Modification of the surface composition of molybdenum oxynitride during hydrocarbon catalysis

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With an oxygen containing molybdenum nitride catalyst, the rate of hydrogenation of propylbenzene increases with time. This is attributed to the carburization of surface during reaction. Both surface reactivity in chemisorption and superficial chemical composition change during the activation of the catalyst.

Keywords: molybdenum; oxynitride; carburization; hydrogenation; activation

1. Introduction

In catalytic reactions of hydrocarbons on metals, the rate of reaction per unit surface area often decreases with time of reaction. The common explanation is that carbonaceous deposits block active sites as a result of side reactions. Thus, observations of the opposite effect, namely the increase of reaction rate with time, are worthy of note.

In fact, such observations prompted interest in examining carbides of transition metals of group VI as catalytic materials for reactions normally catalyzed by noble metals of groups VIII and IX. The first such observation was that 1,1,3-trimethylcyclopentane over a film of tungsten was rearranged to xylene only after an induction period explained by the formation of surface tungsten carbide [1]. Similarly, the rate of ethane hydrogenolysis over a molybdenum metal catalyst was found to increase with time as bulk Mo_2C was formed by X-ray diffraction [2]. Recently, well reduced molybdenum clusters supported on γ-Al_2O_3, prepared as described by Brenner and Burwell [3] were examined by EXAFS during the hydrogenolysis of *n*-butane [4]. The metallic clusters were transformed to carbide as soon as the reaction mixture was introduced, indicating that the active catalytic phase was Mo_2C. Moreover, Mo_2C powders catalysts have turnover rates for *n*-butane hydrogenolysis comparable to the most active noble metal catalysts of group VIII [5].

The presence of superficial oxygen on carbides and nitrides of transition metals can also have an important effect on their surface reactivity. Indeed, in 1989, Ribeiro [6] reported that addition of oxygen to a WC surface decreases drastically the rate of hydrogenolysis of *n*-hexane and promotes the isomerization of neopentane. Besides, in a study on the dehydrogenation and isomerization of methylcyclohexane on WC modified with surface oxygen, Ribeiro et al. [7] attributed to the bifunctionality of the modified surface its ability to catalyze both types of reactions. Similarly, Frennet et al. [8] have reported that the reforming of *n*-hexane on WC was, in fact, catalyzed by a tungsten oxycarbide, the activity of which was close to that of bifunctional Pt/zeolite. Ledoux et al. [9] have also shown that oxygen containing Mo_2C treated in air at 623 K for 14 h was active for *n*-hexane isomerization.

The present paper reports the substantial increase with time of the rate of hydrogenation of propylbenzene on samples of molybdenum oxynitride where oxygen and nitrogen are present simultaneously, as the surface picks up carbon and adapts to the feed composition. This result is another illustration of the interchangeability of surface carbon, oxygen nitrogen and sulfur as in the hyrodesulfurization of thiophene on Mo_2C during which the surface picks up sulfur [10].

2. Experimental

Materials

MoO_3 (Janssen 99.998%) was used as a precursor for catalysts preparation. It has an orthorhombic structure and its specific surface area is about 0.7 m^2 g^{-1}. Gases and reactants were used without prior purification: H_2 (Air Liquide, Custom grade, 99.95%), He (Air Liquide, Custom grade, 99.5%), O_2 (Air Liquide, Custom grade, 99.5%), NH_3 (Air Liquide, Custum grade, 99.5%), 1 vol% CH_4/H_2 (Air Liquide, Custom grade, 99.5%), propylbenzene (Fluka), benzene (Prolabo), and cyclohexane (Janssen) were used as reactants.

Powder X-ray diffraction (XRD)

A Siemens D500 automatic diffractometer with a Cu K_α monochromatized radiation source was used for the XRD powder patterns of the various solid phases. The identification of the different phases was made using the JCPDS for γ-Mo_2N (No. 25-1366), MoO_2 (No. 05-0452), Mo_2C cubic (No. 15-0457) and Mo_2C hexagonal (No. 11-0680).

