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Thermal and chemical stability of titanium-substituted MCM-41

Chang Houn Rhee and Jae Sung Lee [1]

Department of Chemical Engineering, Pohang University of Science and Technology (POSTECH)
and Research Institute of Industrial Science and Technology (RIST),
San 31, Hyoja-dong, Pohang, 790-784 Korea

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The thermal and chemical stability of a titanium-substituted MCM-41 (TiMCM-41) with Si/Ti mole ratio of 39 and pore diameter of 2.4 nm was studied with the small-angle X-ray diffraction and X-ray absorption near-edge structure techniques. The TiMCM-41 was stable in helium flow below 1273 K and under gas-phase reaction conditions of ethanol dehydrogenation (ethanol/O_2 = 1 mol/mol, 373–723 K). Under liquid-phase reaction conditions of phenol hydroxylation (phenol/35% H_2O_2/acetone in moles = 3 : 1 : 7, 333 K), however, it lost the MCM-41 structure and titanium was leached out of the silicalite framework.

Keywords: Ti-substituted MCM-41; stability; dehydrogenation of ethanol; hydroxylation of phenol; XRD; XANES

1. Introduction

MCM-41 is the collective name for a family of crystalline mesoporous molecular sieve materials with hexagonal structure recently invented by Mobil [1,2]. The materials possess a hexagonal array of uniform pores with the diameter ranging from 1.5 to 10 nm. Their silicate framework could also be modified by partial isomorphous substitution with such elements as Al, Ti, V, Sb, Fe or Pd [3–5]. Substitution with Ti is particularly interesting because of the success of Ti-substituted zeolites in the oxidation of various organic substrates [6,7]. Due to their larger pores compared to zeolite-based materials, Ti-substituted MCM-41 (TiMCM-41) could be applied to the oxidation of bulky substrates usually employed in the synthesis of fine chemicals. Despite these attractive properties of MCM-41 materials, their stability is considered to be the limiting factor in the potential application of these materials to several types of hydrocarbon processing and adsorption processes requiring heavy-duty regeneration [8]. The thin wall in the vicinity of 1 nm appears to be the main cause of their limited stability.

There have been a few reports which address some aspects of the stability of MCM-41 [8–10]. Yet, to the best of our knowledge, there has not been a systematic study. In this paper, we report the thermal and chemical stability of TiMCM-41. The structural change of the material was monitored by small angle X-ray diffraction (XRD) and X-ray absorption near-edge structure (XANES) after heating under He flow or after catalytic reactions. Since TiMCM-41 is a potentially useful oxidation catalyst, two oxidation reactions were tested: gas-phase dehydrogenation of ethanol and liquid-phase hydroxylation of phenol with H_2O_2. Two aspects of the stability of TiMCM-41 were considered: the stability of the MCM-41 structure and that of isomorphously substituted titanium. The former was probed by XRD and the latter by XANES.

2. Experimental

TiMCM-41 samples were synthesized following a procedure similar to those described by Beck et al. [1,2] and Corma et al. [5]. A template solution $C_{12}H_{23}(CH_3)_3NBr/OH$ was prepared by partial ion exchange of $C_{12}H_{23}(CH_3)_3NBr$ (Sigma) with Amberlite IRA-400 (OH) (Aldrich, 3 meq. per g of template). Tetraethylorthosilicate and tetrabutylorthotitanate were dissolved into the solution and stirred for 0.5 h. Zeosil (an amorphous silica, Hanbul Chemicals) was added and stirred for another 0.5 h. The relative composition of the starting materials was template/Si mole ratio of 0.5 and Si/Ti mole ratio of 39. The resulting mixture was heated statically at 393 K for 3 days. Solid products were recovered by filtration, washed with water, and then dried in an oven at 333 K for a day. Finally, the synthesized samples were calcined at 813 K in helium for 2 h and then in oxygen for 6 h to remove the organic template from the pores of TiMCM-41. A sample of TS-1 (Ti-substituted MFI-type zeolite) with Si/Ti mole ratio of 33 was employed for comparison.

Ethanol dehydrogenation was carried out in a Pyrex flow reactor. One gram of catalyst was charged and heated in helium flow at 473 K for 1 h. When the desired reaction temperature was reached, the ethanol/O_2 (1 : 1 in moles) feed was established at a flow rate of 25 μmol s^{-1}. Products were analyzed by an on-line gas chromatograph with a flame-ionization detector. The hydroxyla-

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[1] To whom correspondence should be addressed.

tion of phenol was performed at 333 K in a stirred 100 ml glass reactor in batch mode. The reaction mixture consisted of 1 g of catalyst and 30 ml of phenol/H_2O_2/acetone in mole ratio of 3/1/7. The liquid sample of the products was analyzed by a gas chromatograph with a flame-ionization detector.

