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Ti-Si CATALYSTS FOR THE LIQUID-PHASE OXIDATION OF ORGANIC COMPOUNDS WITH MOLECULAR OXYGEN

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Abstract:*The transformation of organic compounds into oxygen-containing products such as epoxides, alcohols, ketones, and carboxylic acids is a key process in the production of both bulk and fine chemicals. In this work, titanium-incorporated mesoporous silica (Ti-MCM-41) catalysts were prepared using a direct hydrothermal synthesis approach and investigated for their efficiency in liquid-phase oxidation reactions employing environmentally friendly oxidants, particularly molecular oxygen. The effects of important synthesis variables, including titanium loading, surfactant-to-silicon ratio, and template removal conditions, on the structural and catalytic properties of the materials were systematically studied. A range of characterization methods was applied to analyze the physicochemical features of the catalysts, with special attention given to the coordination state of Ti (IV) species within the silica framework. The findings indicate that both the dispersion and the local environment of titanium centers significantly influence catalytic performance, including activity, selectivity, and stability. The synthesized materials demonstrated effective catalytic behavior in selective oxidation reactions, reflecting the advantages of combining homogeneous and heterogeneous catalytic features through isolated active sites. Overall, this study advances the development of efficient and sustainable catalytic systems for liquid-phase oxidation and provides valuable insights into the rational design of single-site catalysts based on mesoporous structures.*
Keywords:*Ti-MCM-41, mesoporous silica, titanium-incorporated catalysts, hydrothermal synthesis, liquid-phase oxidation, molecular oxygen, selective oxidation, heterogeneous catalysis.*

İNTRODUCTION

Organic compounds with oxygen-such as epoxides, sulfoxides, alcohols, ketones, quinones, and carboxylic acids—play a crucial role as products and intermediates in the synthesis processes of both bulk and fine organic materials [1]. In today's chemical industry, around 25% of key chemical products are produced through catalytic oxidation processes, and the proportion of these processes is steadily rising [2]. Approximately 50% of these processes occur in the liquid phase, where soluble transition metal salts are mainly utilized as catalysts [3].

Catalytic techniques for producing oxygen-containing compounds using eco-friendly oxidants, such as molecular oxygen and hydrogen peroxide, are of significant interest [4]. A significant challenge in contemporary liquid-phase oxidation catalysis is creating solid-phase catalysts that integrate the benefits of homogeneous and heterogeneous catalysis while demonstrating elevated activity, selectivity, and stability in reaction conditions [5,6]. Methods for addressing this issue have arisen at the boundary between homogeneous and heterogeneous catalysis, reflected in the idea of "single-site catalysis". This idea suggests that a perfect catalyst must be composed of structurally and compositionally uniform, well-distributed, and separate active sites that are securely attached to the surface of a solid substrate.

This study focuses on creating efficient catalytic systems for the selective oxidation of organic compounds in the liquid phase utilizing environmentally friendly oxidants, and on clarifying the fundamental catalytic mechanisms involved. The primary aim of the study is to create novel, highly effective, selective, and stable catalytic systems for the oxidation of organic substances in the liquid phase with molecular oxygen present. In this context, the development of environmentally friendly and economically sustainable oxidation processes has been recognized as a major priority [6].

Mesostructured silicates have been researched since the early 1990s and are noted for their well-ordered structures [7]. Their formations are generally created via hydrothermal synthesis that include inorganic precursors and surfactants [. When the surfactant is eliminated—through either calcination or extraction—consistent mesopores at the nanometer scale are formed within the substance [8]. Mesoporous metal silicates in the mesophase, especially titanosilicates, are typically produced through this hydrothermal method, in which a gel made of a silica precursor, a structure-directing agent, and a transition metal source undergoes crystallization. This procedure takes place at high temperatures (25–200 °C) and under greater pressure [9].

