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TiO₂-supported molybdenum carbide: an active catalyst for the aqueous phase hydrogenation of succinic acid

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HIGHLIGHTS

- Small crystallites (< 5nm) of cubic MoC on TiO₂ were obtained by temperatureprogrammed carburization using 20%v/v C₂H₆/H₂ at 700°C
- Full succinic acid conversion is reached after 22h at 240°C and 150 bar $H_{\rm 2}$ in water
- The preparation conditions affect the catalytic performance
- Higher carbon content favors the formation of butyric acid over γ-butyrolactone
- Recovering the catalyst under inert atmosphere limits the deactivation

ABSTRACT

TiO₂-supported Mo carbides "MoC/TiO₂" were prepared by impregnation of Mo salt followed by temperature programmed reduction-carburization using 20% v/v C₂H₆/H₂. Catalysts were characterized by XRD, XPS, TEM, STEM, ICP, Raman, BET, and carbon elemental analysis. The catalytic activity was evaluated for aqueous phase hydrogenation of succinic acid at 160-240 °C, and 90-150 bar of H₂ in batch reactor. MoC/TiO₂ is active for this reaction. The main products after 24 hours are γ -butyrolactone, and more remarkably butyric acid. These intermediates are then converted to tetrahydrofuran, butanol, 1,4-butanediol and butane. The reaction conditions (temperature, pressure) do not impact the products distribution. A larger amount of butyric acid is formed when catalysts were synthesized with a higher gas hourly space velocity. The deactivation observed while recycling the catalyst was mainly attributed

to a decrease in the amounts of carbidic molybdenum and carbidic carbon, as demonstrated by XPS analysis.

Keywords: Succinic acid, butyric acid, hydrogenation, aqueous phase, Mo carbide, TiO₂ supported catalyst.

1. Introduction

The worldwide environmental concerns about the sustainable production of fuels and chemicals, combined with the diminishing fossil resources, urged the development of environmentally friendly processes for the production of valuable chemicals based on renewable raw materials. The fermentation of lignocellulosic biomass using bacteria (e.g. Anaerobiospirillum succiniciproducens) produces succinic acid "SA" [1–3]. The catalytic hydrogenation of the fossil-based maleic anhydride used to be the conventional route in industries for SA production. However the cost of production of bio-based SA at the present time is lower than that of the petrochemical one when the oil price is above \$30 per barrel [4]. Currently, bio-SA is produced commercially by several companies including Myriant, Reverdia, Succinity, and BioAmber. It has been estimated that the global SA market would steadily grow at a compound annual growth rate around 27% and reach 768 million tons at \$2.3/kg in 2025 [3].

SA can be hydrogenated to valuable products including γ -butyrolactone (GBL), 1,4butanediol (BDO) and tetrahydrofuran (THF) [5–8]. These chemicals are mainly employed as solvents (e.g. THF), food additives, intermediates for polymer synthesis (e.g. BDO and THF) and pharmaceuticals (e.g. GBL) [2,9,10]. Water is preferably chosen as solvent for this reaction since after fermentation, SA is obtained in aqueous phase. It is then necessary for the catalysts to be stable under the severe hydrothermal conditions (T \geq 160 °C, P \geq 80 bar, water) that are required for this reaction. Noble metal supported catalysts have principally been studied for the hydrogenation of SA in aqueous phase [5–8]. The selectivity to the products varies according to the catalyst used and the reaction conditions. The main limitations to the use of noble-metal catalysts are their scarcity and high prices. For an economically viable

valorisation of biomass derivatives, it would be interesting to replace group VIII (8 to 10) metals.

A review of the literature dealing with the formulation of catalysts for heterogeneous processes revealed the development and use of transition metal carbides "TMCs" [11–13]. TMCs display catalytic activity approaching those of group VIII metals, but with unique catalytic pathways and different products selectivity [13]. Experimental and theoretical examinations of these materials in literature confirm that the introduction of carbon into the lattice of the early transition metals results in an expansion of the lattice parameter. Density functional theory (DFT) calculations have shown that the hybridization between metal d-orbitals and the carbon s- and p-orbitals causes a broadening of the d-band structure, providing characteristics approaching the d-band of Pt [14].

Among TMCs, molybdenum and tungsten carbides are known to be active in hydrodesulfurization (HDS), hydro-denitrogenation (HDN), water–gas shift, isomerization, and Fischer Tropsch reactions [15–18]. Recently, they have emerged as efficient hydrodeoxygenation (HDO) catalyst for the selective deoxygenation of biomass-derived oxygenates such as vegetable oils, phenolic compounds (e.g. guaiacol, m-cresol) and furanic compounds (e.g. furfural, HMF) [12,19–21]. They are often employed for gas phase reactions or in organic solvent, and their use for the aqueous conversion of biomass derivatives to chemicals is limited. However, Teixeira da Silva et al., investigated molybdenum carbide supported on activated carbon for the aqueous hydrogenation of levulinic acid. The catalyst exhibited high conversion (~99%), with selectivity towards γ -valerolactone above 85% at 200 °C and 30 bar in aqueous phase [22].

The challenging aspect for the preparation of TMCs, is controlling their crystallographic structure and morphology. Molybdenum carbide systems consist of different phases, most of which have two compositions, MoC and Mo₂C, which may co-exist [23]. The main crystallographic phases observed are the hexagonal, cubic, and orthorhombic molybdenum carbide phases [24]. The composition can directly affect the performance of the catalyst. For example a study of CO_2 hydrogenation reaction using molybdenum carbide showed that hexagonal close packed structure is more active than the face centered cubic system. Moreover, the former one showed higher selectivity to methane while the latter one showed higher selectivity to methanol [25]. These materials are usually prepared by a temperature programmed reduction-carburization method. The metal oxide powder is placed under a reductive-carburizing gas flow, while raising the temperature slowly in a uniform heating ramp until reaching the maximum temperature needed [26]. This temperature-programmed

carburization process is sensitive to many parameters that make the choice of the preparation conditions critical. The carbon sources, composition of the mixture (i.e. % v/v HC/H₂), heating rate, maximum carburization temperature, and holding time have direct influence on the structure and physicochemical properties of the final material [26–31]. For example, the nature of carbon source and its concentration along with the maximum temperature affect the crystallographic structure, the carbon content of the material, and its crystallite size. On the other hand, the heating rate and holding time affect the surface area and morphology of the metal carbide formed.

The use of a support in the preparation of the catalyst can increase the exposed surfaces that lead to a global increase of the activity. Highly dispersed molybdenum carbide supported on varied supports such as Al_2O_3 [32], ZrO_2 [33], and carbon nanotubes [22,34] may be prepared by depositing a precursor on a high surface area support, followed by carburization. TiO₂ has previously been used as a support due to its stability under hydrothermal conditions for the aqueous phase hydrogenation of SA [6].

