The carburization of transition metal molybdates (M_xMoO_4 , $M = Cu, Ni$ or Co) and the generation of highly active metal/carbide catalysts for CO_2 hydrogenation

Wenqian Xu^a, Pedro J. Ramírez^{a, b}, Dario Stacchiola^a, Joaquín L. Brito^c, and José A. Rodríguez^{a, *}

^aChemistry Department, Brookhaven National Laboratory, Upton, NY 11973, USA

^bFacultad de Ciencias, Universidad Central de Venezuela, Apartado 20513, Caracas 1020-A, Venezuela.

^cCentro de Química, Instituto Venezolano de Investigaciones Científicas (IVIC), Apartado 21827, Caracas 1020-A, Venezuela.

*email: Rodríguez, Jose [rodriguez@bnl.gov]

ABSTRACT: A new approach has been tested for the preparation of metal/ Mo_2C catalysts using mixed-metal oxide molybdates as precursors. Synchrotron-based *in situ* time-resolved X-ray diffraction was used to study the reduction and carburization processes of $Cu_3(MoO_4)_2(OH)_2$, α - $NiMoO_4$ and $CoMoO_4 \cdot nH_2O$ by thermal treatment under mixtures of hydrogen and methane. In all cases, the final product was β - Mo_2C and a metal phase (Cu, Ni, or Co), but the transition sequence varied with the different metals, and it could be related to the reduction potential of the Cu^{2+} , Ni^{2+} and Co^{2+} cations inside each molybdate. The synthesized Cu/ Mo_2C , Ni/ Mo_2C and Co/ Mo_2C catalysts were highly active for the hydrogenation of CO_2 . The metal/ Mo_2C systems exhibited large variations in the selectivity towards methanol, methane and C_nH_{2n+2} ($n > 2$) hydrocarbons depending on the nature of the supported metal and its ability to cleave C-O bonds. Cu/ Mo_2C displayed a high selectivity for CO and methanol production. Ni/ Mo_2C and Co/ Mo_2C

were the most active catalysts for the activation and full decomposition of CO₂, showing high selectivity for the production of methane (Ni case) and C_nH_{2n+2} (n > 2) hydrocarbons (Co case).

KEYWORDS: Molybdenum carbide, molybdenum oxide, molybdate, nickel, copper, cobalt, CO₂ hydrogenation

Introduction

Metal carbides are fascinating materials which have aroused continuous research interest for decades owing to their amazing physical and chemical properties.¹⁻³ Since the 1970s, it is known that some transition metal carbides (TMCs) can display a chemical behavior which is reminiscent of platinum and other transition metals such as Pd, Ru or Rh and in addition can exhibit important advantages over these bulk transition metals in terms of catalytic selectivity or resistance to poisoning during the transformation of carbon-containing molecules.^{4,5} Thus, they perform well as hydrogenation and dehydrogenation catalysts,⁶ and display remarkable activity in hydrotreatment processes of oil-derived feedstocks.⁶⁻⁹ Molybdenum carbide is one of the most studied metal carbides in the area of catalysis.^{2,5-11} Molybdenum carbide can adopt a variety of crystal structures, but it is commonly seen in two types, β -MoC_y (y $\approx$ 0.5) with a hexagonal close-packed structure, and α -MoC_{1-x} (x < 0.5) with a face-centered cubic (fcc) structure like NaCl.^{10,12,13} The Mo/C ratio in the carbide affects its chemical and catalytic properties.^{10,14} Although MoC and Mo₂C are both active catalysts for the hydrogenation of CO₂,^{10,14} the catalytic activity increases when going from a Mo/C ratio of 1 to 2. As a CO₂ hydrogenation catalyst, Mo₂C produces CO, CH₄ and CH₃OH as reaction products, while only CO and CH₃OH are observed on a MoC catalyst.¹⁴