Specific surface area measurements

A Quantachrome-Quantasorb Jr was used for the surface measurements in dynamic conditions. After a pretreatment of the molybdenum oxynitride or oxycarbonitride in flowing nitrogen at high temperature, the amount of nitrogen adsorbed and desorbed was determined by using a catharometer detector. The specific surface area was obtained from the nitrogen desorbed at different partial pressures by means of the BET method.

Chemical analysis

Elemental analysis of the solids, before and after catalysis was obtained from the Service Central d'Analyse du Centre National de la Recherche Scientifique à Vernaison (France). Oxygen, nitrogen, hydrogen and carbon amounts were determined by a combustion method and analysis of the effluent gases. Molybdenum analysis was performed by plasma emission spectroscopy.

Temperature programmed desorption (TPD) in vacuum

TPD of propylbenzene (PB) and benzene (B) pre-adsorbed on oxynitride and oxycarbonitride were performed with a quadrupolar mass spectrometer (Delsi Nermag Anagaz 200). Before adsorption, the catalysts were pretreated in flowing H_2 at atmospheric pressure and 693 K for 2 h. Adsorption of PB or B was carried out by flowing helium saturated in PB or B at room temperature. The quartz reactor was then flushed in pure helium closed by stopcocks and connected to the mass spectrometer of the TPD setting without contacting air. The temperature of the furnace was controlled with a programmable temperature controller (Setaram type TGC 85) and TPD was conducted up to 1173 K at a heating rate of 7.5 K min^{-1}. The desorbed molecules were introduced into the spectrometer via a microvalve. Mass scanning, between 1 and 50 or 200 (M/e) was carried out every 9 s. The data were saved, processed, and plotted as desorption curves for all the characteristic fragments included in the selected mass range.

Preparation method

MoO_3 powder (2 g) was placed in a quartz reactor and nitrided in pure flowing ammonia, at a volume hourly space velocity (VHSV) of about 37500 h^{-1}. The preparation followed Volpe and Boudart's work [11]: the temperature was increased in three steps, first rapidly from 290 up to 630 K (17 K min^{-1}), then more slowly from 630 up to 730 K (33 K h^{-1}) and from 730 up to 970 K (100 K h^{-1}). The temperature was held at 970 K for 3 h. The system was then cooled to room temperature (RT) in flowing NH_3, then flushed in helium for half an hour. The sample was passivated by flowing 1 vol% O_2/He to avoid bulk oxidation. As it contained substantial amounts of oxygen, possibly as a result of the passivation, it is called a *molybdenum oxynitride*.

Molybdenum oxycarbonitride was prepared following nitridation of MoO_3 with NH_3: the temperature was decreased in flowing NH_3 and a reactive mixture of 1 vol% CH_4/H_2 was used to perform the carburization. The VHSV was about 3×10^4 h^{-1}. The temperature was slowly increased up to 970 K (1 K min^{-1}) and held at this temperature for 1 h. To remove polymeric surface carbon [12], temperature was decreased to 870 K and the sample was heated in flowing H_2 for 1 h. After flushing with He for 0.5 h at RT, the sample was passivated by 1 vol% O_2/He. As it contained C, O and N, it is called *oxycarbonitride*.

Standard catalytic run

The hydrogenation of PB was performed as a gas–solid process and was carried out in a stainless steel reactor [13] at a total pressure of 50 bar (hydrogen at 41.4 bar, cyclohexane at 8.5 bar, PB at 0.06 bar) between 540 and 670 K. The catalyst was pressed, ground and sieved to yield grains between 180 and 355 μm. Hydrogen flow was controlled by a mass flow controller Brooks 5850 TR and the H_2 pressure by a pressure controller Brooks 5866 located after the reactor. Because of the needs of a companion study [3], the feed consisted of a 1 wt% solution of propylbenzene in cyclohexane. This solution was delivered, as a liquid mixture, to the flow manifold by a piston pump (Gilson model 302). To ensure complete vaporization of this liquid feed, the connecting tubes from the pump to the reactor were maintained at about 520 K. The flow rate of H_2 was 25 ml min^{-1} and liquid flow rate was 0.025 ml min^{-1} with about 0.25 g of catalyst.