In this paper, we report the preparation of TiO₂-supported molybdenum carbide catalysts via impregnation followed by temperature-programmed reaction using 20% v/v C₂H₆/H₂. These catalysts were studied for the aqueous phase hydrogenation of succinic acid. The effect of the preparation conditions of the catalyst, i.e. Gas Hourly Space Velocity (GHSV) and passivation, on its properties and its catalytic performance in terms of activity, and products selectivity was investigated. The stability of the catalyst was also studied under harsh reaction conditions (240 °C, 150 bar H₂, in water).

2. Experimental section

2.1. Preparation of catalysts

Commercial TiO₂ P25 (specific surface area 55 m².g⁻¹, supplied by Degussa-Evonik) was used as the support. MoC/TiO₂ catalysts were prepared by impregnation followed by temperature programmed reduction carburization. To prepare 12% w/w MoC/TiO₂, 1.2 g of ammonium molybdate tetrahydrate (NH₄)₆Mo₇O₂₄.4H₂O (Aldrich Chemical Co, 99.98% trace metals basis) was mixed with 5 g of TiO₂ and 60 mL of water and stirred for 2 h at room temperature. Water was evaporated under vacuum and the solid was dried in an oven at 80 °C overnight. For the second step, the powder was placed in a quartz cell under a reductive-carburizing gas stream (20% v/v C₂H₆/H₂, 60-140 mL.min⁻¹). GHSV was calculated based on gas flow rate (mL.h⁻¹) divided by the volume of catalyst bed (1.1-5.5 mL). GHSV was varied

in the range of 1527-7636 h⁻¹. The temperature was raised at 0.5 °C.min⁻¹ until 700 °C, held for 2 h, and then cooled down to room temperature under argon. The non-passivated (NP) samples were transferred to a glovebox and kept under nitrogen. The other samples were passivated for 4 h under 1% v/v O_2/N_2 mixture, and then kept in a vial, in N₂ atmosphere. For comparison, a MoO₃/TiO₂ solid was prepared by impregnation, followed by calcination under air at 0.5 °C min⁻¹ till 600 °C, held for 2 h, then cooled down to room temperature.

2.2. Characterization of catalysts

The Mo content of the catalysts was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) by using an ACTIVA instrument (HORIBA Jobin Yvon). Before analysis, the samples were mineralized by fusion with lithium tetraborate in Pt-Au crucibles at 1100 °C, and then soaked with 20% HCl.

Carbon elemental analyses were conducted via a LECO micro-analyzer SC144. The total combustion of the samples was done at 1050 °C under a stream of helium/oxygen and under pressure. The carbon was converted to carbon dioxide and quantified by a thermal conductivity detector.

Oxygen analysis was done with a EMGA 620 W analyzer (HORIBA Jobin Yvon). The system uses fusion in a helium pulse furnace to extract oxygen. The sample falls into a graphite crucible heated to a high temperature between 2500 °C and 2800 °C. Oxygen which is converted into carbon monoxide by combining with the carbon of the crucible, is measured by a non-dispersive infrared cell, then oxidized to CO_2 and trapped.

BET surface areas (S) of the samples were determined from the N_2 physisorption at -196 °C using an ASAP 2020 Micromeritics apparatus. Before the measurements, the catalysts were desorbed at 150 °C for 3 h under ultra-high vacuum (10⁻⁴ mbar).

Powder XRD patterns of the catalysts were recorded in the range $2\theta = 20-80^{\circ}$ at $0.04^{\circ}.s^{-1}$ using a Bruker D8A25 X-ray diffractometer and a CuK_a radiation source (λ =1.54184 Å). Phase identification, lattice parameters, and mean crystallite sizes (d = 4/3 * LVol-IB; with LVol-IB the volume averaged column height) were obtained by performing Rietveld refinement using the Topas 5 software.

TEM and STEM images were obtained using Environmental Transmission Electron Microscope: FTI TITAN ETEM instrument operated at 80-300 kV, equipped with a X-MAX SDD EDX detector from Oxford-Instrument and a Tridiem ERs GIF from Gatan. Samples

were prepared by dispersing the solid in ethanol and then depositing them onto carbon-coated grids.

The surface chemical composition and oxidation states of Mo in catalyst samples were analyzed by XPS with monochromatized AlK_{α} source (hv = 1486.6 eV) using a commercial instrument (AXIS Ultra DLD KRATOS). The binding energies (± 0.5 eV) were referred to the C1s line set at BE = 284.6 eV. Peaks decompositions, fittings and quantitative determinations were performed using the Casa XPS and Igor Pro software. The non-passivated samples were transferred after synthesis to a glovebox for preparation and then to the XPS chamber. There was no contact with oxygen as the samples stayed under inert gas (Ar or N₂).

Raman spectra were recorded at room temperature using a LabRam HR (Jobin Yvon– Horiba) spectrometer equipped with a CCD detector cooled at -76 °C. Measurements were carried out under microscope with a 50x objective that focuses the laser beam on the sample surface and collects the scattered light. The exciting line at 514.53 nm of a Ar⁺ laser was used with a power limited at 100 microW. It was previously checked that the samples laser heating was negligible with such power. A 300 grooves/mm grating was used to disperse light leading to band position accuracy within 4 cm⁻¹.

2.3. Catalytic testing

SA with purity above 99% was purchased from Aldrich. The aqueous catalytic hydrogenation experiments were performed using a 300 mL high-pressure batch (Parr 4560) Hastelloy autoclave, equipped with a magnetically driven impeller and a liquid sampling system. The reaction temperature is monitored by a thermocouple probe which sites inside a thermowell, in the reactor. A 100 mL aqueous solution of SA (0.12-0.14 M; pH = 2.3) and 0.6 g of the catalyst were loaded into the reactor. After sealing, the autoclave was purged three times with Ar, heated up to the desired reaction temperature (160-240 °C), pressurized with H₂ (90-150 bar) and stirred at 900 rpm. The reactions were conducted for 22-32 hours and samples were collected periodically every 2 hours during the day in order to follow the evolution of the reaction.

Analyses of the reaction products in the liquid samples were performed using a GC Agilent Technologies 6890N with a flame ionization detector employing a VF-WAXms column (30 m \times 0.25 mm \times 0.25 µm). The temperature was increased up 190 °C, under helium as a carrier gas. The concentration of SA was monitored using a Shimadzu LC 20A HPLC connected to UV and RI detectors. The separation was achieved using ICSep Coregel 107H column (7.8 \times

300 mm) heated at 40 °C. A solution of H₂SO₄ (0.001 mol L⁻¹) in ultra-pure ELGA water was used as the mobile phase at a flow rate of 0.5 mL min⁻¹. After some reactions, the gases were collected in a gas-bag and analyzed using a micro-GC SRA with MS Agilent 5975 detector. Three columns were set up: Alumina (10 m × 3 µm) at 90 °C for C₃–C₄ hydrocarbons, Poraplot U (8 m × 30 µm) for C₂–C₃ compounds and CO₂, and MolSieve 5A (10 m × 12 µm) for H₂, CO, and CH₄.

