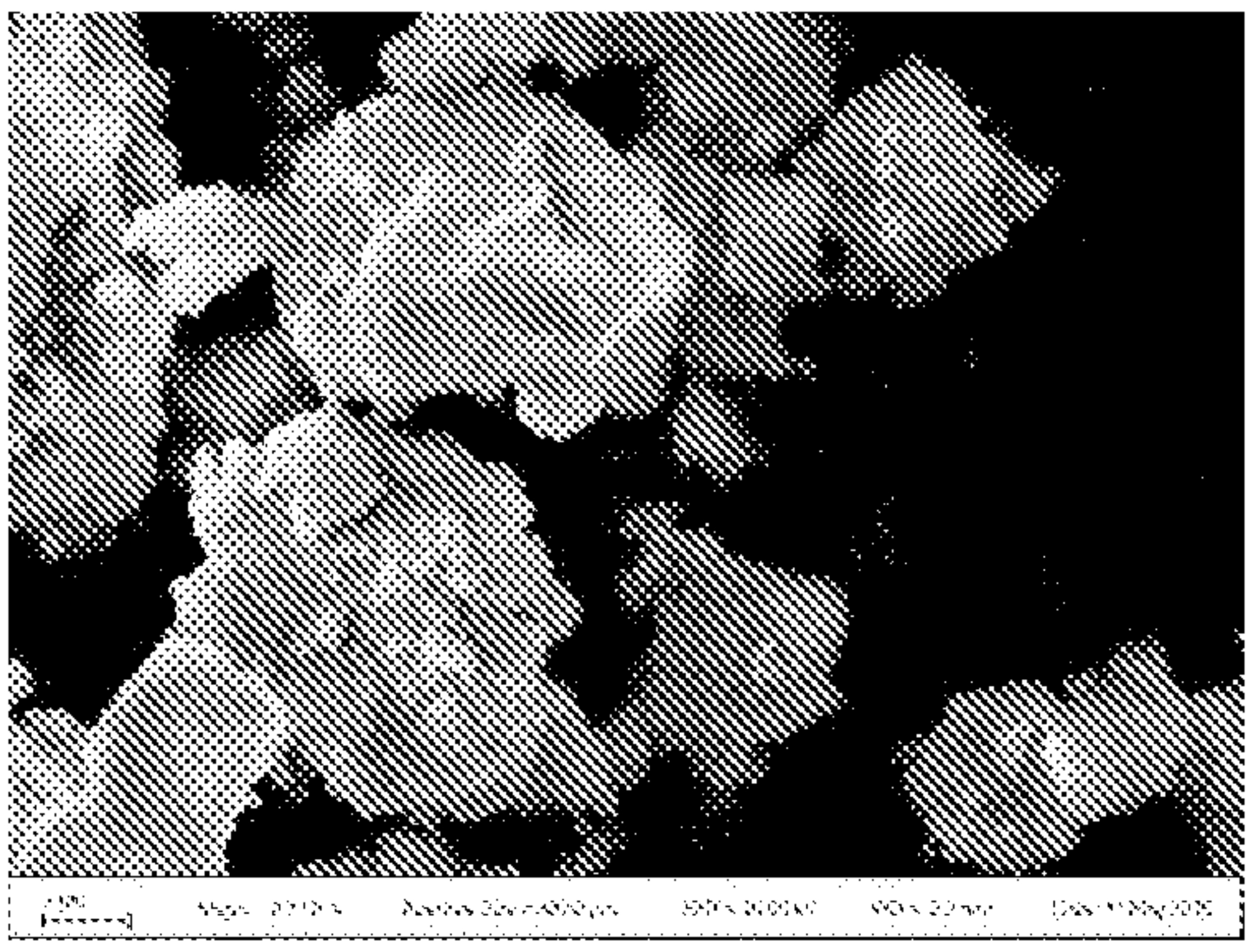

FIG. 2A

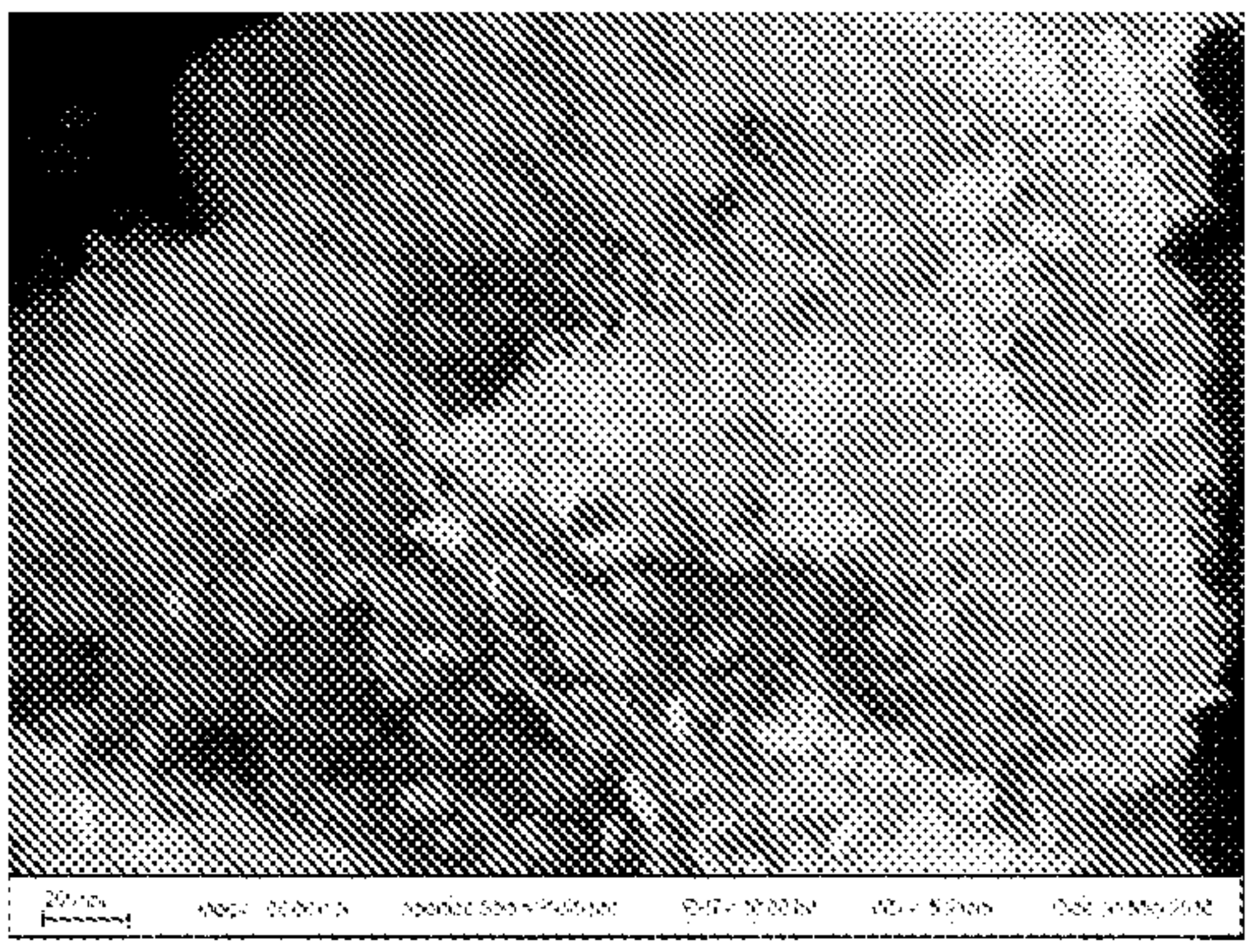

