In-Situ Synthesis of ZSM-5 Catalyst to Form SCR Catalyst Membrane and it's Application in NOx Reduction

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Abstract: Zeolite Socony Mobil-5 (ZSM-5) is a synthetic Aluminium silicate zeolite belonging to the pentasil family of zeolite. The vertices are Al or Si and an O is assumed to be bonded between the vertices. In the present work, ZSM-5 was prepared by using Colloidal Silica and sodium aluminate as silicon and aluminium sources respectively. Since, ZSM-5 acts as catalyst even at prolonged high temperature, the ZSM-5 is used for the Selective Catalytic Reduction of (SCR) of NOx in the exhaust pipe of diesel engine. A thin film of ZSM-5 was developed on the metal sheet by hydrothermal method forms a Selective Catalytic Reduction (SCR) catalyst of plate type of structure. The characterization of SCR catalyst is carried by subjecting to X-ray diffraction, BET test, erosion test. The surface area per unit weight for uncalcined sample was $40.635 \, m^2/g$. The X-ray diffraction shows that the topology of the prepared silicate-1.

INTRODUCTION

Selective Catalytic Reduction (SCR) is a means of converting Nitrogen Oxides (NOx) with the aid of a catalyst into diatomic Nitrogen (N_2) and Water (H_2O). Selective word is used because the catalyst only works for the NOx gas and it has lower reactivity towards all other gases. A gaseous reductant, typically anhydrous ammonia, aqueous ammonia or urea is added to a stream of flue or exhaust gas and is adsorbed on to a catalyst. More recent applications of SCR technology include diesel engines, such as those found on large ships, diesel locomotives, gas turbines and even automobiles[1].

In general, the SCR unit is located between the furnace economizer and the air heater and the ammonia is injected into the catalyst chamber through an ammonia injection grid (Fig. 1).
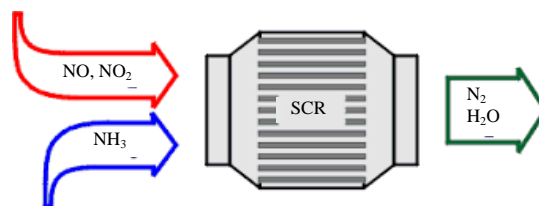

Fig. 1: Block diagram of SCR reactor[2]

As in other SCR applications, the temperature of operation is critical. Ammonia slip is also an issue with SCR technology used in power plants. Other issues that must be considered in using SCR for NOx control in power plants are the formation of ammonium sulphate and ammonium bisulphate due to the sulphur content of the fuel as well as the undesirable catalyst-caused formation

of SO_3 from the SO_2 and O_2 in the flue gas[3, 4]. SCR catalysts are made from various ceramic materials used as a carrier such as titanium oxide and active catalytic components are usually either oxides of base metals (such as vanadium, molybdenum and tungsten) zeolites or various precious metals. Base metal catalysts such as the vanadium and tungsten, lack high thermal durability but are less expensive and operate very well at the temperature ranges most commonly seen in industrial and utility boiler applications. However, they suffer with disadvantage of high catalyst activity to oxidize SO_2 into SO_3 which can be extremely damaging due to its acidic properties[5, 6].

On the other hand, zeolite catalysts have the potential to operate at substantially higher temperature than base metal catalysts; they can withstand prolonged operation at temperatures of 900 K and transient conditions of up to 1120 K. They also have a lower potential for potentially damaging SO_2 oxidation. They have low potential towards the SO_2 reduction[7]. In this regard, the objectives of present work were:

- In situ synthesis of Zeolite Socony Mobil-5 (Silicate-1) on a metal plate
- Thin filming of TiO_2 by hydrothermal treatment to form SCR catalyst
- Characterization of ZSM-5 (Silicate-1) compound by X-ray diffraction, BET and FTIR t
- Conduction of erosion test and NOx gas test

MATERIALS AND METHODS

Experimental

Preparation of precursor solution: Colloidal silica and Tetra propyl Ammonium Hydroxide (TPAOH) (which is a template ion or a surfactant) were mixed in various ratios in a 500 mL beaker. The solutions were continuously stirred for 3 h until a clear solution was obtained. The pentasil structure of the resulted compound was called as "Silicate-1" which is an important intermediate for the synthesis of the ZSM 5.

