Catalysis Letters 55 (1998) 165–168

Hydrogenation of crotonaldehyde over carbon-supported molybdenum nitrides

A. Guerrero-Ruiz [a], Y. Zhang [b,c], B. Bachiller-Baeza [b] and I. Rodríguez-Ramos [b]

[a] *Departamento Química Inorgánica, Facultad de Ciencias, UNED, 28040 Madrid, Spain*
E-mail: aguerrero@ccia.uned.es
[b] *Instituto de Catálisis y Petroleoquímica, CSIC, Campus Cantoblanco, 28049 Madrid, Spain*
[c] *State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, PR China*

Received 23 July 1998; accepted 22 September 1998

The gas-phase hydrogenation of crotonaldehyde has been performed over unsupported Mo_2N and over Mo_2N supported on two carbonaceous materials, an activated carbon (AC) and a high surface area graphite (G). These catalysts were *in situ* prepared by the temperature-programmed reaction of MoO_3 and carbon-supported Mo precursors with NH_3. It is found that selectivity to the unsaturated alcohol is maximum for the Mo_2N/G sample, where crotylalcohol selectivities exceed the 60% during all time in reaction. Higher selectivity surface sites are associated with the (200) planes of the γ-Mo_2N crystallites.

Keywords: molybdenum nitride catalysts, crotonaldehyde hydrogenation

1. Introduction

The catalytic hydrogenation of α,β-unsaturated aldehydes to produce the unsaturated alcohols has been the subject of several investigations in the latter years because of its interest in the fine chemical industry and as catalytic test. In general, supported group-VIII-metal catalysts have been the most studied. Different factors such as the nature of the support [1], metal particle size [2], presence of different promoters or addition of a second metal [3–6] seem to modify the catalytic performance. In the case of copper-based catalysts the presence of sulphur poisons is required to achieve high selectivity to crotylalcohol [7]. The question is how to activate preferentially the CO bond achieving then a higher selectivity to the desired unsaturated alcohol. In fact, the thermodynamic constraints that conduce to the easier hydrogenation of the C=C function instead of the C=O one only can be surpassed by the preferential adsorption of the carbonyl on the catalyst surface. Then, the morphology and polarity of the catalyst surface as well as electronic and steric factors are important parameters that may control the adsorption structure of the reactant.

Inorganic metal nitrides and carbides (Mo_2C, Mo_2N, WC, W_2C, etc.) have also attracted much attention in the fields of material science and catalyst synthesis. The presence of nonmetal atoms (N or C) in these materials, which change electrical, magnetical and adsorptive properties of transition metals (i.e., Mo), convert them in metallic interstitial alloys, and give them new properties as catalysts. Most of the efforts have focused on synthesis and characterization of high surface area materials [8–10] and, more recently, on their application as catalysts for reactions such as CO hydrogenation, hydrodesulfurization or hydrodenitrogenation [11–13]. Molybdenum nitrides exhibit bulk and surface properties similar to noble metals [8] and these may be tailored by changing the preparation methods and synthesis conditions. For instance, the solid-state reaction of MoO_3 with NH_3 leads to the topotactic transformation of MoO_3 to Mo_2N, which originates solids with specific particle morphologies (face-centered-cubic crystals) and with high surface areas [14]. In addition, the catalytic performance of molybdenum nitrides can modify by supporting them on a high surface area carrier [15]. On the other hand, a recent hydrogen adsorption microcalorimetric study has shown that these materials based on Mo_2N are able to chemisorb hydrogen with various adsorption strengths depending on the sample preparation [16]. Thus, we speculate that these nitrides with hydrogenating properties could preferentially activate the C=O bond of unsaturated aldehydes leading to an enhanced selectivity toward the unsaturated alcohol. In this work, we report the structural and catalytic properties of Mo_2N itself and supported on carbonaceous materials for the gas-phase crotonaldehyde hydrogenation reaction.

