Nano-sized Silicalite-1: novel route of synthesis, metal impregnation and its application in selective oxidation of toluene

MAAZ NAWAB, SUNITA BAROT and RAJIB BANDYOPADHYAY*

Department of Science, School of Technology, Pandit Deendayal Petroleum University, Raisan, Gandhinagar, Gujarat 382 007, India

E-mail: rajib.bandyopadhyay@sot.pdpu.ac.in

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Abstract. The novel route of synthesis and catalytic performance of nano-sized Silicalite-1 are presented. Nano-sized Silicalite-1 was initially obtained from a clear solution using sodium silicate as silica source and tetrapropylammonium hydroxide as a template. The effects of silica source on the product yield, purity, crystallization rate and crystallinity were investigated. Effect of seeds in the synthesis was also studied. Nucleation time decreased to 6 h from 24 h using 4% seed, with yield and crystallinity 70% and 90%, respectively. The catalyst was characterized by XRD, FE-SEM, TG, FTIR and N₂ adsorption–desorption techniques. Transition metals like Fe, Cu and Mo were impregnated by wet impregnation method. Cu-impregnated nano-sized Silicalite-1 was found to be highly active for the oxidation of toluene with H₂O₂.

Keywords. Nano-sized Silicalite-1; toluene oxidation; liquid phase; zeolite.

1. Introduction

The selective oxidation of organic compounds is considered as a crucial transformation in organic synthesis. Benzaldehyde is used as a raw material or intermediate in pharmaceutical,¹ perfumery,² dyestuff, agrochemicals and plastic industries. Toluene can be oxidized into several derivatives such as benzyl alcohol, benzaldehyde, benzoic acid, etc., in which benzaldehyde is the essential industrially used aromatic aldehyde among all the oxidized products. The chlorination of toluene and hydrolysis of benzylchloride are the conventional industrial processes for the production of benzaldehyde, which generally cause chlorine contamination that directly affects the production of benzaldehyde. Some of the drawbacks of this process are harsh conditions, formation of toxic acid, tedious and expensive separation procedure and lower yield of benzaldehyde.³ Vapor phase reaction at high temperature and pressure is the alternate oxidation method for toluene with the flow of oxygen. However, the mentioned method seems too difficult for the improvement of benzaldehyde selectivity.^{4,5}

Liquid phase oxidation of toluene using potential oxidizing agents like air, organic peroxides, hydrogen peroxide, etc., provide better scope to the industrial processes under mild reaction conditions. Several methods are reported with the homogeneous catalysts such as iridium(III) chloride,⁶ metal complexes,^{7–9} 10-methyl-9-phenylacridinium ion,¹⁰ xanthone,¹¹ and polyoxometalate.¹² Some other heterogeneous catalysts are also reported for this reaction such as supported metal complexes^{13–15} and metal containing molecular sieves.^{16–20} Song *et al.*²¹ reported oxidation of toluene over copper nanoparticle supported graphene. Compared to other organic oxidants, hydrogen peroxide is widely used in liquid phase oxidation reactions due to its easy handling, cost-effectiveness and environment-friendly qualities. Du *et al.*,²² have used sodium treated ZSM-5 and Li *et al.*,²³ have used various iron-supported zeolites along with the use of hydrogen peroxide as an oxidant for the oxidation of toluene. There are other reports available using hydrogen peroxide along with metal-loaded/metal-free zeolites like [Cu(terpy)]²⁺@Y, Co₃O₄@HZSM-5, Sn-Beta, Fe/ZSM-5, TS-1, VS-1, Sn-Silicalite-1(MFI),

*For correspondence

Sn-Silicalite-2(MEL), Sn-MTW, metal free Silicalites, Sn-ZSM-12, ZSM-12, Sn-ZSM-48 (Al free), etc.^{24–33}

