Styrene oxidation with H_2O_2 over Fe- and Ti-SBA-1 mesoporous silica

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ABSTRACT

The catalytic activity of M-SBA-1 (M = Fe and Ti), synthesized using silatrane as the precursor, was studied in the liquid phase oxidation of styrene using hydrogen peroxide as the oxidant. The influence of time-on-stream, affecting the catalytic activity and the selectivity of styrene, was studied. At 80 °C, the selectivity for benzaldehyde and styrene oxide reached 74% and 11%, respectively, at a styrene conversion of 67 ± 1.49% over 4 wt% Fe in SBA-1, while that for benzaldehyde and styrene oxide reached 50% and 48%, respectively, at a styrene conversion of 69 ± 2.20% over 2 wt% Ti in SBA-1.

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1. Introduction

Since the incorporation of transition-metal ions in a silica framework may improve the catalytic performance of an SBA-1 support, many researchers have tried to introduce transition-metal into the silica framework of SBA-1 [1–3]. SBA-1 is an ordered mesoporous material possessing a three-dimensional cubic structure with a space group of $Pm\bar{3}n$, which is the most important property, thus it can introduce a heteroatom, such as titanium, onto a silica framework. Recently, metal ion-incorporated SBA-1 has attracted much attention as an oxidation catalyst [4–6], especially tri-substituted molecular sieves displaying redox catalytic activities [6–8]. These studies have shown that the incorporation of transition-metal ions into the framework of porous materials is a viable method for the designable preparation of novel catalysts [9].

Styrene epoxidation is of interest to both academic and commercial fields for the synthesis of two important products – styrene oxide and benzaldehyde – in the presence of hydrogen peroxide [8–11]. The use of hydrogen peroxide for oxidizing organic substrates generates various types of products, depending on the catalyst and the reaction conditions used [7]. The aim of this study was to investigate the oxidation of styrene in the presence of hydrogen peroxide over Fe and Ti-SBA-1, synthesized via the sol–gel process.

A comparison was made of the catalytic performance obtained from the catalysts synthesized via impregnation and sol–gel methods.

2. Experimental

2.1. Preparation of catalysts M-SBA-1 (M = Fe³⁺, Ti⁴⁺)

The catalyst synthesis via the sol–gel process is described in the literature [12]. The incorporation of metal (M = Fe^{3+}, Ti^{4+}) onto the SBA-1 support by incipient wetness impregnation was carried out following the procedure described in Ref. [13], using 2 wt% titanium glycolate [14] and 2 wt% $FeCl_3$ precursors. The precursor was dissolved in water and dropped onto the catalyst support, SBA-1. Evaporation of the water from the mixture was carried out at 100 °C in an oven for 12 h, followed by calcination (600 °C/5 h) in a Carbolite Furnace (CFS 1200) at a heating rate of 10 °C/min.

2.2. Catalyst characterization

The catalyst products were characterized using a Rigaku X-ray diffractometer (XRD) with patterns accumulated at a scan speed of 1°/s using CuKα radiation over the range of $2\theta = 1.8–8°$. Specific surface area and average pore size were determined using the Brunauer–Emmett–Teller (BET) method on a Quantasorb JR instrument. Diffuse reflectance UV–visible spectroscopic measurements were recorded on a Shimadzu UV-2550 spectrometer fitted with an ISR-2200 integrating sphere attachment from 200–600 nm referenced to $BaSO_4$.

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2.3. Activity study

The epoxidation of styrene was carried out in a 50 ml glass flask to be heated with an oil bath. In a typical run, styrene (1.04 g, 10 mmol) and aqueous 30% H_2O_2 (1.14 g, 10 mmol) were mixed in 10 ml of CH_3CN. The catalyst (50 mg) was added to the mixture and heated at 80 °C with continuous stirring. During the reaction, the products were analyzed (by withdrawing small aliquots after specific time intervals) using a gas chromatography (GC) equipped with a capillary column (DB-WAX, 30 M × 0.25 mm) and an FID detector.