The small-angle XRD ($2\theta = 1$–$10°$) was performed on a Mac Science X-ray diffractometer M18XHF with Cu K_α radiation. In order to reduce the total reflectance in scanning such small angles, small divergence and scattering slits of 0.5° were employed. X-ray absorption spectra were taken in a transmission mode for the K-edge of titanium at beamline 7C of the Photon Factory in Tsukuba, Japan. The data were analyzed by the UWXAFS 2.0 package. The prepared TiMCM-41 had a surface area of 1426 m^2g^{-1} determined by the N_2 BET method and a pore diameter of 2.4 nm obtained from N_2 physisorption.

3. Results and discussion

3.1. Thermal stability

The thermal stability of TiMCM-41 was tested by heating calcined samples at a temperature of 873–1273 K for 1 h under helium flow. Each sample was analyzed by XRD and XANES. Fig. 1 shows the effect of the heating temperature on the XRD pattern. All the patterns except the one heated at 1273 K show three peaks which could be indexed as the (100), (110), and (200) planes of a hexagonal unit cell. These results are consistent with the regular hexagonal array of uniform channels characteristic of MCM-41 [1,2]. From the difference between the interplanar spacing d_{100} (2.99 nm for samples heated below 1173 K) and pore diameter measured by N_2 adsorption (2.4 nm), an average wall thickness of 0.6 nm could be calculated.

The position of the peaks does not change much until 1173 K where the (100) peak shifts substantially to a lower angle. The best defined XRD pattern is obtained at 1073 K, indicating the highest regularity of MCM-41 structure. It appears that dehydroxylation from the surface silanol group adds additional Si–O–Si (or Ti) units to improve the regularity of the MCM-41 framework. Upon heating at 1273 K, the XRD pattern loses all the peaks except a broad one at low angle. This suggests that the MCM-41 structure has collapsed at 1273 K.

As mentioned, another aspect in the stability of TiMCM-41 is the stability of isomorphously substituted titanium. In properly-prepared TiMCM-41, like in Ti-substituted zeolites [6,7], titanium is expected to replace silicon at the tetrahedral sites of the framework of MCM-41. XANES of titanium K-edge provides a convenient signature of coordination environment around titanium [11]. Tetrahedrally-coordinated titanium gives rise to a strong pre-edge peak at 4668 eV. In contrast, octahedral titanium in titanium oxides (rutile, anatase, or brookite) shows three weak pre-edge peaks.

The XANES spectra shown in fig. 2 indicate that tita-

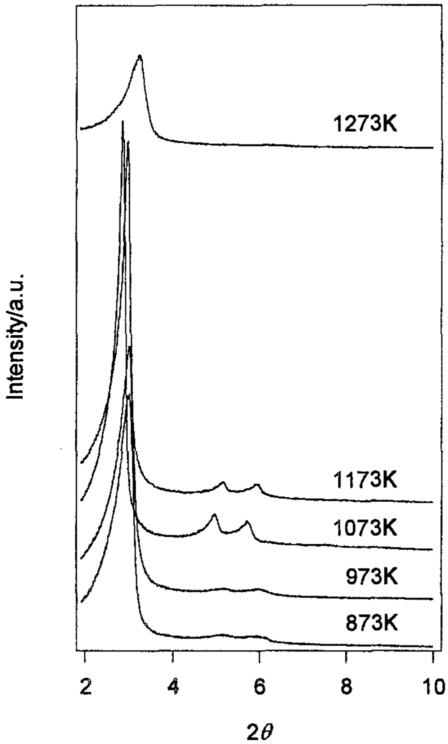

Fig. 1. XRD patterns of TiMCM-41 treated at different temperatures in helium flow.

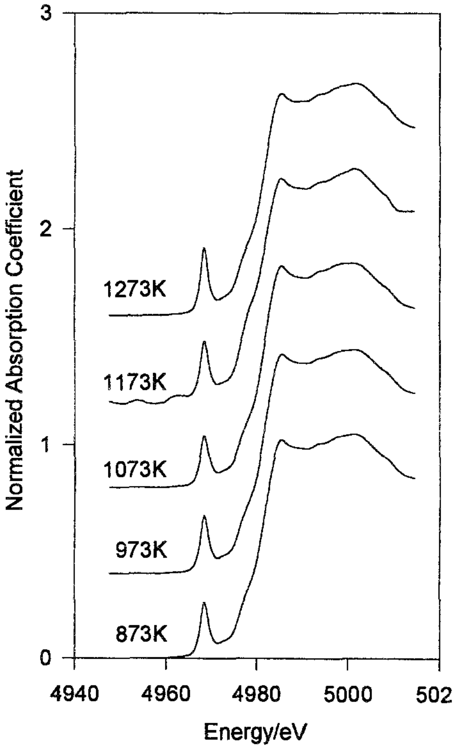

Fig. 2. Titanium K-edge XANES spectra of TiMCM-41 treated at different temperatures in helium flow.

nium in all TiMCM-41 samples resides at tetrahedrally-coordinated framework sites. There is no appreciable change in XANES features upon heating at temperatures of 873–1173 K. There is a gradual increase in the intensity of the pre-edge peak as shown in fig. 3. This could be interpreted as the improved regularity in the tetrahedral symmetry upon heating. Particularly interesting is the fact that titanium coordination is stable at 1273 K where the MCM-41 structure is collapsed. Thus, from XRD and XANES results, we can conclude that TiMCM-41 is thermally stable up to 1173 K under inert conditions maintaining both the MCM-41 structure and the tetrahedral titanium coordination.