In this research, MCM-41 catalysts containing Ti were synthesized using a direct hydrothermal method and then examined through different characterization techniques. The impact of essential synthesis parameters—including titanium loading, surfactant-to-silicon ratio, and the heat treatment for template removal—on the materials' physicochemical characteristics and catalytic performance was systematically examined [10,11, 12]. Special focus was placed on the local coordination environment of Ti (IV) species incorporated in the mesoporous silica matrix, as this offers valuable insights into the characteristics of the active sites and is essential for appropriately understanding the structural attributes and catalytic efficiency of Ti-MCM-41 materials [13].

EXPERİMENTAL PART

Hydrothermal synthesis is a well-established method for producing Ti-MCM-41 with ordered mesostructured and well-dispersed titanium active sites. It provides strong control over material formation but also presents certain limitations.

On the positive side, this method facilitates the development of highly ordered mesoporous frameworks through controlled self-assembly processes. It also promotes the uniform incorporation of titanium species into the silica network, leading to the formation of isolated Ti (IV) sites that are highly active in oxidation reactions. In addition, synthesis parameters such as temperature, pH, reaction time, and composition can be finely adjusted, allowing tailored control over pore structure, surface area, and metal dispersion. The resulting materials generally possess large surface areas and narrow pore size distributions, which enhance catalytic accessibility.

However, hydrothermal synthesis also has several drawbacks. It typically requires elevated temperatures and autogenous pressure, making the process energy-intensive and dependent on specialized equipment. The synthesis duration is often long, as sufficient time is needed for proper crystallization and framework formation. At higher titanium concentrations, maintaining uniform dispersion becomes difficult, and extra-framework TiO_2 species may form, negativelyi affecting catalytic efficiency. Moreover, the subsequent calcination step needed to remove the template can sometimes compromise structural stability if not carefully optimized. Lastly, scaling up this method for industrial applications can be challenging due to cost, reproducibility, and process

complexity.

Synthesis: Mesoporous materials containing titanium (Ti-MCM-41) were synthesized through a hydrothermal method. Tetraethyl orthosilicate (TEOS) served as the silica precursor, while titanium isopropoxide (TIP) acted as the titanium precursor. The catalysts were derived from a gel with molar ratios of Si/Ti = 10–500, surfactant/Si = 0.20–1.00, and H_2O/Si = 60.

In a standard process, TEOS and TIP were initially combined thoroughly for 30 minutes. Subsequently, a 25 wt% ethanol solution were gradually added while stirring for 3 hours. Subsequently, the leftover TEAOH and water were incorporated, and the blend was heated to 80 °C for 30 minutes to eliminate the ethanol generated during hydrolysis. The gel produced had a pH of 11.5.

The gel prepared was placed into a stainless-steel autoclave lined with Teflon and left to age at 100 °C for 7 days. The solid obtained was subsequently filtered, rinsed, and dried overnight at 60 °C, resulting in the synthesis of Ti-MCM-41. A solely siliceous MCM-41 sample was also created under identical conditions for comparison.

To remove the template, the materials underwent a temperature-programmed process, heated at 2 °C/min to 500 °C and held for 6 hours, followed by calcination in airflow (5 mL/min) for the same temperature and time.

The materials underwent analysis through powder X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), and UV–vis diffuse spectro. The titanium levels in the solid samples were assessed using inductively coupled plasma emission spectroscopy (ICP).

The BET technique was utilized for calculating surface area, while the BJH model was employed for analyzing pore size distribution. FT-IR spectra were recorded in the 3500–500 cm^{-1} range using spectrometer. FT-IR spectra of self-supported Ti-MCM-41 samples (~8 mg/cm^2) were also obtained to verify the existence of Si–OH groups. Samples were positioned in a heating cell fitted with CaF_2 windows and linked to a vacuum system prior to analysis.

RESULTS AND DISCUSSION

1. X-ray diffraction

X-ray diffraction (XRD) is essential for assessing the thermal and hydrothermal stability of mesostructured titanosilicates. Common diffraction patterns of materials like Ti-MCM-41, Ti-HMS, Ti-MMM, which feature hexagonal or layered configurations, exhibit a prominent (100) reflection along with subdued (110), (200), and (210) peaks. These reflections suggest the existence of a structured hexagonal pore arrangement, with the unit cell parameter represented as $a_0=2d_{100}/\sqrt{3}$. In systematically arranged mesoporous structures, this factor typically stays consistent.