In the last decade, it has become clear that the metal carbides can be excellent supports for the dispersion of metal particles.¹⁵⁻²⁰ Of particular interest is the use of metal/MoC_x catalysts in the forward and reverse water-gas shift reactions,¹⁸⁻²⁰ in the hydrogenation of CO₂ to methanol and methane,^{17,21} and in hydrodesulfurization processes.^{15,22} As mentioned above, metal carbides have interesting catalytic properties on their own⁴⁻⁷ and, in addition, they also can modify the reactivity of a supported metal through chemical bonding.²³ This phenomenon has been extensively studied in the case of Au nanoparticles on TiC and MoC_x surfaces.^{17,19,22,23} The formation of Au-C bonds on the surface of the carbide induces a polarization of electrons in the metal.²³ This redistribution of electrons accumulates electronic density towards the vacuum side of the surface making the gold more reactive towards incoming molecules such as thiophene, SO₂ or CO₂.^{17,19,22,23} Theoretical calculations predict electronic perturbations after the adsorption of atoms of Cu, Ni or Co on metal carbide surfaces.²³ Although these electronic perturbations are not as large as those found for gold,²³ they certainly could modify the chemical properties of the deposited metals.^{17,21} For example, surfaces of pure copper do not bind well CO₂,²⁴ but the molecule strongly adsorbs with a η^3 -C,O,O configuration on copper clusters in direct contact with a TiC support.¹⁷ Thus, Cu/TiC catalysts are much more active for CO₂ hydrogenation than catalysts generated by the dispersion of copper on typical oxide supports such as ZnO or Al₂O₃.¹⁷

In the most common route for the preparation of metal/Mo₂C catalysts, Mo₂C is first synthesized by carburizing a Mo oxide material, and then the supported metal is dispersed on the carbide.^{18,20,25} In recent works,^{10,26} we reported a new approach for the synthesis of β -MoC_y ($y \approx 0.5$) and α -MoC_{1-x} ($x < 0.5$) catalysts based on the carburization of hexagonal molybdenum oxide (HMO) with mixtures of hydrogen and methane/ethane. In this study, we explore an alternative synthesis route for the generation of Cu/Mo₂C, Ni/Mo₂C and Co/Mo₂C catalysts

starting from mixed-metal oxide precursors $\{\text{Cu}_3(\text{MoO}_4)_2(\text{OH})_2, \alpha\text{-NiMoO}_4 \text{ and } \text{CoMoO}_4 \cdot n\text{H}_2\text{O}\}$. The oxide $\rightarrow$ carbide transformations are followed using synchrotron-based *in situ* time-resolved X-ray diffraction (TR-XRD). Our results show that the synthesized Cu/Mo₂C, Ni/Mo₂C and Co/Mo₂C catalysts are highly active for the hydrogenation of CO₂. The metal/Mo₂C systems exhibit large variations in the selectivity towards methanol, methane and C_nH_{2n+2} (n > 2) hydrocarbons depending on the nature of the supported metal.

Experimental Methods

A. Synthesis and characterization of the molybdenum carbides: *In situ* time-resolved XRD studies

Cu-molybdate from Sigma-Aldrich® was used without further treatment. Ni- and Co-molybdates were synthesized following the methodology described in refs.²⁷⁻²⁹ X-ray diffraction (XRD) of these samples indicated that they were Cu₃(MoO₄)₂(OH)₂, α -NiMoO₄ and CoMoO₄ · nH₂O, respectively. Carburization was performed with a flow reactor in conjunction with the *in situ* XRD setup at Beamline X7B ($\lambda = 0.3196 \text{ \AA}$) of National Synchrotron Light Source (NSLS) at Brookhaven National Lab (BNL).¹⁰ In a gas flow mixture of 10% methane and 90% hydrogen, samples were ramp-heated to 750 or 850 °C at a rate of 5 °C/min. 2D diffraction images were taken with a PerkinElmer® amorphous silicon detector. XRD data processing and analysis involved usage of the programs Fit 2D³⁰ and GSAS.^{10,31,32}