3.2. Stability under reaction conditions

Probably more relevant to practical applications of TiMCM-41 as catalyst or adsorbent is the chemical stability under reaction conditions. Since TiMCM-41 is a potentially useful oxidation catalyst, two oxidation reactions were tested: gas-phase dehydrogenation of ethanol and liquid-phase hydroxylation of phenol with H_2O_2.

The results of ethanol dehydrogenation are presented in fig. 4 where ethanol conversion and selectivity to acetaldehyde and ethylene are plotted against the reaction temperature for TiMCM-41 and TS-1. At the same temperature, TiMCM-41 shows a higher ethanol conversion and a lower selectivity to acetaldehyde than TS-1. An important factor contributing to the difference may be the specific surface area S_g. The TS-1 has S_g of 300 $m^2\ g^{-1}$, which is much less than the S_g of TiMCM-41 (1426 $m^2\ g^{-1}$). The higher S_g of TiMCM-41 may have caused higher surface concentration of active Ti sites although both samples contain the similar amount of titanium. The higher surface area also appears to be responsible for the impaired acetaldehyde selectivity by exposing a larger area of silicalite sites which are active for the ethanol dehydration to ethylene.

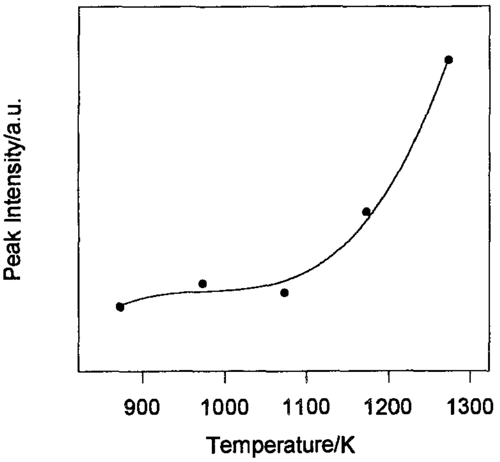

Fig. 3. The intensity of the pre-edge peak in the titanium K-edge XANES of TiMCM-41 treated at different temperatures in helium flow.

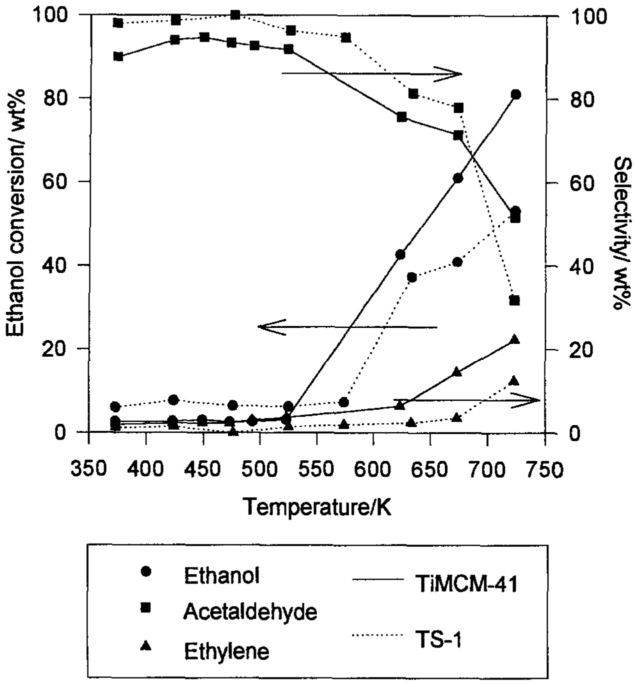

Fig. 4. Ethanol dehydrogenation over TiMCM-41 and TS-1. A 1 : 1 (in moles) ethanol/O_2 mixture was flown at 25 μmol s^{-1} over 1.0 g of catalyst.

