

# Mesoporous titania supported-molybdenum catalysts: The formation of a new mesophase and use in ethanol–oxygen catalytic reactions

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## Abstract

With the aid of dodecylamine as a mesostructure-directing agent, novel catalysts consisting of Mo supported on mesoporous titania were synthesized by the direct co-condensation of the alkoxides (Mo–meso TiO<sub>2</sub>) or by the post-modification technique (Mo/meso TiO<sub>2</sub>). We investigated the phases of the support titania, the local structure of Mo as well as the ethanol–oxygen reaction on these catalysts. Calcination at 673 K induced a new mesophase in both catalysts, with a larger pore size (3.2–4.6 nm) than was originally presented (2.0–2.1 nm). This phase is not similar to any mesoporous titania ever reported previously. X-ray diffraction and Raman spectroscopy revealed that the phase transitions that occur at 573 K and 673 K in Mo/meso TiO<sub>2</sub> are from the amorphous to rutile and from the rutile to anatase phases, respectively. Changes from the rutile to the anatase phase with increasing temperature have rarely been observed before. In contrast, it was shown that Mo–meso TiO<sub>2</sub> is transformed from the amorphous to the anatase phase at 573 K, and that the size of the crystallites increased at 673 K. The intensity of pre-edge peak of the Mo K-edge was measured in vacuum and in air. These mesoporous titania-supported Mo catalysts in the newly-observed mesophase were then used to the catalyst for ethanol–oxygen reactions. Although acetaldehyde was almost exclusively formed on a 4.0 wt.% Mo/P-25 catalyst (which agrees with the result in the literature) ethylene was selectively formed on 3.9 wt.% Mo–meso TiO<sub>2</sub> and on 4.0 wt.% Mo/meso TiO<sub>2</sub>.

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## 1. Introduction

Transition metal-substituted mesoporous silica molecular sieves are currently of interest as catalysts for the oxidation of a variety of compounds [1,2]. Their uniform mesopore channels, which vary from 2 to 10 nm, and large surface area, usually more than 800 m<sup>2</sup> g<sup>-1</sup>, are advantageous characteristics for catalyst supports because the mesopores can accommodate molecules of various sizes, and a high dispersion of chemically active species can easily be achieved. Since supported molybdenum catalysts have been studied for the metathesis of olefins [3–6], the selective oxidation of hydrocarbons [7–10], the oxidative dehydrogenation of alcohols [11,12] and mixed alcohol formation in CO

hydrogenation [13], a number of recent studies have been devoted to the synthesis and characterization of Mo-substituted mesoporous silicas, such as MCM-41 [12–21], MCM-48 [22,23], FSM-16 [24], SBA-1 [25] and SBA-15 [26].

Mesoporous transition metal oxides have been investigated much less frequently than mesoporous silicas for use as catalyst support materials. Considering that the effects of support materials has been a widely disputed issue in the chemistry of solid catalysis, it is important that we investigate the properties of mesoporous transition metal oxides when they are used as catalyst supports. The specific catalytic properties of supported molybdena catalysts can be attributed to the coordination environment of the Mo species, as well as to the nature of oxide support, which strongly influences the structure of molybdenum species [27–36]. However, it is more difficult to synthesize mesoporous transition metal oxides with an ordered

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mesostructure and a high surface area than to prepare mesoporous silicas.

Mesoporous titania has been successfully prepared using a primary amine template [37,38] in which the BET surface area can exceed  $1200 \text{ m}^2 \text{ g}^{-1}$  and the uniform pore channels vary from 2.3 to 3.4 nm. The bulk phase of titania is inevitably amorphous [38] and approximately 37% of the titanium atoms are fivefold coordinated [39]. These features have been found in neither the rutile nor the anatase phases, which are composed of sixfold coordinated Ti. Such an anomalous valence of Ti will provide a unique coordination environment for catalytic active species. XANES and ESR studies of vanadium-substituted mesoporous titania have showed abnormal stability of tetravalent V and a high activity when used for catalytic oxidation [40]. Since the catalysis of molybdenum oxide is also sensitive to the valence and coordination of the Mo ions, mesoporous titania could possibly exhibit extraordinary properties as a support material for molybdenum catalysts [38].

It has been demonstrated that amorphous titania, in which the surface area is extremely extended, is changed into the anatase phase by heating at 673 K in air. This transition is accompanied by a drastic decrease in the surface area down to  $\approx 200 \text{ m}^2 \text{ g}^{-1}$  [38]. It is well known that mesoporous anatase-titania with a surface area of around  $100\text{--}200 \text{ m}^2 \text{ g}^{-1}$  can be prepared by templating with a triblock copolymer. This type of mesoporous titania appears to be a coagulation of anatase particles, and most of its characteristics as a catalyst support can be explained by the known properties of anatase. However, to the best of our knowledge, there has been no studies on the structure and catalytic properties of anatase-titania originating from mesoporous amorphous titania. Another important point to be investigated is to evaluate how different from conventional non-porous titania supports the catalytic properties of this thermally induced mesoporous anatase actually are.