B. Catalytic tests for CO₂ hydrogenation

Surface areas of the metal/Mo₂C catalysts were measured by the BET method using N₂ and were all in the range of 1.5-2 m²/g. These surfaces areas reflect the initial properties of the mixed-metal oxide precursors and are not a main consequence of the carburization process.¹⁰ High pressure CO₂ hydrogenation was performed with a flow type fixed bed micro-reactor at temperatures of 200, 250 and 300 °C, with a pressure of 2 MPa and a flow rate of 30 ml/min of a reaction mixture of 10 % Ar/ 15% CO₂/ 75% H₂.¹⁰ Before CO₂ hydrogenation, 0.2 g of the mixed-metal oxide precursor were loaded into the micro-reactor and treated with mixtures of CH₄/H₂ at 700 (Cu/Mo₂C) or 850 °C (Ni/Mo₂C and Co/Mo₂C) to produce different types of catalysts (see below). After the synthesis of the metal/Mo₂C systems, the sample was cooled to the temperatures for CO₂ hydrogenation indicated above under a flow of hydrogen and then exposed to the reaction mixture of Ar/CO₂/H₂. The effluent gas from the micro-reactor was analyzed by gas chromatography and mass spectrometry.^{10,25}

Results

A. Oxide → carbide transformation: *In situ* time-resolved XRD studies

A.1. Carburization of NiMoO₄

Figure 1 shows the evolution of XRD patterns as a function of temperature for the carburization of α-NiMoO₄. The initial sample underwent three stages of transition before it reached the final state at 850 °C, which is a mixture of pseudo-hexagonal β-Mo₂C and metallic Ni. The initial NiMoO₄ phase was reduced to a mixture of nanocrystalline Ni and Mo oxyhydroxide (MoO_xH_y) at 350 to 470 °C. From peak profile fitting with the GSAS code, crystallite size of Ni and MoO_xH_y were estimated to be 4 nm and 2 nm, respectively. The

MoO_xH_y phase is a face-centered cubic structure and has been documented in previous studies when a Mo oxide was isothermally treated in hydrogen at 350 to 400 °C.^{10,33} This phase was further carburized to α-MoC_{1-x} at 620 to 670 °C. α-MoC_{1-x} is isostructural with MoO_xH_y but has a larger lattice constant, 4.28 Å versus 4.10 Å of MoO_xH_y. In XRD, this transition is evidenced by the shift of the MoO_xH_y peaks to lower 2-θ angles (Figures 1 & 2). On the other side, Ni remained in metallic state without being carburized. Starting at 740 °C, α-MoC_{1-x} was transformed into β-Mo₂C. This process was accompanied by growth of crystallinity in the products as indicated by the sharpening of the XRD peaks. A crystallite size of 26 nm was estimated for β-Mo₂C. For Ni, the value was 22 nm.

A.2. Carburization of Cu₃(MoO₄)₂(OH)₂

The complete *in situ* XRD series for the Cu molybdate carburization process is plotted in Figure 2. The initial sample is matched to Cu₃(MoO₄)₂(OH)₂ (ICSD: 40084). This starting phase was destabilized at 200 °C and turned into a short-lived amorphous state at around 230 °C (bottom of Figure 2, trace at 237 °C). This is followed by a rapid growth of Cu metal phase at 240 °C. The Cu peaks are dominantly intense in the XRD and the other weak broad features are assigned to the cubic MoO_xH_y phase (bottom of Figure 2, trace at 269 °C). From 520 to 600 °C, MoO_xH_y was reduced to a Mo metal phase, which was further carburized to β-Mo₂C at 620 to 680 °C. The Cu metal phase underwent no more phase changes after its formation at 240 °C. The crystallite sizes of Cu and β-Mo₂C are estimated to be 17 nm and 7 nm, respectively.