In highly ordered structures, the diffraction peaks appear quite sharp, exhibiting a full width at half maximum (FWHM) of roughly 0.07–0.09° 2θ, near the limits of instrumental resolution. Among the materials examined, Ti-MMM generally exhibits a greater level of structural ordering than Ti-MCM-41. This is evident in the sharper and more symmetrical peaks with FWHM values between 0.08–0.18° 2θ.

Reported data suggest that Ti-MCM-41 displays a wider (100) reflection (0.40–0.70° 2θ), whereas Ti-HMS presents an even broader peak around 0.50° 2θ. Moreover, Ti-HMS typically shows weak (110), (200), and (210) reflections, indicating a framework with lower order.It is known that the lattice parameter of ordered titanosilicates like TS-1, Ti-ZSM-48, Ti-MCM-41, and Ti-HMS rises in proportion to titanium content until

reaching approximately 2–2.5%. This trend is linked to isomorphic substitution, where Si is replaced by Ti in the framework; the larger ionic radius of titanium causes the lattice to expand. With increased titanium loading, this expansion effect lessens, suggesting the presence of additional-framework titanium species.

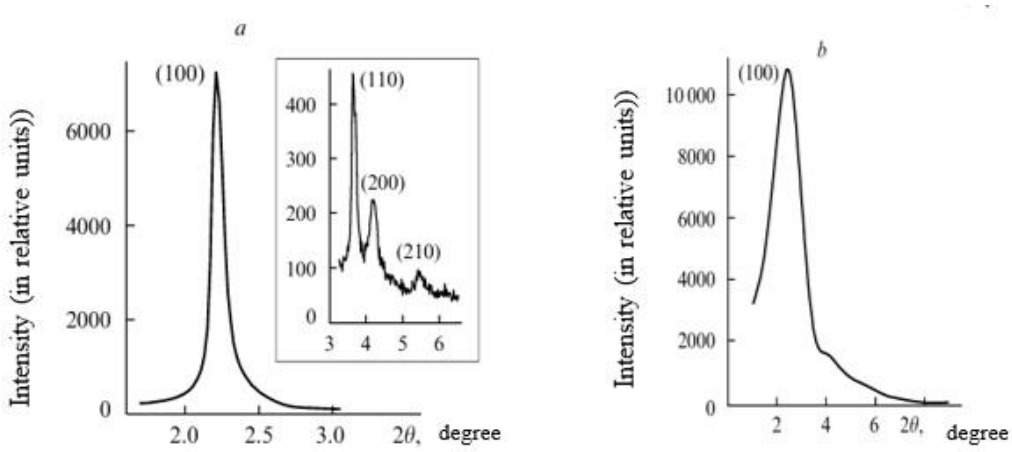

Fig. 1. X-ray difraction (XRD) results: Ti-MMM, b: Ti-MCM-41

2. Nitrogen adsorption at low temperatures

Textural properties like specific surface area pore volume and average pore diameter of titanosilicates were assessed via low-temperature nitrogen adsorption (77 K).

The reported total pore volume and surface area for Ti-HMS and Ti-MCM-41 are about 1.11 $cm^3\ g^{-1}$ and 0.03 $cm^3\ g^{-1}$.

