



Hydrothermal Stability of Mesoporous SBA-15 Modified with Alumina and Titania

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Abstract — Hydrothermal stability of alumina or titania modified SBA-15 was studied. Al_2O_3 and TiO_2 were introduced into the SBA-15 structures either by post-synthetic deposition or isomorphous substitution. Appropriate isopropoxides were applied as the reagents for modifications. In all cases surface area and pore volume on non-modified SBA-15 decreased significantly after hydrothermal treatment. Surface decreased by more than 60% after 2 hs at 975 K. Stabilization effect was found only after introduction of titanium and aluminum ions *via* sol-gel technique. Here, the decrease of surface area was only 20% of the initial one. Independently from the stabilization effect of the SBA-15 structure the creation of surface acidity was also possible. In contrast, the stabilization effect after isomorphous substitution was negligible. All samples were studied with XRD, TEM, nitrogen sorption at 77 K, TPD of ammonia. Hydrothermal stability was tested under water vapour at temperatures up to 975 K.

Keywords— SBA-15, hydrothermal stability, alumina, titania, porous structure, acidity.

I. INTRODUCTION

Siliceous uniform mesoporous structures attracted much attention since their discovery in 1992 [1]. The most comprehensive review concerning synthesis, properties and possible application of MCM-41 type materials is given by Corma [2]. Due to relatively thin walls and poor hydrothermal stability, the catalytic applications of these materials were significantly limited. Exposition of this siliceous structure to water vapour at elevated temperatures cause an instant collapse of the hexagonal array of parallel channels. In contrast, due to the thicker walls and regular structure of the mesoporous siliceous SBA-15 [3] shows much higher hydrothermal stability than MCM-41 structure [4]. This property, as well as much larger pores of SBA-15 desirable for more bulky molecules, makes this material suitable for catalytic purposes. However, synthesis of SBA-15 requires strongly acidic conditions which are an obstacle for introduction other than silicon ions. Therefore, introduction of such ions as aluminum, titanium or zirconium into the framework of SBA-15 is very difficult. It is well known that creation of acidic or basic surface sites can influence the activity of heterogeneous catalyst. On the other hand, an introduction of foreign ions into the basic framework of SBA-

15 by isomorphous substitution or external deposition can significantly improve hydrothermal stability of these materials.

This paper compares hydrothermal stability of alumina and titania modified SBA-15 with the non-modified one. The special emphasis was focused on methods of aluminum and titanium ions introduction. Moreover, it can be created the change of surface acidity inside the SBA-15 channels.

Recent studies showed that titania modified SBA-15 can be applied in PROX [5] catalysts or as photocatalysts in water splitting [6].

II. EXPERIMENTAL

Pure siliceous material of SBA-15 was synthesized according the procedure of Zhao et al. [3] applying Pluronic P-123 as template and TEOS as source of Si. The product after few days of drying in air was calcined at 825 K for 6 hours. Heating rate was 1K min^{-1} .

A. Modification with Al^{3+} ions

Two methods of modification of SBA-15 with aluminum ions were applied:

a/ post-synthetic by the incipient wetness of SBA-15 with alumina sol [7],
 b/ isomorphous substitution during SBA-15 synthesis.
 During deposition of alumina on internal walls of SBA-15 (method a) four different concentrations of alumina sol were applied (Si/Al were 36, 72, 144 and 288). Samples after drying at room temperature were calcined at 825 K for two hours. These samples are designated as Al-SBA-15.
 The SBA-15 samples containing Al³⁺ ions and obtained during isomorphous substitution were generated at the initial stage of synthesis. Here, after complete dissolution of Pluronic 123 in HCl solution, the known amount of aluminum isopropoxide was added to the reaction mixture. After complete hydrolysis of TEOS and Al-iso-PrOH, samples were dried in air and calcined at 825 K for 2 hours. These samples are designated as SBA-15-Al. In all cases number after the symbol indicate the Si/Al ratio.

B. Modification with Ti⁴⁺ ions

Samples modified with titanium ions were obtained either by the incipient wetness with titanium isopropoxide followed by calcination, impregnation with titanium isopropoxide followed by hydrolysis with subsequent calcination, introduction by sol-gel method and isomorphous substitution. In the incipient wetness method samples of dry SBA-15 were saturated with solutions of titanium isopropoxide in dried isopropanol. Different concentration of Ti-iso-PrOH provided appropriate final content of TiO₂ (8, 12, 16 or 24 wt. %). Samples after drying in air were calcined at 675 K. These samples are designated as Ti-SBA-15.