Pre-treatment of autoclave reactor and substrate: In the present work, the zeolite reaction has been conducted in alkaline medium. Hence, prior to conduct the reaction, the reactor was flashed with concentrated alkali solution. A 4 N NaOH solution was transferred to autoclave reactor and was heated to 150°C for 2 h. A 10'×11' rectangular SS 304 plate having 24 opening per inch was used as substrate. It was cleaned with ethyl alcohol prior to experiment to remove the dust and other particular matter and also to improve the adhesion of catalyst coating.

Hydrothermal coating: Pre-treated pre-cursor solution containing 30% silica along with substrate was placed in
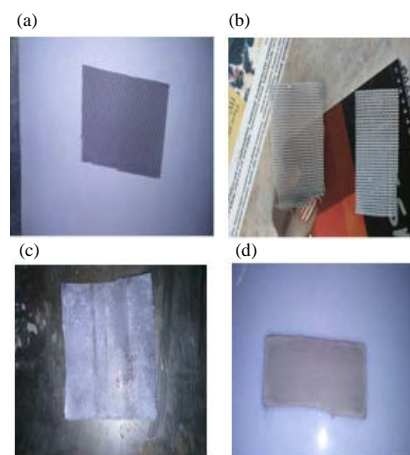

Fig. 2(a-d): (a) Pre-treated metal substrate, (b) ZSM coated Metal substrate, (c) ZSM coated Metal substrate and (d) TiO_2 coated metallic substrate plate

autoclave reactor. The reactor was heated to desired temperature for known time. After the reaction, the reactor was sudden cooled using chilled water. The substrate was washed several times with distilled water, until the pH of washings reached 7. The coated substrate was then dried at 130°C in hot air oven. The production solution was filtered to get zeolite powder.

Coating of TiO_2 catalytic paste: The hard TiO_2 was mixed with appropriate quantity of Polyethylene Glycol (PEG) which acts as plasticizer and the mass was extruded by passing through extruder to get noodles of catalyst paste which was applied uniformly on the metal substrate. The coated metal substrate was then passed through passed through a set of rollers to get uniform thickness of 1 mm and dried at room temperature.

Calcination: Calcination of coated substrate was done by heating metal substrate in Muffle furnace at 650°C for 4 h at a heating a rate of 0.5°C/s. The calcination is carried to remove template ion. For any analysis the template ion should be removed. Figure 2a shows the pretreated metallic substrate pretreated with ethanol. Figure 2b depicts two samples. The left side is single coated sample (at 423 K). The right side sample is substrate coated thrice with the ZSM at 423 K. Figure 2c depicts the substrate coated with ZSM-5 while Fig. 2d illustrates the substrate with TiO_2 substrate. The coating efficiency was higher at 473 K than 423 K. The results of different trials are shown in Table 1.

First 3 trials were carried at 150°C and for 48 h. The weight% gain in the first trial was higher (Average = 4.4%) as compared to second trial which was carried in a 300 mL autoclave reactor wherein the weight

Table 1: Weight% gain in various trials

Trial No	Residence time (sec)	Temperature (°C)	SiO$_2$:Al, O$_2$:H, O (Molar ratio)	Weight% gain
1	48	150	15:1:160	4.37
2	48	150	13:1:130	2.76
3	48	150	15:1:160	4.49
4	24	200	13:1:150	12.12
5	24	200	8:1:30	14.36

Wet ammonia gas → Catalytic conversion reactor → Nitrogen and other gases

NO gas, air → Catalytic conversion reactor → Concentration of different molecules

