Solid–Solid Wetting: a Simple and Effective Method for the Preparation of Molybdenum Sulphide/Alumina Catalysts

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The spreading of MoS_2 on an Al_2O_3 support under thermal treatment at 723 K in the presence of a CS_2–H_2 atmosphere results in a dispersed phase, which exhibits activity for thiophene hydrodesulphurisation comparable with a conventional catalyst.

The economic relevance of hydrodesulphurisation (HDS) makes molybdena/alumina catalysts one of the technologically most important catalyst systems being studied.[1–4] These catalysts are normally prepared by impregnation of the alumina support with an aqueous solution of $(NH_4)_6Mo_7O_{24}$ followed by drying and calcination at temperatures around 773 K. The resulting oxidic precursor of the catalyst is then transformed into the actual HDS catalyst by an *in situ* sulphiding treatment with a mixture of H_2S–H_2 or thiophene–H_2.[3,4] It is generally accepted that the dispersed MoS_2 is the actual active catalyst, with reactive sites modified in some way by the promoter atoms (Ni or Co).[3]

Xie *et al.*[5,6] first observed that heating a physical mixture of crystalline MoO_3 and γ-Al_2O_3 near 670 K led to the disappearance of the X-ray diffraction (XRD) patterns of MoO_3 and this phenomena was interpreted as monolayer dispersion of MoO_3 on the surface of Al_2O_3. Knözinger *et al.*[7–10] further demonstrated that dispersed supported molybdena/alumina catalysts can also be obtained from simple physical mixtures by the spreading of MoO_3 on the surface of an Al_2O_3 support. This spreading process was phenomenologically termed as 'solid–solid wetting' and the driving force for this phenomena was proved to be due to the decrease in surface free energy.[10] In this communication we report, for the first time, a much more simplified method of making of MoS_2/Al_2O_3 catalysts by the spreading of MoS_2 on the surface of Al_2O_3 support.

Physical mixtures of MoS_2 (Fluka, Switzerland, AR grade) and γ-Al_2O_3 (Harshaw Al-III-61, USA) were prepared by first tumbling and then grinding the powders in an agate mortar for 30 min. These mixtures were treated in different ways. A nominal quantity of 8 wt% Mo was chosen in order to obtain a single monolayer of MoS_2 on Al_2O_3 support.[4] A vertical flow Pyrex glass reactor of 8 mm internal diameter and 20 cm long was used for thermal treatments under normal atmospheric pressure conditions. In a typical experiment *ca.* 2 g of sample mixture was placed in the reactor (in between the quartz wool plugs, and the empty portion of the reactor was filled with quartz chips) and heated to 723 K (10 K min^{-1}) in a flow of purified N_2 (35 cm^3 min^{-1}). Then N_2 was replaced with a stream of H_2 (35 cm^3 min^{-1}; pretreated with Pd Deoxo and 4 Å molecular-sieve zeolite) saturated with CS_2 vapour (maintained at 298 K). After heat treatment at a final temperature of 723 K for several hours the CS_2–H_2 was replaced by N_2 and flushed for 6–8 h. The sample was then allowed to cool to room temperature in N_2 flow and preserved under N_2 atmosphere for analysis.

The impregnated catalyst was prepared by adopting the standard incipient wetness method using a stoichiometric quantity of aqueous ammonium heptamolybdate (J. T. Baker, USA, AR grade) solution. The impregnated sample was dried at 393 K for 16 h and calcined at 773 K for 12 h in an air circulation furnace.

X-Ray powder diffraction patterns were recorded on a Philips PW 1051 diffractomer using Ni-filtered Cu-Kα radiation. Oxygen chemisorption (at 195 K) and N_2 Brunauer–Emmett–Teller (BET) surface area (at 77 K) measurements were made on a conventional static volumetric high vacuum system. A double isotherm method[11] was used to calculate the amount of O_2 chemisorbed at 195 K. More details of the experimental procedure are described elsewhere.[12] Before the O_2 chemisorption measurement the thermally treated MoS_2/Al_2O_3 catalyst sample (transferred to the chemisorption cell with minimum exposure to air) was evacuated (10^{-6} Torr) for several hours. The impregnated MoO_3/Al_2O_3 catalyst was presulphided *in situ* with a mixture of thiophene–H_2 at 673 K for 6 h before oxygen chemisorption and activity measurements. Catalytic tests were carried out in a previously described[13] flow microreactor system interfaced to a gas chromatograph by a six-way gas sampling valve and operating under normal atmospheric pressure. Thiophene conversion was kept within a 10% level and the rates were measured under steady-state conditions in the absence of any diffusional effects.