Similar method was applied for hydrolysed samples. Here, SBA-15 was placed in the solution of Ti-iso-PrOH and dry isopropanol. After 2 hours of stirring, the water-isopropanol (10:1) was added in excess leading towards complete hydrolysis of Ti-iso-PrOH. The absence of Ti⁴⁺ ions in the solution after hydrolysis was checked with the XRF method. These samples are designated as Ti-H-SBA-15.

In the sol-gel method an appropriate amount of TiO₂ sol prepared according the method of Dai et al. [8] was used during deposition on SBA-15. The colloidal suspension of TiO₂ and SBA-15 was evaporated initially at 325 K for 2 hours and next dried at 395 K for 10 hours. The obtained material was finally calcined at 825 K. The Ti-S-SBA-15 is the symbol of these samples.

The isomorphous substitution occurred post-synthetically applying SBA-15 and toluene solution of Ti-iso-PrOH. All steps of the reaction were performed under argon and with extremely dry solutions. Reaction was performed at 384 K for one hour under reflux and argon atmosphere. The obtained material after exposition to air was next calcined at 825 K. These samples are designated as SBA-15-Ti.

C. Hydrothermal stability and characterization

Hydrothermal stability was tested with granulated samples (grains 0.4 -1.0 mm). 1 gram of granulated sample was placed in quartz vertical tube (diameter 11 mm) connected with vessel containing boiling water under atmospheric pressure. In routine experiments each sample was kept in water vapour at indicated temperature for 2 hours (from 375 to 975 K). After cooling, hydrothermally treated samples were characterized with XRD (AXS D8 Advance from Bruker,) nitrogen

adsorption-desorption (ASAP-2000 from Micromeritics) and TPD of ammonia. Surface area was determined from adsorption isotherms by the BET method, whereas pore volume and their distribution were determined from desorption isotherms by BJH method. Micropore volume was calculated from t-plot.

III. RESULTS AND DISCUSSION

Data presented in Table 1 as well as the adsorption-desorption isotherms of nitrogen at 77 K (Figure 1) indicate that hydrothermal stability of non-modified SBA-15 is rather stable until 575 K.

TABLE I
SBA-15 AFTER HYDROTHERMAL TREATMENT

Sample	Temp. [K]	BET [m ² g ⁻¹]	Pore vol. [cm ³ g ⁻¹]	Micropore vol. [cm ³ g ⁻¹]	Aver. diam. [nm]
1*	-	807	0.92	0.098	6.8
2*	-	785	0.89	0.089	6.2
3	375	739	0.88	0.087	6.1
4	475	748	0.89	0.081	6.2
5	575	732	0.87	0.081	6.3
6	675	668	0.85	0.054	6.4
7	775	460	0.74	0.023	7.0
8	875	400	0.65	0.015	7.2
9	975	390	0.52	0.012	7.8

* - SBA-15 before granulation

* - SBA-15 after granulation

Hydrothermal treatment at 675 K of pure SBA-15 result in almost 20% lower value of BET surface area. Further increase of temperature up to 775 K causes the surface area decrease by 50% and significant changes in micropore volume. Moreover, average pore diameters calculated by the BJH method show an increase. The decrease of pore and micropore volumes with simultaneous increase of average pore diameter after hydrothermal treatment was observed after 2 hours of exposure of non-modified SBA-15 in rather extreme hydrothermal conditions. Similar experiments were performed

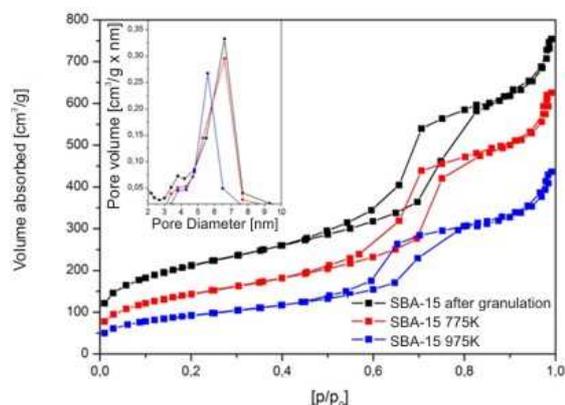


Fig. 1 Nitrogen adsorption-desorption isotherms of non-modified SBA-15 after hydrothermal treatment.

by other group [9] at room temperature for prolonged exposure of SBA-15 to water vapour. Significant changes both in the surface area and structure were observed.

