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Catalysis Today 65 (2001) 195–200

CATALYSIS TODAY

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Tetralin hydrogenation catalyzed by Mo_2C/Al_2O_3 and WC/Al_2O_3 in the presence of H_2S

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Abstract

Supported molybdenum and tungsten carbides were synthesized by temperature-programmed reactions. These materials were characterized by XRD, EDS analysis, HRTEM and CO chemisorption. Hydrogenation of tetralin was carried out at a total pressure of 4 MPa (3.06 MPa of H_2), at 573 K, without or with sulfur (200 ppm of sulfur as DMDS). The resulting activities were compared with those of MoS_2/Al_2O_3 and Pt (1% (w/w) metal loading) supported on Al_2O_3 or SiO_2. In the absence of sulfur, WC/Al_2O_3 showed an initial activity similar to that of Pt/SiO_2, higher than that of MoS_2/Al_2O_3 but lower than that of Pt/Al_2O_3. In the presence of H_2S, WC/Al_2O_3 showed a steady-state activity similar to that of Pt/Al_2O_3 (which suffered a marked deactivation). Post-reaction characterization did not show any sulfur poisoning of the supported carbides. Therefore the supported carbides are sulfur-tolerant and promising catalysts for the hydrogenation of aromatics in diesel fuels in the presence of small amounts of S-containing compounds. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Supported carbides; Hydrogenating function; Sulfur-resistant materials

1. Introduction

New regulations on the composition of diesel fuels in Europe and the United States of America require a reduction of the content of aromatic compounds. Common hydrogenating catalysts such as noble metals are inefficient in the presence of H_2S, always present in petroleum feedstocks. Moreover, molybdenum-based sulfides, widely used in hydrotreating, are ineffective in the presence of a low partial pressure of dihydrogen sulfide. Transition metal carbides have been shown to be as active as noble metals for various reactions. Therefore, a new kind of supported metal carbide less sensitive to sulfur poisoning and exhibiting interesting activity for aromatic hydrogenation has been proposed [1,2].

In this study, the hydrogenation of aromatics in diesel fuels was modeled by that of tetralin at 573 K, in the presence or in the absence of dihydrogen sulfide. The catalysts used were tungsten and molybdenum carbides supported on alumina. The activities were compared with that of molybdenum sulfide supported on alumina and of platinum supported on silica. Supported carbides were characterized by CO chemisorption measurements, X-ray diffraction

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PII: S0920-5861(00)00593-9

(XRD), electron microscopy (HRTEM) and energy dispersive spectroscopy (EDS).

2. Experimental

2.1. Catalyst preparation

Ammonium heptamolybdate and ammonium metatungstate were used as precursors. The support consisted of γ-alumina provided by Procatalyse. Supported molybdenum (10% (w/w) metal loading) and tungsten (18% (w/w) metal loading) materials were prepared using the incipient wetness method. The impregnated samples were dried at 393 K for 12 h. Carbides were prepared by temperature-programmed reaction (TPR), using a modification of the procedure described elsewhere [3]: after impregnation samples were dried in flowing argon, then carburized by a 20% CH_4/H_2 (v/v) mixture.

For molybdenum samples, the carbide synthesis was divided into two steps. First, the impregnated extrudates were quickly heated in flowing argon (flow rate: 60 $cm^3\,min^{-1}$) and held at 673 K for 8 h. The material was then carburized by a TPR in flowing CH_4/H_2 (total flow rate: 60 $cm^3\,min^{-1}$), the temperature being raised linearly from 673 to 950 K. At this final temperature the CH_4/H_2 flow was switched to hydrogen and the system cooled rapidly to room temperature (RT). After cooling to RT the hydrogen flow was switched to a O_2/Ar mixture (1%, v/v) for a passivation step (1 h) before characterization or catalysis experiments. A similar procedure was applied to tungsten samples. The dried materials were quickly heated in flowing argon (flow rate: 60 $cm^3\,min^{-1}$) and held at 773 K for 5 h. Carburization was then performed (temperature raised linearly from 773 to 1123 K) in flowing CH_4/H_2 (total flow rate: 83.3 $cm^3\,min^{-1}$). The samples were held at 1123 K for 3 h, and treated as described for molybdenum materials. The TPR procedures are presented in Fig. 1. The choice of a high final temperature of carburization for supported tungsten carbides is justified by the existence of two carbides, W_2C and WC [4], the alumina-supported WC requiring a higher temperature. Extrudates of supported carbides were crushed and sieved between 0.25 and 0.4 mm. These powders were used for characterization and catalysis tests.

