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Synthesis and characterization of mechanically activated bulky molybdenum sulphide catalysts

Synthèse et caractérisation de catalyseurs massifs à base de disulfure de molybdène par activation mécanique

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ABSTRACT

Bulky catalysts on the basis of MoS_2 nano-crystallites have been obtained for the first time from commercial molybdenite in one-step synthesis using mechanical-chemical treatment with small additives of polar liquids. Physical and chemical properties of the synthesized catalysts were studied using sedimentation analysis, XRD, XPS, TEM and thermal analysis. The catalytic activity of the catalysts was examined in the course of dibenzothiophene hydrodesulphurization followed by the GC–MS analysis of the reaction products. Correlations between the catalytic activity and the methanol quantity added in the course of mechanical-chemical activation were established. The pathways of dibenzothiophene hydrodesulfurization reactions over the synthesized catalysts were proposed.

Mots-cles:
Activation mécanique
Disulfure de molybdène
Catalyseurs massifs
Hydrodésulfuration
Microadditifs de solvant polaires

RÉSUMÉ

Pour la première fois, des catalyseurs massiques à base de nano-crystallites MoS_2 ont été synthétisés à partir de molybdénite commerciale par activation mécanique en phase solide en une étape. Des liquides polaires ont été aussi additionnés en petites quantités comme adjuvants. Les propriétés physicochimiques des catalyseurs synthétisés ont été caractérisées par analyses par sédimentation, radiocristallographique et thermique, ainsi que par microscopie électronique à transmission et spectroscopie photoélectronique par rayons X. Les activités des catalyseurs dans une réaction modèle d'hydrogénolyse du dibenzothiophène ont été mesurées par analyse GC–MS. La corrélation entre l'activité catalytique et la quantité de methanol ajoutée au cours de l'activation mécano-chimique a

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été déterminée et discutée. Des hypothèses ont été émises sur les chemins réactionnels de l'hydrogénolyse des dibenzothiophènes à l'aide des catalyseurs synthétisés.

1. Introduction

Currently, nano-sized molybdenum disulphide attracts vivid attention as a catalyst in hydrotreatment, as well as a photosensitive element in light-electric solar transducers and optronic devices [1]. Various methods for obtaining highly dispersed MoS_2 powders were reported [2–7]. Highly dispersed MoS_2 in a form of nano-sized spheres or tube-like structures can be formed in the course of hydrothermal synthesis from ammonium heptamolybdate ($[NH_4]_6Mo_7O_{24}\cdot 4H_2O$), elemental sulphur and lithium hydroxide in pyridine in the presence of ammonium carbonate and hydrazine hydrate [3]. Recently developed methods for self-spreading high-temperature synthesis of MoS_2 from electroblasted nano-powder mixtures of molybdenum and elemental sulphur [4] and mechanical-chemical Mo sulphidation [5] are very attractive. Mechanical grinding of MoS_2 synthesized by various methods using liquid dispersion media (heptane, butanol, ethanol, etc.) is a widely used method. Compared to solid-phase mechanical activation (MA), the solvent provides MoS_2 nano-particles' stability in suspensions. For example, coarse MoS_2 powders formed at the stage of thermal decomposition of ammonium tetrathiomolybdate (ATTM) [2] are subsequently subjected to mechanical grinding in ethanol. In this paper, the shortcomings of nano-crystalline MoS_2 are discussed, as well as its activity variations in reactions of hydrogenation, alkene isomerization and deuterium exchange dependent on ATTM decomposition conditions. The experimental results most relevant to the present research concerning synthesis and application of mechanically activated MoS_2 nano-particles were reported in [6–7]. The authors prepared the final product by milling commercial MoS_2 bulky particles in a specially designed mill in butanol. The obtained MoS_2 had a high concentration of defects, and did not concede to commercially available supported catalysts in its catalytic activity in dibenzothiophene hydrodesulfurization (DBT HDS) and hydrotreating of heavy oil fractions. In spite of the advance made in these studies, the authors of the present article failed to find later publications on the subject.

It is commonly known that the MoS_2 slab consists of S-M-S layers linked by weak Van der Waals bonds. Various components intercalated into the Van der Waals gap between the layers essentially affect the physical and chemical properties of the material. Thus, potassium intercalation into MoS_2 is favourable for the use of the material as an active component of the catalyst for the conversion of syngas to higher alcohols and other oxygenates used as additives to motor fuels and precursors in petrochemical synthesis [8]. Those catalysts are resistant to poisoning by an ultra-low sulphur content in crudes in contrast to conventional ZnCr and ZnCu catalytic systems.

One of the effective ways to split a multilayer MoS_2 slab into monolayer structures is lithium intercalation followed by exfoliation of $LiMoS_2$ layers in water. The formed monolayers with a thickness of about 0.6 nm are stacked up to nano-sized particles by centrifugation [9]. These nano-particles showed essential catalytic activity not only in reactions of naphthalene hydrogenation and hydrogenolysis of DBT and quinolone, but also in hydrotreatment of heavy oils and bitumen [10]. The ultra low concentration of the MoS_2 nano-particles in the reaction zone limits their commercial usage. Any manipulation aiming to convert nano-particles to nano-powders causes particle agglomeration and decreases catalytic activity.

The methods of solid intercalation or exfoliation of MoS_2 nano-slabs under mechanical-chemical activation conditions were not reported in the literature and even a possibility to realize these processes has not been discussed yet.

The objective of current communication is to report the recent experimental results regarding the effects of the conditions of mechanical-chemical activation of both macrocrystalline MoS_2 and its composition with micro-additives of methanol on the structural properties of nano-crystallites and their activity in DBT HDS.

2. Experimental

2.1. Catalyst preparation

Catalysts were prepared from commercial coarse powder of molybdenum disulphide (MoS_2, fine grade, DMI-7). The content of the main substance (MoS_2) is 99.72%, and the content of the fraction below 7 μm is as high as 99.00%. MoS_2 was subjected to mechanical activation (MA) in an inert atmosphere of argon in a vertical vibratory mill at a powder-to-ball weight ratio of 1:60, frequency 16 Hz, and amplitude 2 mm. Small additives of polar liquids, CH_3OH and H_2O, were added to MoS_2 in amounts of 100 and 200 μL, and 100 μL per 3 g of molybdenite, respectively. The weight ratios of the reagents in MoS_2:CH_3OH and MoS_2:H_2O were = 38:1 and 18:1, respectively. Durations of MA were 1.5, 3.0, 5.0, and 8.0 h for 100 μL of methanol, and 5, 8, 12, and 16 h for 200 μL of methanol, while 100 μL of water were mechanically activated for 8.0 h. The activated samples were stored in a dry container filled with argon.

The following notations of the catalysts in the text are used: the asterisk in $^*MoS_2 + 100\ CH_3OH(8)$ denotes the mechanically activated sample, and $100\,CH_3OH(8)$ means the addition of 100 μL of methanol to MoS_2 in the course of mechanical co-activation for 8 h.