Complete disappearance of (110) and (200) and significant decrease of (100) reflexes, as well as a decrease of surface area by 50 % after 48 hours exposition to water vapour indicate rather poor hydrothermal stability of non-modified SBA-15.

Changes in the structure of hydrothermally treated of non-modified SBA-15 can be observed in XRD patterns of the selected samples (Fig. 2b). The positions of the characteristic reflexes are shifted towards higher values of 2θ . This indicates that significant changes in wall thickness occur. The group of Cassieres [10] indicate that among different mesoporous silicas the SBA-15 with relatively thick walls (~3 nm) indicate much better hydrothermal stability than those presented earlier [11]. It is believed that such structural degradation can be caused by hydrolysis of Si-O-Si bonds [9] with formation of siloxane bridges [12].

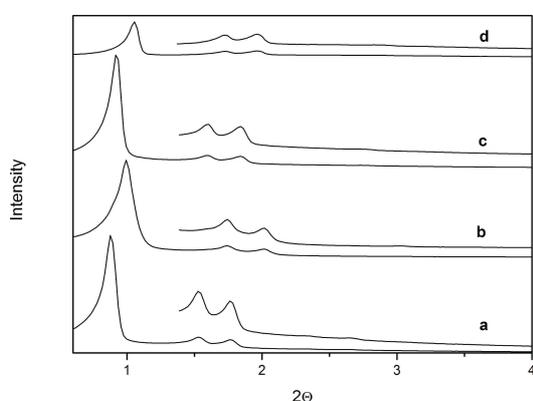


Fig. 2 XRD diffraction patterns of (a) non-modified SBA-15, (b) after hydrothermal treatment at 875 K, (c) Al-SBA-15; Si/Al = 288, (d) Al-SBA-15; Si/Al = 36.

In order to improve the hydrothermal properties of SBA-15 the incorporation of foreign ions into the siliceous structures was proposed in many laboratories. In this paper an attempt to improve hydrothermal stability applying Al^{3+} and Ti^{4+} oxide structures with SBA-15 has been made.

TABLE II
HYDROTHERMAL STABILITY OF SBA-15 MODIFIED WITH TITANIUM AND ALUMINIUM IONS BY SOL-GEL TECHNIQUE

Sample	BET [$m^2 g^{-1}$]	Pore vol. [$cm^3 g^{-1}$]	Micro-pores [$cm^3 g^{-1}$]	Aver. diam. [nm]	Wall thick [nm]
SBA-15	785	0.89	0.089	6.8	3.7
SBA-15 (975 K)*	390	0.52	0.012	7.8	1.9
Ti-S-SBA-15	678	0.94	0.066	6.6	3.8
Ti-S-SBA-15(975 K)*	564	0.86	0.039	6.7	3.6
Al-SBA-15	733	0.85	0.075	6.1	3.8
Al-SBA-15 (975 K)*	607	0.80	0.050	6.4	3.4

* - temperature of hydrothermal treatment

Data presented in Table II show the results of surface studies with samples of SBA-15 loaded with TiO_2 or Al_2O_3 . The decrease of surface area and micropores volume suggests deposition of thin films inside the channels of SBA-15 structure. Although the amount of the adsorbed nitrogen obtained from the adsorption-desorption isotherms presented on Fig. 3 (SBA-15 modified with sol of alumina) decreases after deposition of alumina, the characteristic shape of hysteresis loop is well preserved. Especially the position and the shape of hysteresis loop is indicative that hexagonal array of the SBA-15 channels is not damaged in large extent. Similar curves (not shown in this paper), with the same tendency, were obtained for Ti-S-SBA-15 samples. Data presented in Table II and the amount of adsorbed N_2 at low p/p_0 indicate the decrease in micropores volume for the modified samples. Results presented on Fig.4 and 5 show this effect in more details. Here are presented the results of the granulated samples under 100 bars. The instant collapse of micropore structure of SBA-15 after hydrothermal treatment is well documented. Small discrepancies in the values on the isotherms of non-modified SBA-15 originate from the use of two similar but different initial batches.

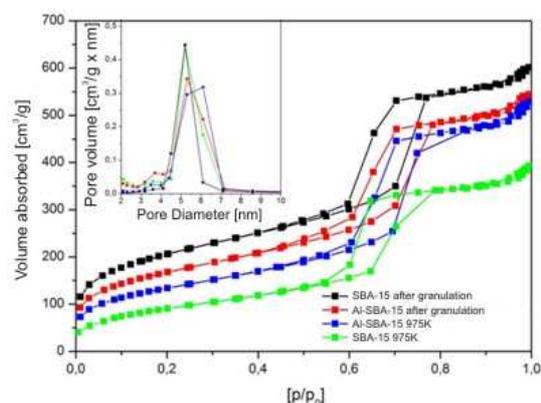


Fig. 3 Nitrogen adsorption-desorption isotherms (77K) for alumina modified SBA-15 (sol-gel method).