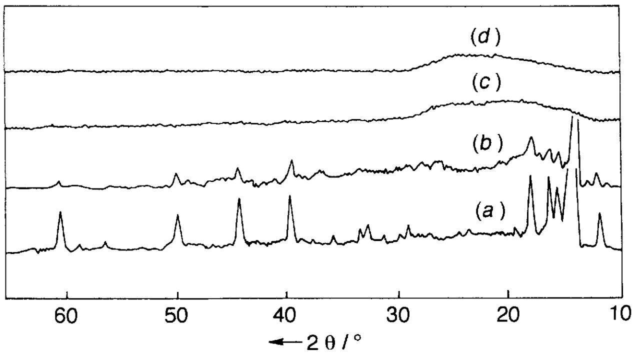

Fig. 1 X-Ray diffraction patterns of MoS_2/Al_2O_3 catalysts: (*a*) MoS_2 + Al_2O_3 physical mixture (PM); (*b*) thermally treated PM in CS_2–H_2 for 8 h; (*c*) thermally treated PM in CS_2–H_2 for 18 h; (*d*) conventionally impregnated and presulphided in thiophene–H_2

XRD patterns of MoS_2 + Al_2O_3 physical mixtures and thermally treated mixtures under CS_2–H_2 gas atmosphere are shown in Fig. 1. The XRD profile of the conventionally impregnated Mo/Al_2O_3 catalyst presulphided with a mixture of thiophene–H_2 is also shown in Fig. 1 for comparison. In the case of simple physical mixtures, characteristic XRD lines due to the crystalline MoS_2 phase[14] can be seen. Upon thermal treatment at 723 K for 8 h in CS_2–H_2 a rapid decline in the intensity of MoS_2 lines was observed. A total disappearance of the XRD lines due to crystalline MoS_2 phase can be seen on further treatment of the sample for 18 h. The XRD pattern of this sample is very similar to the one obtained for the conventionally impregnated sample. It is generally known that the conventionally impregnated Mo/Al_2O_3 catalyst (8 wt% Mo) upon presulphiding gives an XRD pattern without the presence of any crystalline material.[4,15] Thus, the present XRD results give an indication of spreading (highly dispersed state) of MoS_2 on Al_2O_3 surface under thermal treatments. The commercial MoS_2 sample used in this study also contains a small quantity of Mo_2S_3, whose XRD lines[14] are also observed and disappeared upon subsequent thermal treatments in CS_2–H_2 mixture.

Oxygen uptake, BET surface area, equivalent MoS_2 surface area (EMA), apparent MoS_2 surface coverage and thiophene HDS rate are shown in Table 1. An increase in O_2 uptake from 3.2 μmol g^{-1} catalyst to 43.6 μmol g^{-1} upon thermal treatment of physical mixtures at 723 K in the presence of CS_2–H_2 gas atmosphere can be noted. Interestingly, the maximum O_2 uptake observed on the 18 h treated mixture sample is close to the value obtained on the conventionally impregnated sample. The numerical values of EMA and MoS_2 surface coverages are also the same within experimental error both for the conventionally impregnated sample (equivalent to literature data[15]) and the solid–solid wetting sample. Another interesting point to note from Table 1 is the observation of similar thiophene HDS rates on both the samples. In fact, the solid–solid wetting sample appears to show better catalytic performance than the

Table 1 O_2 uptake, BET surface area, MoS_2 surface coverage and HDS rate on various MoS_2/Al_2O_3 catalysts

Sample	O_2 uptake /μmol g^{-1} cat.	BET area /m^2g^{-1}	EMA[b] /m^2g^{-1}	MoS_2 coverage (θ)[c]	HDS activity $10^3\gamma_{HDS}$ /mol g^{-1} cat. h^{-1}
MoS_2/Al_2O_3 (PM)[a]	3.2	151	3.8	0.03	1.1
MoS_2/Al_2O_3 (8 h)	18.2	142	31.5	0.22	6.2
MoS_2/Al_2O_3 (18 h)	43.6	128	75.4	0.59	15.1
MoS_2/Al_2O_3 (Impr.)	42.1	131	72.8	0.56	14.8

[a] MoS_2 + Al_2O_3 physical mixture; N_2 BET SA of Al_2O_3 is 175 m^2g^{-1} and MoS_2 is 4.1 m^2g^{-1}. [b] Equivalent MoS_2 (surface) area determined from inverse site density for unsupported MoS_2 (ref. 15) of 1.73 m^2 μmol^{-1} O_2. [c] Apparent MoS_2 surface coverage or dispersion = EMA/BET area (refs. 11 and 15).

equivalent impregnated sample. Thus, the combined O_2 uptake, BET SA, XRD and HDS activity data from this study provide a reasonably consistent picture regarding the similarities in the dispersion and morphology of the MoS_2/Al_2O_3 catalysts obtained *via* two different routes. Most interestingly, the impregnated and thermally spread material both develop identical HDS activities and O_2 chemisorption capacities.

Thus, the method of solid–solid wetting appears to be a promising one towards the preparation of highly dispersed MoS_2/Al_2O_3 catalysts.

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