Characterization The High Dispersion Molybdenum Oxide On Silica Surface Using XRD Technique

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Abstract

The X-ray powder diffraction method is thus ideally suited for characterization and identification of polycrystalline phases. The main use of powder diffraction is to identify components in a sample by a search/match procedure.

Silica (SiO_2) supported molybena (MoO_3) catalysts at loading varying between 3 and 6 wt% were prepared by impregnating support silica (SiO_2) with an aqueous solution at different acidity levels (pH = 2, 4 and 6) of ammonium hepta molybdate. After stirring for 3 h, the excess water was slowly evaporated at 100°C. Moreover, the impregnated supports were further dried at 120°C for 24 h. The products thus obtained were calcined at 700 °C for 2 h in static atmosphere of air. X-ray powder diffractogram (XRD) for support (SiO_2), supported (MoO_3) and different loading levels (3, 4, 5 and 6 wt% MoO_3/SiO_2) catalysts at different PH`s were investigated.

The results clearly revealed that the formation of highly dispersed MoO_3 phase on the SiO_2 surface at a loading levels of 3 wt%, at pH = 2, for 4 wt%, at pH = 4 and 5 wt%, at pH = 6. This indicts that, a weaker dispersion of MoO_3 on SiO_2 surface at low pH. Given that, at low pH = 2 the formation of MoO_3 phase crystallites was observed at 2 wt%. Whereas, at high pH = 6 the form of MoO_3 crystallites was observed at 6 wt%. These results can be reorganized on the basis of the different surface chemical properties of the oxide support and nature of oxide supported.

Keywords: *Dispersion, SiO_2, MoO_3, pH, XRD.*

1. Introduction

All basic XRD applications start with making an appropriate scan [1]. Even if for quantitative analysis only a measurement on a single or a few peaks would be necessary, setting up the analysis requires a complete scan to be made. There are a number of parameters that need attention, these are: Scan range, step size, time per step or total scan time and slit sizes. To choose the right parameters information is needed from a preliminary scan. This scan can be fast, but gives already much information about the sample and while the real scan is being made analysis can already be started [1, 2].

In X-ray diffraction analysis a lot of different samples are measured in various application fields. These samples can vary from largely bulky samples to samples of even less than one milligram, solid samples, odd shaped samples, plates, sheets, filters and even slurries or fluids. The final quality of an analysis depends on the quality of the data (measurements and other knowledge) obtained. The quality of the measured data depends on the choice, preparation method and handling of the sample [2, 3].

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The samples in their turn should be a good representation of the analytical problem, although in some cases the sample itself poses the analytical problem.

In gAeneral it can be stated that the sample preparation and handling determines for more than 50 % the final quality, hence it is the most important part of the analysis [3].

According, to above consideration, X-ray diffraction analysis can be used for detect lower and high dispersion of supported material. Many of these materials have been described as so-called monolayer catalysts [4]. They are typical prepared by impregnation or mechanical mixed of the support oxide with an appropriate salt from aqueous solution. Obviously, the initial interaction of the parent species with the support at the solid/solution interface will be critically controlled by the surface chemical properties of the support [5-8]. Strong interfacial interactions lead to specifically adsorbed species that form stable surface complexes upon drying [6]. Whereas, a high temperature treatment may lead to chemical transformation resulting in materials containing molecularly dispersed oxide species [6]. Consequently, a simple though used advance toward estimating the dispersion of supported oxide at least qualitatively, is X-ray diffraction analysis.

A factor that may be expected to be essential in determining the structure of the supported material is the acidity (pH) of the impregnating solution. This is can be affects in both the suport surface acidity and the nature of the supported species in solution. Other parameters such as the loading level of the active component, the nature and concentration of promoters will be of important. However, there is still considerable scope for the determination of the physicochemical properties, and of such parameters as activity, selectivity and regneration of the system [9]. Whereas, stable surface compounds may thus be formed [10], such as e.g. surface poly-anions or spinals, in which the activity and selectivity can be determined [11].