A.3. Carburization of CoMoO₄

Figure 3 displays a series of time-resolved XRD patterns for Co molybdate carburization. The starting sample is matched to CoMoO₄ • 0.75H₂O (ICSD: 153169). At 360 °C, the initial

phase started to transform to a new phase with a pronounced peak at 5.4° . The transition was complete by 420°C . The new phase could not be identified in the ICSD database, but is most probably a Co molybdate phase^{28,31} with less or no water content (bottom of Figure 3, trace at 452°C). From 490 to 530°C , the unidentified Co molybdate phase decomposed to nano oxide mixtures. CoO is clearly seen in XRD as shown by the trace at 557°C in Figure 3. The form of the Mo oxide/oxyhydroxide is uncertain since no observed peaks can be unambiguously assigned to it. The CoO peaks at 7.5° and 8.7° show asymmetric features that are most probably due to scattering from the nano Mo oxide phase, which is unlikely to be the MoO_xH_y phase that has appeared in the reduction of Ni and Cu molybdate. Increasing the temperature to 720°C induced another step of transition in which CoO was reduced to Co metal while the nano Mo oxide was carburized to $\alpha\text{-MoC}_{1-x}$ (bottom of Figure 3 trace at 753°C). The $\alpha\text{-MoC}_{1-x}$ was not stable and transformed into $\beta\text{-Mo}_2\text{C}$. The final carburized sample was composed of $\beta\text{-Mo}_2\text{C}$ and Co metal with a crystallite size of 30 nm and 14 nm, respectively.

B. Catalytic tests for CO_2 hydrogenation

In a previous studies, we found that plain $\beta\text{-Mo}_2\text{C}$ was very active as a catalyst for the hydrogenation of CO_2 .^{10,14} It displayed a catalytic activity better than that of unsupported Cu and Cu/ZnO catalysts.¹⁴ At temperatures between 200 and 300°C , the hydrogenation of CO_2 on $\beta\text{-Mo}_2\text{C}$ yielded CO, methane and methanol as the main reaction products, with some other oxygenates and alkanes (see Table 1). The activity and selectivity of the $\beta\text{-Mo}_2\text{C}$ catalyst were strongly sensitive to the reaction temperature. An increase in temperature from 200 to 300°C made the catalyst four times more active and favored the formation of methane, substantially reducing the generation of CO and methanol.¹⁰

Table 1 summarizes the product distribution for the hydrogenation of CO₂ on Cu/Mo₂C, Ni/Mo₂C and Co/Mo₂C catalysts at temperatures between 200 and 300 °C. Under the H₂-rich conditions used in our experiments (reaction mixture of Ar/CO₂/H₂ with a proportion of 10 % / 15 % / 75%), we did not observe deactivation of the catalysts after 5 hours of reaction. The addition of Cu to Mo₂C produced a small decrease in the total conversion of CO₂ but the Cu/Mo₂C system was still more active than a Cu/ZnO test catalyst. On the other hand, the total conversion increases when Ni and Co are present on the surface. For the total conversion of CO₂, one has the following trend in activity: Cu/Mo₂C < Mo₂C < Ni/Mo₂C < Co/Mo₂C. As it will be shown below, this trend matches well the relative reactivities towards CO₂ of Mo₂C and the supported metals. In test studies, we found that our metal/Mo₂C catalysts were 3-5 times more active than metal/Al₂O₃ catalysts with similar metal loadings. The enhancement in catalytic activity is probably a consequence of the intrinsic ability of Mo₂C to bind and hydrogenate the CO₂ molecule.¹⁴