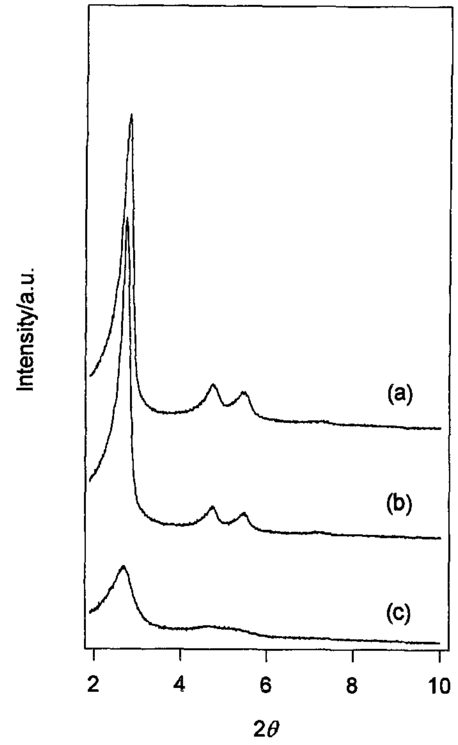

Fig. 5. XRD patterns of TiMCM-41: (a) before reaction (calcined); (b) after ethanol dehydrogenation at 375–725 K for 7 h; (c) after phenol hydroxylation with H_2O_2 (phenol/35% H_2O_2/acetone = 3/1/7 in moles) at 333 K for 24 h.

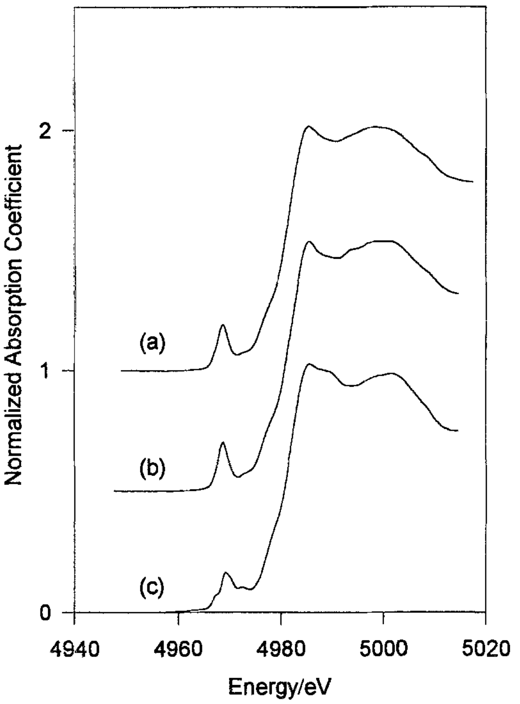

Fig. 6. Titanium K-edge XANES spectra of TiMCM-41: (a) before reaction (calcined); (b) after ethanol dehydrogenation at 375–725 K for 7 h; (c) after phenol hydroxylation with H_2O_2 (phenol/35% H_2O_2/acetone = 3/1/7 in moles) at 333 K for 24 h.

The TiMCM-41 was also tested for the hydroxylation of phenol at 333 K with a 35% aqueous H_2O_2 solution in acetone solvent. TS-1 showed stable activity for the formation of catechol and hydroquinone. The same products were also observed with TiMCM-41 with much less yields. A more serious problem with TiMCM-41 was the difficulty in obtaining reproducible results. Hence, the results were not quantified.

After each catalytic reaction, TiMCM-41 was recovered from the reactor and analyzed by XRD and XANES. Fig. 5 shows the results of XRD. Gas-phase ethanol reaction for 7 h does not alter the XRD structure of TiMCM-41. However, liquid-phase phenol reaction for 24 h appears to destroy the MCM-41 structure of TiMCM-41. The XANES spectra in fig. 6 also show that the gas-phase ethanol reaction does not do any harm to the coordination sphere of titanium. Yet, the liquid-phase phenol reaction completely changes the pre-edge feature of Ti K-edge XANES. The single pre-edge peak of fresh TiMCM-41 turns into triple peaks, indicating the presence of octahedrally coordinated titanium. It appears that titanium has been leached out of the silicalite framework. This phenomenon has also been reported for a vanadium containing mesoporous molecular sieve [10].

Hence, it is clear that the chemical stability of TiMCM-41 depends more heavily on the nature of the reaction medium than on the reaction temperature. The collapse of MCM-41 is known to start from the local hydrolysis of Si–O–Si bonds [8]. The hydrolysis of Si–O–Ti bonds should lead to the leaching of titanium from the silicalite framework. Hence, the presence of water in the reaction mixture appears to be the major factor responsible for destabilizing TiMCM-41. H_2O_2 may also promote the leaching of titanium due to its interaction with titanium sites.

4. Conclusions

TiMCM-41 is thermally stable under an inert atmosphere below 1273 K and under the gas-phase reaction conditions of ethanol dehydrogenation at 373–723 K. Under the liquid-phase reaction conditions of phenol hydroxylation with H_2O_2 at 333 K, however, the MCM-41 structure is collapsed and titanium is leached out of the silicalite framework by hydrolysis.

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