The products were analyzed on-line by a gas chromatograph with a 50 m long 0.32 mm i.d. capillary column (Methyl Silicone Gum). Before each run the catalysts were pretreated under H_2 at atmospheric pressure, at 693 K, for 2 h.

3. Results

Characterization of the catalysts

By elemental chemical analysis, the composition of molybdenum oxynitride and oxycarbonitride, after synthesis and passivation, corresponds respectively to the chemical formula: $MoN_{0.7}O_{0.7}$ and $MoC_{0.27}N_{0.14}O_{0.76}$, indicating a high amount of oxygen in both cases. Furthermore, powder X-ray diffraction patterns showed that the oxynitride presented a crystal structure close to that of γ-Mo_2N but with a cubic lattice parameter $a_0 = 419$ pm, higher than that of the stoichiometric γ-Mo_2N ($a_0 = 416$ pm). This difference can be due to the presence of oxygen in the lattice. The specific surface areas of the oxynitride and oxycarbide were 110 $m^2\ g^{-1}$ and 75 $m^2\ g^{-1}$ respectively.

Propylbenzene (PB) hydrogenation on molybdenum oxynitride

Several runs were performed, successively, on the same sample, in the standard conditions previously described.

Fig. 1a (run 1a) shows the conversion of PB into propylcyclohexane (PCH) versus time of run, at 540 K. The conversion is about 80% at the start and decreases to 0% after 100 min. The thermodynamic data (fig. 1b) show that it is possible to convert PB completely to PCH at 540 K under our experimental conditions. Thus, the oxynitride of molybdenum was active at the start and lost activity rapidly.

