

CHARACTERIZATION OF TITANIA AND ZIRCONIA SUPPORTED MOLYBDENUM OXIDE
CATALYSTS BY LOW TEMPERATURE OXYGEN CHEMISORPTION

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Low temperature oxygen chemisorption (LTOC) has been applied to characterize a series of TiO_2 and ZrO_2 supported Mo-oxide catalysts. The monolayer coverage of the surface is completed when the Mo loading reaches 6% and 4% on the TiO_2 and ZrO_2 supports, respectively. The results are explained with the help of a "Patch" model of the Mo-oxide phase.

Низкотемпературная хемосорбция кислорода использовалась для характеристики серии Мо-окисных катализаторов на TiO_2 и ZrO_2 носителях. Монослойное покрытие поверхности завершается когда содержание Мо на TiO_2 и ZrO_2 носителях достигает 6% и 4%, соответственно. Результаты объясняют на основе модели "Patch" Мо-окисной фазы.

INTRODUCTION

Supported molybdenum oxide catalysts are used in many reaction systems, such as hydrodesulfurization, coal liquefaction, hydrogenation, polymerization, partial oxidation and disproportionation of olefins. The most efficient utilization of any supported catalyst depends on the dispersity of the active component on the surface of the support. This dispersity is often controlled, among other factors, by the extent of loading and the nature of the support. Although much research activity has been devoted towards understanding surface structure of Mo-oxide phase on alumina support [1-3], similar studies on other supports like titania and zirconia are scarce. Pursuant to our earlier low temperature oxygen chemisorption studies on Mo/Al_2O_3 catalysts [4,5], an investigation has been made with the Mo/TiO_2 and Mo/ZrO_2 systems by this technique in order to gain some information on the surface structure of the Mo-oxide phase and its dispersity on the two

different supports.

EXPERIMENTAL

The supported Mo-oxide catalysts were prepared by an incipient wetting technique: an appropriate amount of ammonium heptamolybdate (spectroscopic grade, Baker) calculated to yield the desired percentage of the Mo on the support, was dissolved in a predetermined volume of distilled water. The ammonium heptamolybdate solution was added to the support, well mixed for 30 min and then allowed to stand for 1 h. The impregnated samples thus obtained were dried at 120°C for 16 h and then calcined in air for 12 h at 540°C. The titania support used was the commercial Harshaw titania (S.A. 161 m²/g; P.V. 0.36 cm³/g). The ZrO₂ support was prepared by precipitating Zr-hydroxide from ZrOCl₂.8H₂O by dilute ammonia solution. The zirconium hydroxide precipitate was freed from chloride ions, dried at 120°C for 24 h and finally calcined at 540°C for 4 h in air.

A conventional static high vacuum (up to 10⁻⁶ Torr) system, with the facility for reducing the samples in situ by flowing hydrogen (30 cm³/min) was applied for low temperature oxygen chemisorption, which was performed at -78°C by following the procedure of Parekh and Weller [2]. The same apparatus was used to measure the BET surface areas of the catalysts by N₂ (0.162 nm²) adsorption at -196°C. The details of the experimental set-up and the chemisorption procedure have been given elsewhere [6].

The x-ray diffractograms were recorded on a Philips PW 1051 diffractometer by using Ni-filtered CuK_α radiation.

RESULTS AND DISCUSSION

The oxygen uptake values as a function of catalyst composition are presented in Figure 1. The oxygen uptake per gram of catalyst increases as a function of Mo loading up to a certain level (about 5% on TiO₂ and about 3.5% on ZrO₂) and then levels off. This saturation level indicates the completion of a monolayer coverage of the active support surface by Mo-oxide. The monolayer composition corresponds to about 9 μmol Mo m⁻² and 13 μmol Mo m⁻² on TiO₂ and ZrO₂ support surfaces, respectively. These values are more than about twice as high as the corresponding value for Mo/Al₂O₃ catalysts [4]. The maximum oxygen uptakes by the Mo/TiO₂ and Mo/ZrO₂ catalysts are found to be about 1 μmol m⁻² and 3 μmol m⁻² as compared with about 0.3 μmol m⁻² for

Mo/Al₂O₃ catalysts. These results therefore indicate that Mo-oxide is dispersed better on ZrO₂ than on TiO₂ and on Al₂O₃.