SA concentration (%) and conversion (%) are based on initial concentration of SA ([SA]₀) and defined by,

 $SA \ concentration \ (\%) = \frac{[SA]_t}{[SA]_0} \times 100 \quad \text{and} \quad SA \ conversion \ (\%) = \frac{[SA]_0 - [SA]_t}{[SA]_0} \times 100 \quad (1)$ where $[SA]_t$ refers to the concentration of SA at time *t*.

Selectivity and yield of a product *i* are given by,

Selectivity $(\%) = \frac{[P_i]_t}{[SA]_0 - [SA]_t} \times 100$ and Product yield $(\%) = \frac{[P_i]_t}{[SA]_0} \times 100$ (2)

where $[P_i]_t$ refers to the concentration of the product *i* at time *t*.

The carbon balance (CB) is given by,

$$CB (\%) = \frac{4*[SA]_t + \sum_i n_i * [P_i]_t}{4*[SA]_0} \times 100$$
(3)

where n_i refers to the number of carbon of the product *i*.

The initial reaction rate was calculated based on the slope of the linear curve (up to 6-8h), at low conversion (< 40%),

$$V_0(\text{mmol}_{\text{Substrate}} \ g_{\text{Mo}}^{-1} \ h^{-1}) = \frac{\text{mmole of reactant}}{\text{mass of Moxtime}}$$
(4)

The total organic carbon (TOC) in solution was measured by using a Shimadzu TOC-VCSH analyzer and use to check the carbon balance in the liquid phase and the possible formation of gaseous products. The samples were diluted by a factor of 70 before TOC analysis.

Repeated reactions delivered conversion and products yield reproducible within \pm 3%. Therefore the selectivity is given with an error of \pm 3% and the reaction rate with an uncertainty of 1 .0 mmol_{SA} g_{Mo}^{-1} h⁻¹. Carbon balance and TOC values are given with a precision of 8%.

3. Results and discussion

3.1. Preparation and characterization of the catalysts

The supported molybdenum carbide catalysts were prepared by impregnation of ammonium heptamolybdate tetrahydrate on TiO₂ at room temperature. The impregnation occurs at pH = 5.3 which is slightly lower than the PZC of TiO₂ P25 (pH_{PZC} = 6.3) [35]. The predominant species in solution at that pH should be Mo₇O₂₄⁶⁻ [36,37]. The support must bear a slight positive charge which should favor the interaction with the anionic species. Water was removed by rotary evaporator in order to insure the total deposition of Mo, which was confirmed by ICP-OES analysis of the final materials (~12 wt.% Mo, Table 1).

Table 1. GHSV employed during the catalysts synthesis	. Mo and C content (% wt.), surface area (S), and
mean crystallite size of MoC, anatase TiO ₂ , and rutile TiO	2.

Catalysts	Synthesis	Characterization			Synthesis Characterizatio					
							Crystallit	te size ^e (nm)	
	GHSV ^a (h ⁻¹)	% Mo ^b	% C ^c	$S^d(m^2.g^{-1})$	Cubic MoC	Anatase TiO ₂	Rutile TiO ₂			
MoC-I/TiO ₂	1527	11.8	2.2	45	4	50	45			
MoC-II/TiO ₂	2545	12.0	3.7	47	4	45	25			
MoC-III/TiO ₂	7636	11.9	5.3	46	4	50	11			

^a GHSV of 20% v/v C₂H₆/H₂ during the reduction-carburization process

^b ICP analysis

^{*c*} Carbon elemental analysis

^d BET surface area

^e Rietveld refinement

The powder obtained after impregnation and drying was then placed under a reductivecarburizing gas stream (20% v/v C_2H_6/H_2) while raising the temperature up to 700 °C. The effect of GHSV has been widely studied for bulk molybdenum nitride [38]. It has been demonstrated that a decrease in space velocity during the reaction causes a loss of surface area. The use of high space velocities would facilitate the removal of H₂O from the vicinity of the solid surface, thus reducing the potential for hydrothermal sintering [38,39]. However we could not find any report on the effect of GHSV on the synthesis of supported molybdenum carbide. In the case of TMCs, the GHSV factor might also affect the carbon content of the catalyst. A series of TiO₂-supported molybdenum carbides, catalysts were synthesized by changing the GHSV (1527 h⁻¹, 2545 h⁻¹, and 7636 h⁻¹) and were denoted MoC-I/TiO₂, MoC-II/TiO₂, and MoC-III/TiO₂, respectively (Table 1). The three catalysts exhibit similar BET surface area of 45-47 m².g⁻¹, slightly lower than the support TiO₂ (Table 1).



Figure 1. XRD diffraction patterns of the support P25 TiO₂ P25 and the catalysts: a) MoC-I/TiO₂, b) MoC-II/TiO₂, c) MoC-III/TiO₂. Note: peaks associated with \bullet Anatase, \circ Rutile, * Cubic MoC phase.

Rietveld refinement allowed us to conduct a quantitative identification of the different crystalline phases present in the catalysts. Concerning the support, the main peaks corresponding to TiO_2 anatase and rutile phases were observed (Figure 1). For the three catalysts, the composition anatase/rutile was the same as for the support P25 (75%/25%). Anatase is known to convert to rutile at temperature between 600 and 700 °C [40]. However in the presence of a dopant, such as metal oxide, this temperature is increased [41]. Therefore the presence of the Mo species at the surface might stabilize the anatase phase during the gas treatment at high temperature (700 °C). The lattice parameters of the anatase and rutile phases are similar in the three samples (Table A.1 in appendices). It is however worth noting that the mean crystallite size of the minor rutile phase decreased from ca. 45 nm (bare support and MoC-I/TiO₂) to 11 nm (MoC-III/TiO₂) when increasing the GHSV during the preparation (Table 1), while the anatase phase was not affected.

Regarding the Mo crystalline carbides, the main peaks attributed to cubic Mo carbide phase at $2\theta = 36.4^{\circ}$, 42.2° and 61.3° were detected for all the catalysts. They can be associated with the planes (111), (002), and (022), respectively. The peaks were broad and overlapped with the ones from the supports, which might alter the analysis. Rietveld refinement confirmed the presence of the cubic Mo carbide phase (> 10 %) with crystallite size below 5 nm (Table 1). The presence of molybdenum oxides, such as MoO₂ or MoO₃, was not detected, which suggests full carburization.