As the crystal size of zeolite reduces, all other associated properties like external surface area, surface charge, and ionic charge show remarkable enhancement. These changes enable the reaction of bulky molecules on the zeolite surface, which is not possible due to the microporous nature of zeolite crystal. The transport of the molecules from the surface to the center of the crystals is a slow process due to the presence of these narrow pores. Consequently, adsorption and reaction occur primarily at the outer shell of the zeolite crystals while the interior is hardly used, reducing the total effectiveness of the zeolite catalyst and limiting the effect of the pore selectivity for reactants or products. In order to utilize the entire zeolite crystal and to decrease the total adsorption/desorption time, one can lower these diffusion limitations by using smaller crystal size, e.g., nanocrystals, or by the synthesis of mesoporous zeolites. It is also possible to combine zeolite with other binders and supports, and increase its usability in other fields.^{34–36}

Silicalite-1 has a pentagonal 10-membered ring structure. The framework is a combination of two intersecting channels; one elliptical-shaped straight channel with a cross section $0.53 \text{ nm} \times 0.56 \text{ nm}$, and another zig-zag channel with cross section $0.51 \text{ nm} \times 0.55 \text{ nm}$.³⁷ Here, we report the synthesis of nano-sized Silicalite-1, and selective oxidation of toluene over metal-impregnated nano-sized Silicalite-1 using hydrogen peroxide as an oxidant in a liquid phase at mild condition.

The novelty of the present study is the synthesis of nano-sized Silicalite-1 using H_3PO_4 as a promoter in minimum time with good crystallinity as well as exploring the effect of metal impregnated nano-sized Silicalite-1 as a catalyst in the oxidation of toluene.

2. Experimental

2.1 Materials

Tetra propyl ammonium hydroxide (TPAOH, 40 wt% solution) was procured from Tritech Catalyst and Intermediate Pvt. Ltd. Sodium silicate (26.7% SiO_2 , 14.4% Na_2O) and phosphoric acid (85%) was procured from SD Fine Chem. Ltd. Ferric nitrate (98%), copper nitrate (98%), ammonium heptamolybdate (97%), acetonitrile (99%), toluene (99%) and hydrogen peroxide (30% solution) were purchased from Merck. All the chemicals were of analytical grade and used as obtained without further purification.

2.2 Catalyst synthesis

Synthesis of nano-sized Silicalite-1 was carried out with the molar gel composition 1 SiO_2 : 0.25 TPAOH: 1.042 NaOH: 0.271 H_3PO_4 : 30 H_2O and was prepared by mixing water, TPAOH and H_3PO_4 to Na-Silicate solution. The pH of the final gel was adjusted at 11.5 by adding H_3PO_4 . H_3PO_4 was added as a promoter to reduce the synthesis time and obtain good crystallinity in a short time period which has not been explored so far for the Silicalite-1 system. The synthesis gel was further stirred for 4 h at room temperature. The hydrothermal synthesis was carried out at 160°C for 24 h until complete crystallization. The nanocrystals were collected by centrifugation. After discarding the supernatant liquid, the solid product was recovered, dried at 90°C overnight, followed by calcination at 550°C for 5 h.

Copper nitrate, Ferric nitrate and ammonium heptamolybdate were used as a source of metal and doped on nano-sized Silicalite-1 by wet impregnation technique. An aqueous solution of each metal source containing 3% transition metal ions was stirred at room temperature with nano-sized Silicalite-1 for 1 h and the solution was evaporated to dryness. The solid was dried and grinded at 100°C overnight followed by calcination for 5 h at 550°C .

2.3 Effect of seed amount on crystallization time

Effect of seed amount on the hydrothermal synthesis of nano-sized Silicalite-1 was studied by taking different seed weight percentage in terms of SiO_2 . Initially, 4% seed was fixed with varying the hydrothermal synthesis time (i.e., 10 h, 18 h, 24 h, and 30 h) to study the crystal growth and crystallinity of the Silicalite-1. The yield of the product at 10 h was very less compared to 18 h. Further synthesis time (18 h) was fixed and seed amount was varied in terms of SiO_2 (i.e., 1%, 2%, 3%, and 4%) to study the growth and crystallinity of the nano-sized Silicalite-1 (Table 1).