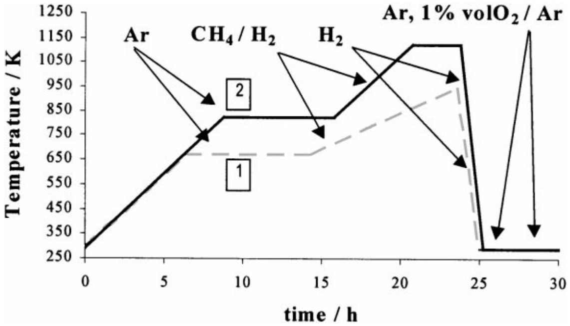

Fig. 1. TPR schedule for synthesis of supported molybdenum [1] and tungsten [2] carbides.

2.2. Characterization of catalysts

The passivated catalysts, before and after reaction, were characterized by XRD, CO chemisorption, TEM and EDS analysis. Powder XRD was carried out on a Siemens model D-500 diffractometer with Cu Kα radiation. The selective chemisorption of CO was used to titrate active metal sites before runs and was performed by a pulse technique at 293 K. The titration was carried out by passing a known volume of CO controlled by an automatic valve, through a quartz reactor containing the material (0.3 g), He being used as carrier gas. A catharometric cell detected the remaining non-adsorbed CO at the outlet of the reactor. Hence, the consumption of CO could be determined and the amount of CO chemisorbed by the sample deduced. Prior to chemisorption, the passivated Mo_2C/Al_2O_3 was reduced in flowing H_2 (12 $cm^3\,min^{-1}$) at 773 K for 4 h; WC/Al_2O_3 was pretreated similarly at 873 K for 2 h.

High-resolution transmission electron microscopy (HRTEM) was performed to determine the particle size of molybdenum and tungsten carbides supported on alumina and to check the dispersion of the supported carbides. HRTEM studies were performed on a JEOL-JEM 100 CXII apparatus associated with a top entry device and operating at 100 kV.

EDS analysis (STEM mode) was performed with the same apparatus using a LINK AN 10000 system, connected to a silicon–lithium diode detector, and multichannel analyzer. The EDS analyses were obtained from large domains of samples (150×200–$400 \times 533\,nm^2$). Chemical analysis was performed at the

"Service Central d'Analyses du CNRS" in order to determine the Mo, W and C contents for both the fresh and spent catalysts.

2.3. Hydrogenation reaction

Tetralin hydrogenation was chosen as a model reaction for the hydrogenation of aromatics in diesel fuels. The reaction was carried out at 573 K, at a total pressure of 4 MPa. Tetralin was diluted in *n*-heptane, the mixture being injected by a high-pressure pump (GILSON Pump, model 307). Partial pressures of tetralin, *n*-heptane and hydrogen were 0.01, 0.93 and 3.06 MPa, respectively. Contact times ranged from 0.2 to 0.4 s. To hydrogenate tetralin in the presence of H_2S, dimethyldisulfide (200 ppm sulfur) was added to *n*-heptane [5].

The liquid products of the reaction were collected periodically (every hour) and analyzed by gas chromatography (VARIAN) using a flame ionization detector (FID) and a capillary column (DB1, J&W Scientific). Before reaction, 0.2 g of supported carbides were pretreated in situ, at 423 K and 4 MPa in flowing hydrogen ($1\,l\,h^{-1}$) to remove the passivation layer.