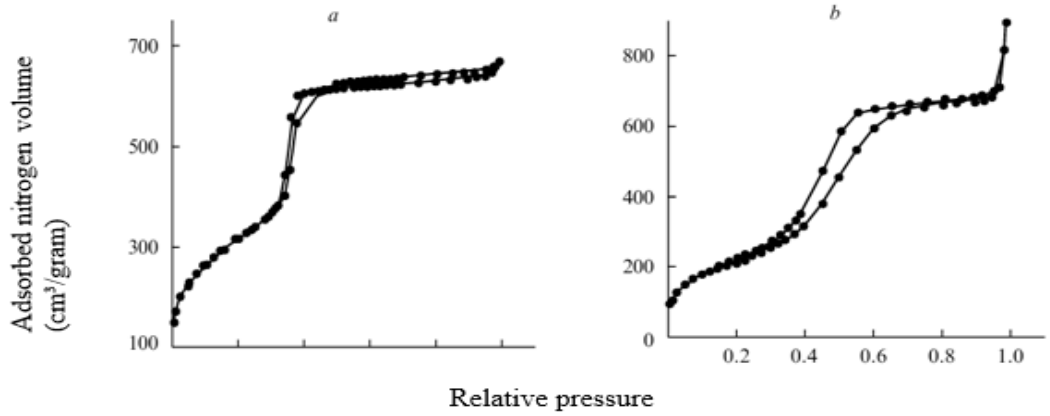

Fig. 2. Nitrogen adsorbtion results a: Ti-MMM, b: Ti-MCM-41

According to IUPAC classification, materials like Ti-MCM-41, Ti-MMM and Ti-HMS exhibit a mesoporous structure characterized by type IV adsorption isotherms.

In the analyzed samples, hysteresis loops are detected within the relative pressure range, suggesting the existence of mesoporosity. In structured materials, the hysteresis loop is tight, indicating a consistent distribution of pore sizes. In comparison, disordered structures exhibit wider hysteresis loops, reflecting pore variability.

The adsorption characteristics indicate that these materials possess both micro- and mesoporous structures. The distribution of pore sizes is usually determined through techniques like those based on the Kelvin equation, which are often used for mesoporous silica substances.

3. Water absorption

The surface properties and degree of hydrophilicity primarily dictate the adsorption behavior of titanosilicates, affecting their catalytic efficiency as well. Based on their makeup and structural characteristics, these materials can show either hydrophilic or hydrophobic properties.

Earlier research indicates that TS-1 typically has a hydrophobic surface because of isolated titanium species integrated within a purely siliceous framework characteristic of microporous materials. Conversely, mesoporous materials like Ti-MCM-41 exhibit greater hydrophilicity due to the increased quantity of silanol (Si–OH) groups located on the pore walls and defect sites. In mesostructured silica systems, silanol groups are found in various configurations, such as isolated, adjacent (vicinal), and hydrogen-bonded species. The quantity and availability of these groups are crucial in influencing how water molecules are adsorbed onto the surface. In numerous instances, solely the surface-accessible silanol groups engage actively with water molecules or modifying agents.

Hydrophilicity directly influences adsorption ability: materials with higher hydrophilicity typically absorb water more readily, leading to swift pore saturation and quicker equilibrium achievement. In contrast, hydrophobic samples show reduced water absorption and slower adsorption rates.

In general, the water adsorption characteristics of titanosilicates like Ti-MCM-41 are influenced by pore structure and surface chemistry, with titanium inclusion and silanol arrangement playing a crucial role in the interaction with water molecules.

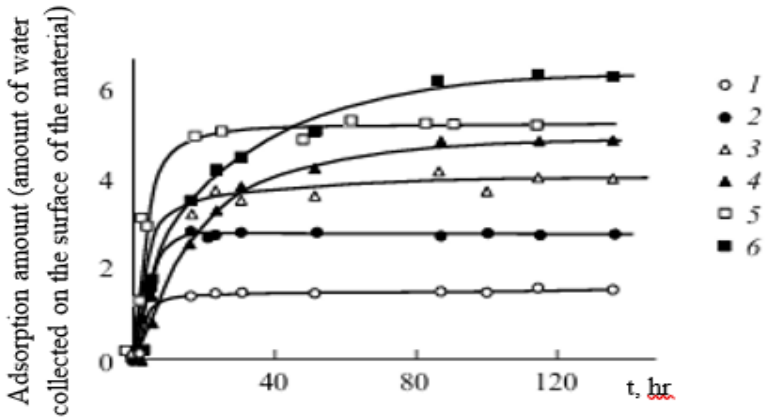

Fig. 3. Water absorption results: 1 – hydrophobized TiO_2–SiO_2 aerogel, 2 – Ti-MMM, 3 – Ti-MCM-41, 4 – TiO_2–SiO_2 xerogel, 5 – Ti-MMM-2, 6 – TiO_2–SiO_2 aerogel