FIG. 2B

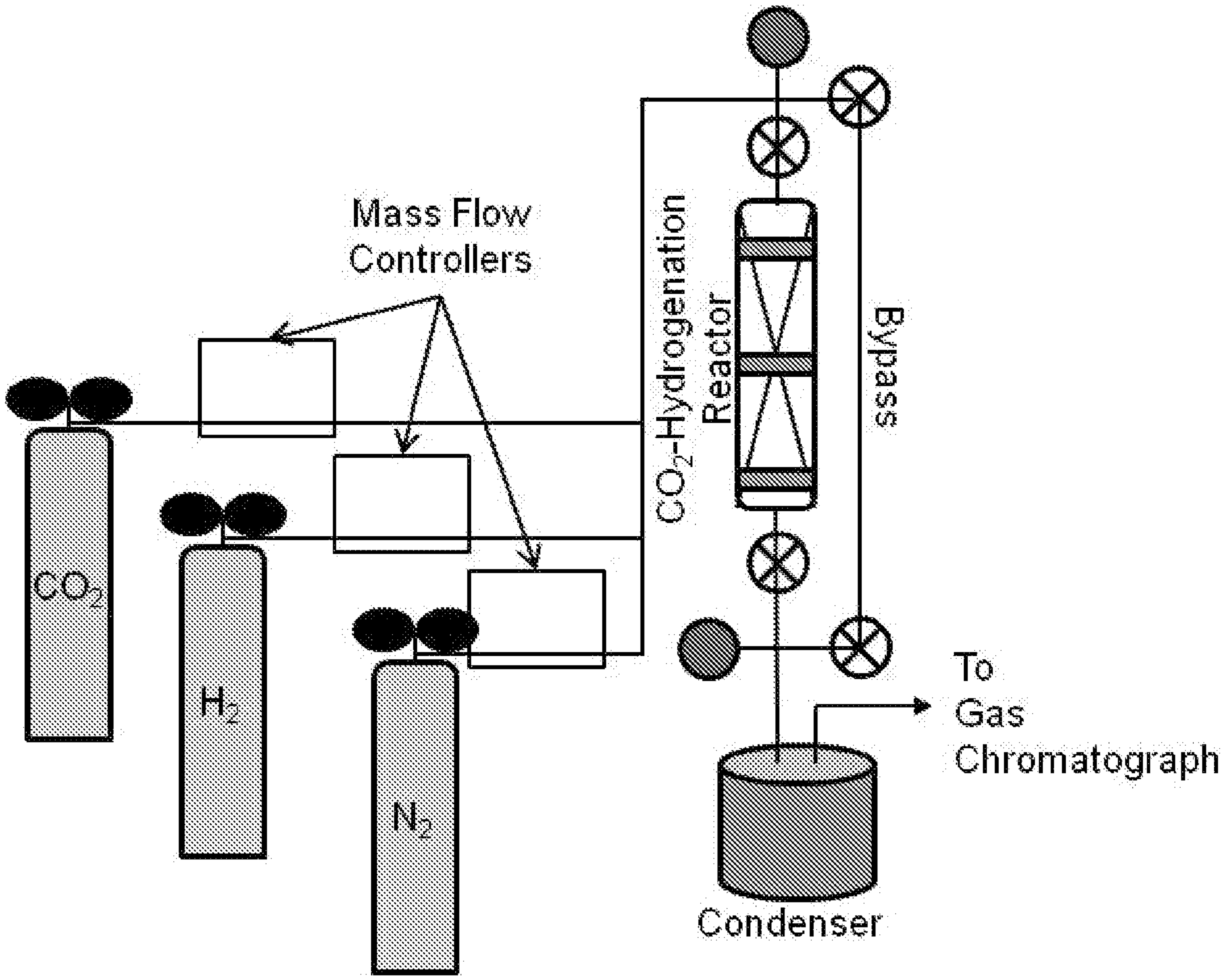
Mass Flow Controllers
CO$_2$-Hydrogenation Reactor
Bypass
CO$_2$
H$_2$
N$_2$
To Gas Chromatograph
Condenser