The reports in the literature on the effects of carburizing agent on the structure of bulk TMCs show that the type and concentration of the carbon source affect the crystallographic structure [27,28,31]. When increasing the chain length of the carburizing agent, lower temperatures are required for the complete transformation from molybdenum oxide to carbide [27]. The hexagonal hcp phase is usually obtained when conducting the carburization with CH₄, while carburizing agent with longer chain, such as C₄H₁₀ and heptane, or aromatics, such as toluene, favor the formation of the cubic fcc phase [27,31,42,43]. Carburization with C₂H₆/H₂ generates a mixture of fcc and hcp phases at low concentration of carbon 10 % v/v [28], while pure cubic phase is obtained at 20 % v/v [25].

The literature dealing with molybdenum carbides supported on TiO₂ is really limited [44–46]. One study reported the formation of large crystallite (~ 25 nm) of hexagonal Mo₂C on TiO₂ using 20% v/v CH₄/H₂ at 650 °C [44]. The preparation of MoC_{1-x}/TiO₂ with 20% v/v C₃H₈/H₂ generated a mixture of particles of fcc and hcp phases with a mean crystallite size around 15 nm [45]. It is worth noting that the carburization at 700 °C in CH₄/H₂ can generate small crystallites (< 5 nm) of cubic MoC over activated carbon [34] and carbon nanotubes [47]. Therefore, we report the first synthesis of small crystallites (< 5 nm) of cubic MoC over TiO₂, by employing 20 % v/v C₂H₆/H₂ at 700 °C.



Figure 2. Representative TEM image (a, a.1), electron diffraction (a.2), and STEM image (b) of MoC-III/TiO₂.

Spot	h k l	α (°)		d (nm)	
		Exp.	Theo.*	Exp.	Theo.*
1	200	0.00	0.00	0.212	0.213
2	220	44.37	45.00	0.150	0.150
3	020	89.40	90.00	0.214	0.213
4	-220	134.49	135.00	0.153	0.150

Table 2. Lattice parameters obtained from TEM analysis.

* Theoretical values corresponding to cubic MoC

Representative TEM and STEM images of MoC-III/TiO₂ are shown in Figure 2 and Figure A.1. Small particles (< 5 nm) are dispersed on the support. Local EDX analyses and diffractogram patterns (Table 2, Table A.2) revealed that these are particles of MoC with cubic phase, which is in agreement with XRD results. An excess of graphitic carbon was clearly seen in the images (Figure 2-a). The TEM and STEM analyses of the three catalysts, MoC-I/TiO₂, MoC-II/TiO₂, and MoC-III/TiO₂, exhibited similar results, i.e. presence of cubic MoC particles and excess of carbon on the surface (Figure A.2 and Table A.3).

Carbon elemental analysis was conducted to estimate the carbon content of the catalysts. The results in Table 1 show that the samples contained between 2.2 and 5.3 wt. % of carbon while the theoretical carbon content for MoC/TiO₂ with 12 wt. % of Mo should be 1.5 %. This reflects an excess of free-carbon in the catalysts, as observed on the TEM pictures with the presence of graphitic carbon. Moreover the carbon content increased from 2.2% to 5.3% while increasing the GHSV during the preparation from 1527 to 7636 h⁻¹ (Table 1). The presence of free carbon at the surface of TMCs is well known. It is deposited on the surface during the synthesis, as ethane starts to decompose from 590 °C [28]. The temperature for complete formation of bulk molybdenum carbide is around 630 °C when using 10% v/v C₂H₆/H₂, however, supported catalysts often require more severe conditions [26,28]. The presence of Ti dopant can facilitate hydrocarbon decomposition and carburization [48]. Thus, the excess of carbon is not surprising after synthesis at 700 °C with high concentration of hydrocarbon (20% v/v C₂H₆/H₂).

Due to their pyrophoricity, TMCs are typically passivated prior to use in order to facilitate their handling. However, it has been shown that the passivation treatment can affect the catalytic results. For example, Nagai et al., have shown that passivated molybdenum carbide catalysts supported on alumina were less active for CO₂ hydrogenation reaction than the non-

passivated catalysts [49]. On the contrary, Mehdad et al. showed that after the removal of the passivation layer of molybdenum carbide, the catalyst exhibited identical performance as the non-passivated one for toluene hydrogenation [50]. Therefore, two catalysts were also synthesized without passivation treatment (NP is added to the same catalysts labelling) in order to investigate the effect of this treatment on the properties and performance of the catalyst in SA hydrogenation. Limited characterization could be performed on these two non-passivated catalysts as they cannot be exposed to air, except for XPS analysis. For the latter one the samples were transferred directly after synthesis to the XPS chamber.

	Atomic concentr	ation %	Mo species %		C species %		Ratio $C = \frac{\delta^+}{\delta^+}$	
Catalyst	Mo	С	Mo^{δ^+}	Mo ⁴⁺	Mo ⁶⁺	Carbide	Graphite	C Carbide/M0 ⁰⁺
MoC-III/TiO ₂	3.3	46.5	47	8	45	8	74	1.4
NP-MoC-III/TiO2	3.9	49.2	88	12	0	16	65	1.6
NP-MoC-I/TiO ₂	4.8	22.4	76	13	12	17	47	0.7

Table 3. XPS analysis: atomic concentration of Mo and C, and the abundance of Mo and C species.

XPS analyses were conducted on 3 catalysts in order to assess the differences resulting from the passivation (MoC-III/TiO₂ vs. NP- MoC-III/TiO₂) and from variation of the GHSV (NP- MoC-I/TiO₂ vs. NP- MoC-III/TiO₂). The Mo 3d and C 1s spectra of MoC-III/TiO₂, NP- MoC-III/TiO₂ and NP- MoC-I/TiO₂ are presented in Figure 3. The chemical states of the catalyst components and their relative abundance are compiled in Table 3.

In Figure 3-a-1, the Mo 3d spectrum of MoC-III/TiO₂ exhibits two peaks at BE = 228.7 eV and 231.9 eV which correspond to Mo $3d_{5/2}$ and Mo $3d_{3/2}$ peaks of Mo⁸⁺. The former value falls within the range 227.6 - 228.9 eV which is attributed to carbidic Mo (Mo next to carbon) in the literature [51,52]. In addition, contributions assigned to Mo⁴⁺ (BE = 230.2 eV and 233.5 eV) and Mo⁶⁺ (BE = 232.7 eV and 235.8 eV) were also observed [53,54]. The difference between the passivated and non-passivated catalysts is clearly noticeable when comparing Mo 3d spectra of MoC-III/TiO₂ and NP- MoC-III/TiO₂ in Figure 3-a-1 and Figure 3-b-1, respectively. The absence of Mo⁶⁺ for the fresh sample (non-passivated), confirms that the presence of Mo⁶⁺ in the passivated sample is due to the passivation treatment. The absence of