Fig. 3: Process flow of NOx test

Table 2: Jet erosion test results of zeolite uncoated sample

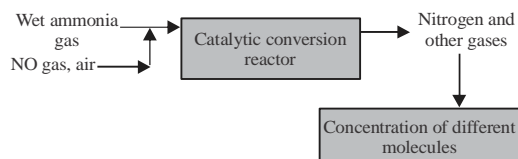| Angle (°)	Erosion rate (g min^{-1})			
	Uncoated	Single coated	Double coated	Standard sample
15	0.20	0.12	0.08	0.0012
30	0.28	0.20	0.15	0.0063
45	0.32	0.24	0.24	0.0373

gain 2.7%. Highest coating efficiency of 14.21% was obtained in Trials 5 (conducted at 200+C for 24 h).

NOX tests: The NOx test was carried by passing through the catalytic converter chamber which contains a stack of plates that contains SCR catalytic particles (Fig. 3). Initially the NO gas other gas such as oxygen, carbon dioxide, carbon monoxide were passed through the catalytic chamber. The chamber is maintained at specific temperature. The concentrations of the different gasses were noted down using a probe in the units of ppm. The concentrations of the gases were noted down at the time intervals of two minutes until the concentration of the nitrogen oxide gas reaches a constant value. After nitrogen oxide value reaches a constant value, ammonia gas is passed through certain flow rate through an inlet and again the concentrations of the different gasses were noted down using the probe. The concentrations of the gases were noted down at the time interval of two minutes until the concentration of the nitrogen oxide reaches a constant value. The % conversion is calculated by using following formula:

$$\text{Converson of NO} = \frac{\text{NO concentration in inlet-NO Concentration in outlet}}{\text{NO concentration in inlet}} \times 100$$

RESULTS AND DISCUSSION

Figure 4 shows the XRD pattern of ZSM-5 sample prepared by using TPAOH/Si ratio value of 0.125. Figure 5 is the FTIR spectrum for the ZSM-5 (prepared by using TPAOH/Si ratio value of 0.125).

Comparing the FTIR spectra reveal absorption bands of both the samples, at 1634, 1225, 1150-1050, 796, 549 and 456 cm^{-1}. The absorption bands at 1225 cm^{-1} (external asymmetric stretch), 1100 cm^{-1} (internal asymmetric stretch), 796 cm^{-1} (external symmetric stretch) and 456 cm^{-1} (T-O bend) corresponded to siliceous materials. The framework vibration band at

549 cm^{-1} which has been assigned to the five-membered rings of MFI zeolites can be used to determine the crystallinity of ZSM-5 zeolites. The other vibration bands present in Fig. 2a are may be because of presence of impurities. Hence, from both X-Ray diffraction and Fourier transformed infrared spectroscopy, it is confirmed that the synthesized material is silicate-1.

Jet erosion test: The results of jet erosion tests were shown in Table 2. The tests were carried for 3 different samples in which the results are compared to the erosion test of the standard sample.

As can be observed from Table 2, uncoated sample had highest corrosion rates at all angles while single and double coated samples had similar equal corrosion rate at 90°. The double coated sample had lesser corrosion rate at 15° and 30° as compared to single coated sample. Any of the values of the upper three curves is difficult to compare with the yellow curve values because the values are almost 100 times less than that of those values. But in the sample of the yellow curve which is imported one is having a film of cement material on the catalyst surface which is piousness to the catalyst and decrease the conversion rate. Due to that cement material, the erosion rate is so less of that sample. Hence, the conversion and the amount of conversion are vice versa in the values. The imported one is having less conversion and the samples of zeolite coated are having comparatively high erosion rate and conversion with the imported one.