2. Experimental

Two carbon-supported molybdates were prepared by impregnation of a commercial microporous activated carbon (Merck, $S_{\mathrm{BET}} = 960\ \mathrm{m^2\,g^{-1}}$) and of a high surface area graphite (HSAG-300 from Lonza Ltd., $S_{\mathrm{BET}} = 299\ \mathrm{m^2\,g^{-1}}$). An aqueous solution of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (Aldrich) with the appropriate concentration to obtain a loading of ca. 10 wt% MoO_3 was used. The samples were dried overnight at 383 K. The starting material of the unsupported Mo nitride was a commercial MoO_3 from Merck.

The carbon-supported molybdenum nitrides (Mo_2N/AC and Mo_2N/G) and the unsupported molybdenum nitride (Mo_2N) were *in situ* prepared by temperature-programmed reaction of their corresponding metal oxide precursors with NH_3. Briefly, the oxidic samples (600 mg) were heated in a tubular quartz microreactor under flowing NH_3 (60 $cm^3\,min^{-1}$) from room temperature to 573 K in 1 h. Then the temperature was raised up to 973 K at a 1 $K\,min^{-1}$ and kept for 1 h. Finally, the furnace was opened and the sample rapidly cooled in flowing NH_3. Before reaction tests, samples were treated at 673 K under H_2 (25 $cm^3\,min^{-1}$) for 2 h and then cooled down under hydrogen to the reaction temperature.

The hydrogenation of crotonaldehyde was carried out at atmospheric pressure in the 313–353 K reaction temperature range. Catalysts were contacted with a reaction mixture (flow of 50 $cm^3\,min^{-1}$) containing helium, hydrogen and crotonaldehyde which was prepared by bubbling the H_2/He gas through a thermostabilized saturator (277 K) containing the aldehyde. The H_2/crotonaldehyde molar ratio was 30. The effluents were analyzed by gas chromatography using a Varian 3400 GC equipped with a FID detector and a Carbowax 20M on Chromosorb WHP packed column for separation. The conversion was kept below 10%. The main products of this reaction were crotylalcohol (CROTOL), butanol (BUTOL), butanal (BUTAL) and butane (BUNE). For comparative purpose a graphite-supported platinum catalyst (Pt/G) with a 3.2 wt% of metal loading and a metal dispersion of 0.11 (determined from H_2 chemisorption) was also studied. Details about the preparation and characterization of this sample are given elsewhere [17].

The BET surface areas of catalysts, both oxidic precursors and samples used in reaction, were determined by N_2 adsorption at 77 K using a Micromeritics ASAP 2000 equipment. X-ray diffraction (XRD) pattern of samples used in reaction and air exposed were measured in a Siefert 3000 P apparatus using Ni filtered Cu $K\alpha$ radiation and a graphite monochromator. Average Mo_2N crystallite sizes were determined measuring the width of the (200) diffraction peak, by application of the Scherrer equation with Warren's correction for instrumental broadening.

3. Results and discussion

Figure 1 shows the overall activities (μmole of crotonaldehyde transformed per second and gram of active phase (Pt or Mo_2N)) at 333 K for the catalysts in the gas-phase hydrogenation of crotonaldehyde. It can be observed that all catalysts suffer a significant deactivation, which may be due to carbon accumulation on the catalyst surface with the consequent decrease in active sites able to carry out the hydrogenation reaction. A decrease in the rate of reaction of about 80% of the initial rate was observed during the first 90 min on stream for the carbon-supported and unsupported molybdenum nitrides, while this was 30% for the Pt/G sample. After this initial period catalytic activities become stabilized. It should be noted that the sample Mo_2N/AC exhibited no catalytic activity at 313 K; the support took up the CROTAL from the gas phase. Neither the reactant nor products were observed in the stream exit after about 100 min. This uptake of CROTAL suggests that the activated carbon pores were steadily filled by the reactant during its exposure to the catalyst. However, when the reaction temperature was increased up to 333 K, a catalytic activity similar to that of the Mo_2N/G sample was observed (figure 1). Further increase in the reaction temperature up to 353 K, brought about a sudden desorption of the condensed CROTAL since its concentration in the exit stream was much higher than the initial feed concentration.

