Catal Lett (2008) 120:137–142
DOI 10.1007/s10562-007-9264-9

Synthesis, Characterization and Catalytic Activity in the Hydrogenation of Cyclohexene with Molybdenum Carbide

Espinoza-Monjardín · J. Cruz-Reyes · M. Del Valle-Granados · E. Flores-Aquino · M. Avalos-Borja · S. Fuentes-Moyado

Received: 15 August 2007 / Accepted: 1 September 2007 / Published online: 15 September 2007

Abstract Two series of molybdenum carbides are prepared from MoO_3 by temperature programmed reduction (TPR), differing in feed gas composition (20 and 40% CH_4/H_2). The heating ramp consists of two steps, one from ambient temperature to 973 K, at a rate of 10 K/min; the second from 973 K up to the final temperature (1023, 1073, 1123, 1173 K), at a rate of 0.5 K/min. The Mo_2C (hcp) phase is identified for the series prepared with 20% CH_4/H_2 at different temperatures, with surface areas between 20 and 27 m^2/g. Also found is a mix of the MoC and Mo_2C (hcp) phases for the series prepared with 40% CH_4/H_2 at temperatures above 1023 K, with surface areas between 9 and 19 m^2/g. Both series of catalysts reach 100% conversion of cyclohexene in 5 h or less, with those catalysts prepared with a 40% CH_4/H_2 gas mix reaching maximum conversion in the least time. Catalysts are compared to a commercial molybdenum carbide reagent as a reference.

Keywords Molybdenum carbide · Molybdenum carbide catalysts · Cyclohexene hydrogenation · TPR

1 Introduction

Transition metal sulfides (TMS) have been used as catalysts in hydrotreatments and some hydrogenation reactions as well. Most of the research on TMS catalysts up to the early 1970s is found in a classic reference [1]. The hydrogenation of ethylene and other linear and cyclic olefins in the gas phase has been studied in a variety of systems using transition metals and their compounds as catalysts, including zinc oxide, different Group 8–10 metals, cobalt–molybdenum catalysts and sulfided Al–Ni–W catalysts, sulfided cobalt–molybdenum catalysts and palladium sulphide [2]. Until recently, the literature on transition metal compounds as catalysts for hydrogenation reactions has mostly dealt with single and multi-phase oxides and sulphides [3].

The search for new materials with better catalytic properties has lead to two new catalyst families. One of them is based on transition metal carbides, the other on transition metal nitrides. These compounds, especially those of the Group 6 transition metals, have catalytic properties similar to those of the precious metals [4, 5]. One of the first carbides to merit attention was tungsten carbide [4], which has properties similar to those of the noble metals. This catalytic behavior was also found in other carbides and nitrides [6]. These compounds can be synthesized to yield low or high surface areas. Thus, low surface area Mo_2C can be produced by the direct combination of metal and nonmetals, whereas reactions of metals or compounds with gas-phase reagents give Mo_2C with a greater surface area [7, 8]. A notable advance was achieved when these compounds were synthesized by temperature programmed reduction (TPR), a method that yields higher surface area nitrides and carbides [9, 10]. Molybdenum carbides have a tendency to oxidize in air and it has recently been theorized that oxicarbides have enhanced catalytic activity for the water-gas-shift reaction compared to clean Mo_2C surfaces [11].

Carbides can not only be formed from the corresponding oxides, but also from their nitrided species. This is the case

Espinoza-Monjardín · J. Cruz-Reyes (✉) · M. Del Valle-Granados
Facultad de Ciencias Químicas e Ingeniería de la UABC, Tijuana, BC, Mexico
e-mail: juancruz@uabc.mx

E. Flores-Aquino · M. Avalos-Borja · S. Fuentes-Moyado
Centro de Ciencias de la Materia Condensada de la UNAM, Ensenada, BC, Mexico

of the W_2N and Mo_2N precursors, which in adequate contact with a CH_4/H_2 mix have lead to the formation of the β-$WC_{(1-x)}$ and α-$MoC_{(0.45)}$ carbides with surface areas of 55 and 185 m^2/g, respectively [12]. In order to increase the reduction of Mo and obtain new properties, MoO_3 has been co-impregnated with an aqueous solution of ortho-platinic acid $H_2PtCl_6 \cdot 6H_2O$, generating a high surface area α-$MoC_{(1-x)}$ phase of about 200 m^2/g [13].