High dispersed molybdenum oxide supported on SiO_2 surface catalyst represents a class of catalysts of industrial interest. For instance, MoO_3 /SiO_2 catalyst have been used in trans-esterification of dimethyl oxalate with phenol to form biphenyl oxalate [12] and trans-esterification of diphenyl carbonate for the production of polycarbonate by polymerization process [13-15]. In addition, MoO_3 /SiO_2 catalyst have been used for hydro-desulfurization [16–18], oxidative dehydrogenation [19-21] and in selective oxidation of hydrocarbons reactions [22].

The present work differs from previous studies on the preparation and properties of filled monolayer. Hence, this study concering about of different loading levels and surface acidity for dispersion of MoO_3 on SiO_2 surface. The monolayer was prepared by a method of solvent assisted spreading (impregnation method). The adsorption of molybdate species on SiO_2 from the slurry ammonium hepta molybdate.

In the present work I will attempts to use the useful and easily accessible information by using X-ray diffraction to characterize the high dispersion of MoO_3 supported on SiO_2 surface.

2. Experimental and Technique

2. 1. Catalyst Preparation

Silica (SiO_2) was used as support material, obtained from BDH product (99%). Whereas, highly pure (99.9%) ammonium hepta molybdate (AHM) ($(NH_4)_6Mo_7O_{24}$. 4 H_2O) was used as supported material, obtained from BDH product. AHM used for the preparation of unsupported molybdenum oxide (MoO_3) which calcined at 700 °C for 2 h as well as the make up of the impregnating solutions.

The support material (SiO_2) was impregnated with aqueous solutions of AHM at pH = 2, 4 and 6 to yield final materials containing (3, 4, 5 and 6 wt%) MoO_3 catalysts. The pH of the solution was modified to a values of 4 and 6 by the addition of ammonium hydroxide. After stirring for 3 h, the excess water was slowly evaporated at 100°C. Prior to calcination, the impregnated supports were further dried at 120°C for 24 h. The product thus obtained was manually ground in an agate mortar and calcined at 700 °C for 2 h in static air. The calcination temperature was chosen on basis of thermal analysis results for AHM. For convenience, the calcined supported samples are referred to in the text as **x%** MoO_3/ SiO_2 pH= **y**, where **x** is the loading level and **y** is value of pH.

2. 2. Apparatus and technique

2.2.1. X-ray diffractometry (XRD)

X-ray powder diffraction were recorded using a Model PW/1710 Philips diffractometer monochromatic, Ni-filtered, Cuk_α radiation (λ = 1.54056 Å) and operated at (40 kV, 35 mA) was employed. The diffractometer was operated with 2° diverging and receiving slits at a scan rate of 2°/min and a continuous intensity trace was recorded as a function of 2θ. The diffraction patterns, derived as relative intensity (I/I^o) versus 2θ were compared, for identification purposes, with the relevant ASTM and JCPDS [Joint Committee on Powder Diffraction standards) [23, 24].

3. Results and Discussion

In our previous paper [25] we discussed the effects of acidity and loading level on the properties of MoO_3 supported on alumina. These studies give this interest to find the highest percent dispersion of supported catalyst over support surface material. Moreover, we concluded that, the highly dispersion of supported depend on the preparative and pretreatment conditions, as well as the nature of support material, and the acidity medium of the impregnating solution. Also, the solution of AHM enable to form of MoO_4^{2-} monomers in high pH solution, as in the case of 12% MoO_3/Al_2O_3 at pH=11. Whereas, the solution of ammonium hepta molybdate enables the formation of a variety of polymeric species at low pH solution, as in the case of 12% MoO_3/Al_2O_3 at pH = 9. In this paper I will make a compression between the effects of acidity for the dispersion of MoO_3 on SiO_2 and Al_2O_3.

3.1 X-ray Diffraction

The previous study for the TG curve [25] of pure ammonium hepta molybdate, $(NH_4)_6Mo_7O_{24}.4H_2O$ obtained at a heating rate of $10^oC\ min^{-1}$ under a dynamic atmosphere of air, confirmed that (MoO_3) formed at temperature higher than 500^oC according to the equation:

$$(NH_4)_6Mo_7O_{24}.\ 4\ H_2O \rightarrow 7MoO_3+6NH_3+7H_2O$$

Accordingly, I chose 700 ^{o}C for the calcinations temperature for the samples under investigation.