NOx reductions: As can be observed from Table 3, concentration of NO reaches highest concentration at 6 min (336 ppm). After this, the ammonia gas is passed and the concentration of the nitrogen oxide starts to decrease and it remains constant after 8 min at 25 ppm. The total conversion value is around 92.4%. The concentration of the other gas such as carbon monoxide, nitrogen dioxide or oxygen does not vary much with time. The concentration of the oxygen remains almost constant with time. The variation in the carbon monoxide is due to variation in the flow rate of the air and other experimental

Table 3: Concentration of gases before ammonia passing

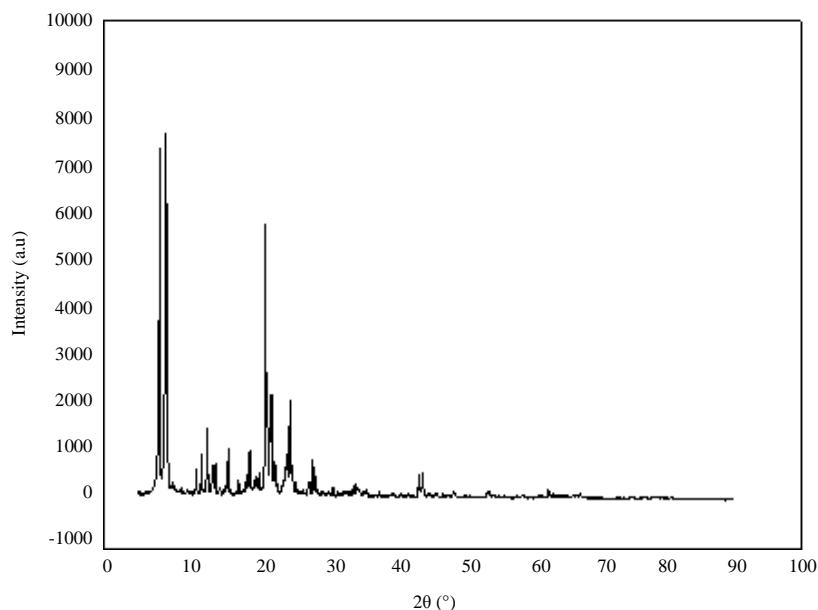| Time (min)	Initial Concentration of gases (ppm)				Concentration of gases after passing through catalytic reactor (ppm)			
	O_2	NO_2	NO	CO	O_2	NO_2	NO	CO
2	20.8	6.3	321.8	28.70	20.8	6.9	336.4	103.0
4	20.8	5.9	318.2	92.60	20.8	2.9	125.4	28.70
6	20.8	6.5	320.0	99.10	20.8	1.1	94.00	92.60
8	20.8	6.9	336.4	103.0	20.8	0.7	96.00	99.10

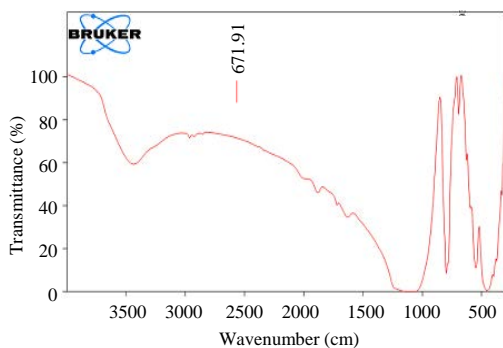Fig. 4: X-ray diffraction of the synthesis material synthesized at 200°C FTIR of ZSM-5

Fig. 5: FTIR spectrum of sample synthesized at 200°C

errors. Concentration of the nitrogen dioxide gas does not vary much since, the concentration of the gas is very less. NOx test was carried by passing air, ammonia and Nitrogen oxide and nitrogen dioxide gasses. Air was sent at the flow rate of 10 standard liter per minute and nitrogen oxide was sent at 0.07 standard LPM. The test was carried at 350°C.

CONCLUSION

The synthesized sample is ZSM-5 (silicate-1) material was confirmed by X-ray diffraction and FTIR spectrum and BET test. Thin TiO_2 film was applied on the metal mesh and erosion test, NOx were carried and results shown that erosion decreased as No. of layers of coating increased. COMSOL modeling was done for the catalytic conversion and the values of velocity, pressure and concentration was noted down.

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