The distribution of products was very sensitive to the intrinsic nature of the admetals present on β-Mo₂C surface. In fact, the effect of the admetal did overcome the effect of temperature on the product distribution of β-Mo₂C. Figure 4 shows how the production of CO through the reverse water-gas shift reaction (CO₂ + H₂ → CO + H₂O) changes when going from pure β-Mo₂C to the metal/β-Mo₂C systems. The best catalyst for the production of CO is Cu/Mo₂C at 200 or 300 °C. The selectivity towards the production of CO increases following the sequence: Co/Mo₂C < Ni/Mo₂C < β-Mo₂C < Cu/Mo₂C. The deposition of Ni and Co on β-Mo₂C enhances the conversion of CO₂ and there is a clear tendency towards the cleavage of both C-O bonds in the molecule, especially at 300 °C. The lowest conversion of CO₂ in Table 1 is seen on

Cu/Mo₂C but the drop in chemical reactivity can be useful to prevent the cleavage of both C-O bonds in the reactant molecule.

Figure 5 compares the selectivity for the production of methanol on pure β -Mo₂C and on the metal/ β -Mo₂C carbides. The trends are similar to those found in Figure 4 for the generation of CO. Since Cu/Mo₂C is only efficient for the cleavage of one C-O bond in CO₂, it becomes automatically the best catalyst for the production of methanol. The amount of methanol produced on the Co/Mo₂C and Ni/Mo₂C catalysts is very small, even smaller than in pure β -Mo₂C. A relatively easy decomposition of the CO molecule on Co/Mo₂C and Ni/Mo₂C makes very difficult a CO $\rightarrow$ CH₃OH hydrogenation on these surfaces.

As shown in Figure 5, Ni/Mo₂C and Co/Mo₂C are the best catalysts for the production of methane and higher alkanes, respectively. The two main products over Ni/Mo₂C are methane and CO and it appears as a very good catalyst for CO₂ hydrogenation. Co/Mo₂C is the most active catalyst in Table 1, but is not very selective in the type of products that it yields and in addition to methane there are substantial amounts of ethane and propane. In any event, it is clear that by choosing the admetal properly one can tune the selectivity of the catalyst for the production of methanol, methane or higher hydrocarbons.

Discussion

A. Oxide $\rightarrow$ carbide transformations

Figure 7 shows the evolution of phases versus onset transition temperatures for the three mixed-metal oxides studied. In all cases, the final products of the carburization β -Mo₂C and a

metal phase (Cu, Ni, or Co), but the intermediates and transition sequences changed with the different metals, and it was apparently related to the reduction potential of the Cu^{2+} , Ni^{2+} and Co^{2+} cations in each molybdate. Reduction of the metal cations led to the destruction of the molybdate structure to form a mixture of metal and metal oxide. Cu^{2+} was reduced to a metallic state at a temperature as low as 240 °C, and grew in crystallinity right after reduced. Ni^{2+} was reduced to Ni at 350 °C, but the size of Ni remained very small (4 nm) until the formation of $\beta\text{-Mo}_2\text{C}$ at 740 °C (Figure 1). The interaction between Ni and MoO_xH_y and $\alpha\text{-MoC}_{1-x}$ may inhibit the growth of Ni particle size at earlier stages like Cu. As for Co^{2+} , it is the only one that stayed at an oxidized state after the molybdate decomposed at 490 °C, the highest decomposition temperature of all the three studied molybdates. The CoO was further reduced to Co metal at 720 °C along with the formation of $\alpha\text{-MoC}_{1-x}$ phase. In a previous work,³¹ it was found that both $\beta\text{-CoMoO}_4$ and $\text{CoMoO}_4 \cdot x\text{H}_2\text{O}$ became reduced in hydrogen through a mixture of lower molybdates ($\text{Co}_2\text{Mo}_3\text{O}_8$ plus Co_2MoO_4) which could be transient species in the carburization process.