3. Results and discussion

3.1. Catalyst characterization

The physical properties of all the samples are summarized in Table 1. The N_2 adsorption–desorption isotherms (Fig. 1) of all M-SBA-1 samples showed the type IV mesopore characteristic, with a narrow pore size distribution and a pore diameter of about 21 Å. These results are in good agreement with our previous study [13]. The XRD patterns of M-SBA-1 (Fig. 2) reveal three well-resolved diffraction peaks in the region of $2\theta = 1.5–3°$, indexed as {2 0 0}, {2 1 0}, and {2 1 1} reflections, with respect to a cubic lattice [15]. The diffuse reflectance UV–visible spectra of these samples are shown in Fig. 3. The Fe-SBA-1 showed a strong UV band at ~220 nm, associated with a shoulder at 260 nm, consistent with Laporte-allowed ligand-to-metal charge-transfer, involving isolated $Fe^{3+}O_4$ co-ordination [4]. A characteristic band above 320 nm, typical of octahedral co-ordination ($Fe^{3+}O_6$), was absent in the samples synthesized via the sol–gel process, indicating that these materials are free of the ferric oxide species similar to those found in iron hydroxide, iron oxyhydroxide, and iron oxide. However, this band can be observed in the samples synthesized via the impregnation method, meaning that the ferric oxide species was formed [4,16]. The Ti-SBA-1 samples show an absorption band centered at 220 nm, characteristic of the charge-transfer transition associated with the regular $Ti^{4+}O_4$ framework tetrahedra. Octahedral co-ordination ($Ti^{4+}O_6$) as a distinctive feature at 330 nm is missing [6–8]. All of the above characterizations clearly indicate that the metals are incorporated into the silica framework of SBA-1. It is worth noting that the impregnation method also provided Ti or Fe incorporated inside the SBA-1 framework, as indicated by the UV results.

3.2. Catalytic activity of M-SBA-1 in styrene epoxidation

The catalytic results of the epoxidation of styrene over Ti- and Fe-SBA-1 with various amounts of metals are presented in Table
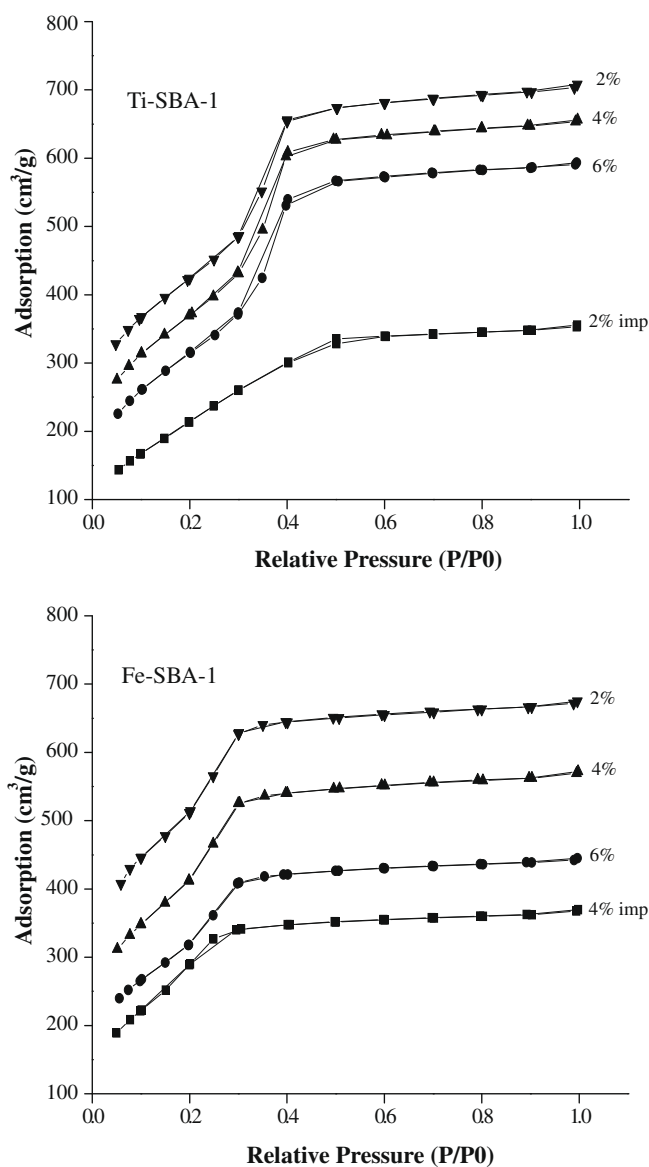