Although the TPR method has been able to produce materials with better properties, these depend noticeably on the conditions of synthesis, which can vary from one laboratory to the next, like the nature of the gas feed, the ratio between reactor and sample volumes, the heating temperature ramp, the final temperature of synthesis, and the time the sample is heated at this final temperature [14].

Cyclohexene hydrogenation is a model hydrogenation test. It is known that cyclohexene hydrogenation can be carried out by the use of classical catalysts like Ni–W sulphide [15], complexes of transition metals like Pd, Rh [16], and more recently, amine metal complexes [17]. Molybdenum carbide catalysts prepared by TPR have been studied in different reactions, among them the hydrogenation of cyclohexene [7], benzene [18], toluene [19], and carbon monoxide [14]. Other reactions include simultaneous hydrodesulfurization (HDS), hydrodeoxidation (HDO) and hydrogenation [20], dehydronitrogenation of indol [21], and conversion of methane to synthesis gas [22].

In the case of the cyclohexene, hydrogenation is reported in liquid phase by diluting with n-heptane at 309 K and pressurizing to 115 kPa (92% H_2), using only the α-$MoC_{(1-x)}$ phase as catalyst and a flow reactor to measure activity [7]. However the influence of parameters like gas feed, feed mixture on this reaction are open to further study. Since the structure generally has an influence in the catalytic activity, variations in synthetic methods are of continuing interest. In this work a tubular furnace is used to study the effect of varying the CH_4/H_2 mix and the synthesis temperature on the formation of molybdenum carbide phases, their surface area and their catalytic activity, using a batch reactor for the hydrogenation of cyclohexene as the model reaction. Activity was compared with that of commercial Mo_2C (Aldrich).

2 Experimental

2.1 Sample Preparation

A ceramic boat containing 1.0 g of MoO_3 (99%, Aldrich), is placed in an alumina tube inside a high temperature tubular furnace with programmable temperature (Lindberg Blue). Through the tube is flowed a CH_4/H_2 gas mix. Passivation is done by treatment with a flow of 1 vol%f O_2/N_2 at ambient temperature for 2 h. All carbide products are immediately kept under nitrogen atmosphere prior to analysis.

MoO_3 is heated from ambient temperature to 923 K with a heating ramp of 10 K/min, followed by a heating ramp of 0.5 K/min which takes it to 1023, 1073, 1123 and 1173 K, using a CH_4/H_2 20% (v/v) gas mix (Series I) or 40% (v/v) gas mix (SeriesII).

2.2 Characterization of Samples

Specific surface area is meassured with a Micromeritics Gemini 2060 instrument. The X-ray diffraction patterns of the prepared samples are obtained with a Philips X'Pert analytical diffractometer for powder samples using Cu Kα radiation. Their phases are identified with reference to the data base of the International Centre for Diffraction Data.

2.3 Catalytic Activity

Catalytic activity for cyclohexene hydrogenation is tested in a high pressure 300 mL Parr reactor by placing 20 mL of ciclohexene with 0.3 g of catalyst. The reactor is purged of residual air with H_2 then pressurized to 35.91 KPa (750 psi) with the same gas. The reactor is then heated to the reaction temperature of 523 K. The advance of the reaction is monitored by taking samples every 15 min during the first hour, then every 30 min for the next four hours. Catalytic activity is expressed in terms of % conversion of cyclohexene.

2.4 Gas Chromatography

Samples obtained from the reactor are analyzed using a Hewlett-Packard 5890 gas chromatograph with FID detector. A low polarity J&W DB624 capillary column, 30 m long, 0.53 mm diameter, 3.0 μm thick liquid phase is employed. Column temperature is 373 K, using a N_2 carrier gas flow of 3 mL/min and a split rate of 1:10.