Deposition of titanium or aluminium oxide causes partial clogging of certain micropores (red lines on Fig. 4 and 5) but simultaneously protect mesoporous structure against structure collapse in dramatic hydrothermal conditions (975 K). The protective activity of thin films of Al_2O_3 or TiO_2 build inside the hexagonal mesopores originate from formation of Al-O-Si or Ti-O-Si bonds on external surface of channels. This way the hydrolysis of Si-O-Si bonds is significantly weaker. The attempts of isomorphous substitution of SBA-15 with titanium or aluminium ions during initial stage of synthesis showed that application of this method leads towards less stable hydrothermal materials. In comparison with the sol-gel technique samples obtained in "one pot" synthesis and containing Al^{3+} and Ti^{4+} ions show during nitrogen adsorption much lower values (see Fig. 6 and 7). Moreover, the flat shape of the hysteresis loops for sample isomorphically substituted indicate a presence of different geometry in mesoporous structure. This effect is well documented for samples containing aluminium ions (Fig. 7). Here, the pore size distribution (see insert) clearly indicate a non-uniform shape of the pores. Although the amount of incorporated Al^{3+} (1.4 wt. % expressed as Al_2O_3) and Ti^{4+} (1.8 wt. % expressed as

TiO₂) ions is very low in comparison with the sol-gel technique, the changes caused by incorporation of foreign ions are significant. Location of foreign ions within the

strated by the absence of TPD maxima. The increasing amount of deposited Al₂O₃ (lower Si/Al) causes higher acidity (curves b/c/d/, Fig. 8). Two characteristic maxima

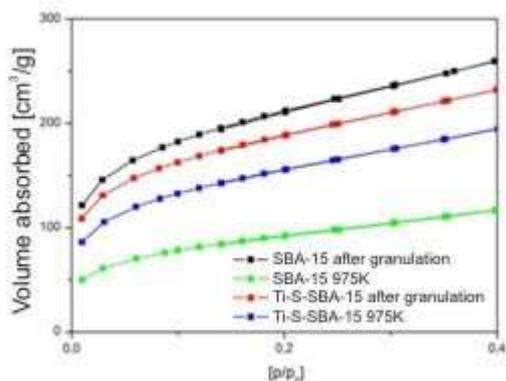


Fig.4 Adsorption isotherms of N₂ (77 K) for TiO₂ modified SBA-15.

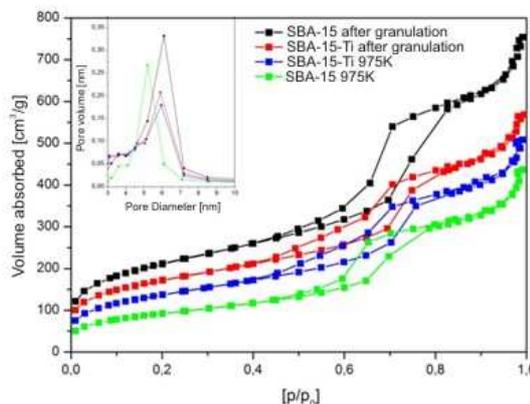


Fig. 6 Nitrogen adsorption-desorption isotherms (77 K) of SBA-15-Ti samples (isomorphous substitution).

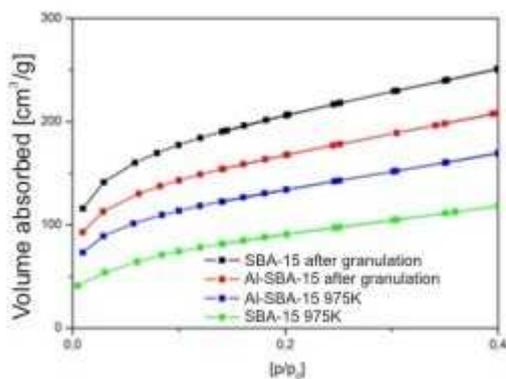


Fig.5 Adsorption isotherms of N₂ (77 K) for Al₂O₃ modified SBA-15.