Different reaction products could be obtained. Under our conditions, the only products of transformation were decalins (*trans*- and *cis*-decalin, hydrogenation products) and a small amount of naphthalene (dehydrogenation product), as already reported for supported alumina catalysts [6]. The supports (alumina or silica) were tested, no catalytic activity in tetralin hydrogenation was found.

3. Results and discussion

3.1. Characterization of fresh catalysts

As reported in Table 1, the C/M ratios of supported molybdenum and tungsten carbides are lower than the theoretical values. These unexpectedly low values suggest a strong interaction between the support and the molybdate or the tungstate [7]. In the literature, the theoretical ratio is never observed and supported carbides are never stoichiometric [8].

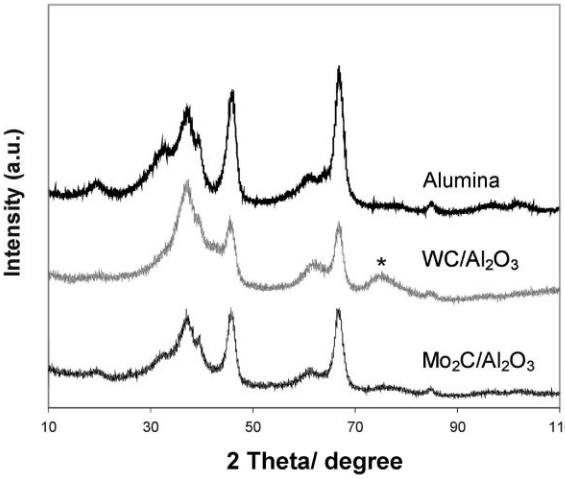

Fig. 2. XRD patterns of WC/Al_2O_3 and Mo_2C/Al_2O_3 (∗: tungsten carbide phase).

The only detectable peaks in the XRD pattern (Fig. 2) for the alumina-loaded materials were due to γ-Al_2O_3, presumably because the carbide domains were highly dispersed. However, for the supported tungsten carbide, a diffraction peak could be identified at $2\theta = 75°$. This tungsten carbide XRD line is not well defined and cannot be clearly attributed to either WC or WC_{1-x}.

EDS measurements and chemical analysis reported in Table 1 show that Mo/Al and W/Al ratios are quite constant throughout the sample ($Mo/Al = 0.07$ and $W/Al = 0.065$) indicating a homogeneous distribution of the carbides on the alumina surface. No molybdenum carbide particles were detected by HRTEM, whereas tungsten carbide particles with sizes ranging from 20 to 40 Å were detected as shown in Fig. 3. This obviously contributes to the differences previously

Table 1
Supported carbide analyses (M*: molybdenum or tungsten)

Catalysts	M*/Al ratio (EDS analysis)	M*/Al ratio (chemical analysis)	C/M* ratio (chemical analysis)
Mo_2C/Al_2O_3	0.070	0.068	0.35
WC/Al_2O_3	0.065	0.068	0.68

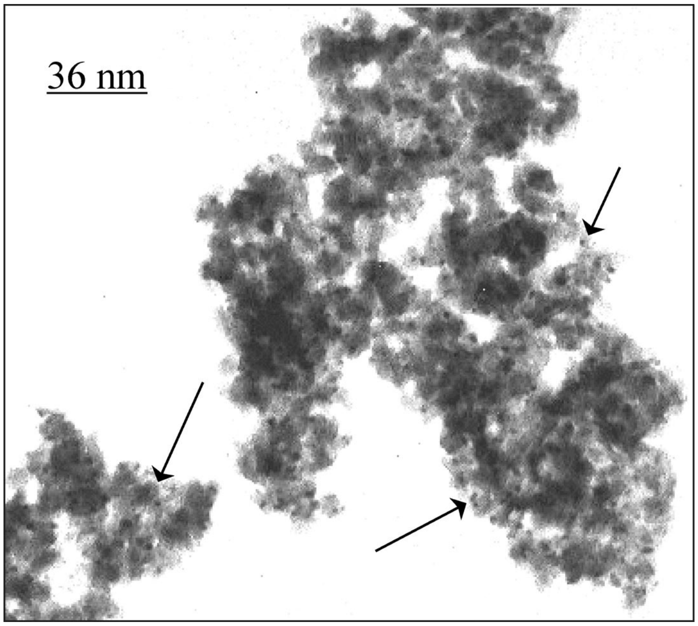

Fig. 3. HRTEM micrograph of WC/Al_2O_3.