FIG. 3

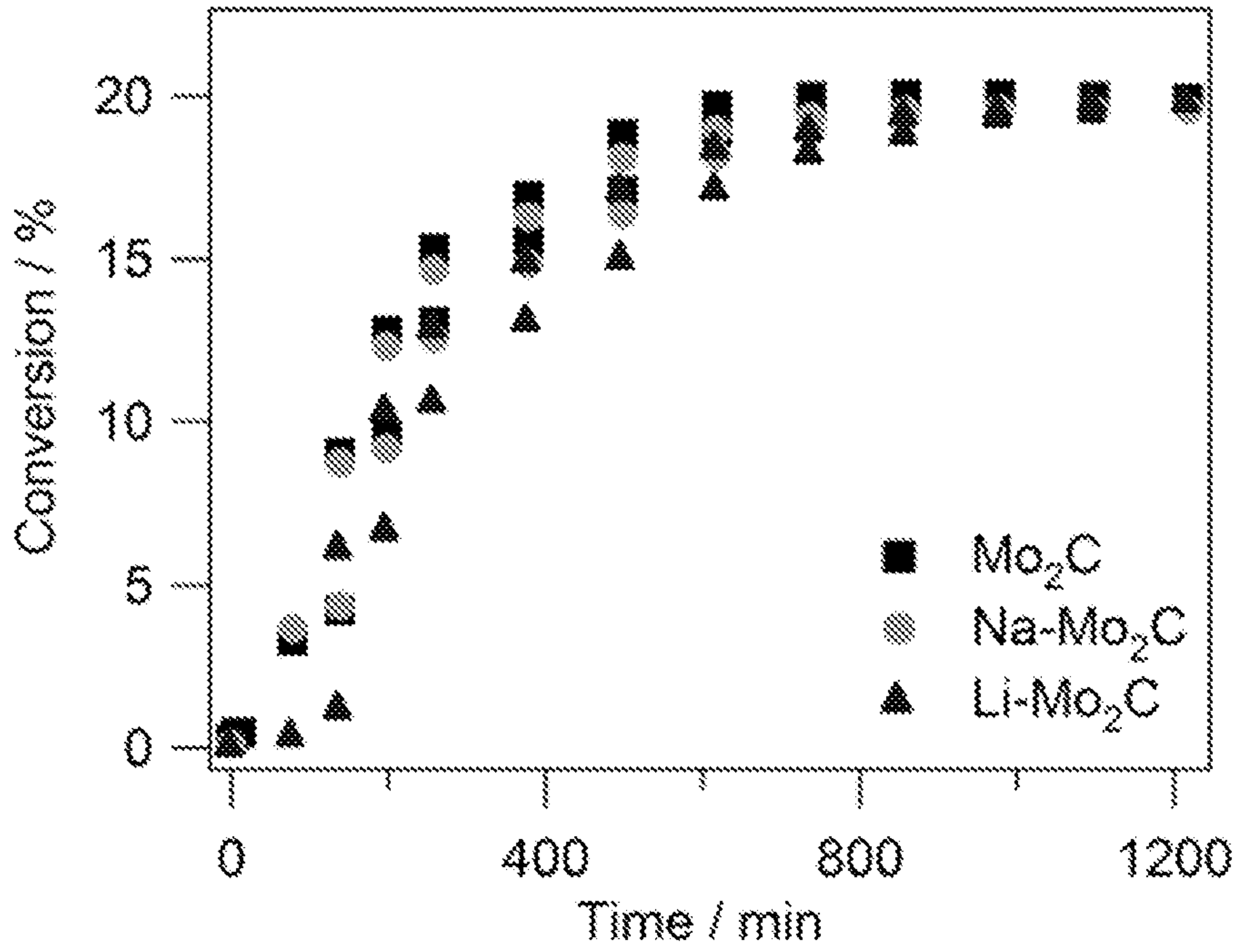
Conversion / %
0
5
10
15
20
0
400
800
1200
Time / min
■ Mo_2C
● $Na\text{-}Mo_2C$
▲ $Li\text{-}Mo_2C$