3 Results and Discussion

3.1 X-ray Diffraction and Surface Area

Figure 1 shows the XRD pattern of the molybdenum trioxide reagent (Aldrich) compared to the computer-simulated XRD pattern of orthorhombic molybdenum trioxide derived from the PDF file. The XRD spectrum of MoO_3, Fig. 1a, is formed by a set of well defined and

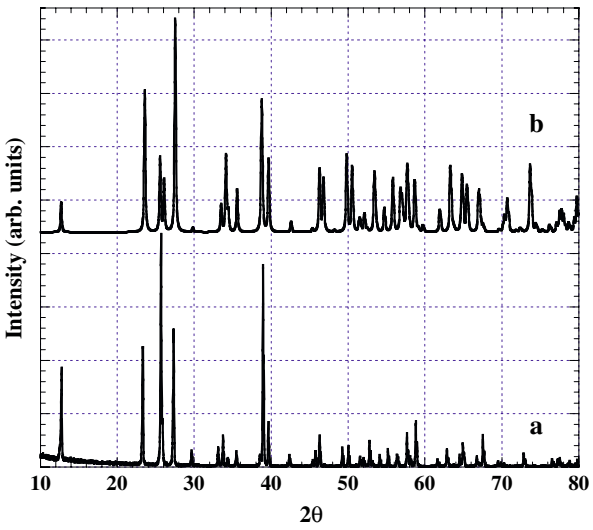

Fig. 1 XRD pattern of (a) molybdenum trioxide reagent, and (b) computer-simulated orthorhombic MoO_3 from PDF file 5-0508

narrow peaks, typical of crystalline materials. The principal reflections (020), (110), (040), (021), (060) are found to be in agreement with the simulated XRD pattern, Fig. 1b, derived from PDF card 5-0508.

Figure 2 shows the XRD pattern of the molybdenum carbide found in all the Series I products, compared to the computer-simulated XRD pattern of α-phase molybdenum carbide derived from the corresponding PDF file. The experimental XRD pattern has broader peaks, which are related to the presence of smaller crystals. The experimental interplanar spacings agree with the theoretical ones for the α-Mo_2C (hcp) (PDF 35-787) phase, with the (100), (002), (101), (102), (110), (103), (112), and (201) reflections outstanding. It should be pointed out that in all Series I samples only the presence of the α-Mo_2C (hcp) phase is detected.

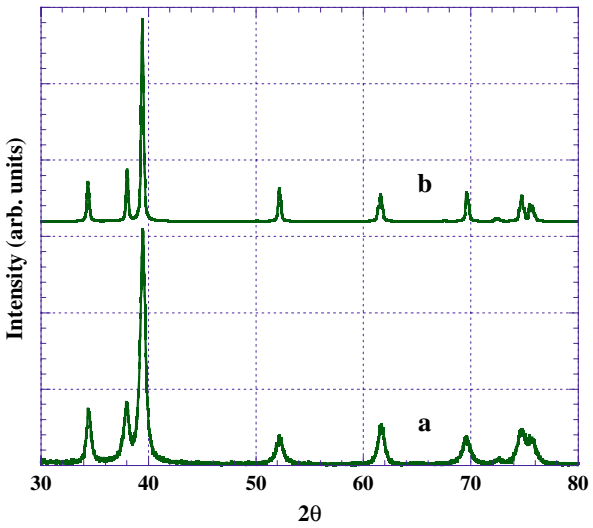

Fig. 2 XRD pattern of (a) molybdenum carbide found in Series I samples, and (b) simulated α-Mo_2C

This phase has been previously detected in similar catalysts [10, 23], where MoO_3 conversion was monitored by TPR when heating oxide in a mix of CH_4/H_2 (1:4), using a 1 K/min heating ramp and a heating range of 573–990 K, while the present work uses a 0.5 K/min heating ramp and a heating range of 923–1023 K. The same authors point out that the transformation of MoO_3 involves two steps. The first one is a reduction to MoO_2 (880 K), without the participation of CH_4. Above this temperature, methane begins to react yielding CO_2 and CO, becoming noticeably consumed at 950 K, and leads to the β-Mo_2C (hcp) phase at 990 K. In this step, the reduction of MoO_2 with CH_4 gives CO and CO_2, and with H_2 forms water. The reduction of MoO_2 to Mo consumes the carbon from the methane, generating Mo_2C. In our case, the absence of the MoO_2 and Mo phases can be explained by the use of a higher synthesis temperature than the one used by these research groups.

The XRD patterns of Series I samples are nearly identical, corresponding to the α-Mo_2C (hcp) phase and having about the same crystal size. According to Table 1, the surface area values of the compounds prepared from 1023 to 1173 K are very similar (24–28 m^2/g). Preparation at 1223 K gives a slightly lower surface area (21 m^2/g), possibly due to sintering. These values are considerably higher than the 3.7 m^2/g obtained for β-Mo_2C under somewhat different conditions by Li et al. [10] and the 7.5–15 m^2/g obtained by Mamede et al. [19].