2.4 Oxidation of toluene

Oxidation of toluene was carried out in an RB flask equipped with reflux condenser and magnetic stirrer. Catalyst, acetonitrile and toluene were added in the desired proportion and

Table 1. Effect of seed on crystallization time.

No.	Seed amount	Crystallization time (h)	% Yield	% Relative crystallinity
1	–	24	65	100
2	1%	18	65	92
3	1%	12	54	90
4	2%	18	74	93
5	2%	12	67	85
6	3%	18	79	92
7	3%	12	69	91
8	4%	6	70	90

Figure 1. XRD of Silicalite-1; Pattern number corresponds to entry number in Table 1.

heated at the set temperature. Hydrogen peroxide was added dropwise to the reaction mixture at regular intervals. Reaction samples were drawn at regular time intervals and analyzed using GC (Shimadzu 2025). The solid catalyst was separated by centrifugation while liquid samples were injected to GC with HP5 capillary column and FID detector. Conversion of toluene and yield of benzaldehyde were measured by manual calibration curve method. Product identification was done over GCMS (Agilent 7890).

3. Results and Discussion

3.1 Characterization of catalyst

Figure 1 shows the XRD patterns of nano-sized Silicalite-1 (pattern number corresponds to an entry in Table 1), which confirm the MFI structure. Seed concentration on the reaction time reveals that pure MFI phase with good crystallinity was obtained in minimum reaction time of 6 h by using 4% seed with a good yield. Yield increased to 79% using 3% seed

Figure 3. FTIR spectrum of Silicalite-1.

and in 18 h reaction time. Crystallinity was not much affected while using the seed to decrease the crystallization time. The seeding effect resulted in the pure and uniform sized crystals under the reduced crystallization time.

The XRD patterns of all samples showed five distinct peaks at 7.98° , 8.87° , 23.18° , 23.98° , and 24.43° corresponding to (101), (020), (501), (151), and (303) reflections which represent MFI structure.^{38,39} The average crystallite size of Silicalite-1 and Cu loaded Silicalite-1 calculated by Scherrer equation^{40–42} was found to be 40 nm and 64 nm, respectively.

As shown in FE-SEM (Figure 2), individual crystals of 30–40 nm size were agglomerated to form clusters of approximately 150–200 nm. The decrease in crystal size enhances the surface area with more number of active sites.

The FTIR spectra of nano-sized Silicalite-1 is shown in Figure 3. Vibration bands at 439.05, 799.67, 1079.68 and 1226.81 cm^{-1} were observed and assigned to

Figure 2. FE-SEM images of Silicalite-1.

Figure 4. TG of Silicalite-1.

Si-O-Si bending, Si-O-Si symmetric stretching (outer SiO_4 tetrahedron), Si-O-Si asymmetric stretching (inner SiO_4 tetrahedron), and Si-O-Si asymmetric stretching (outer SiO_4 tetrahedron) of a condensed silica network, respectively. The absorption peaks at around 977.57 and 545.31 cm^{-1} are assigned to the stretching vibration of the Si-OH group and MFI-structure, respectively.^{38,39}

Thermal stability of as-synthesized catalyst was studied by thermogravimetric (TG) analysis. The TG curve (Figure 4) shows the initial weight loss of about 4.67% below $200\text{ }^\circ\text{C}$ due to evaporation of physisorbed and structural water from the surface. The second weight loss of 9.82% between 350 and $560\text{ }^\circ\text{C}$ is due to the decomposition of organic moieties within the framework. No significant weightloss was observed after $560\text{ }^\circ\text{C}$, indicating good thermal stability of the material.

Physical properties such as BET surface area, micropore and mesopore area, micropore volume, total pore volume and average pore diameter of Silicalite-1 and Cu loaded Silicalite-1 are reported in Table 2. Adsorption isotherm and pore size distribution of the samples are also compared in Figure 5. Copper loaded Silicalite-1 shows a decrease in surface area, pore volume and pore diameter compared to Silicalite-1 due to partial blocking of pores and surface by copper ions. The isotherms showing some mesoporosity with H1 type hysteresis loop at high pressure is not very common for microporous Silicalite-1 samples. However, it may be due to the presence of inter-particle void space between the elementary crystalline particles. Such type of H1/H4 type high-pressure hysteresis was observed in MFI phases by other researchers also resulting from swelling of microporous fissured regions or between large parallel crystal slabs.^{43,44}

Table 2. Physical characteristics of Silicalite-1 and Cu Silicalite-1.