Fig. 1. Nitrogen adsorption–desorption isotherms of calcined Fe-SBA-1 and Ti-SBA-1 samples prepared at different degrees of loading.

2. The reaction without metal loading occurred at a very low rate. The main product was benzaldehyde, resulting from the nucleophilic attack of H_2O_2 on styrene oxide, followed by a cleavage of the intermediate hydroxy–hydroperoxystyrene, and also from a cleavage of the C=C bond [8]. As can be seen, when increasing the Ti content up to 2 wt%, the conversion of styrene was increased to a maximum of 69 ± 2.20%, and the selectivities for benzaldehyde and styrene oxide were 50% and 48%, respectively. These results were consistent with those reported by Ji and coworkers [6], showing a maximum styrene conversion of 45.1% and an epoxidation selectivity of 40%. Compared to our study of Ti-SBA-1 (synthesized using a small head group of template and home-made metal alkoxide precursors under much milder acidic condition) the same amount of catalyst (2 wt% Ti) provides higher conversion, at a styrene conversion of 70% and an epoxidation selectivity of 48%. It is worth noting that the catalyst with 2 wt% Ti synthesized by Ji and coworkers showed an XRD result with a distorted pattern, indicating some collapse of the SBA-1 structure. This may be a reason why their styrene conversion and epoxidation selectivity were less. The Ti-SBA-1 at 2 wt% Ti content synthesized by impregnation was also
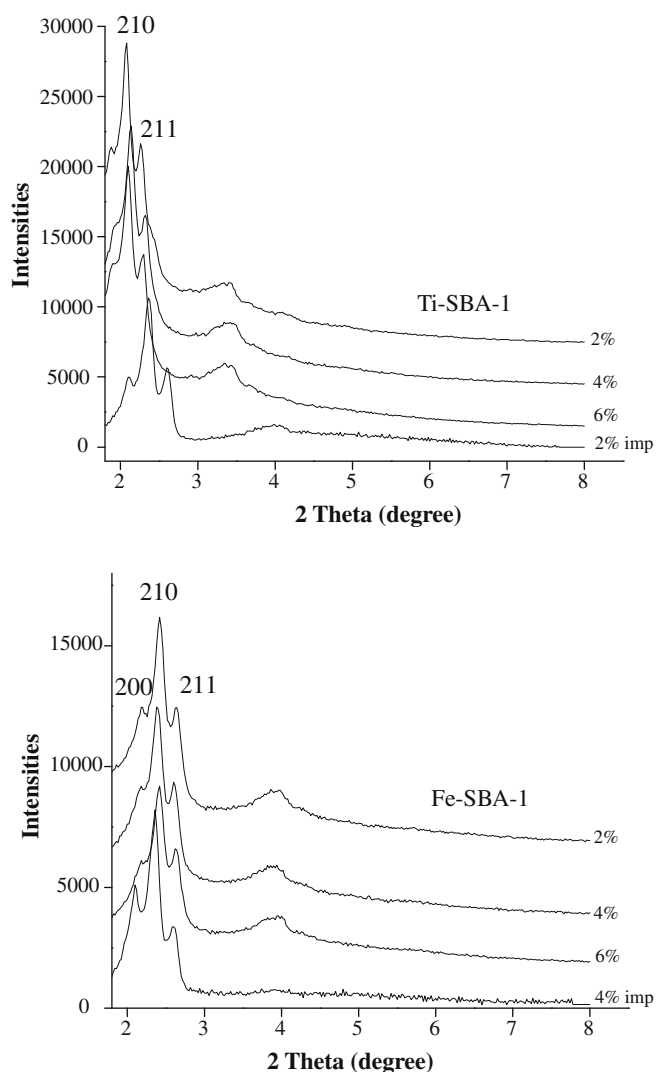
Table 1
BET analysis of M-SBA-1 synthesized at different degrees of loading.