In this study, X-ray diffraction will be use to identify the effects of surface acidity for the high loading level dispersion of MoO_3 on SiO_2 surface. Additionally, establish the appropriate loading level (%) for the formation of monolayer and fully dispersion of MoO_3 on SiO_2 surface.

The XRD pattern (Fig.1) for the calcined ammonium hepta molybdate, $(NH_4)_6Mo_7O_{24}.4H_2O$ at 700°C show lines matching very well those assigned to crystalline, orthorhombic MoO_3 (JCPDS No. 05-0508) [23, 24]. Figure 1, also shows the powder diagram of SiO_2 display lines matching well those assigned to crystalline SiO_2 (JCPDS No.11-695) [23, 24].

The powder diagrams of MoO_3 dispersed on SiO_2 catalysts at pH = 2 for different loading levels (3–6%) are shown in Fig.1. X-ray diffractogram for 3% MoO_3/SiO_2 at pH=2 confirmed that no separate molybedena phase existed on that sample. In contrast, 4% MoO_3/ SiO_2 displayed the similar pattern of pure SiO_2 with some significant minor changes due to the formation of MoO_3 phase. These minor changes are manifested by the newly emerged weak diffraction, which for the convenience are cross labeled. This indicates that the formation of MoO_3 like phase is formed.

At higher loading level of 5, 6 % MoO_3/SiO_2 at pH=2, bulk phase of MoO_3 can be easily formed. This indication may reveal that, 4% MoO_3/SiO_2 is suffer to form more than monolayer on SiO_2 surface, at acidity (pH=2). While, at less than 4% MoO_3/SiO_2 is properly to form monolayer and fully dispersion of MoO_3 on SiO_2 surface at pH=2.

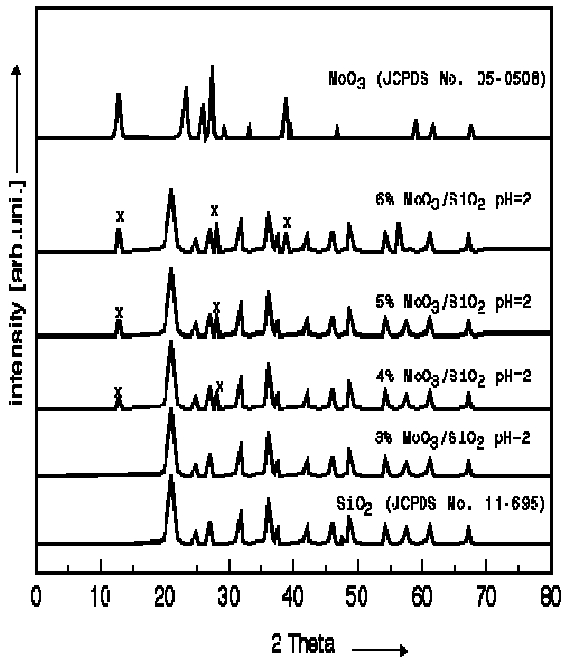

Fig.1. X-ray diffractograms of the calcinations products of AHM at 700 °C for 2h dispersed on SiO_2 surface at pH= 2.

Fig. 2, shows X-ray diffractograms for (3–6%) MoO_3/SiO_2 at pH=4. The X-ray diffractogram for 3 and 4% MoO_3/SiO_2 at pH=4 definite that no separate molybedena or poly-molybdate phase initiate on the surface of these samples. Whereas, up on increasing the loading level up to 5% MoO_3/SiO_2 the poly-molybdate in a bulky form (MoO_3) can be detected. This confirms that a separate molybedena phase existed on that sample.

X-ray analyses (Fig.2) shows more molybedena phase (cross labeled) when the loading level increased up to 6% MoO_3/SiO_2 at pH=4. This indicates that 5% MoO_3/SiO_2 suffer to form high dispersion of MoO_3 on SiO_2 surface at pH=4.