In order to check the origin of such a loss of conversion, the initial feed was

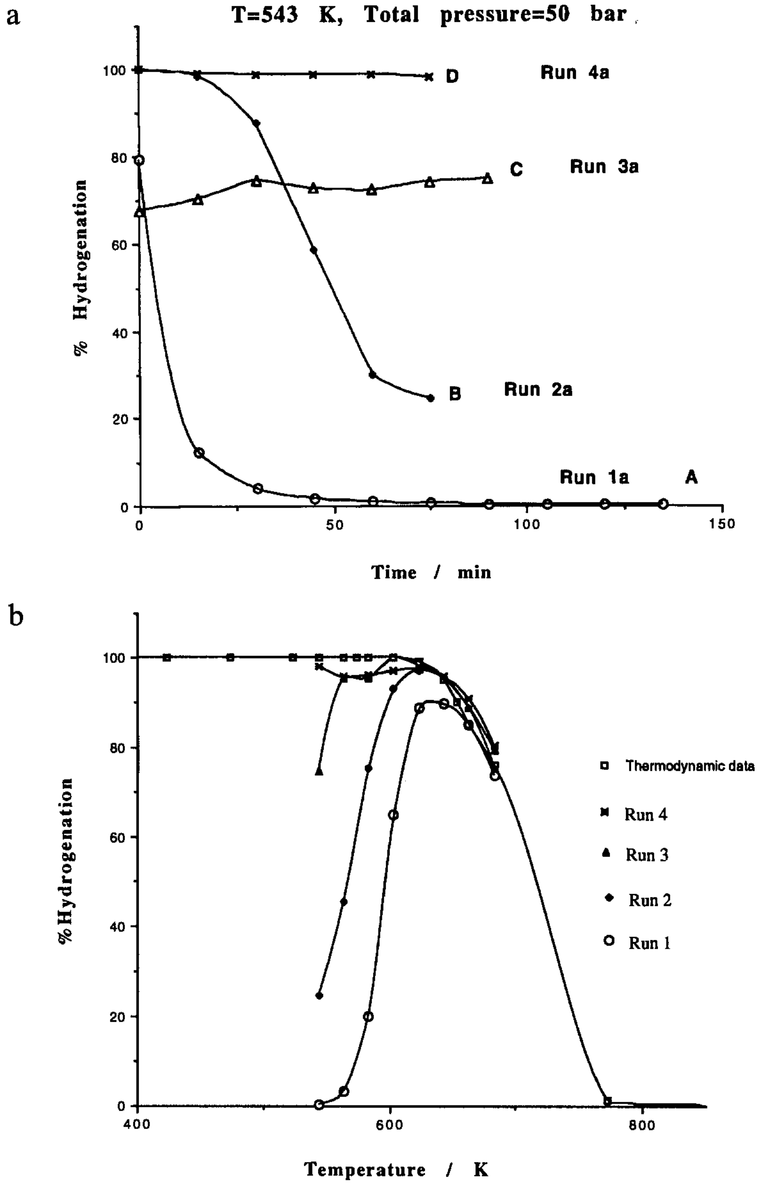

Fig. 1. Hydrogenation of propylbenzene (PB). (a) Conversion to propylcyclohexane (PCH) in successive catalytic runs, at 540 K and 50 bar, versus time of run (same sample of molybdenum oxynitride). (b) Conversion to propylcyclohexane (PCH) in successive catalytic runs, versus temperature, at 50 bar (same sample of molybdenum oxynitride). Points A, B, C, D correspond to points A, B, C, D in (a).

kept flowing in the reactor and the temperature of the catalyst was increased linearly. In fig. 1b (run 1b) the A point corresponds to the A point in fig. 1a (run 1a). Fig. 1b (run 1b) shows that the conversion increases with temperature. At about

640 K, the thermodynamic value of conversion is obtained. Above 640 K up to 680 K, the conversion decreases, following the thermodynamic values of conversion versus temperature.

The catalyst was then cooled down to 540 K in flowing pure hydrogen. At 540 K, PB was again introduced into the reactor under the standard conditions and a second run started. Fig. 1a (run 2a) shows that the conversion of PB into PCH is 100% at the start and more slowly decreases in a much less drastic way than in the case of run 1a, to attain 30% after 75 min (point B, fig. 1a). At that time, temperature was linearly increased, as seen in fig. 1b (run 2b, starting point B). The same phenomena then occurs as for run 1b, but with higher values of conversion between 540 and 600 K. The final temperature of run 2b was 680 K.

The catalyst was then cooled down again in flowing pure hydrogen to 540 K, PB was re-introduced and a third run was initiated. As can be seen in fig. 1a (run 3a) the conversion attains about 70%, without any decrease during 90 min (fig. 1a, run 3a, point C). At that time, temperature was increased (fig. 1b, run 3b, starting point C) and the conversion reached about 100% at a temperature as low as 550 K, then followed thermodynamic values from 550 to 680 K. After cooling down to 540 K in flowing pure hydrogen, and introducing PB in standard conditions, the catalyst starts at 100% and remains at that level as the run proceeds (fig. 1a, run 4a).

In order to understand such an enhancement of activity, PB hydrogenation on the molybdenum *oxycarbonitride* previously described was studied.

Propylbenzene hydrogenation over molybdenum oxycarbonitride

Conversion was already 100% in the first run at any temperature between 540 and 620 K. No change in conversion was observed even after 12 h of run at 540 K. Furthermore, conversion was close to that observed on MoN_xO_y after the fourth run, as observed above.

Reactions of cyclohexane during propylbenzene hydrogenation on molybdenum oxynitride

Dehydrogenation, isomerization and cracking of cyclohexane occurred simultaneously with PB hydrogenation. At high temperatures, above 620 K, light compounds (molecular weights less than 84), coming from the *cracking* of cyclohexane (molecular weight 84) could be observed.