Carburization of Mo is affected by the transition metal species. MoO_3 without other metals carburized at the same condition (10% CH_4 in H_2) undergoes this path: $\text{MoO}_3 \rightarrow \text{Mo}_4\text{O}_{11} \rightarrow \text{MoO}_2 \rightarrow \beta\text{-Mo}_2\text{C}$.¹⁰ MoO_xH_y can only be formed under isothermal treatment at around 350 to 400 °C.^{10,33,34} However, when carburized as Ni or Cu molybdate, MoO_xH_y is the favored reaction intermediate. A second difference is that MoO_xH_y is initially carburized to $\alpha\text{-MoC}_{1-x}$ when Ni is present; without Ni, to obtain $\alpha\text{-MoC}_{1-x}$ one needs higher carbon concentration or heavier hydrocarbon species in the reduction gas.^{10,35} Nonetheless, $\beta\text{-Mo}_2\text{C}$ is thermodynamically more stable than $\alpha\text{-MoC}_{1-x}$ and a transition to $\beta\text{-Mo}_2\text{C}$ is seen as temperature goes beyond 740 °C. The transformation of the Mo species in Co molybdate is different from the other two in that MoO_xH_y

did not form as the intermediate Mo oxide phase. Though not identified, the intermediate (Co-)Mo species was carburized to α -MoC_{1-x} then β -Mo₂C like seen in the Ni molybdate carburization series.

An important result of the approach used for the carburization of the metal mixed-metal oxides is that it leads to systems in which the second metal (Cu, Ni or Co) remains in a metallic state on top of the β -Mo₂C substrate. This is the desired product if one is interested in the generation of catalysts for CO₂ hydrogenation.^{17,21} On the other hand, there are methods reported for the generation of bimetallic carbides through the carburization of sulfate precursors which contained the Ni-Mo and Co-Mo pairs.¹⁵ XRD showed the formation of Ni₆Mo₆C₂ and Co₆Mo₆C₂ phases which were active as hydrodesulfurization catalysts.¹⁵ Interestingly, when nitrate precursors which contained Ni-Mo and Co-Mo were carburized, the products of the process were metallic Ni and Co on top of β -Mo₂C,¹⁵ as seen in the present study for the carburization of NiMoO₄ and CoMoO₄. A CoMo bimetallic carbide has been observed by XRD during the carburization CoMoO₄ dispersed on activated carbon but it was not a single phase and transformed into Co and β -Mo₂C at temperatures above 700 °C.³⁶ Thus, different precursors (sulfates, nitrates, oxides) probably lead to different intermediate species that can make possible or impossible the formation of bimetallic carbides which have limited thermochemical stability.

B. Catalytic activity and selectivity

On β -Mo₂C, carbon dioxide undergoes sequential decomposition

The results of density-functional calculations for the adsorption of CO₂ on a β -Mo₂C(001) surface show that the cleavage of the first C-O bond of the CO₂ molecule, reaction (1), occurs spontaneously to yield CO and O on the surface.¹⁴ On the other hand, the cleavage of the second C-O bond, reaction (2), is an activated process,^{14,37} which only can occur at very high temperatures. Thus, at 300 °C, a sequential CO₂ $\rightarrow$ CO $\rightarrow$ C $\rightarrow$ CH₄ transformation is the most important reaction pathway for the hydrogenation of CO₂ on a β -Mo₂C catalyst.^{15,25}

Commercially, methanol is synthesized from syngas (CO–CO₂–H₂) over a Cu–ZnO/Al₂O₃ catalyst at 220–300 °C and 5–10 MPa.³⁸ It has been shown that CO₂ is the predominant carbon source for methanol under industrial conditions by means of isotope labeling experiments.³⁹ Fundamental studies of the hydrogenation of CO₂ on Cu(111), Cu(100) and Cu(110)^{40–43} have been reported in the literature. CO₂ interacts weakly with copper surfaces,^{44,45} exhibiting a desorption temperature of -170 °C.⁴⁶ In general, extended surfaces of copper exhibit a low activity for CO₂ hydrogenation producing mainly CO with methanol as a minority product.^{40–43} The deposition of Cu on TiC(001) induces a drastic increase in the reactivity of Cu towards CO₂.¹⁷ Cu/TiC(001) binds CO₂ strongly in a η^3 -C,O,O configuration and is a better catalyst for a CO₂ $\rightarrow$ CH₃OH transformation than a Cu/ZnO(000 $\bar{1}$) surface.¹⁷ The deposition of Cu on β -Mo₂C may also enhance the reactivity of the admetal.²³ In Table 1, there is a small drop in reactivity when going from Mo₂C to Cu/Mo₂C, but the selectivity towards the production of methanol improves substantially. The supported Cu particles probably block sites of the carbide surface which are highly active for the full dissociation of CO₂ and catalyze a CO₂ $\rightarrow$ CH₄ transformation.