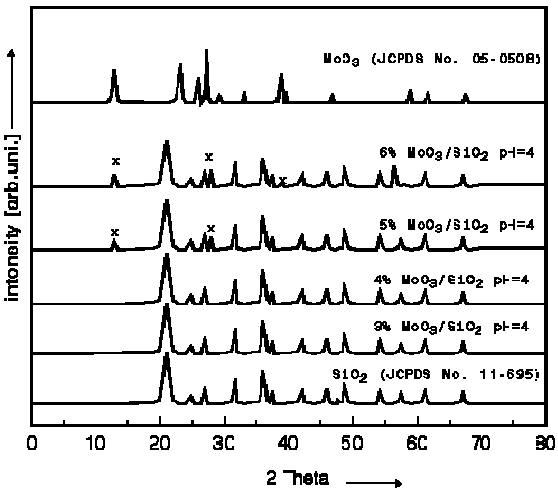

Fig. 2. X-ray diffractograms of the calcination products of AHM at 700°C for 2h dispersed on SiO_2 surface at pH= 4.

The X-ray diffractograms of different loading levels (3-6%) MoO_3/SiO_2 samples prepared at pH = 6 are shown in Fig. 3. The X-ray diffractograms for 3,4 % MoO_3/Al_2O_3 displays the same characteristic peaks of the support SiO_2. Also, the pattern for 5% MoO_3/SiO_2 exhibit the same pattern of support SiO_2, and no MoO_3 bulk phase any other features could be seen in the pattern. Whereas, the X-ray diffractograms pattern for 6% MoO_3/SiO_2 at pH = 6 catalyst shows some considerable changes. These changes due to the newly emerged weak diffractions due to the formation of MoO_3 bulk phase (cross-labeled).

Accordingly, to the above interpretation the polymeric form of MoO_3 on SiO_2 surface can be formed at each of the loading levels of 4% MoO_3/SiO_2 at pH = 2, for 5% MoO_3/SiO_2 at pH = 4 and 6% MoO_3/SiO_2 at pH = 6. This indicates that the high dispersion of MoO_3 on SiO_2 surface is effected by the acidity of the support surface and the nature of the molybdenum species in solution.

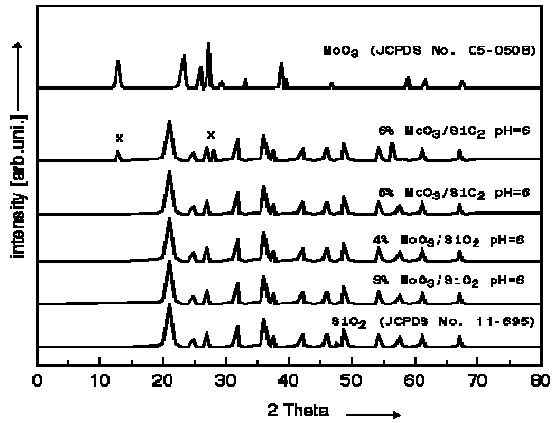

Fig. 3. X-ray diffractograms of the calcination products of AHM at 700°C for 2h dispersed on SiO_2 surface at pH= 6.

As a comparison, the previous results [25] show that the high dispersion of MoO_3 on Al_2O_3 surface at pH=6 was less than 8 wt%. Where at pH = 9, was less than 12 wt%, and at pH=11 less than 16 wt%. Whereas, in this study the high dispersion of MoO_3 on SiO_2 surface at pH=2 was less than 4 wt%. Where at pH = 4, was less than 5 wt%, and at pH=6 less than 6 wt%. This indicates that, the solution acidity of AHM with SiO_2 is completely different from the solution acidity of Al_2O_3. In case, of Al_2O_3 the high dispersion of MoO_3 needs more pH than in case of dispersion of MoO_3 on SiO_2 surface. For instance, the high dispersion of MoO_3 on SiO_2 surface appear to be at pH=6 in this study. Whereas, the high dispersion of MoO_3 on Al_2O_3 surface appear to be at pH=11 in this the pervious study. Accordingly, the high dispersion of MoO_3 on Al_2O_3 surface needs high pH medium than the high dispersion of MoO_3 on SiO_2 (low pH).

4. Conclusion

The present investigation indicates that:

1- X-ray diffraction can provide qualitative information on the dispersion of molybdena on the silica surface.

2- The poor dispersion of molybdena on silica surface at 3% MoO_3/SiO_2 at pH = 2.