It has been reported that in the presence of ammonia, molybdenum trioxide can be transformed into a high surface area (220 m^2/g) molybdenum nitride, Mo_2N (fcc), which in turn can be transformed into a molybdenum carbide, α-MoC_{1-x}, with a similar surface area [13]. It has also been found that adding platinum, nickel, palladium to the molybdenum trioxide (using the impregnation method) in a CH_4/H_2 atmosphere, leads to the α-MoC_{1-x} phase with a surface area of about 200 m^2/g [24]. The β-Mo_2C phase is obtained by passing a CH_4/H_2 mix over the molybdenum trioxide. The presence of the Mo_2C phase, considered to be the most stable, can show variations in surface area due to

Table 1 Crystalline phases and surface areas found in Series I (20% CH_4/H_2)

Synthesis temperature, K	Phases found (%)	Surface area, m^2/g
1023	α-Mo_2C (100)	27.4
1073	α-Mo_2C (100)	27.1
1123	α-Mo_2C (100)	24.0
1173	α-Mo_2C (100)	28.3
1223	α-Mo_2C (100)	20.7

the change in the composition of the CH_4/H_2 mix. Thus, the TPR carburization using a 20% CH_4/H_2 mix leads to the formation of Mo_2C (hcp) with a surface area of 60 m^2/g. An improved surface area is achieved by using an 80% CH_4/H_2 mix, yielding molybdenum carbide with a layer of polymeric carbon. Removal of this surface layer with hydrogen produced a molybdenum carbide with a greater surface area of 84 m^2/g [10].

Another variable which affects surface area is the carburizing agent. Márquez et al. [18] report the synthesis of high surface area molybdenum carbide (β-Mo_2C) with a surface area of 170 m^2/g. using a 10% C_2H_6/H_2 mix and a heating ramp of 1 K/min until the synthesis temperature of 900 K is reached, maintaining the isothermal heating for 3 h. This direct carburization using an C_2H_6/H_2 gas mix has been shown to reduce the synthesis temperature and increase the surface area of the carbides as compared to those synthesized using a CH_4/H_2 mix [25].

The XRD patterns of Series II products are nearly identical among all the samples carburized at 1073, 1123 and 1173 K. The experimental XRD pattern shown in Fig. 3a is found to be a composite of the XRD patterns of two known carbide phases: the α-Mo_2C (hcp) phase, simulated in Fig. 3b, and the MoC (hcp) phase (PDF 06-0546), simulated in Fig. 3c. The sample treated at 1023 K produced the α-Mo_2C (hcp) phase only.

While all the XRD patterns of the Series I samples correspond to the single α-Mo_2C (hcp) phase, the XRD patterns of the Series II samples in Fig. 2a, prepared in the range of 1073–1173 K, show the presence of two phases: the α-Mo_2C phase (hcp) (90%) and the MoC (hcp) phase (10%). Figures 2b and c show the simulated XRD patterns for each

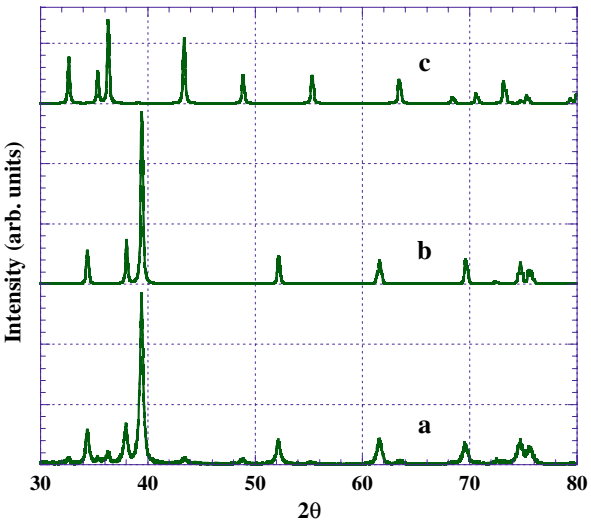

Fig. 3 XRD patterns of (a) carbides found in Series II samples (except for the one prepared at 1023 K), (b) simulated α-Mo_2C, and (c) simulated MoC

phase. This fact suggests that the increase of methane in the mix induces the formation of the MoC phase, although the MoC/Mo2C ratio (1:9) clearly favors the Mo_2C phase. The presence of the β-Mo_2C phase has also been found after MoO_3 was treated with a CH_4/H_2 (20%) mix at 773 K to form MoO_2 and, with increased temperature, the β-Mo_2C phase [23]. Although MoO_2 is present at temperatures below 773 K, it does not become molybdenum carbide by direct carburization. Instead, the β-Mo_2C phase occurs at 973 K by using a heating ramp of 1 K/min.