In this paper, we have prepared mesoporous titania-supported molybdenum catalysts, heated them to induce the phase transition from amorphous to anatase and found the formation of a new mesoporous phase. The structures of the molybdenum(VI) ions that are incorporated into the support oxide are explored by Mo K-edge XANES spectroscopy. The catalytic performances of these catalysts for ethanol dehydrogenation/dehydration reactions are investigated. The catalysts were prepared either by direct incorporation or by post-synthetic impregnation, and the experimental results are compared with those of molybdenum oxide supported on non-porous titania.

## 2. Experimental section

### 2.1. Chemicals

Dodecylamine  $\text{C}_{12}\text{H}_{25}\text{NH}_2$  (reagent grade Tokyo Kasei Kogyo Co., Ltd.), titanium tetraisopropoxide  $\text{Ti}(\text{O}^i\text{Pr})_4$  (Chameleon Reagent, >99%), molybdenum pentaethoxide  $\text{Mo}(\text{OC}_2\text{H}_5)_5$  (Aldrich, >98%) and *p*-toluenesulphonic acid

(Tokyo Kasei Kogyo Co., Ltd., >99%) were commercially available. These reagents were used as-received, without further purification. A conventional titania support, P-25 was also used. Its composition is  $\text{TiO}_2 > 99.5\%$ ,  $\text{Al}_2\text{O}_3 < 0.3\%$ ,  $\text{SiO}_2 < 0.2\%$ ,  $\text{Fe}_2\text{O}_3 < 0.01$ ,  $\text{Cl} < 0.3\%$  and heavy metals  $< 5 \text{ ppm}$ . The average particle size is  $\approx 21 \text{ nm}$ , the specific surface area is  $50 \pm 15 \text{ m}^2 \text{ g}^{-1}$  and the isoelectric point is  $\text{pH} = 6.6$ . The bulk phase is mainly anatase.

### 2.2. Synthesis of Mo-meso $\text{TiO}_2$ by direct incorporation

A typical procedure is as follows. Forty grams of water was added slowly to a mixture of titanium tetraisopropoxide (8.0 g), molybdenum pentaethoxide (0.301 g for  $\text{Ti}/\text{Mo} = 30$ , 0.904 g for  $\text{Ti}/\text{Mo} = 10$ ) and dodecylamine (2.6 g) at 273 K. After the addition of 0.1 M HCl ( $1.6 \text{ cm}^3$ ), the mixture was allowed to stand overnight and transferred to a Teflon bottle in an oven at 333 K. After 4 d, the solution was filtered and washed with methanol and diethyl ether. The white solid was collected and dried in an oven at 373 K for 1 d, before being transferred into a Pyrex test tube, which was evacuated at 453 K using a vacuum pump. After evacuation for 2 h, the tube was sealed by heating. The dehydration and co-condensation of the alkoxides of titanium and molybdenum were completed by heating the powder in the tube at 453 K for 10 d. The resulting solid was denoted as “thermally treated.” This solid was treated with *p*-toluenesulphonic acid to extract dodecylamine. The powder was then dried at 473 K for 2 h and calcined at 573 K or 673 K for 2 h. No nitrogen (<0.05%) was detected by elemental analysis after the template extraction. The loadings of molybdenum in thermally treated and extracted Mo-mesoporous  $\text{TiO}_2$  (denoted as Mo-meso  $\text{TiO}_2$ ) were determined by ICP analysis. These were found to be 3.9 and 9.8 wt.% (loading based on the weight of  $\text{MoO}_3$  in catalyst) for  $\text{Ti}/\text{Mo} = 30$  and 10, respectively.

Pure mesoporous titania was obtained if no molybdenum pentaethoxide was added into the starting mixture.

### 2.3. Preparation of Molmeso $\text{TiO}_2$ and MolP-25 impregnation catalysts

Pure mesoporous titania prepared by the method described above was impregnated with a 2-propanol solution of molybdenum pentaethoxide. After standing overnight, the mixture was dried, (and, at the same time, decomposed and oxidized) at 473 K for 2 h and then calcined at 573 K or 673 K for 2 h. In addition to this Mo/mesoporous  $\text{TiO}_2$  catalyst (denoted as Mo/meso  $\text{TiO}_2$ ), a conventional non-porous impregnation catalyst was prepared with a P-25 support by the same procedure.

### 2.4. Characterization

The X-ray diffraction (XRD) patterns of the catalysts were recorded using an XL Labo diffractometer (MAC Science Co., Ltd.) with  $\text{CuK}_\alpha$  radiation. The nitrogen

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