Sample	BET surface area (m^2/g)	Micropore area (m^2/g)	Mesopore area (m^2/g)	t-Plot micropore volume (cm^3/g)	Total pore volume (cm^3/g)	Average pore diameter ($\text{\AA}$)
Silicalite-1	350	239	111	0.12	0.25	131
Cu Silicalite-1	277	201	76	0.10	0.20	121

Figure 5. (a) N_2 Adsorption-desorption isotherms and (b) BJH pore size distribution of Silicalite-1 and Cu Silicalite-1.

Figure 6. Selectivity and conversion at various temperature and metal loading (Cu, Fe and Mo). Reaction conditions: Time 6 h, 0.2 g catalyst, Acetonitrile 12 mL, Toluene 0.87 mL, Toluene to H₂O₂ molar ratio 1:3.

Table 3. Effect of solvent on oxidation of toluene.

Solvent	Conversion of toluene (%)	Selectivity (%)	
		Benzaldehyde	Others
Water	2.6	98.1	1.9
Ethanol	25.8	47.2	52.8
Acetonitrile	22.2	27.9	72.1
DMSO	8.6	8.7	91.3
Cyclohexane	7.0	0.9	99.1
DMF	1.9	39.7	60.3

Reaction conditions: Time 6 h, 0.2 g catalyst, Solvent 12 mL, Toluene 0.87 mL, Toluene to H₂O₂ molar ratio 1:3.

3.2 Catalytic activity of metal loaded nano-sized Silicalite-1 towards selective oxidation of toluene

In order to get optimized catalyst in the selective oxidation of toluene, the reaction parameter was varied by studying the effect of different transition metal ions (Cu, Fe and Mo) loading on nano-sized Silicalite-1, catalyst amount (0.1–0.3 g), reaction temperature (70–110 °C), time (6–24 h) and Toluene/ H₂O₂ molar ratio (1:1–1:5).

The effect of impregnation of transition metal ions (Cu, Fe and Mo) on nano-sized Silicalite-1 in the reaction was studied by varying the temperature from 70 °C to 110 °C. Figure 6 shows the influence of transition metal ions and temperature in the conversion of toluene and benzaldehyde selectivity. Iron and molybdenum impregnated nano-sized Silicalite-1 show very good selectivity towards benzaldehyde with very less conversion. On the other hand, copper impregnated nano-sized Silicalite-1 show very good conversion and good selectivity towards benzaldehyde. It is observed that the conversion of toluene increased from 17% to 31% with increasing the reaction temperature from 70 °C to 110 °C. However, the selectivity of benzaldehyde decreased from 30.8% to 26.5%. The low conversion

of toluene at 70 °C may be due to the thermal effect of kinetically controlled reaction. Thus, conversion of toluene increases with the increase in reaction temperature. It is considered that more by-products form due to an increase in temperature. To achieve optimum toluene conversion and benzaldehyde selectivity, 70 °C temperature and copper impregnated nano-sized Silicalite-1 as the catalyst was fixed for further evaluation of the catalyst.

The effect of solvents are shown in Table 3. The conversion of toluene was increased from 1.9% in a weak polar solvent such as DMF to 2.6% in a strong polar solvent such as water, and then to 22.2% in a medium polar solvent such as acetonitrile. In strong polar solvent like water, main oxidation product, benzaldehyde was 98.1%, but the conversion was only 2.6%. In weak polar solvents such as DMSO and DMF, the conversion was increased from 1.9% to 8.6%, while selectivity was drastically decreased to 39.7% from 8.7%. Significant conversion and selectivity (22.2% and 27.9%, respectively) were obtained in a medium polar solvent such as acetonitrile.