Using these methods, it has been established that the hydrophobicity of titanosilicates depends on their pore structure and the presence of hydrophilic groups on the surface. For example, TiO_2–SiO_2 xerogel and Ti-MCM-41 samples exhibit higher

hydrophilicity. In contrast, Ti-MMM-2 and hydrophobized TiO_2–SiO_2 aerogel show more hydrophobic character.

4. Electron Microscopy

Both scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were employed to analyze the samples regarding particle size, shape, and distribution.

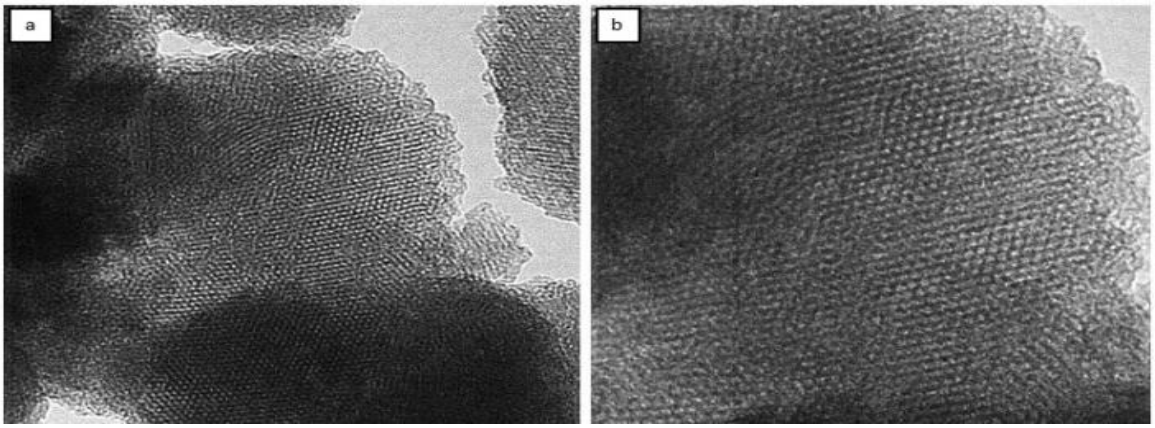

Fig. 4. TEM image of Ti-MCM-41 mesoporous material (a) 50 and (b) 20 nm

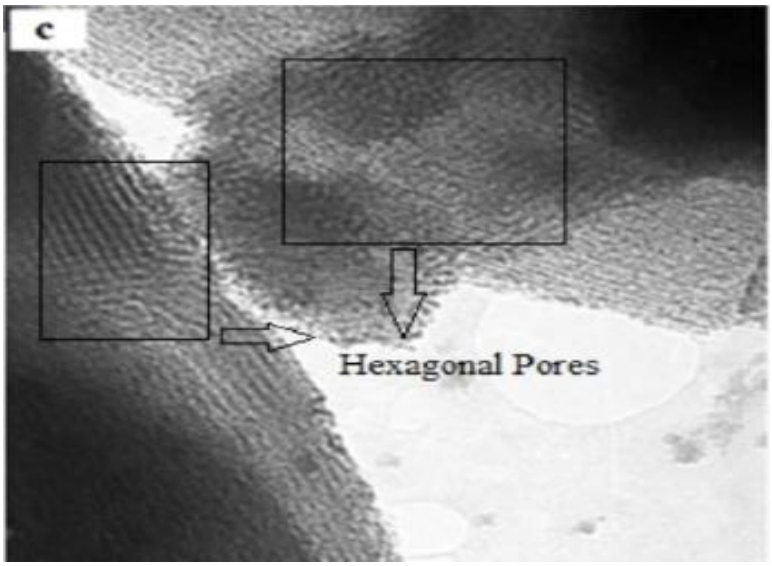

Fig. 5. TEM image of Ti-HMS

The results demonstrate distinct variations in the morphology of Ti-HMS and Ti-MCM-41 materials. SEM images show that Ti-HMS is primarily made up of spherical particles, whereas Ti-MCM-41 displays a more organized structure with relatively smaller particles. The degree of structural organization is significantly high in Ti-MCM-41.