Well-defined surfaces of nickel^{46–48} and Ni-based catalysts⁴⁹ are active for the hydrogenation of CO₂ producing methane instead of methanol as a dominant product. On Ni, the

CO₂ hydrogenation barrier is much smaller than on common Cu metal-based catalysts.⁴⁷ Upon adsorption of CO₂ at ~ 90 K on Ni(110), the molecule weakly chemisorbs and undergoes a geometrical distortion, bending into a nonlinear geometry.⁵⁰ This geometrical distortion is triggered by electron transfer from the substrate to the molecule and the formation of an anionic CO₂⁻ molecule.⁵⁰ The CO₂⁻ anion-molecule reacts with adsorbed H atoms to form formate,⁵⁰ a species that undergoes chemical transformations to yield methyl, methoxy and methane moieties.⁴⁷ On top of β -Mo₂C, Ni is essentially a CO₂ methanation catalyst. The main product is methane with CO as the second species produced, specially a 300 °C. In Ni/Mo₂C, the admetal and substrate are efficient for the full dissociation of CO₂ and the hydrogenation of C to CH₄ but neither of them is very active in the generation of C-C bonds. Thus, Ni $\leftrightarrow$ Mo₂C interactions may enhance the chemical activity of Ni towards CO₂ without increasing the ability of the metal to catalyze C-C bond formation.

Cobalt is an active catalyst for the hydrogenation of CO₂⁵¹ and the Fischer-Tropsch synthesis.⁵² In Table 3, Co/Mo₂C is the catalyst that produces the smallest amount of CO and methanol and the largest amount of alkane molecules. In fact, when going from β -Mo₂C to Co/Mo₂C, the amount of CH₄ produced drops while the production of C₂H₆ increases substantially. Among the three admetals investigated, Co is the only one that has the ability for catalyzing C-C bond formation. Thus, Cu, Ni and Co exhibit very different catalytic properties when supported on β -Mo₂C. The results of or catalytic studies indicate that one can tune the catalytic performance of a β -Mo₂C catalyst for CO₂ hydrogenation by adding the proper type of admetal.

Conclusions

A new approach has been tested for the preparation of metal/Mo₂C catalysts using mixed-metal oxides as precursors. *In situ* XRD methods were used to study the reduction and carburization processes of Cu₃(MoO₄)₂(OH)₂, α-NiMoO₄ and CoMoO₄•nH₂O by thermal treatment under mixtures of hydrogen and methane. In all cases, the final product was β-Mo₂C and a metal phase (Cu, Ni, Co), but the transition sequence vary with the different metals, and it could be related to the reduction potential of the Cu²⁺, Ni²⁺ and Co²⁺ cations inside each molybdate. Cu²⁺ was reduced to metallic form at a temperature as low as 240 °C. Ni²⁺ was transformed into Ni at 350 °C. As for Co²⁺, it stayed in an oxidized state up to 720 °C. At temperatures between 620 and 720 °C, MoO_xH_y species transformed into molybdenum carbides with β-Mo₂C present at the end of the carburization process.