In order to understand these modifications, comparative thermodesorptions of propylbenzene and benzene were made on both catalysts (oxynitride and oxycarbonitride of molybdenum) as explained in the next paragraph.

Temperature programmed desorption (TPD) of propylbenzene (PB) and benzene (B)

TPD of PB on molybdenum oxynitride (fig. 2). PB was adsorbed at room temperature on a passivated MoN_xO_y subsequently reduced in flowing H_2 at 720 K.

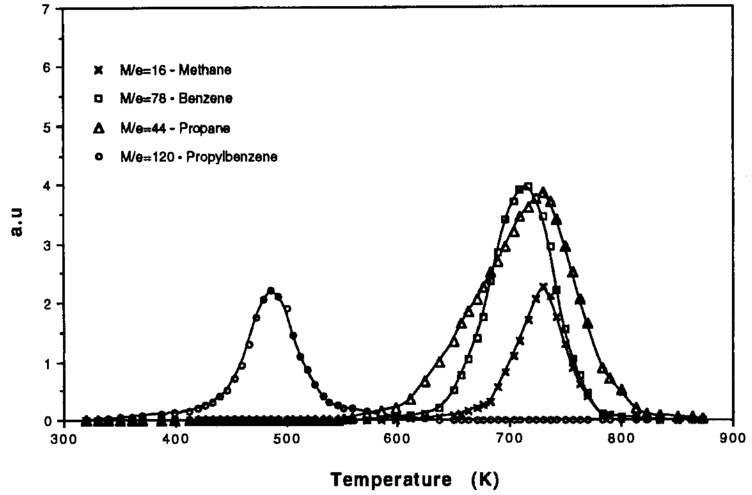

Fig. 2. Temperature programmed desorption in vacuum of propylbenzene (PB) on molybdenum oxynitride. $M/e = 120$ (PB) and $M/e = 78$ (benzene) are plotted.

PB, B, C_3H_8 and CH_4 were detected by their parent peaks ($M/e = 120, 78, 44$ and 16 respectively). Fig. 2 shows that PB desorbs at 490 K. At a higher temperature B is detected at 710 K whereas propane and methane are simultaneously observed in the same range of temperature.

TPD of B on molybdenum oxynitride. Fig. 3 shows that benzene preadsorbed at RT, desorbs at low temperature (350 K) and no other peak appears up to 710 K.

TPD of PB on molybdenum oxycarbonitride. No adsorption/desorption of PB from RT to 710 K was observed on the oxycarbonitride.

Elemental chemical analysis

Pertinent results are shown in table 1 where all values are expressed in mole per mole of Mo.

The chemical analysis of a passivated molybdenum oxynitride just after preparation shows a low percentage of carbon (table 1). The chemical composition of a

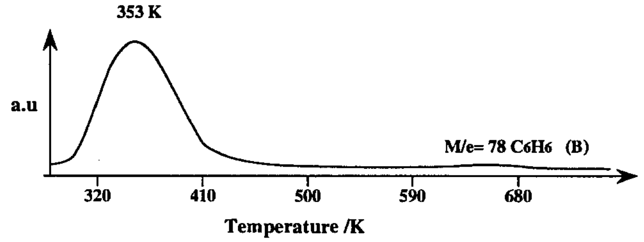

Fig. 3. Temperature programmed desorption in vacuum of benzene (B) on a molybdenum oxynitride. $M/e = 78$ (B) is reported.

Table 1
Chemical composition of catalysts (mole per mole of molybdenum). (A) MoN_xO_y passivated just after preparation. (B) MoN_xO_y passivated after 1080 h of reactions in hydrocarbons. (C) Passivated molybdenum oxycarbonitride

	N	O	C	H
A	0.75	0.69	0.03	0.55
B	0.67	0.55	0.45	0.6
C	0.13	1.13	0.29	0.6

passivated molybdenum oxynitride after reaction during 1080 h in hydrocarbons shows a higher C content (0.45%). The composition of a passivated molybdenum oxycarbonitride prepared by carburization of the corresponding oxynitride in a CH_4/H_2 mixture shows a carbon content of 0.29%. Hydrogen was also detected in the global chemical analysis of all compounds.