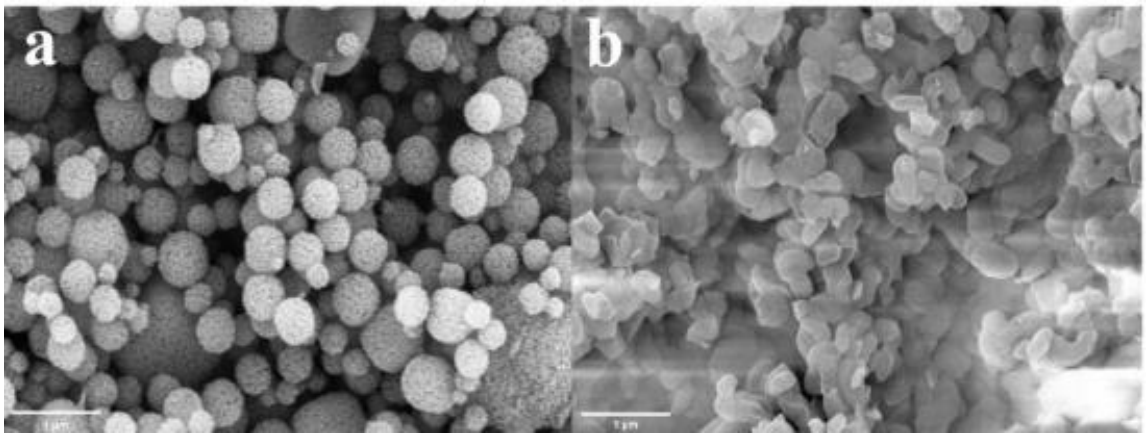

Fig. 6. SEM images of (a) Ti-HMS, (b) Ti- MCM-41

TEM analysis offers a perspective on the arrangement of crystalline phases in heterogeneous samples. Results from electron diffraction verify the existence of both the anatase and rutile phases of titanium dioxide.

CONCLUSION

In this study, titanium-containing mesoporous silica materials were synthesized and systematically characterized to evaluate their structural, textural, and surface properties relevant to liquid-phase oxidation processes. The X-ray diffraction analysis confirmed the formation of mesostructured frameworks with varying degrees of order depending on the synthesis method and titanium content. An increase in titanium loading led to partial deterioration of structural order, indicating the formation of extra-framework titanium species at higher concentrations.

Nitrogen adsorption–desorption measurements revealed that all samples exhibit typical mesoporous characteristics with type IV isotherms, confirming the presence of well-developed pore systems. Differences in hysteresis behavior highlighted variations in pore size distribution and structural uniformity, with more ordered materials showing narrower pore distributions and higher surface regularity.

Water adsorption studies demonstrated that the surface properties of the synthesized materials are strongly influenced by the presence of silanol groups and titanium incorporation. Mesoporous titanosilicates, particularly Ti-MCM-41, exhibited pronounced hydrophilic behavior, which can significantly affect their catalytic performance in liquid-phase reactions.

Electron microscopy analysis provided further insight into the morphology and microstructure of the samples. The results showed clear differences in particle size, shape, and degree of aggregation depending on the synthesis approach. More ordered materials displayed uniform and smaller particles, while less structured samples exhibited larger and more irregular morphologies. The presence of titanium dioxide phases and their dispersion within the silica matrix were also confirmed.

Thus, the results obtained demonstrate that synthesis conditions and titanium incorporation play a important role in determining the structural organization, surface properties, and morphology of mesoporous titanosilicates. These factors are important for creation efficient and stable catalytic systems in selective oxidation processes.

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