Synthesis of novel Ag modified MCM-41 mesoporous molecular sieve and beta zeolite catalysts for ozone decomposition at ambient temperature

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Mesoporous molecular sieve Na-MCM-41 with Si/Al ratio 20 and 50 and Na-beta zeolite with Si/Al ratio 11 were synthesized and characterized using X-ray powder diffraction, scanning electron microscope and nitrogen adsorption. The Ag (5 and 2 wt%) modifications of H-MCM-41-20, H-MCM-41-50 and H-beta-11 catalysts were carried out using impregnation method. The catalysts were tested in the decomposition of ozone at ambient temperature. The 5 wt% Ag-H-MCM-41 catalyst showed a very high decomposition of ozone (~98%). The 5 wt% Ag-H-MCM-41-50 catalyst exhibited higher decomposition rate than 2 wt% Ag-H-MCM-41-50. The Ag modified H-MCM-41 catalyst with higher Si/Al ratio showed higher reaction rate than the catalyst with lower Si/Al ratio. The H-MCM-41 catalyst without Ag exhibited the lowest decomposition of ozone indicating an important role of Ag in the reaction.

1. Introduction

Ozone is a toxic compound and is environmentally unfriendly because it can cause breathing problems, headaches and photo-chemical smog. Hence the catalytic decomposition of ozone is of great importance in order to keep the environment clean. There are several reports in the patent and open literature on the gas phase and aqueous solution (photo catalytic) decomposition of ozone. The Pt, Pd, Cu, Co, Fe and Ni supported SiO_2, Al_2O_3 and TiO_2 and activated carbon catalysts have been studied for this reaction [1–5].

Metal modified and proton form zeolite catalysts are used in the petrochemical industry and have potential applications in the synthesis of fine chemicals and environmental catalysis. Several transition and noble metal modified zeolite catalysts have been used in the solving of environmental related problems such as investigation of the removal of NO_x, CO and unburnt hydrocarbons from emissions of exhaust gas. The Cu-ZSM-5 zeolite catalyst has been investigated in the NO_x decomposition [6–8]. Na-MCM-41 is a new mesoporous molecular sieve invented at Mobil Company [9]. The mesoporous molecular sieve material because of its high surface area, uniform pores, tunable acidity and high thermal stability has attracted attention of researchers in industry and academia as a catalytic material. Metal modified and proton forms of MCM-41 have been investigated for several catalytic reactions such as hydrogenation of cinnamaldehyde, isomerisation of linoleic acid, reduction of NO using hydrocarbons, ring opening of decalin and isomerisation of 1-butene to name a few [10–14]. The decomposition of ozone over silver modified catalysts has been reported in the literature [15].

There are only few reports in the literature where high silica zeolites such as ZSM-5 and mordenite have been used as adsorbents of ozone in filters [16]. However, there are no reports in the open literature regarding the application of metal modified MCM-41 mesoporous molecular sieve in the catalytic decomposition of ozone.

In this work we report the synthesis of novel Ag modified MCM-41 mesoporous molecular sieve and beta zeolite catalysts and their application for the gas phase catalytic decomposition of ozone at ambient temperature of 296 K. Furthermore the influence of Ag loadings and acidity of MCM-41 on the decomposition of ozone is reported.

2. Experimental

2.1. Catalyst synthesis and characterization

Synthesis of Na-MCM-41 mesoporous molecular sieve was carried out in laboratory using the method mentioned in reference [17] with some modifications. The reagents used in the synthesis were fumed silica (Aldrich), tetramethyl ammonium silicate (Sachem), sodium silicate (Merck), cetyltrimethyl ammonium bromide (Aldrich), and aluminum isopropoxide (Aldrich) and distilled

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water. A gel mixture was prepared and introduced in a 300-mL autoclave (Parr). The synthesis of Na-MCM-41 was carried out in an oven at 373 K. After the completion of synthesis, the autoclave was quenched, and mesoporous material was filtered and washed with distilled water. Drying of the sample was carried out at 383 K and calcination at 823 K. The Na-MCM-41 was ion-exchanged with 1 M NH_4Cl solution, washed with distilled water to remove chloride ions and dried at 373 K. The H-MCM-41 catalyst was obtained by calcination of NH_4-MCM-41 at 813 K.

Na-beta zeolite was synthesized as mentioned in Ref. [18] with some modifications. Solution A was prepared by mixing Ludox As 40 (Aldrich) with distilled water. Solution B was prepared by dissolving sodium aluminate in distilled water and adding tetraethylammonium hydroxide (Fluka). Solution A was added to B and stirred for a required amount of time. The gel formed was transferred in a teflon cup, which was inserted in a stainless steel autoclave. The synthesis of Na-beta zeolite was carried out 423 K. After completion of synthesis, autoclaves were quenched, crystalline product filtered, washed with distilled water, dried and calcined 823 K. Proton form of beta was obtained by ion-exchange of Na-Beta, using 1 M NH_4Cl solution, followed by removal of Cl^- by water, drying at 383 K and calcination of NH_4-beta at 773 K.