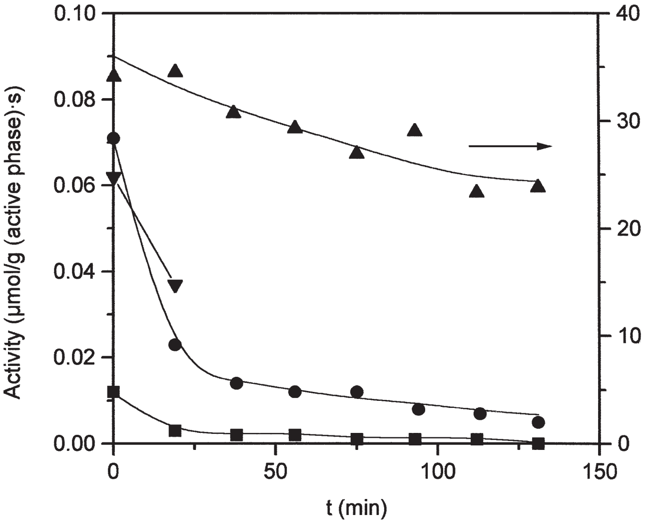

Figure 1. Catalytic activity in the hydrogenation of crotonaldehyde at 333 K for catalysts: (■) Mo_2N, (●) Mo_2N/G, (▲) Pt/G and (▼) Mo_2N/AC.

The products obtained in the gas-phase hydrogenation of crotonaldehyde in the conditions used in this study are mainly the primary products, CROTOL and BUTAL. More hydrogenated products, BUTOL and BUNE, are produced in much lower amounts (below 5%), which are similar for all the catalysts. The trends of the CROTOL selectivity with the time on stream are shown in figure 2. For unsupported and graphite-supported molybdenum nitrides the selectivity to CROTOL increased in the early stages of the reaction and then decreased, seeming to reach a steady state after approximately 300 min on stream. However, for the Mo_2N-AC sample the CROTOL selectivity was very low (ca. 5%) and increased steadily until the end of the experiment after 220 min reaction time. The CROTOL selectivity of the Pt/G sample increased during the first 40 min of reaction and then became constant. Comparison of the CROTOL selectivity of the different catalysts at steady-state conditions shows that the unsupported Mo_2N itself has selectivity towards CROTOL of ca. 25%, which is slightly higher than that of the PT/G sample (ca. 20%). When the molybdenum nitride is supported on graphite, the selectivity to CROTOL is hugely enhanced (ca. 60%), the unsaturated alcohol being therefore the main product yielded by the Mo_2N-G sample. By contrast, the activated-carbon-supported molybdenum nitride showed a very poor

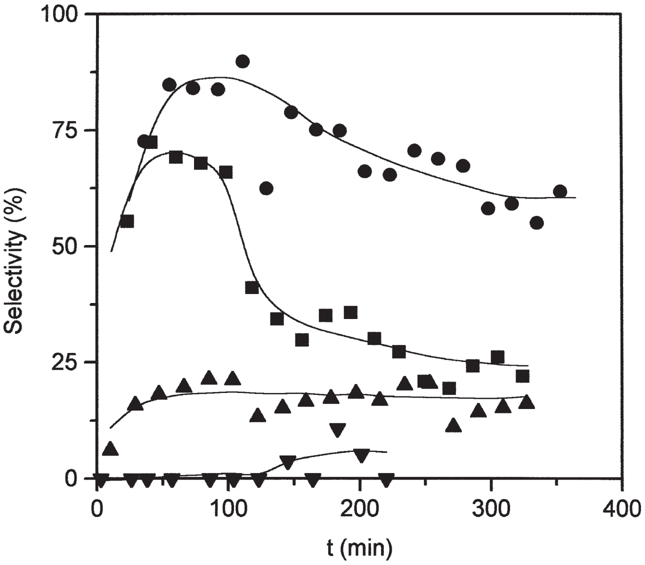

Figure 2. Selectivity to crotylalcohol as a function of time on stream for catalysts: (■) Mo_2N, (•) Mo_2N/G, (▲) Pt/G and (▼) Mo_2N/AC.

Table 1
Structural properties of unsupported and carbon-supported molybdenum nitrides.