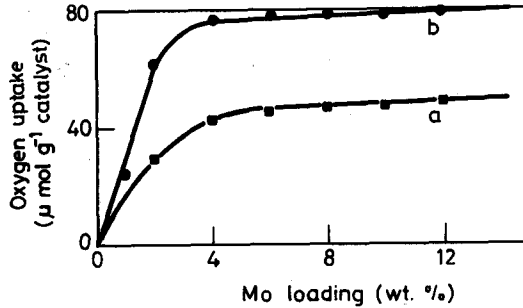


Fig. 1. Oxygen uptake at -78°C as a function of Mo loading. (a) TiO₂ (b) ZrO₂. All the data are corrected for the contributions by the support

The equivalent molybdenum area (EMA), derived from oxygen uptake, and BET surface areas of the reduced catalysts are given in Table 1. It is also evident that the EMA values also increase up to monolayer coverage and then level off with the Mo-loading. It is to be expected since, the EMA values are only derived from oxygen chemisorption data. The decrease in BET surface areas with molybdenum loading also indicates a monolayer formation following arguments presented by Weller [7] for Mo/Al₂O₃ catalysts.

Based on the 'Patch' model of Hall [3] the nature of oxygen chemisorption of Mo/Al₂O₃ catalysts has recently been discussed by Nag [8]. Under the tenet of this model we propose that a similar mechanism operates in the present Mo/TiO₂ and Mo/ZrO₂ systems, and the results can be explained with the help of the same concept. At lower Mo loadings small patches of Mo-oxide, two-layer thick are formed on the support surface. Upon reduction coordinatively unsaturated sites (CUS) are generated by the removal of oxygen from the edge and corner sites of the patches. These are the sites upon which oxygen chemisorption takes place. As the Mo-loading increases the number of these patches increases with attendant increase in the number of CUS up to the monolayer level. Beyond the monolayer level these patches grow three dimensionally, thus decreasing the dispersity of Mo-oxide, as shown in Table 1. This growth in size of the small patches, rather than in number is expected.

Table 1

O₂ Chemisorption Results on Reduced Mo/TiO₂ and Mo/ZrO₂

Catalyst ^a	Mo loading (wt.% Mo)	Oxygen uptake ($\mu\text{mol g}^{-1}\text{cat.}$)	BET Surface (m^2/g)	EMA ^b (m^2/g)	D ^c
MT-1	2	30.3	56.8	9.25	29.07
MT-2	4	42.8	55.6	13.06	20.53
MT-3	6	46.4	55.7	14.14	18.84
MT-4	8	46.8	51.4	14.28	11.22
MT-5	10	47.7	49.8	14.55	9.15
MT-6	12	48.2	49.1	14.69	7.71
MZ-1	1	24.5	30.3	7.48	47.01
MZ-2	2	62.0	29.0	18.90	59.47
MZ-3	4	77.2	28.3	23.53	37.04
MZ-4	6	78.1	27.3	23.80	24.98
MZ-5	8	78.1	25.1	23.80	18.73
MZ-6	10	78.5	24.0	23.94	15.06
MZ-7	12	80.8	24.7	24.62	12.92

- MT-1 to MT-6 are TiO₂ supported catalyst and MZ-1 to MZ-7 are ZrO₂ supported catalysts.
- Equivalent molybdene area, obtained by multiplying the oxygen uptake value (ml STP/g) by the factor $13.6 \text{ m}^2/\text{cm}^3$
- Percentage dispersity: is the ratio of number of chemisorbed 'O' atoms to the total number of Mo atoms multiplied by 100

not to add new CUS per unit Mo as a function of Mo loading. It is also worth mentioning here that indeed XRD lines of reduced Mo-oxide were detectable only with samples containing Mo-oxide greater than the monolayer level.

The following conclusions can be derived from this study: (1) as in the case of Mo/Al₂O₃ system, the CUS on highly dispersed Mo-oxide on ZrO₂ and TiO₂ can be titrated by LTOC; (2) LTOC data can precisely determine the

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Mo level where the formation of monolayer attains completion and (3) Mo-oxide is dispersed better on ZrO_2 support than on TiO_2 and Al_2O_3 .

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