molybdenum bulk oxides phases (by XRD) suggest that the passivation treatment results in a thin layer of oxide on the surface. It is assumed that oxygen adsorbs on top of Mo atoms and hollow sites that are not occupied by C [50]. From the literature, it is expected to see a small amount of Mo⁴⁺, even for the non-passivated sample [51]. Oxygen elemental analyses were also conducted and no difference was observed for the two catalysts. However the fact that the support is an oxide limits the efficiency of the analysis. As expected, MoC-III/TiO₂ and NP- MoC-III/TiO₂ present similar Mo and C atomic concentration knowing that the Mo theoretical atomic concentration of 12% w/w MoC/TiO2 is 3.6 (Table 3). The C atomic concentration is in excess due to the presence of graphite on the surface. The C 1s spectrum of MoC-III/TiO₂ displayed in Figure 3-a-2 exhibits a peak at BE = 283.4 eV which corresponds to the carbon in the carbidic form [52]. The broad peak at BE = 284.6 eV along with the peak at 289.5 eV refer to graphitic carbon. The additional peak at 286 eV can be attributed to carbon in C-O or C=O groups [52,55]. The ratios of carbidic carbon to Mo carbide are shown in Table 3 and are around 1.5 for the two samples. The Ti 2p spectrum of MoC-III/TiO₂ is shown in Figure A.3 as an example. The peak at BE = 459.1 eV refers to Ti⁴⁺ and no peak corresponding to Ti^{3+} (BE = 457.5 eV) was observed.

The sample NP- MoC-I/TiO₂ synthesized at lower GHSV (Figure 3-c, Table 3) presents



Figure 3. XPS spectra of catalysts a) MoC-III/TiO₂, b) NP- MoC-III/TiO₂, and c) NP- MoC-I/TiO₂ over 1) Mo 3d and 2) C 1s.

similar compositions as NP- MoC-III/TiO₂. However, the presence of a small amount of Mo^{6+} suggests that the carburization was not complete. When looking at the atomic concentration determined by XPS, it is noticeable that the carbon content on the surface of the catalyst is lower (22% vs. 49%) when decreasing the GHSV. This result is in agreement with the carbon elemental analysis. Moreover the fraction of carbon graphite is slightly lower (from 65% to 47%) in favor of carbon as carbonyl/carbonate groups. The lower Mo % surface concentration on MoC-III/TiO₂ might be related to the higher concentration of carbon in the sample. Indeed, the excess of carbon on the surface might be masking the Mo particles because only few nanometers are probed by XPS.

3.2. Catalytic results

3.2.1. Hydrogenation of succinic acid over MoC/TiO₂

The catalytic performance of MoC-II/TiO₂ catalyst was evaluated for the aqueous phase hydrogenation of succinic acid (SA) at 240 °C and 150 bar. Without catalyst, no conversion was observed (< 1%). A typical temporal evolution of the substrate and products in solution is presented in Figure 4. In the presence of the catalyst, SA was progressively converted with time and full conversion was achieved after 22 h. From the start of the reaction, parallel formation of γ -butyrolactone (GBL) and unexpectedly butyric acid (BA) were observed. After 8 h of reaction, 60% conversion was achieved with 38% yield of GBL and 26% yield of BA. Proceeding more in the reaction, the two intermediates started disappearing along with the formation of butanol (BOL), tetrahydrofuran (THF), and 1,4-butanediol (BDO). After 32 h, 22% of GBL, 6% of BA, 21% of BOL, 14% of THF, and 4% of BDO are present in solution. Traces of propionic acid were also observed, close to the detection limit (< 0.5%). The carbon balance (CB) started decreasing after 18 h and only 66% of the products were still present in



liquid phase at the end of the reaction. This was confirmed by qualitative GC-MS analysis of the gas phase where butane as well as traces of propane were detected. All the catalytic results were reproducible within 5%. The CB calculated based on GC and HPLC analysis were always very close to the TOC measured, which means that all the products in liquid phase were identified and analyzed (Figure A.4).

Figure 4. Hydrogenation of succinic acid over MoC-II/TiO₂ at 240 $^{\circ}$ C and under 150 bar H₂: temporal evolution of the concentrations of SA, the products yield and the carbon balance (CB). Aqueous solution of SA (0.12 M, 100 mL), 0.6 g of catalyst.

The selectivity to the products was distinct from the results reported in literature for SA hydrogenation over group VIII metals catalysts. For example, at 160 °C and 150 bar over Pd/TiO₂, SA is converted to GBL with 94% selectivity [6]; under the same reaction conditions, introducing Re to this catalyst favours the conversion of GBL to BDO with 83% selectivity [7]. On the other hand, using Re/C at 240 °C and under 80 bar of H₂ generates THF with 86% selectivity [8] (Scheme 1). In the literature dealing with the hydrogenation of SA, BA is usually not observed. A couple of studies reports the formation of small amounts of BA (< 3%), e.g. over Au-Pt/TiO₂ [9], Pd-ReO_x/TiO₂ [56], FeO_x/C + Pd/C [57], and Pd/SiO₂-NH₂ [58]. A combined selectivity of 18% towards propionic acid and butyric acid (at 80% conversion) was reported during the hydrogenation of SA over Pd/alumina xerogel, in dioxane ($P_{H_2} = 60$ bar, T = 240 °C) [59]. In another study over Pd/alumina, they reported that the selectivity towards the acids increased with increasing palladium dispersion on the surface [60]. BOL was observed as by-product (< 5%) in a couple of studies, e.g. over Re/C [61] and, with maleic acid as reactant, over Pd/TiO₂ and Re/TiO₂ [62]. The formation of butane has not been reported in the literature before. These reflect major differences with the selectivity obtained over carbide catalyst.



Scheme 1. Suggested reaction pathway for the aqueous phase hydrogenation of SA over MoC/TiO₂.

GBL is formed as intermediate through hydrogenation and dehydration of SA [7]. Dehydration reactions are usually favored on acid sites while hydrogenation is favored on metal sites. BDO is formed by further ring opening and hydrogenation of GBL. This might be due to the simultaneous activation of both oxygens of GBL, as it has been proposed over Re-Pd/TiO₂ [7]. THF can be formed by dehydration of BDO in the presence of acid catalysts. The direct hydrogenation of the carbonyl group of GBL is more likely in water. BOL, n-propanol, BA and propionic acid can be formed as further by-products. It was proposed that BA and propionic acid are formed from SA or GBL, while BOL and propanol are formed by hydrogenation of BDO or the monoacids [63]. BOL is usually obtained from further hydrogenolysis of BDO, favored by acid sites [64]. It can generate n-propanol by C-C bond cleavage [8], e.g. over Re [63]. In a series of publications, Liang ad co-workers [8,61,63] investigated the reaction pathway of the aqueous hydrogenation of SA over Pd/C, Re/C, Ru/C, Re-Ru/C and Pd-Re/C, at 240 °C and under 80 bar H₂. Starting from GBL, high selectivity towards THF was observed over Re/C, while a mixture of BDO and THF was obtained over Re-Ru/C. Starting from BA, 100% selectivity towards BOL was observed, over all the catalysts. The conversion of BDO generated mainly THF over Re/C, while propanol was also formed in the presence of Ru based catalyst. The conversion of THF was negligible.