Other important factors, which influence the oxidation of toluene, are reaction time and catalyst amount. Figure 7 shows the effect of reaction time (6 h to 24 h)

Figure 7. Effect of reaction time and amount of catalyst. Reaction conditions: Temperature 70 °C, Toluene to H₂O₂ molar ratio 1:3, Acetonitrile 12 mL, Toluene 0.87 mL.

Figure 8. Effect of reaction time and Toluene/H₂O₂ molar ratio. Reaction condition: Temperature 70 °C, catalyst 0.2 g, Acetonitrile 12 mL, Toluene 0.87 mL.

and catalyst amount (0.1 g to 0.3 g) on the oxidation of toluene using copper impregnated nano-sized Silicalite-1. Conversion of toluene increases with the increase in reaction time and catalyst amount. No remarkable change was observed in the conversion of toluene with an increase in the reaction time further from 18 h to 24 h. The conversion of toluene is lower with 0.1 g catalyst, which is due to insufficient active sites. However, with increasing the catalyst amount from 0.1 g to 0.3 g, the conversion remarkably increased from 27% to 52%. While taking 0.2 g and 0.3 g catalyst, no significant conversion difference was observed; therefore, 0.2 g catalyst and 18 h reaction time were considered as the ideal condition for optimizing the reaction parameters.

Influence of the molar ratio of Toluene/H₂O₂ with respect to time on the oxidation of toluene was also studied by keeping other parameters constant (Figure 8). Conversion of toluene increased as reaction time increased in each set of molar ratio. The conversion of toluene was lower when toluene to H₂O₂ molar ratio was 1:1. This is due to complete utilization of H₂O₂ during the oxidation of toluene. When the molar ratio of toluene to H₂O₂ increased from 1:1 to 1:5, the conversion of toluene starts increasing. This result

clearly indicates that conversion of toluene increases with increasing the amount of H₂O₂. This is due to the liberation of the high amount of oxygen on the decomposition of H₂O₂, which is responsible for oxidizing toluene. At the same time, an excess amount of liberated oxygen favors further oxidation of benzaldehyde that leads to the formation of benzoic acid. Therefore, the optimum molar ratio for this reaction was found to be 1:3.

Copper loaded Silicalite-1 was also tested for reusability in the oxidation of toluene at optimized reaction condition. In a typical experiment (after completion of each reaction) catalyst was recovered by centrifuge, washed with methanol, dried at 100 °C for overnight and used two times. Figure 9 shows the catalytic activity after each reaction cycle. Conversion of toluene decreased to 33.3% from 52.6% and selectivity of benzaldehyde decreased to 17.4% from 30.2% after 2nd cycle. The decrease in catalytic activity in the subsequent run may be due to partial metal leaching during the reaction and workup process. The XRD patterns (Figure S5, Supplementary Information) after each reaction revealed that the copper loaded Silicalite-1 retained its crystallinity throughout.

Figure 9. Catalyst reusability at optimized reaction conditions: Temperature 70 °C, catalyst 0.2 g, Acetonitrile 12 mL, Toluene 0.87 mL, Toluene/H₂O₂ molar ratio 1:3, Time 18 h.

4. Conclusions

Nano-sized Silicalite-1 having MFI structure was successfully synthesized by a novel method using H₃PO₄ as a promoter. Structural, thermal, morphological and other characteristics of the catalyst were confirmed by using XRD, TG, FE-SEM and FTIR techniques. Effect of seed amount on crystal growth and crystallinity during the synthesis was found to be significant. Selective oxidation of toluene was found to be strongly influenced by the type of impregnated metal, reaction time, catalyst amount, temperature and toluene to H₂O₂ molar ratio. Copper impregnated nano-sized Silicalite-1 showed superior catalytic activity compared to its iron and molybdenum impregnated counterparts.

Supplementary Information (SI)

The results comprising effect of metal loading and reaction temperature on oxidation of toluene (Table S1); effect of reaction time and amount of catalyst (Table S2); effect of various reaction time, toluene to H₂O₂ molar ratio (Table S3), catalyst reusability (Table S4) and XRD patterns of reused catalyst (Figure S5) are available in Supplementary Information at www.ias.ac.in/chemsci.

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