The Na-MCM-41 mesoporous molecular sieve and Na-beta zeolite as well as silver containing materials were characterized by X-ray powder diffractometer (Philips PW 1800), X-ray fluorescency spectrometer (Siemens SRS 303) and the specific surface area was determined by nitrogen adsorption using a Sorptometer 1900 (Carlo Erba Instruments). The modification of H-MCM-41 and H-beta with Ag was carried out by an incipient wetness impregnation catalyst preparation method using an aqueous solution of silver nitrate. The H-MCM-41-20 and H-MCM-41-50 mesoporous molecular sieves nominally loaded with 2 and 5 wt% Ag, and H-beta-11 loaded with 5 wt% was dried at 373 K and calcined at 723 K in an oven for 2 h.

2.2. Catalytic experiments

The catalytic activity of the Ag modified MCM-41 and Beta zeolite catalysts was investigated in an isothermal plug flow reactor (4.2 mm i.d.) permitting work under steady state conditions without temperature gradients. The catalyst amount and grain size (0.042 cm^3, 0.2–0.4 mm, prepared by tabletting at 9.5 tons/cm^3 and sieving) were chosen in conformity with the reactor diameter as well as with the volume rate (mean value GHSV = 133 300 h^{-1}, calculated on the total catalyst bed volume) in order to reduce the effect of external diffusion. Conversion and first order rate constant for plug flow reactor were calculated on the basis of equations:

$$\text{conversion } (\%) = 100 * (C_{\text{inlet}} - C_{\text{outlet}})/C_{\text{inlet}}$$
$$\text{rate constant } (h^{-1}) = -\text{GHSV} * \ln(1 - \text{conversion})$$

where C_{inlet} and C_{outlet} are ozone concentrations of ozone in inlet and outlet of reactor. The inlet concentration of ozone was 9.4 g/m^3 in 5.6 L/h O_2. Ozone concentration was analyzed with an Ozomat GM (Germany) ozone analyzer. The initial activity of the catalysts was measured after 15 min. The detail description of catalyst testing of ozone can be found in Ref. [19].

3. Result and discussion

3.1. Catalyst characterization results

X-ray powder diffraction patterns of Na-MCM-41 mesoporous molecular sieve and Na-Beta zeolites were found to be similar to those given in literature. Hence it was concluded that the synthesized material had indeed MCM-41 and Beta zeolite structures. The Si/Al ratio of Na-MCM-41-20, Na-MCM-41-50 and Na-Beta-11 zeolite were determined to be 20, 50 and 11, respectively, as measured by X-ray fluorescency. The surface area of Na-MCM-41 and 5 wt% Ag-H-MCM-41-20 mesoporous molecular sieve catalysts were determined to be 1214 and 957 m^2/g, respectively. The X-ray powder diffraction pattern of 5 wt % Ag-H-MCM-41-20 mesoporous molecular sieve is given in figure 1. The main characteristic peaks of MCM-41 was found in 5 wt% Ag-H-MCM-41-20 between 2θ value of 0.5° and 7°, however, there were extra peaks at 2θ value between 8° and 45.5°. The peak at 2θ value of 38° is attributed to Ag.

The surface area of Na-beta and 5 wt% Ag-H-Beta-11 zeolite catalysts were determined to be 730 and 574 m^2/g, respectively. The X-ray powder diffraction pattern of 5 wt% Ag-H-Beta-11 is given in figure 2. The XRD pattern of 5 wt% Ag-H-Beta-11 is similar to that of pure beta-11, indicating that Ag is highly dispersed in the beta zeolite structure. The scanning electron micrograph (SEM) of Na-Beta zeolite showed around spherical shape crystals. The SEM of Na-beta zeolite is given in figure 3.

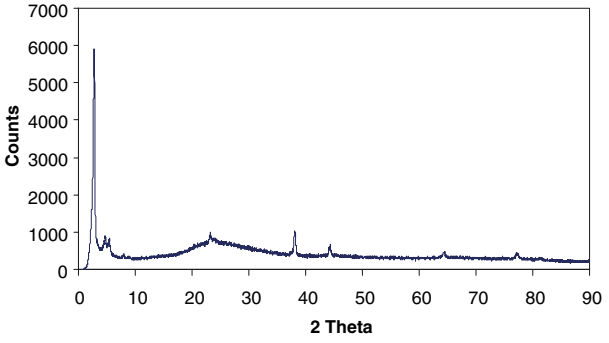

Figure 1. X-ray powder diffraction pattern of 5 wt% Ag-H-MCM-41-20 mesoporous molecular sieve catalyst.

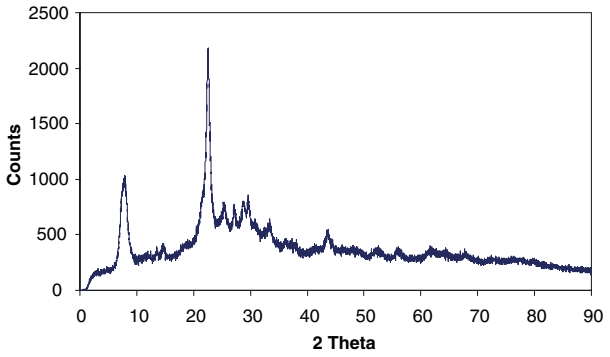

Figure 2. X-ray powder diffraction pattern of 5 wt% Ag-H-beta-11 zeolite catalyst.