Since the products selectivity observed during the hydrogenation of SA over MoC/TiO₂ is distinct from over noble metals catalysts, the reaction pathway was investigated in more detail. The hydrogenation reactions of GBL, BA, and BDO were conducted under the same reaction conditions as before. Figure 5 compares the product distributions at around 50-60% conversion and the initial rates of reaction (V₀) for the hydrogenation reactions of these intermediates and SA. The temporal evolution of these reactions are included in Figure A.5.



Figure 5. Selectivity to the products at 50-60% conversion and initial rate of reaction (V_0) for the hydrogenation reactions of SA, GBL, BA, and BDO, at 240 °C and 150 bar. Aqueous solution of reactant (0.12 M, 100 mL), 0.6 g of MoC-II/TiO₂ catalyst.

THF (31%) was the main product during the hydrogenation of GBL, in addition to BOL (28%), BA (16%) and BDO (14%). BOL and BA were formed simultaneously which suggest that BOL can be formed directly from GBL. The hydrogenation of BA generated solely BOL in liquid phase, as reported elsewhere [63]. The hydrogenation of BDO gave mainly THF (57%) in addition to BOL (10%). Lastly, THF was stable in these reaction conditions where barely 7% was converted to BDO after 30 h of reaction. The hydrogenation of the intermediates suggests that BA can be formed directly from SA as well as from GBL. Moreover gaseous products (i.e. butane) are mainly formed from BA. The rate of reaction follows the order: V_0 (SA) > V_0 (BA) > V_0 (BDO) > V_0 (GBL) >> V_0 (THF) (< 0.1 mmol_{THF} g_{Mo}⁻¹ h⁻¹). These reactions lead to the proposal of the reaction pathway shown in Scheme 1.

Molybdenum carbide catalysts are known to be active for C=O hydrodeoxygenation reaction. It was proposed that the hydrogenation steps occur over metallic sites, while the dehydration occurs over Brønsted acid sites [65]. The hydrodeoxygenation of acrylic acid to propane has been studied in gas phase over Mo₂C [32]. The experimental and theoretical results suggested that the hydrogenation/dehydration of the carboxylic acid generates

adsorbed aldehyde, which undergoes further hydrogenation/dehydration and forms propane. Therefore BA might be formed via successive hydrogenation/dehydration of SA, without desorption of the intermediate aldehyde.

In the literature, the conditions for aqueous phase hydrogenation of SA in the presence of noble metal catalysts are in the range of 80-150 bar of H₂ and 160-240 °C [5,6,8,63]. The effects of temperature and pressure were investigated over MoC-II/TiO₂. The reaction was conducted at different temperatures (160, 200, and 240 °C) and H₂ pressures (90, 110, 150 bar) for 22 h (Table 4). The initial rate of reaction (V₀) increased with temperature and pressure. According to the Arrhenius plots (Figure A.6), the apparent activation energy is 55 kJ mol⁻¹ for MoC-II/TiO₂. It is worth to mention that the effects of temperature and pressure were only limited on the activation of SA. Indeed, Figure 6 represents the selectivity towards the products in function of conversion, for all the reactions conducted over MoC-II/TiO₂. The selectivity values were similar, independently of the reaction conditions, implying that the products distribution is not affected by the change of temperature and pressure. When going from 2 to 85% of conversion, the selectivity towards BA decreased slightly (from 52 to 43%). Above 90% SA conversion, GBL and BA started to be converted and the products BOL, BDO and THF appeared. It is well known that there is a competitive adsorption of SA and GBL. Indeed, it is usually observed that GBL starts to be converted when SA has disappeared [56]. In the same manner, we observed that the conversion of BA to BOL occurred only when SA was almost fully converted. It is also worth noting that fare less gaseous products were observed when working at 90 or 110 bar of H₂. This was confirmed by the fact that the TOC measured and the carbon balance remained close to the initial value (Figure A.7). This is due to the fact that at low conversion, hardly any butanol, hence butane, were formed.

Т	Р	Vo	SA Conversion ^a	Pr	oducts yiel	ds (%) ^a			
(°C)	(bar)	(mmol _{SA} g _{M0} ⁻¹ h ⁻¹)	(%)	Gl	• GBL	• BA	. E	BOL .	THF
160	110	0.4	4 80)1	2	0	0	0	
200	110	1.6	20	12	8	0	0	0	
240	110	4.5	61 S 60) = 3	26	1	1	0	
240	90	3.4	48	24	24	1	0 •	0	
240	150	12.5	100 5 40)45	17	15	9•	2	
^a after	22 h reac	tion: aqueous solution	of SA (0.12 M 300 m	L), (0.6 g of MoC	C-II/TiO ₂	catalyst	•	
			20 <u>Sei</u> e)					
									:
			()	· · · · ·	_		••	18
				Ō	20	4	0	60	80
					(Conve	ersio	on (%)	

Table 4. Effect of temperature and pressure on initial rate (V₀), SA conversion and product yields

Figure 6. Selectivity to GBL, BA, BOL, and THF as function of SA conversion, for all reactions conducted over MoC-II/TiO₂ catalyst, at different pressure and temperature (see Table 4). Aqueous solution of SA (0.12 M, 100 mL), 0.6 g of MoC-II/TiO₂ catalyst.

3.2.2. Effect of preparation conditions of the catalyst on its performance in succinic acid conversion

The initial rate and products distribution of MoC-II/TiO₂ were then compared to those of MoC-I/TiO₂ and MoC-III/TiO₂, at 240 °C and 110 bar of H₂ and the results are included in Table 5. For these reactions the CB was always over 90%. By increasing GHSV of C₂H₆/H₂ during the carburization of the catalyst from 1527 h⁻¹ (MoC-I/TiO₂) to 7636 h⁻¹ (MoC-III/TiO₂), V₀ increased from 1.6 to 7.8 mmol_{SA} g_{Mo}^{-1} h⁻¹ and the selectivity shifted towards BA. Indeed, when comparing the selectivity at ca. 23% conversion, MoC-III/TiO₂ gave selectivity towards BA of 71% while 44 and 49% were obtained over the other two catalysts. In the catalyst characterization section it was shown that as the GHSV increases, the carbidic Mo and the free-carbon contents increase. Therefore the degree of carburization and/or the presence of free carbon must have a strong impact on activity and selectivity. A supported Mo oxide catalyst MoO₃/TiO₂ was also prepared and tested for comparison (Table 5). High selectivity to GBL was observed (95%). This shows that the carbon content has direct effect on shifting the selectivity towards BA.