The formation of molybdenum carbide α-$MoC_{(1-x)}$, fcc phase has also been achieved by using a 4 L/h flow of ammonia gas, while heating in the range of 773–973 K at a rate of 1 K/min and isothermic temperature of 973 K for 3 h. This intermediate is finally taken to an atmosphere of CH_4/H_2 at 20% and 973 K. The intermediate γ-Mo_2N (fcc) is transformed to η-Mo_3C_2 by using the same conditions except for the synthesis temperature, which in this case is 1173 K [26].

Tables 1 and 2 show that the surface areas of catalysts obtained by treating with 40% CH_4/H_2 are slightly smaller than those obtained with 20% CH_4/H_2, whereas the opposite behavior has been reported for similar treatments with 20% and 80% CH_4/H_2 [10]. In the same work it has been noted that two conditions must be satisfied in order to obtain a high surface area material: (a) the transformation of the solid must occur at the lowest temperature in order to reduce any unnecessary particle movement that might lead to their growth, and (b) a moderate heating ramp, not too small that it takes too much time and allows particles to grow. Preferably, the presence of metallic intermediates should be avoided due to their tendency to sinter.

The XRD patterns of commercial molybdenum carbide and computer-simulated molybdenum carbide from PDF card 35-787 are identical, as shown in Fig. 4. The surface area of the comercial Mo_2C (hcp) phase is <1 m^2/g. The surface area of the MoO_3 reagent is also <1 m^2/g.

3.2 Catalytic Activity

Figure 5 shows the catalytic activity results of Series I (20% CH_4/H_2) catalysts prepared from ambient temperature up to

Table 2 Crystalline phases and surface areas found in Series II (40% CH_4/H_2)

Synthesis temperature, K	Phases found (%)	Surface area, m^2/g
1023	α-Mo_2C (100)	19.4
1073	α-Mo_2C (90), MoC (10)	17.5
1123	α-Mo_2C (90), MoC (10)	15.2
1173	α-Mo_2C (90), MoC (10)	9.4

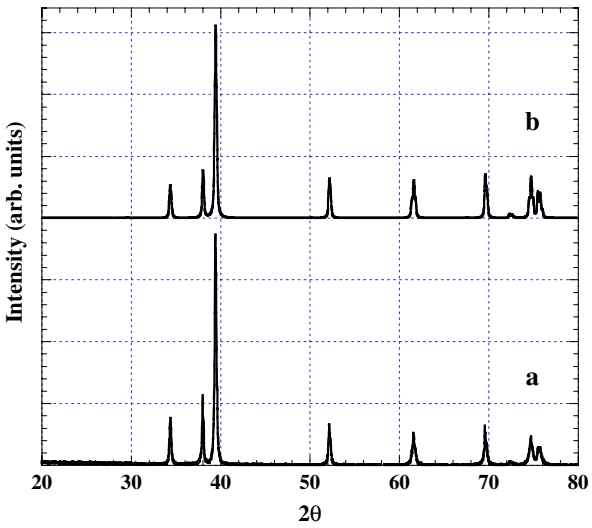

Fig. 4 XRD patterns of (a) commercial molybdenum carbide, and (b) simulated α-Mo_2C

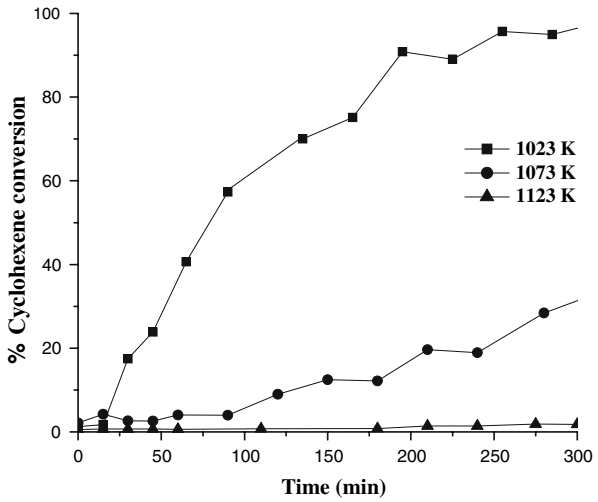

Fig. 5 Catalytic activity results of Series I (20% CH_4/H_2) for the catalysts prepared from ambient temperature up to 923 K (ramp, 10 K/min) with gradual heating 0.5 K/min to 1023, 1073 and 1123 K