Catalyst	S_{BET}[a] ($m^2\ g^{-1}$)	Crystallite size (nm)	$I(200)/I(111)$
Mo_2N	107 (<1)	6.5	1.12
Mo_2N/AC	692 (923)	2.5	2.32
Mo_2N/G	91 (133)	2.7	–

[a] Between parentheses BET surface areas of oxidic precursors.

selectivity for the production of the unsaturated alcohol and yielded mainly butanal and saturated products (>90%).

Table 1 shows the values of surface areas for the supported and unsupported molybdenum nitride catalysts after the hydrogenation reaction and for their corresponding oxidic precursors. The unsupported molybdenum nitride catalyst possesses a high surface area as it is expected from the synthesis conditions employed [9,18]. The XRD pattern for the unsupported sample is shown in figure 3. This latter is characteristic of high surface area crystalline γ-Mo_2N constituted by plate-like crystallites extended out in the (100) direction [9]. This type of texture is a consequence of the pseudomorphic nitridation of the MoO_3 particles into γ-Mo_2N [15]. The incorporation of the molybdenum precursor to the AC support does not seem to modify its surface area, but for the G support it is diminished by about 50%. After nitridation the catalysts show surface areas lower than that of the oxidic precursors (table 1). These results suggest that the pores of the carbon supports are modified during nitridation by NH_3 at 973 K. The XRD patterns of supported molybdenum nitride catalysts (figure 3) show small and broad diffraction lines assigned to the (111) and (200) planes of crystalline γ-Mo_2N for the Mo_2N/G sample. While for the sample supported on activated carbon is only observed a wide band at $2\theta = 43.1$ attributed to the (200) plane of γ-Mo_2N. These supported molybdenum nitrides have crystallites of much smaller average size

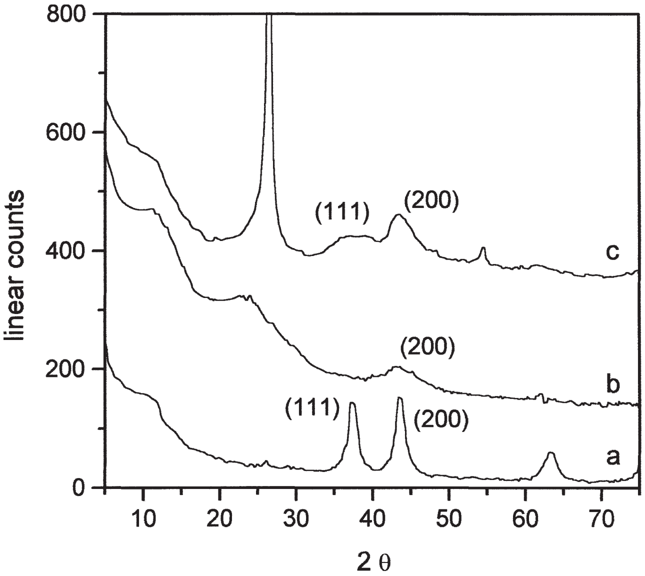

Figure 3. XRD patterns after reaction for: (a) Mo_2N, (b) Mo_2N/AC, (c) Mo_2N/G catalysts.

(2.5–2.7 nm) than the unsupported counterpart (6.5 nm). However, no large difference in Mo_2N crystallite size is found between the two carbon-supported catalysts in spite of the much higher surface area of the activated carbon. This latter fact indicates that the narrow microporosity of the activated carbon does not participate in the dispersion of the molybdenum nitride phase. From this standpoint, there is no advantage in the use of activated carbon as a support. Moreover, the higher value of the ratio of intensities of the (200) and (111) diffractions, $I(200)/I(111)$, for the Mo_2N/G sample compared with the unsupported sample indicates an enhanced preferential orientation of the γ-Mo_2N crystallites in the (100) direction. This picture agrees with that observed for unsupported Mo nitrides, where the predominance of large plate-like particles increased with decreasing average size of Mo_2N particles [9,18].