Catalyst	V ₀	Time ^a	Selectivit	ty ^a (%)					
	(mmol _{SA} g _{M0} ⁻¹ h ⁻¹)	(h)	GBL	BA	BOL	THF			
MoC-I/TiO ₂	1.6	22	56	44	0	0			
MoC-II/TiO ₂	4.5	10	51	49	0	0			
MoC-III/TiO ₂	7.8	6	29	71	0	0			
MoO ₃ /TiO ₂	4.1	10	95	1	0	0			

Table 5. Effect of GHSV during catalyst carburization on the initial rate and selectivity at 110 bar and 240 °C.

^a at 22-25 % conversion

The effect of the passivation treatment on the catalytic results was investigated under 110 bar of H₂. Figure 7-a presents the results obtained over MoC-III/TiO₂, which was used directly after passivation. The non-passivated catalyst "NP- MoC-III/TiO₂" (Figure 7-b) was transferred to the reactor in a glovebox, directly after synthesis, without passivation treatment. It is obvious that the two catalysts exhibited really similar catalytic response in terms of activity and selectivity. The conversion reached 87-92% after 24 h reaction for both samples

and the initial rates was of $7.6 \pm 0.2 \text{ mmol}_{SA} \text{g}_{Mo}^{-1} \text{h}^{-1}$ (the difference is within experimental error $\pm 5\%$). The yield of GBL and BA reached around 30 % and 50%, respectively. Therefore the passivation layer does not affect the catalytic performance of the catalyst. As no pre-activation was conducted on the passivated sample, the reduction of the passivated sample must occur in situ, at the beginning of the reaction. The XPS results showed that no more Mo^{6+} and a lower amount of Mo^{4+} species were present in NP- MoC-III/TiO₂ (Figure 3-b; Table 3). These results suggest that the oxides must be reduced at the beginning of the reaction and the selectivity must depend on the Mo carbide content, which is similar in both catalysts.



Figure 7. Hydrogenation of succinic acid over (a) MoC-III/TiO₂ and (b) NP-MoC-III/TiO₂ at 240 $^{\circ}$ C and under 110 bar of H₂: temporal evolution of the concentrations of SA, the product yields and the carbon balance (CB). Aqueous solution of SA (0.12 M, 100 mL), 0.6 g of catalyst.

3.2.3. Stability of the catalyst

The stability tests were conducted with MoC-II/TiO₂ at 240 °C and 150 bar for 26 h, which are the harshest conditions used in this work. The results obtained during the first run over MoC-II/TiO₂ are shown in Table 6 and Figure A.8. The catalyst was then filtered, washed with distilled water (under air) and dried at 80 °C; this catalyst is denoted R1- MoC-II/TiO₂. The percentage of Mo in the solution recovered after the first run was below 0.1 ppm, which means that no leaching occurred (< 0.1%).

Catalyst oxidation is a possible cause of deactivation for metal carbides catalysts [66]. The hydrothermal stability of Mo₂C in water at 250 °C for 48 h has been investigated in a previous study [67]. The formation of MoO₂ (by XRD) was observed and due to the oxidation by H₂O. In order to assess the presence of oxides in the solids (crystalline or amorphous), Raman analysis were done for the catalyst before (MoC-II/TiO₂) and after reaction (R1- MoC-II/TiO₂). In Figure 8, the bands at 145, 196, 397, 517, and 637 cm⁻¹ correspond to anatase

phase of TiO₂ and the rutile phase is evidenced by two extra broad bands at 440 and 605 cm⁻¹ [68]. The two bands at 1345 and 1597 cm⁻¹ correspond to the disorder D and tangential G bands of graphitic carbon [31,69,70]. The presence of these two bands have previously been reported for molybdenum carbides synthesized under 10% C₂H₆/H₂ at 800 °C [31]. The weak bands at 2654, 2932, and 3209 cm⁻¹ were attributed to second order features [71–73]. As the cubic MoC structure leads to no Raman active band, no bands were detected for MoC-II/TiO₂. Furthermore, the presence of the light absorbing carbon layer can hinder observation of underlying phase [74]. This result implies that the catalyst is covered with an excess of graphite during the synthesis, in agreement with the XPS, elemental analysis and TEM results. The absence of bands attributed to v(Mo=O) vibrations around 950-1000 cm⁻¹ [31,75,76] suggests that MoC-II/TiO₂ is fully carburized. In the spectra of R1- MoC-II/TiO₂, two



additional v(Mo=O) and v(Mo-O-Mo) stretching bands located at 968 cm⁻¹ and 832 cm⁻¹, respectively were observed and attributed to the presence of molecular polymolybdates [77,78]. The recovered catalyst (R1- MoC-II/TiO₂) was tested under the same reaction conditions (240 °C, 150 bar of H₂). After 26 hours, only 24% of SA is converted, with 14% yield of GBL and 7% yield of BA (Figure A.8).

Catalyst	V ₀	Time ^a	Products selectivity (%) ^a				
	$(\text{mmol}_{SA} g_{Mo}^{-1} h^{-1})$	(h)	GBL	BA	BOL	THF	BDO
MoC-II/TiO ₂	11.2	6	60	40	0	0	0
R1- MoC-II/TiO ₂	2.7	26	67	32	0	0	0
R2- MoC-II/TiO ₂	8.5	6	34	60	5	1	0

Table 6. Initial rate (V_0) and product selectivity after recycling

MoC-II/TiO₂ (before reaction), R1- MoC-II/TiO₂ (recovered under air), $R2_{solid}$ - MoC-II/TiO₂ (recovered under N₂) and $R2_{solution}$ - MoC-II/TiO₂ (recovered in solution).