observed in the XRD patterns of the supported carbides. However, for a 30% (w/w) Mo loading diffraction peak for crystalline Mo_2C was observed; large particles were also detected by HRTEM. These results indicate that molybdenum carbide domains on alumina were small and highly dispersed for low molybdenum loading. Increasing the loading did not have a significant effect on the activity. Furthermore, for comparison with commercial catalysts a loading of 10% (w/w) was taken.

Table 2 presents CO chemisorption data for different materials. CO chemisorption uptakes were nearly identical for all supported carbides, ranging from 40 to 41 $\mu mol\,g^{-1}$. These values allowed us to calculate that the percentage of metal exposed for the different catalysts ranges from 3.9 to 4.2%.

Table 2
CO chemisorption measurements

Samples	Pretreatment temperature (K)	CO uptake ($\mu mol\,g_{catalyst}{}^{-1}$)	% Metal exposed[a]
Mo_2C/Al_2O_3	773	40	3.9
WC/Al_2O_3	873	41	4.2

[a] % Metal exposed = CO uptake/total number of metal atoms per gram of catalyst.

3.2. Hydrogenation properties

The reactivities of WC/Al_2O_3 and Mo_2C/Al_2O_3 were tested in the absence and in the presence of H_2S. The only products of the transformation of tetralin were *cis*- and *trans*-decalins and a small amount of naphthalene. For the sake of comparison, tetralin hydrogenation was performed under the same operating conditions with three reference catalysts: molybdenum sulfide supported on alumina (10% (w/w) Mo loading) and platinum supported on alumina or silica (1% (w/w) Pt loading).

Fig. 4 shows the conversions of tetralin hydrogenation in the absence of H_2S vs. time on stream. It can be seen that the hydrogenation activity of WC/Al_2O_3 was initially similar to that of Pt/SiO_2, and then decreased with time. The deactivation of tetralin hydrogenation can be due to a too stable intermediate adsorbed on the active sites of WC (Sabatier's principle). Under our experimental conditions, Pt/Al_2O_3 presents the highest tetralin conversion. The ranking of steady-state

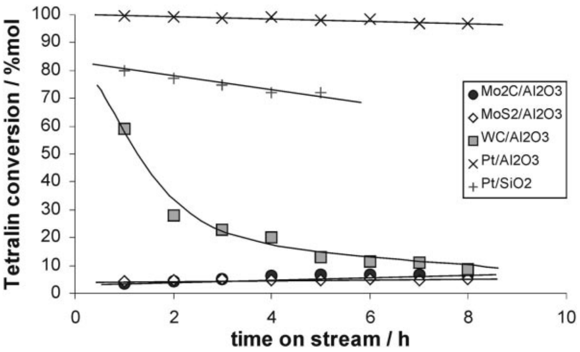

Fig. 4. Tetralin hydrogenation over supported molybdenum and tungsten carbides in the absence of H_2S.

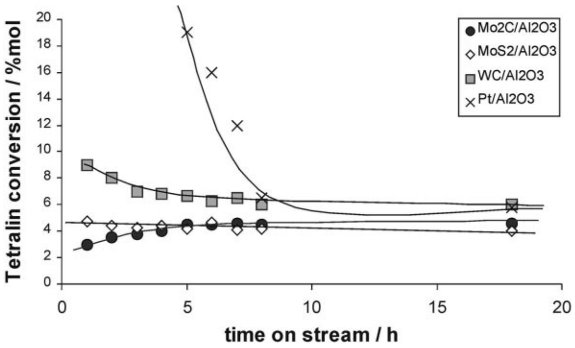

Fig. 5. Tetralin hydrogenation over supported tungsten and molybdenum carbides in the presence of H_2S.