The synthesized Cu/Mo₂C, Ni/Mo₂C and Co/Mo₂C catalysts are highly active for the hydrogenation of CO₂. Their activity for the conversion of CO₂ increases following the sequence: Cu/Mo₂C < β-Mo₂C < Ni/Mo₂C < Co/Mo₂C. The metal/Mo₂C systems exhibit large variations in the selectivity towards methanol, methane and C_nH_{2n+2} (n > 2) hydrocarbons depending on the nature of the supported metal. Although Cu/Mo₂C exhibits a somewhat lower activity than β-Mo₂C for CO₂ activation, it does have a high selectivity for CO and methanol production. On the other hand, Ni/Mo₂C and Co/Mo₂C are more active for the activation and full decomposition of CO₂ than β-Mo₂C, displaying high selectivity for the production of methane (Ni case) and C_nH_{2n+2} (n > 2) hydrocarbons (Co case).

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Table 1. CO₂ Hydrogenation over β -Mo₂C and M/ β -Mo₂C (M= Cu, Ni, Co) catalysts ^a

Catalyst	Temp. (°C)	CO ₂	Selectivity (%)							
		conv(%)	CO	CH ₃ OH	C ₂ H ₅ OH	CH ₃ OCH ₃	CH ₄	C ₂ H ₆	C ₃ H ₈	Others
β -Mo ₂ C	200	6	39	21	1	2	29	5	2	1
	250	17	34	12	0	1	37	9	4	3
	300	24	28	4	0	0	45	13	9	1
Cu/Mo ₂ C	200	4	44	34	1	1	16	1	1	2
	250	13	40	21	1	2	28	4	2	2
	300	19	38	17	0	1	32	6	4	2
Ni/Mo ₂ C	200	8	37	11	0	0	42	8	1	1
	250	21	29	6	0	0	48	11	2	1
	300	29	22	2	0	0	64	10	1	1
Co/Mo ₂ C	200	9	31	9	1	0	28	18	9	4
	250	23	24	5	1	0	32	23	11	4
	300	31	19	1	0	0	37	26	12	5

^a Pressure = 2 MPa; flow rate = 30 ml/min; reaction mixture of Ar/CO₂/H₂ = 10 % / 15 % / 75%.

Figure Captions

Figure 1 Top: Time-resolved XRD patterns for the carburization of NiMoO₄. Bottom: XRD profiles at different stages of the carburization process. Temperature XRD series of Ni molybdate carburization

Figure 2 Top: Time-resolved XRD patterns for the carburization of copper molybdate. Bottom: XRD profiles at different stages of the carburization process XRD profiles at different stages of carburization of Ni molybdate

Figure 3 Top: Time-resolved XRD patterns for the carburization of cobalt molybdate. Bottom: XRD profiles at different stages of the carburization process Temperature XRD series of Cu molybdate carburization

Figure 4 Selectivity for the generation of CO from CO₂ hydrogenation on β -MoC_y, Cu/ β -MoC_y, Ni/ β -MoC_y and Co/ β -MoC_y {Pressure = 2 MPa; flow rate = 30 ml/min; reaction mixture of Ar/CO₂/H₂ = 10 % / 15 % / 75%}.

Figure 5 Selectivity for the generation of methanol from CO₂ hydrogenation on β -MoC_y, Cu/ β -MoC_y, Ni/ β -MoC_y and Co/ β -MoC_y {Pressure = 2 MPa; flow rate = 30 ml/min; reaction mixture of Ar/CO₂/H₂ = 10 % / 15 % / 75%}.

Figure 6 Selectivity for the generation of alkanes from CO₂ hydrogenation on β -MoC_y, Cu/ β -MoC_y, Ni/ β -MoC_y and Co/ β -MoC_y {T= 300 °C; Pressure = 2 MPa; flow rate = 30 ml/min; reaction mixture of Ar/CO₂/H₂ = 10 % / 15 % / 75%}.

Figure 7 Phase evolution diagram for Ni, Cu and Co molybdate carburization

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Fig 1

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