In a second stage, we aimed to assess when the oxidation of the catalyst was taking place. Indeed, the oxidation could occur during the reaction or during the recovery due to the exposure to air in the washing and filtration process. For that, another reaction was conducted with MoC-II/TiO₂ but the used catalyst denoted R2_{solution}- MoC-II/TiO₂ was recovered with the reaction solution. Raman spectra of the solid in solution did not show any peaks associated with molecular or crystalline molybdenum oxides (Figure 8), hence oxidation did not occur during the reaction. The presence of amorphous carbon might inhibit the oxidation of the particles, as observed for iron carbide [79]. In order to test the reusability of the catalyst, the reactor was transferred to a glove bag where the filtration was set up. The catalyst was recovered under inert atmosphere and without washing with water. Raman spectra associated with this solid, R2_{solid}- MoC-II/TiO₂, showed complete absence of molybdenum oxides. It was then concluded that the oxidation of the catalyst occurs during the recovery step, and not during the reaction. However, the relative intensity of the bands of graphitic carbon was higher after recovery suggesting that the quantity of such carbon was increased. R2solid- MoC-II/TiO₂ was then tested for the hydrogenation of SA (Figure A.8, Table 6). 64% conversion was achieved after 26 h. It is clear that the catalyst R2_{solid}- MoC-II/TiO₂ was more active than R1- MoC-II/TiO₂, however it was still less active than fresh MoC-II/TiO₂. The selectivity was also affected as more BA and less GBL were formed. The catalyst exhibited some deactivation, while the characterization of the bulk catalyst after the first run did not show any drastic changes, in terms of XRD, ICP and elemental analysis (C and O contents). Therefore XPS analysis of R2_{solid}- MoC-II/TiO₂ was conducted and the results are presented in Table 7 and Figure A.9. It can be seen that the amounts of carbidic molybdenum and carbidic carbon have decreased in the recovered catalyst in comparison to the fresh one, i.e. from ca. 26 to 20% and from ca. 5 to 2% respectively. Moreover, despite the fact that the bulk carbon content (by elemental analysis) was constant, the surface carbon atomic concentration has increased. Therefore the partial oxidation of the catalysts on the surface, coupled with some

coke formation, could be responsible for the deactivation. A regeneration of the catalyst under a flow of H_2/C_2H_6 at 700 °C might provide a recovery of the catalyst performance.

	Atomic concentration %		Mo species %			C species %	
Catalyst	Мо	С	Mo^{δ^+}	Mo^{4+}	Mo^{6+}	Carbide	Graphite
MoC-II/TiO ₂	3.6	33.9	26	11	63	5	89
R2 _{solid} - MoC-II/TiO ₂	4.7	49.3	20	20	60	2	80

Table 7. XPS analysis: atomic concentration of Mo and C, and the abundance of Mo and C species.

4. Conclusion

In this study, we investigated the hydrogenation of succinic acid in aqueous phase using supported molybdenum carbide catalysts instead of the more conventional noble metals catalysts. MoC/TiO₂ were synthesized by impregnation with (NH₄)₆Mo₇O₂₄.4H₂O followed by hydrogenation / carburization under a flow of 20% v/v C₂H₆/H₂. XRD and TEM showed that particles < 5 nm of cubic phase were obtained. The catalysts were active for the reaction and full conversion was achieved. The results also showed that MoC/TiO₂ catalysts exhibit high selectivity towards butyric acid and butanol, contrary to noble metal catalysts. The effects of H₂ pressure and temperature were investigated and the selectivity does not depend on conversion. The passivation treatment does not have a noticeable effect on the performance, while an increase in GHSV during the synthesis is associated with an increase of in activity and a switch of selectivity towards BA. Molybdenum does not leach during the reaction. After recovering the catalyst under air, deactivation was observed, while keeping it under inert atmosphere limits the deactivation. The promising perspective of this project is replacing noble metals by the non-precious and more abundant Mo carbides.

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Figure A.1. Representative TEM image (a, a.1), and electron diffraction (a.2) of MoC-III/TiO₂.



Figure A.2. Representative TEM image (a, a.1), and electron diffraction (a.2) of MoC-I/TiO₂.



Figure A.3. XPS spectra of MoC-III/TiO₂ over Ti 2p.



Figure A.4. Typical hydrogenation of succinic acid at 240 $^{\circ}$ C and under 150 bar H₂: temporal evolution of (a) the concentrations of SA and the products yield, (b) the carbon balance (CB) and TOC measured. Aqueous solution of SA (0.14 M, 100 mL), 0.6 g of MoC-II/TiO₂.



Figure A.5. Hydrogenation of GBL (a), BA (b), BDO (c) and THF (d) at 240 °C and under 150 bar H₂: temporal evolution of the concentrations of the substrates and products yield. Aqueous solution of substrates (0.12 M, 100 mL), 0.6 g of MoC-II/TiO₂.



Figure A.6. Arrhenius plots for the hydrogenation of SA over MoC-II/TiO₂. Aqueous solution of SA (0.12 M, 100 mL), 150 bar of H₂, 0.6 g of catalyst. The rate constant k (s⁻¹) were calculated, assuming a pseudo-first order: Ln ($[SA]_0/[SA]_t$) = k * t.



Figure A.7. Typical hydrogenation of succinic acid at 240 °C and under 110 bar H₂: temporal evolution of (a) the concentrations of SA and the products yield, (b) the carbon balance (CB) and TOC measured. Aqueous solution of SA (0.13 M, 100 mL), 0.6 g of MoC-II/TiO₂.



Figure A.8. Hydrogenation of succinic acid over (a) MoC-II/TiO₂, (b) R1- MoC-II/TiO₂ and (c) R2_{solid}- MoC-II/TiO₂: temporal evolution of the concentrations of SA, products yield and carbon balance (CB). Aqueous solution of SA (0.14 M, 100 mL), 0.6 g of catalyst, 240°C and 150 bar of H₂.



Figure A.9. XPS spectra of catalysts a) MoC-II/TiO₂, and b) R2_{solid}-MoC-II/TiO₂ over 1) Mo 3d and 2) C 1s.

Appendices

Table A.1. Lattice	parameters of anatase.	rutile TiO ₂ , and cubic	MoC of the support	and catalysts.
	F			

	Lattice pa	rameters (Å)			
Catalyst	Anatase TiO ₂		Rutile TiO	2	Cubic MoC	
	a	c	a	c	a	
TiO ₂	3.784 (1)	9.503 (1)	4.592 (1)	2.957 (1)	-	
MoC-I/TiO ₂	3.787 (1)	9.507 (2)	4.596 (2)	2.960(1)	4.260 (3)	
MoC-II/TiO ₂	3.787 (1)	9.506 (4)	4.596 (2)	2.961 (1)	4.273 (3)	
MoC-III/TiO ₂	3.785 (1)	9.496 (2)	4.594 (2)	2.963 (2)	4.268 (3)	

Spot	h k l	α (°)		d (nm)		
		Exp.	Theo.*	Exp.	Theo.*	
1	11-1	0.00	0.00	0.245	0.2465	
2	200	55.73	54.74	0.210	0.2135	
3	1 -1 1	109.22	109.47	0.240	0.2465	
4	0 -2 2	144.40	144.74	0.148	0.1509	

Table A.2. Lattice parameters obtained from TEM analysis, Figure A.1.

* Theoretical values corresponding to cubic MoC

Spot	hkl	α (°)		d (nm)		
		Exp.	Theo.*	Exp.	Theo.*	
1	11-1	0.00	0.00	0.2431	0.2465	
2	200	54.04	54.74	0.2134	0.2135	
3	1 -1 1	108.82	109.47	0.2495	0.2465	

Table A.3. Lattice parameters obtained from TEM analysis, Figure A.2.

* Theoretical values corresponding to cubic MoC