Material		Physical properties			Crystallographic properties	
Designation	Metal doping (wt%)	BET surface area (m^2/g)	Pore Volume (cm^3/g)	Average pore diameter (nm)	d_{210} (nm)	a_0 (nm)
SBA-1	0	1435	0.75	2.12	3.62	8.09
Fe 2%	2	1164	0.61	2.11	3.65	8.16
Fe 4%	4	1175	0.61	2.11	3.68	8.23
Fe 6%	6	1062	0.54	2.1	3.71	8.3
Fe 4% (imp)	4	1112	0.57	2.05	3.46	7.73
Ti 2%	2	1101	0.57	2.07	3.77	8.43
Ti 4%	4	1029	0.56	2.17	3.8	8.51
Ti 6%	6	880	0.51	2.34	3.83	8.58
Ti 2% (imp)	2	839	0.54	2.16	3.46	7.74

Fig. 2. XRD patterns of calcined Fe-SBA-1 and Ti-SBA-1 samples prepared at different degrees of loading.

Fig. 3. Diffuse reflectance UV–visible spectra of the calcined Fe-SBA-1 and Ti-SBA-1 samples prepared at different degrees of loading.

studied in our case to compare it with the catalyst synthesized via the sol–gel process. It was found that for the impregnation method, the conversion of styrene was 59 ± 2.12%, and the selectivities for benzaldehyde and styrene oxide were 54% and 29%, respectively. It can be concluded that, for the epoxidation of styrene, the Ti^{4+} incorporated inside the framework is more active than that outside the framework.

In the case of Fe-SBA-1, an increased Fe content, up to 4 wt%, increases the conversion of styrene to a maximum of 67 ± 1.49%, with the selectivity for benzaldehyde and styrene oxide at 74% and 11%, respectively. When the Fe content exceeded 4 wt%, the conversion of styrene slightly decreased. Compared to Fe- impregnated SBA-1 at 4 wt%, the conversion of styrene reached 65 ± 2.19%, with the selectivities for benzaldehyde and styrene oxide at 67% and 14%, respectively. The result demonstrates that the metal active sites incorporated inside the framework of SBA-1 probably account for the epoxidation of styrene with hydrogen peroxide [16]. As mentioned earlier, the conversion of styrene over the neat SBA-1 is very low, indicating that Fe^{3+} incorporated inside the framework is indeed the active site for the epoxidation of styrene. This result is in agreement with the conclusion that the tetrahedrally coordinated and atomically isolated iron sites are responsible for the oxidation of styrene [6].
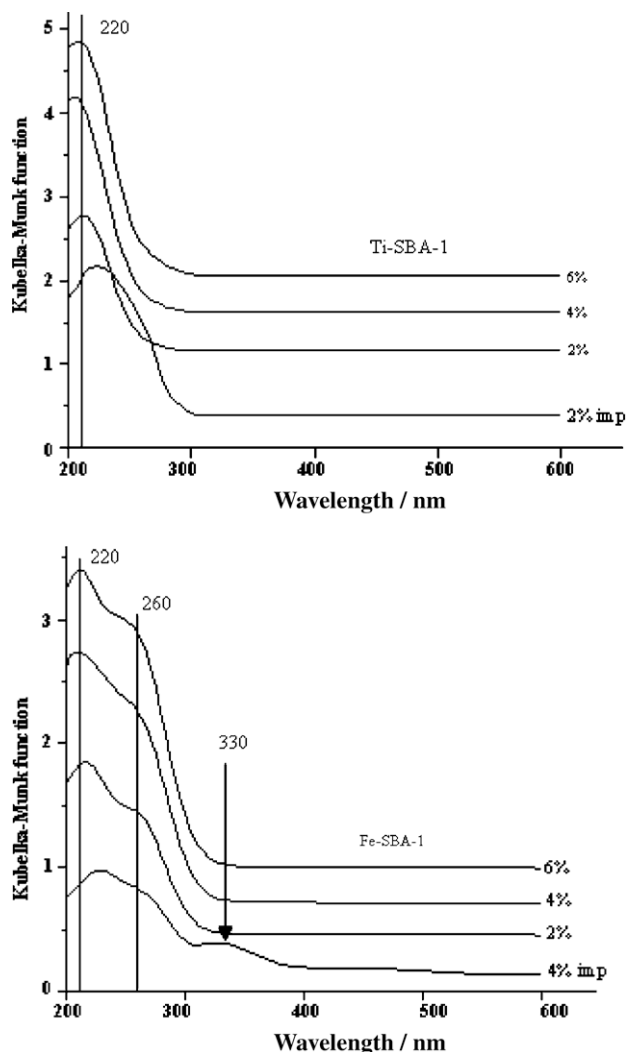
Table 2
Selective oxidation of styrene using 50 mg of the M-SBA-1 catalyst with various metal contents at an 80 °C reaction temperature for 2 h (Ti-SBA-1) and 4 h (Fe-SBA-1) reaction time.