923 K (ramp, 10 K/min) with gradual heating 0.5 K/min at 1023, 1073 and 1123 K. In Fig. 6 are shown the catalytic activity results of Series II (40% CH_4/H_2) for the catalysts prepared from ambient temperature up to 923 K (ramp, 10 K/min) with gradual heating 0.5 K/min at 1023, 1073, and 1123 K.

Comparing the catalytic activity of samples from both series of catalysts, Figs. 5 and 6, cyclohexene conversion using the Series I sample prepared at 1023 K is nearly 100% after 300 min, while the maximum conversion with the sample prepared at 1073 K is about 30% after the same time. A greater activity is found for the Series II sample prepared at 1023 K compared to the Series I sample prepared at the same temperature; similar behavior is also seen

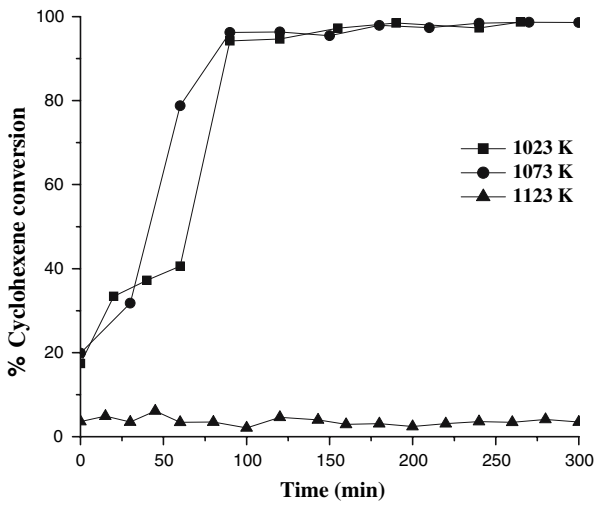

Fig. 6 Catalytic activity results for Series II (40% CH_4/H_2) for the catalysts prepared from ambient temperature up to 923 K (ramp, 10 K/min) with gradual heating 0.5 K/min to 1023, 1073 and 1123 K

when comparing the Series II sample prepared at 1073 K, with the Series I sample prepared at 1073 K. This improvement may be due to an added structural carbon on the surface of the catalysts synthesized with a higher CH_4/H_2 ratio, as proposed by Chianelli [27] for Mo and Ru sulfide catalysts and later by Liu for molybdenum carbides [28]. The Series I and II samples prepared at 1123 K have no significant catalytic activity, attributed to the presence of graphitic carbon formed during the decomposition of methane at this high temperature. The rate constants for the Series I and Series II catalysts prepared at 1073 K are 1.5×10^{-2} s^{-1} and 3.6×10^{-2} s^{-1}, respectively.

In Fig. 7 are shown the catalytic activity results for the cyclohexene hydrogenation reaction using samples of

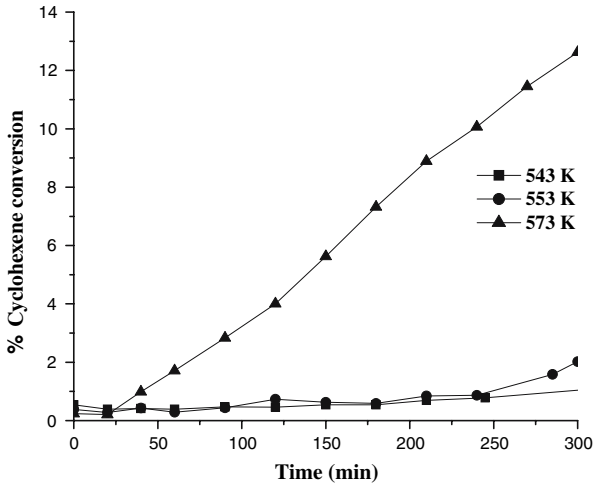

Fig. 7 Catalytic activity results for the cyclohexene hydrogenation reaction using samples of commercial molybdenum carbide as catalysts at temperatures of 543, 553 and 573 K

commercial molybdenum carbide as catalyst at temperatures of 543, 553 and 573 K. The conversion of cyclohexene versus time using commercial molybdenum carbide is similar for temperatures of 543 y 553 K, reaching a final conversion of 1.0% and 1.8% respectively. A reaction temperature of 573 K leads to a 13% conversion. The low catalytic activity of this molybdenum carbide compared to that of the synthesized catalysts partly due to its small surface area (<1 m^2/g).