3- High dispersion of molybdena on silica surface at 4% MoO_3/SiO_2 at pH = 4. Whereas, at 6% MoO_3/SiO_2 at pH = 6 small MoO_3 crystallites was observed.

4- The monolayer formation appear to be largely depending on the acidity and the high reactivity of the support surface toward the oxide species.

5- A maximum dispersion of molybdena on silica surface was shown by 6% MoO_3/SiO_2 at pH = 6.

6- The solution of AHM in the presence of SiO_2 enable to form of MoO_4^{2-} monomers in high pH solution, as in the case of 6% MoO_3/SiO_2at pH = 6. Whereas, the solution of ammonium hepta molybdate enables the formation of a polymeric species at low pH solution, as in the case of 4% MoO_3/SiO_2 at pH = 2.

7- A maximum dispersion of molybdena on alumina surface was shown by 12% MoO_3/Al_2O_3 at pH = 11.

توصيف الانتشار العالي لأكسيد الموليبدنيوم على سطح السيلكا بإستخدام حيود الاشعة السينية

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الملخص العربي

تتعلق هذه الورقة بدراسة تاثير الاس الهيدروجيني علي انتشار أكسيد الموليبدنيوم (موليبدنا) على سطح اكسيد السليكون (SiO_2). وتم اختيار أكسيد الموليدنيوم كمادة مدعومة ذات النشاط الحفزي العالي واكسيد السليكون كمادة داعمة وهي مادة ذات نشاط حفزي منخفض.

تم تحضير العينات بطريقة التشرب التي تعتمد على إضافة محلول المادة المحفزة (سباعي موليبدات الأمونيوم) المتشربة الي المادة الداعمة , ثم غسل وترشح المحلول لإزالة المحلول الزائد من الكبريتات $(SO_4)^{-2}$ وتجفيف المادة عند 120^0م وتكليس المادة عند 700 ^{0}م. وكذا تم استخدام سباعي موليبدات الأمونيوم للحصول على أكسيد الموليبدنيوم (MoO_3) وقد تم التأكد من نواتج الكلسنة لكل التحضيرات وكذلك معرفة التركيب البنائي والخواص التركيبية للعينات والمجموعات الوظيفية للعينات المحضرة باستخدام حيود الأشعة السينية (XRD).

من خلال هذه الدراسة تم الحصول على معلومات عن مدى أنتشار الموليبدنا على سطح السليكا باستخدام تقنية حيود الأشعة السينية (XRD) وهي ظهور أنتشار قليل للموليبدنا على سطح السليكا وذلك لضعف التفاعل المتبادل بينهما, كما يتبين من ظهور منحنيات لاكسيد الموليبدنيوم عند ($3\%\ MoO_3/\ SiO_2$) وأس هيدروجينى =2 وظهور ايضا أنتشار للموليبدنا على سطح السليكا عند ($4\%\ MoO_3/\ SiO_2$) وأس هيدروجينى =4 , وأنتشار اكبر للموليبدنا على سطح السليكا عند ($6\%\ MoO_3/SiO_2$) وأس هيدروجينى =6 , كما تكونت طبقة أحادية (أنتشار متجانس) من الموليبدنا على سطح السليكا معتمد على الحامضية السطحية والنشاطية لسطح المادة الداعمة(SiO_4) , وظهور اعلى أنتشار للموليبدنا على سطح السليكا للعينة ($6\%MoO_3/SiO_2$) عند أس هيدروجينى=6 , كما تكونت جزيئات منفردة من (MoO_4^{2-}) فى محلول سباعى موليبدات الامونيوم عند أس هيدروجينى عالى, كما تبين فى العينة ($6\%MoO_3/SiO_2$) عند أس هيدروجينى =6 , بينما يتكون عديد جزيئات (MoO_4^{2-}) عند أس هيدروجينى منخفض , كما تبين فى العينة ($4\%MoO_3/\ SiO_2$) عند أس هيدروجينى = 2 , كما ان أعلى انتشار من لجزيئات اكسيد الموليبدنيوم على سطح اكسيد الالومنيوم لوحظ عند تحضير نسبة 12% لاكسيد الموليبدنيوم مع اكسيد الالومنيوم ($12\%\ MoO_3/Al_2O_3$) وأس هيدروجينى =11.

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