Catalyst	Styrene conversion (%)	Selectivity (%)		
		Benzaldehyde	Styrene oxide	Other
SBA-1	7.75	93.23	6.23	0.54
Fe 2%	66.34	73.18	11.42	15.40
Fe 4%	67.94	74.01	11.46	14.52
Fe 6%	66.27	71.82	14.63	13.55
Fe 4% (imp)	57.96	69.90	14.55	15.55
Ti 2%	69.95	50.50	48.16	1.35
Ti 4%	68.71	51.11	44.75	4.13
Ti 6%	67.13	53.35	37.16	9.49
Ti 2% (imp)	59.23	54.82	29.56	15.62

Table 3 shows the styrene conversion as a function of reaction time at an 80 °C reaction temperature. When the reaction time is fixed at 4 h, using the 2 wt% Fe catalyst, the styrene conversion is 66 ± 1.53%, and the selectivities for benzaldehyde and styrene oxide are 73% and 11%, respectively; though the reaction time was prolonged, the conversion of styrene and the selectivity for styrene oxide changed only slightly [17]. At 2 h reaction time, the corresponding 2 wt% Ti-SBA-1 catalysts provided styrene conversion,

Table 3
Effect of reaction time on the epoxidation of styrene using 50 mg of the catalyst at an 80 °C reaction temperature.

Catalyst	Reaction time (h)	Styrene conversion (%)	Selectivity (%)		
			Benzaldehyde	Styrene oxide	Other
Fe 2%	2	61.86	76.47	10.25	13.28
	4	66.34	73.18	11.42	15.40
	6	61.44	72.85	11.66	15.49
Ti 2%	2	69.95	50.50	48.16	1.35
	4	63.09	53.10	37.85	9.06
	6	60.78	55.71	32.58	11.71

and the selectivities for benzaldehyde and styrene oxide of 69 ± 1.53%, 50%, and 48%, respectively. The selectivity for styrene oxide decreases with reaction time while that for benzaldehyde increases (with only a slight increase in other products). This could be attributed to the secondary oxidation of the epoxide and the formation of benzaldehyde through the cleavage of the C=C bond [6,8].

4. Conclusions

In summary, both the Fe- and Ti-SBA-1 catalysts show good activity and selectivity in the oxidation of styrene. The selectivity for benzaldehye and styrene oxide reached 74% and 11%, respectively, at a styrene conversion of 67 ± 1.49% over 4 wt% Fe in SBA-1, while that for benzaldehyde and styrene oxide reached 50% and 48%, respectively, at a styrene conversion of 69 ± 2.20% over 2 wt% Ti in SBA-1. However, the Ti-SBA-1 revealed better performance (both in activity and selectivity) in the styrene conversion to styrene oxide. Moreover, when compared to the impregnated catalyst, the sol–gel synthesized catalyst showed better performance for the conversion of styrene.

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