FIG. 4A

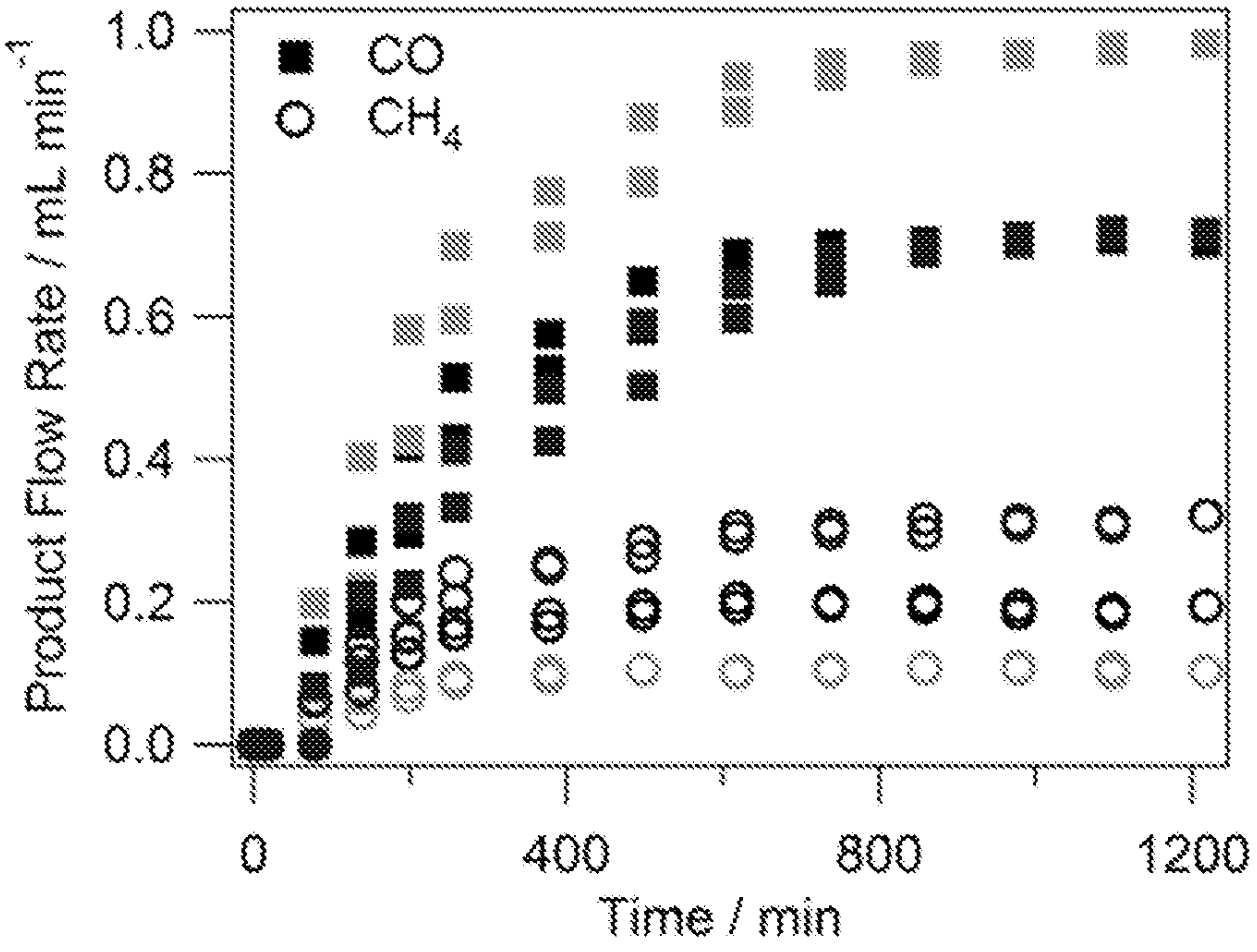
Product Flow Rate / mL min^{-1}
0.0
0.2
0.4
0.6
0.8
1.0
0
400
800
1200
Time / min
■ CO
○ CH_4

FIG. 4B


Co-impregnate γ-Al_2O_3 with $(NH_4)6\mathbf{Mo}_7O_{24}$•$4H_2O$ and **A**-NO_3 solution
Dry at 60 °C and calcine in air at 350 °C
Mo + Alkali Metal/γ-Al_2O_3
Carburize in 21% CH_4 in H_2 at 600 °C
A-Mo_2C/γ-Al_2O_3

FIG. 1