4 Conclusions

In the X-ray diffractograms of the Series I catalysts, no appreciable changes in composition occur with different synthesis temperatures. This series is composed of a molybdenum carbide phase α-Mo_2C (hcp), with a surface area that decreases slightly with increasing temperature. As for Series II catalysts, two phases of molybdenum carbide are found, α-Mo_2C (hcp) and MoC (hcp), with surface areas following the same behavior as Series I. The decrease in surface area may be due to the formation of graphitic carbon on the surface of the catalysts.

Acknowledgments We are very grateful to Eloisa Aparicio for technical assistance in the X-ray laboratory. Also to Dr. C. Márquez-Alvarez of the Instituto de Catálisis y Petroleoquímica, CSIC, Madrid, Spain, for fruitful discussions.

References

1. Weisser O, Landa S (1973) Sulfide catalysts: their properties and applications. Pergamon Press, Oxford, p 470
2. Kiperman SL (1986) In: Cerveny L (ed) Catalytic hydrogenation. Studies in surface science and catalysis, Vol 27. Elsevier, Amsterdam, p 1
3. Zdrazil M (1988) Catal Today 3:269
4. Muller JM, Gault FG (1970) Bull Soc Chim Fran 2:416
5. Levy RB, Boudart M (1973) Science 181:547
6. Oyama ST, Haller GL (1982) Catalysis (Spec Per Repts Roy Soc Chem, Lond) 5:333
7. Oyama ST (1992) Catal Today 15:179
8. Oyama ST (1996) In: Oyama ST (ed) The chemistry of transition metal carbides and nitrides. Blackie, Academic & Professional, Glasgow, Scotland, pp 1–27
9. Volpe L, Boudart M (1985) J Solid State Chem 59:332
10. Lee JS, Oyama ST, Bourdart M (1987) J Catal 106:125
11. Liu P, Rodríguez JA (2006) J Phys Chem B 110:19418
12. Volpe L, Boudart M (1985) J Solid State Chem 59:348
13. Lee JS, Volpe L, Ribeiro FH, Boudart M (1988) J Catal 112:44
14. Kim H, Hee Lee K, Lee JS (2000) Res Chem Intermed 26:427
15. Voorhoeve RJH, Stuiver JCM (1971) J Catal 23:242–252
16. Román-Martínez MC, Díaz-Auñon JA, Argentiere PCL, Salinas-Martínez de Lecea C (2001) Catal Lett 77:41
17. Cagnola EA, Quiroga ME, Liprandi DA, Argentire PCL (2004) Appl Catal A: Gen 274:205
18. Márquez-Alvarez C, Claridge JB, York APE, Sloan J, Green MLH (1997) In: Froment GF, Delmon B, Grange P (eds) Hydrotreatment and hydrocracking of oil fractions. Elsevier Science B.V, p 485
19. Mamede AS, Giraudon J-M, Lofberg A, Leclercq L, Leclercq G (2002) Appl Catal A: Gen 227:73
20. Dhandapani B, St Clair T, Oyama ST (1998) Appl Catal A: Gen 168:219
21. Li S, Lee JS, Hyeon T, Suslick KS (1999) Appl Catal A: Gen 184:1
22. Claridge JB, York APE, Brungs AJ, Marquez-Alvarez C, Sloan J, Tsang SC, Green MLH (1998) J Catal 180:85
23. Li S, Kim WB, Lee JS (1998) Chem Mater 10:1853
24. Jung KT, Kim WB, Rhee CH, Lee JS (2004) Chem Mater 16:307–314
25. Claridge JB, York APE, Brungs AJ, Green MLH (2000) Chem Mater 12:132
26. Oshikawa K, Nagai M, Omi S (2001) J Phys Chem B 105:9124
27. Chianelli RR, Berhault G (1999) Catal Today 53:357
28. Liu P, Rodríguez JA (2004) J Chem Phys 120:5414