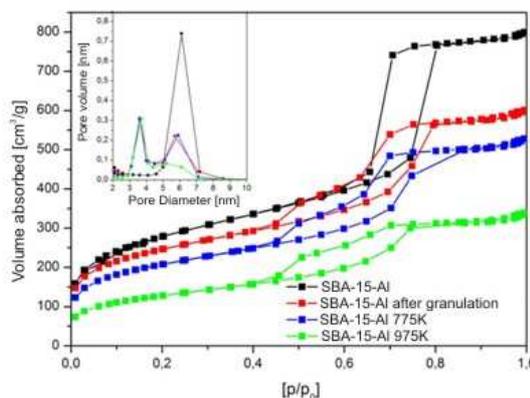


Fig. 7 Nitrogen adsorption-desorption isotherms (77 K) of SBA-15-Al samples (isomorphous substitution).

framework of SBA-15 causes different distortion and tensions between Si and O bonds [13-15].

Isomorphous substitution of SBA-with aluminium ions results in relatively low hydrothermal stability. This can be caused by transformation of structural Al³⁺ ions into agglomerations of surface clusters of Al₂O₃. The presence of too high negative charge which can not be compensated by H⁺ ions lead towards destruction of mesoporous structure [16].

Introduction of titanium ions from Ti-isopropoxide (samples Ti-SBA-15) as well as from hydrolysis of Ti-isopropoxide (samples Ti-H-SBA-15) did not show the improved hydrothermal stability and in many cases all these samples were similar to non-modified SBA-15. However, different methods of titanium ions deposition generated different surface species what was observed as different photocatalytic activity in splitting of water (results not shown here).

Relatively high level of hydroxylation of the modified SBA-15 surface (thermogravimetric measurements) both with TiO₂ and Al₂O₃ obtained by the sol-gel method suggested formation of surface hydroxyl groups with different acidic properties. Therefore, a series of TPD experiments with alumina loaded SBA-15 were performed. Ammonia was chosen as a probe molecule. Pure SBA-15 showed practically the absence of acidic centers (curve a, Fig. 8) what is demon-

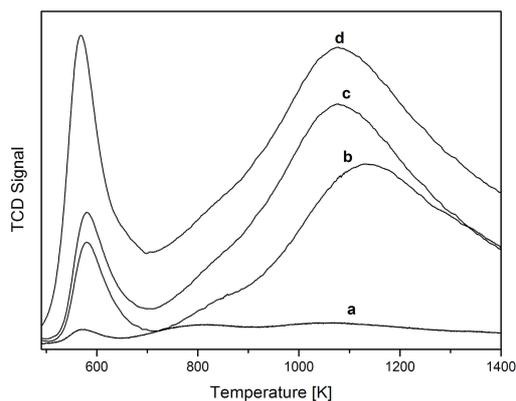


Fig. 8 Temperature programmed desorption of ammonia from Al-SBA-15 samples.

- a/ non-modified SBA-15
- b/ Al-SBA-15 (Si/Al = 144)
- c/ Al-SBA-15 (Si/Al = 72)
- d/ Al-SBA-15 (Si/Al = 36)

at ~590 and ~1100 K originating from ammonia desorption suggest the presence of two acid sites with different strength on the Al-SBA-15 materials. Both sites are of the Lewis sites because additional experiments with FTIR spectroscopy and pyridine as probe molecule did not indicate characteristic vibration for the Brønsted acidity.

The stabilized SBA-15 materials due to their density, uniform hexagonal array of the walls and newly created acidity can be the excellent supports for copper-zinc catalysts for dimethyl ether (DME) synthesis in hybrid systems. The presence of weak acidity of the walls provide the dehydration activity of methanol, synthesized at the same time from CO and H₂. Preliminary experiments proved that such catalyst are active in DME formation when the reaction is performed Cu-Zn-Al-SBA-15 catalysts suspended in inorganic oil

IV. CONCLUSIONS

Mechanical strength of non-modified SBA-15 is affected by compression of the mesoporous silica powder into pellets under increased pressure. Hydrothermal stability of non-modified SBA-15 is well preserved up to 675 K. Hydrolysis of the Si-O-Si bonds above this temperature leads to the destruction of microporous and mesoporous structure. Application of alumina and titania sols during post-synthetic deposition of these oxides as thin films inside the hexagonal channels of siliceous SBA-15 leads to the significant improvement of hydrothermal stability. Moreover, introduction of alumina sol can generate Lewis acidity and the amount of introduced alumina can control the level and strength of acid sites. Isomorphous substitution of Ti⁴⁺ and Al³⁺ ions does not improve significantly the hydrothermal stability of SBA-15.

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