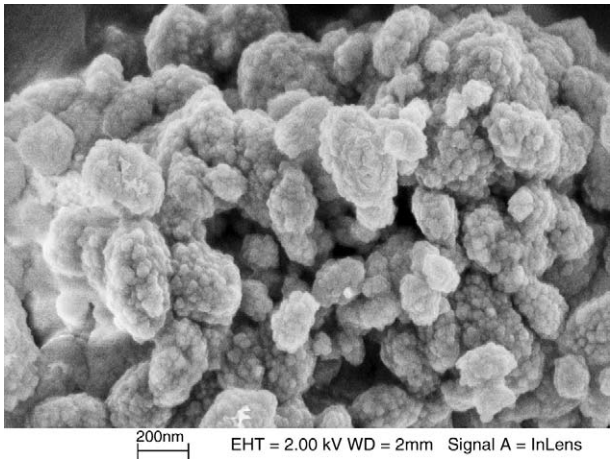

Figure 3. Scanning electron micrograph of Na-beta-11 zeolite.

Table 1
Decomposition of ozone over 5 wt% Ag-H-MCM-41-50, 2 wt% Ag-H-MCM-41-50, 5 wt% Ag-H-MCM-41-20, 2 wt% Ag-H-MCM-41-20, H-MCM-41-20 and 5 wt% Ag-H-beta-11 catalysts at ambient temperature [296 K]

Catalysts	Weight of catalyst [g]	First order rate constant [h^{-1}]	Ozone decomposition, degree [%]
5 wt% Ag-H-MCM-41-50	0.0491	5.07×10^5	97.8
2 wt% Ag-H-MCM-41-50	0.0451	2.35×10^5	82.8
5 wt% Ag-H-MCM-41-20	0.0306	3.33×10^5	91.8
2 wt% Ag-H-MCM-41-20	0.0477	9.1×10^4	49.5
H-MCM-41-20	0.0446	4.89×10^3	3.6
5 wt% Ag-H-beta-11	0.0475	2.97×10^4	44.6

3.2. Ozone decomposition over 5 wt% Ag-H-MCM-41-50, 2 wt% Ag-H-MCM-41-50, 5 wt% Ag-H-MCM-20, 2 wt% Ag-H-MCM-41-20 mesoporous molecular sieves and 5 wt% Ag-H-Beta-11 zeolite catalysts

5 wt% Ag-H-MCM-41-50 catalyst exhibited highest degree of decomposition of ozone (~98%), Table 1. The 2 wt% of Ag-H-MCM-41-50 catalyst showed lower decomposition (~83%) than the 5 wt% Ag-H-MCM-41-50 catalyst indicating that there was an influence of Ag loadings on the degree of decomposition of ozone. The proton form H-MCM-41-20 catalyst showed much lower decomposition of ozone than Ag modified MCM-41 catalyst, pointing to the importance of Ag in the ozone decomposition. Similarly, 5 wt% Ag-H-MCM-41-20 catalyst showed higher ozone decomposition (~92%) than 2 wt% Ag-H-MCM-20 (~49%). The 2 wt% Ag-H-MCM-41-20 catalyst with lower Si/Al ratio i.e. higher acidity exhibited lower ozone decomposition (49.5%) than 2 wt% Ag-H-MCM-41-50 (~83%) with higher Si/Al ratio i.e. lower acidity, elaborating that the lower acidity favored the ozone decomposition. Microporous 5 wt% Ag-H-beta-11 zeolite catalyst which is more acidic than 5 wt% Ag-H-MCM-41-50 and 5 wt% Ag-H-MCM-20 mesoporous molecular sieves showed lower ozone decomposition, further confirming that very high acidity is not beneficial for this reaction.

4. Conclusions

A very high degree of decomposition of ozone at ambient temperature (296 K) was obtained over 5 wt% Ag-H-MCM-41-50, 2 wt% Ag-H-MCM-41-50, 5 wt% Ag-H-MCM-41-20 and 2 wt% Ag-H-MCM-41-20 mesoporous molecular sieves catalysts. The decomposition of ozone increased with increase in Ag loading over H-MCM-41 catalyst with the same Si/Al ratio. The H-MCM-41 catalyst with higher Si/Al ratio exhibited higher degree of ozone decomposition. The unmodified proton form H-MCM-41 mesoporous molecular sieve demonstrated lower ozone decomposition than Ag modified MCM-41 mesoporous molecular sieve catalyst clearly indicating the important role of Ag in ozone decomposition. The Ag modified MCM-41 mesoporous molecular sieve catalyst showed higher ozone decomposition than the microporous 5 wt% Ag-H-Beta-11 zeolite catalyst.

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