On the basis of the catalytic and structural studies of unsupported and graphite-supported molybdenum nitrides, we arrive at the conclusion that the selectivity to crotylalcohol markedly depends upon the molybdenum nitride crystallite size. These results suggest that the hydrogenation of crotonaldehyde over molybdenum nitrides is structure sensitive, as it is over noble metals [19]. With decreasing particle size the fraction of Mo_2N (200) planes increases. Thus, we affiliate the selectivity to crotylalcohol with the abundance of Mo_2N (200) surfaces which would promote the adsorption of crotonaldehyde via the C=O bond. No such high selectivity to CROTOL was observed in the case of the Mo_2N supported on the microporous activated carbon in spite of its small Mo nitride particle size. It appears that the opportunity for prolonged adsorbed crotonaldehyde–hydrogen contact due to significant residence time within the catalyst pores shifted the product selectivity towards the total hydrogenated product. These results agree with those from the 3-methylcrotonaldehyde hydrogenation over zeolite-supported Ru catalysts [20].

In conclusion, molybdenum nitrides, particularly when supported on mesoporous carbon, appear as very selective catalysts to produce the less thermodynamically favored hydrogenation of crotonaldehyde to crotylalcohol very likely because of the preferential activation of the C=O group over the (200) planes of these types of material.

Acknowledgement

This work was supported by DGICYT, Spain (Project no. PB94-0077-CO2-02). YZ thanks the Consejo Superior de Investigaciones Científicas (CSIC) for a postdoctoral fellowship. BBB acknowledges the Ministerio de Educación y Cultura for a scholarship grant.

References

[1] M.A. Vannice and B. Sen, J. Catal. 115 (1989) 65.
[2] S. Galvagno, G. Capannelli, G. Neri, A. Donato and R. Pietropaolo, J. Mol. Catal. 64 (1991) 237.
[3] A. Giroir-Fendler, D. Richard and P. Gallezot, in: *Heterogeneous Catalysis and Fine Chemicals*, eds. M. Guisnet et al. (Elsevier, Amsterdam, 1988) p. 171.
[4] A.B. Da Silva, E. Jordão, M.J. Mendes and P. Fouilloux, Appl. Catal. A 148 (1997) 253.
[5] T.B.L.W. Marinelli, S. Nabuurs and V. Ponec, J. Catal. 151 (1995) 431.
[6] B. Coq, P.S. Kumbnar, C. Moreau and M.G. Warawdekar, J. Mol. Catal. 85 (1993) 215.
[7] G.J. Hutchings, F. King, I.P. Okoye, M.B. Padley and C.H. Rochester, J. Catal. 148 (1994) 453.
[8] G.S. Ranhotra, G.W. Haddix, A.T. Bell and J.A. Reimer, J. Catal. 108 (1987) 24.
[9] J.G. Choi, R.L. Curl and L.T. Thompson, J. Catal. 146 (1994) 218.
[10] X.S. Li, Y.J. Zhang, Q. Xin, C.X. Si, Y.F. Miao and L. Wang, React. Kinet. Catal. Lett. 57 (1996) 177.
[11] G.S. Ranhorta, G.W. Haddix, A.T. Bell and J.A. Reimer, J. Catal. 108 (1987) 40.
[12] H.K. Park, J.K. Lee, J.K. Yoo, E.S. Ko, D.S. Kim and K.L. Kim, Appl. Catal. A 150 (1997) 21.
[13] E.J. Markel and J.W. Van Zee, J. Catal. 126 (1990) 643.
[14] C.W. Colling and L.T. Thompson, J. Catal. 146 (1994) 193.
[15] L. Volpe and M. Boudart, J. Solid State Chem. 59 (1985) 332.
[16] A. Guerrero-Ruiz, A. Maroto-Valiente, Y. Zhang and I. Rodríguez-Ramos, in preparation.
[17] P. Badenes, L. Daza, I. Rodríguez-Ramos and A. Guerrero-Ruiz, in: *Spillover in Surface Science and Catalysis*, eds. C. Li and Q. Xin (Elsevier, Amsterdam, 1997) p. 241.
[18] Y. Zhang, Q. Xin, I. Rodríguez-Ramos and A. Guerrero-Ruiz, Mater. Res. Bull., in press.
[19] M. Englisch, A. Jentys and J.A. Lercher, J. Catal. 166 (1997) 25.
[20] A. Waghray, R. Oukaci and D.G. Blackmond, Catal. Lett. 14 (1992) 115.