catalyst activity for tetralin hydrogenation was found to be as follows:

$$MoS_2/Al_2O_3 < Mo_2C/Al_2O_3 < WC/Al_2O_3 < Pt/SiO_2 < Pt/Al_2O_3$$

There is no evolution of tetralin conversion after 8 h on stream, the steady state being reached. It was possible to calculate a decalin formation rate as a site time yield (STY) at the steady state (18 h). STYs were defined as the number of tetralin molecules converted to decalins per second per active site measured by CO chemisorption. Table 3 reports the tetralin hydrogenation STY for supported carbides. It can be noted that the two supported carbides exhibit nearly identical hydrogenation properties at the steady state.

The effect of H_2S was studied by adding DMDS to the feed mixture (200 ppm). Fig. 5 shows the reactivity of all selected catalysts, as observed, conversion of tetralin decreased with the addition of sulfur. The supported carbide samples were deactivated to a small extent, but Pt/Al_2O_3 suffered serious deactivation upon addition of 200 ppm of sulfur. Supported tungsten carbide exhibited the highest activity at the steady state, similar to that of Pt/Al_2O_3. At the steady state, the tetralin hydrogenation STY for supported carbides was nearly the same without and with 200 ppm of sulfur. It can be seen clearly that the supported carbides reported in this study are sulfur resistant and nearly identical to Pt/Al_2O_3 for extended periods of time.

3.3. *Post-reaction characterization*

The XRD patterns and EDS analysis of the spent supported carbides revealed no evolution of the materials. No coke formation was observed by HRTEM, confirming the possible existence of an adsorbed stable intermediate saturating the active sites, inhibiting tetralin hydrogenation and leading to the deactivation of the material. The average particle size observed and evaluated by HRTEM was increased and ranged from 30 to 50 Å on spent WC/Al_2O_3 materials. No particles

Table 3
Reactivity of carbides in tetralin hydrogenation at 573 K, total pressure: 4 MPa, with and without H_2S

Samples	Without sulfur		With 200 ppm of sulfur	
	Conversion at steady state (mol%)	STY[a] at steady state ($10^4\,s^{-1}$)	Conversion at steady state (mol%)	STY[a] at steady state ($10^4\,s^{-1}$)
Mo_2C/Al_2O_3	6.5	0.8	4.5	0.6
WC/Al_2O_3	8	1.0	6	0.8

[a] STY for tetralin hydrogenation at steady state.

of Mo_2C/Al_2O_3 were detected even after reaction. Sulfidation of molybdenum carbide to molybdenum sulfide (existence of MoS_2 slabs), in the presence of H_2S, was never observed. These data suggest that molybdenum, and tungsten-supported materials are stable and tolerant to sulfur during hydrogenation in the presence of low levels of H_2S.

4. Conclusion

Novel alumina-supported WC and Mo_2C catalysts were synthesized by TPRs and characterized by chemical analysis, XRD, EDS analysis, HRTEM and CO chemisorption. The catalysts were tested in the hydrogenation of tetralin at high pressure with or without sulfur. Platinum-supported catalyst deactivated quickly in the presence of 200 ppm sulfur in the feed, whereas the carbide-supported catalysts showed only a slight deactivation leading to a stable hydrogenation activity. Post-reaction characterization indicated that the materials did not change and hence are stable and sulfur-tolerant. It is concluded that carbide-supported materials have potential for the hydrogenation of aromatics in diesel fuels in the presence of S-containing compounds.

Acknowledgements

The help of Mrs. P. Beaunier and M. Lavergne with the STEM-EDS and TEM measurements is greatly appreciated. This work was carried out in the framework of the program “Hydrodésulfuration des Gazoles” supported by ELF, IFP, TOTAL, PROCATALYSE and CNRS-ECODEV.

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