4. Discussion

TPD of propylbenzene (PB) and inhibition of PB hydrogenation at 540 K

Fig. 2 shows that two species of PB remain adsorbed on MoN_xO_y after preadsorption of PB at RT: the first one desorbs in vacuum at 490 K (maximum of the peak) *as PB*, and a second species desorbs *as benzene* (B) at 710 K, simultaneously with a production of propane and methane. Fig. 3 shows that no benzene species remains adsorbed above 410 K when B is preadsorbed on the oxynitride at RT. These data show that C–C bond scission occurs at 710 K for the second PB species, producing benzene and C_3H_8, and further cracking leads to CH_4 formation.

From these data, it can be assumed that during PB hydrogenation at the lower temperature of 540 K (fig. 1a, run 1a), the second PB species progressively fills the surface and inhibits the surface active sites of MoN_xO_y, leading to a zero conversion after 1 h of run. The initial 80% conversion observed in run 1a (fig. 1a) is probably due to both the hydrogen saturation of the surface of the catalyst after the previous hydrogen pretreatment before run 1a, and the filling of the catalyst bed by PB.

An increase of temperature in the conditions of standard hydrogenation (fig. 1b, run 1b) can restore the accessibility to the active sites by the disappearance of the second PB species, as suggested by the TPD experiment in vacuum when PB desorbs as B + propane (fig. 2). Therefore the surface active sites become accessible and conversion of PB to PCH increases until it reaches its thermodynamic value.

Increase of PB conversion to PCH (fig. 1a, runs 1a to 4a) is attributed to progressive carburization of the molybdenum oxynitride in feed by cracking of hydrocarbons at high temperature, modifying the chemisorptive properties of the molybdenum oxynitride. Clearly, cracking leads to beneficial carburization, not only to coke deposition that would lead to deactivation.

Indeed, blank runs on the behaviour of pure cyclohexane in H_2 at a total pressure of 50 bar and at 680 K [13] indicate that cyclohexane cracks into light hydrocarbons during PB hydrogenation. This result can be correlated to the TPD of PB which transforms into B and propane in the temperature range between 650 and 780 K (fig. 2). Moreover, table 1 shows that molybdenum oxynitride presents a high content of C after runs suggesting surface and bulk carburization of the oxynitride modified surface reactivity.

Thus, the drop in conversion of PB to PCH at 540 K, during the first run (fig. 1a, run 1a) can be due to an irreversible chemisorption of the second PB species. As this drop in conversion is less and less drastic for runs 2a to 4a (fig. 1a), it can be assumed that this second PB species is less and less formed, due to an evolution of surface reactivity. A surface (or bulky) carburization by the mixture hydrocarbons/H_2 can then be considered to occur at the higher temperature (650 to 780 K) justifying the evolution of the solid properties. The value of conversion of hydrogenation of PB on the *oxycarbonitride* of molybdenum, as well as the lack of TPD peaks of PB and B are in good agreement with the enhancement of conversion of PB to PCH over the oxynitride of molybdenum during runs 1a to 4a, due to its progressive carburization.

5. Conclusion

Chemical analysis of oxynitride or oxycarbonitride of molybdenum, TPD of propylbenzene (PB) and benzene preadsorbed at room temperature on these oxynitride and oxycarbonitride, and successive catalytic runs of propylbenzene hydrogenation, indicate that during runs in feed, the surface of the molybdenum oxynitride is chemically modified: an oxycarbonitride is formed without decrease of the specific surface area. As a consequence, sorptive properties of the oxynitride are modified and the conversion of hydrogenation of PB to propylcyclohexane increases. The starting oxynitride of molybdenum is found to pick up carbidic carbon as it adapts to the feed composition, avoiding the irreversible chemisorption of an inhibiting PB species capable of desorbing only at high temperature.

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