SUPPORTING INFORMATION

Control of Carbon Monoxide (CO) from Automobile Exhaust by a Dealuminated Zeolite Supported Regenerative $MnCo_2O_4$ Catalyst

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S1 COMPUTATIONAL EVIDENCE FOR LOW CO ADSORPTION ENERGY ON DAZMS COMPARED TO ZEOLITE

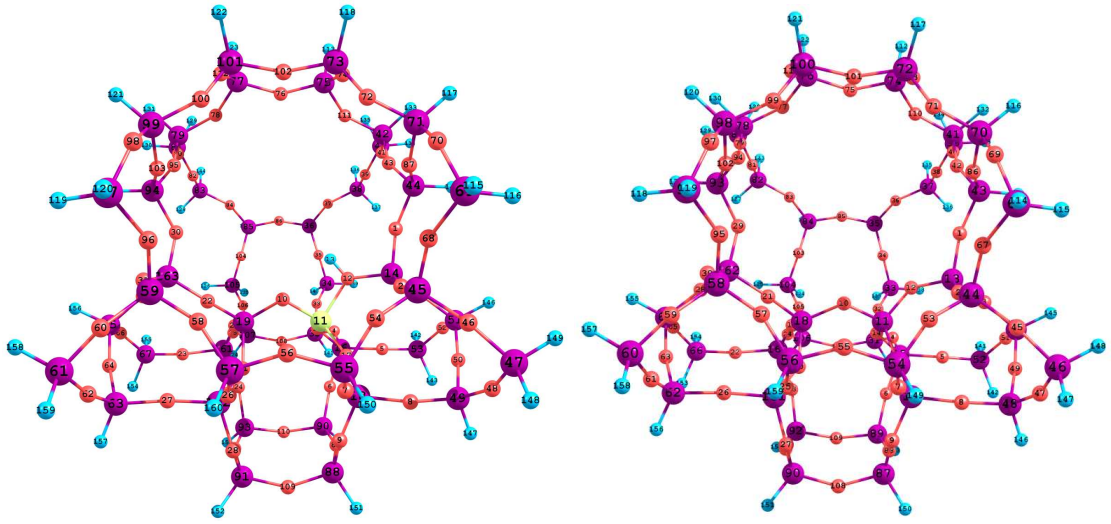
Our preliminary computational study-results evidenced that adsorption energy of CO on DAZMS was less compared to zeolite. Zeolite with a porosity of $5A^0$ (ZSM-5) was selected for the computational study. CO adsorption study was carried out on ZSM-5 and dealuminated ZSM-5.

S1 a. Computational methods and models

All calculations were performed using the standard implementation of the ONIOM method in Gaussian 09 program package. Full geometry optimizations were carried out with the ONIOM (M06L/6-31+G**: MNDO) method for all clusters studied. We had considered ZSM-5 containing 163 atoms and one Bronsted acid site as reported by Mynsbrugge et al [J. V. Mynsbrugge, K. Hemelsoet, M. Vandichel, M. Waroquier, V. V. Speybroeck, J. Phys. Chem. C, 116 (2012), 5499].

The ZSM-5 used in this study was modeled as ($AlSi_{45}H_{49}O_{68}$) cluster. And the dealuminated zeolite was modeled as ($Si_{45}H_{48}O_{68}$) cluster.

S1 b. Optimized structure of ZSM-5 and dealuminated ZSM-5



A **B**

Figure S1-1 Optimized structure of A. ZSM-5 B. Dealuminated ZSM-5 

S1 c. Adsorption energy of CO on ZSM-5 and dealuminated ZSM-5

The adsorption energy of CO on ZSM-5 and dealuminated ZSM-5 was calculated by using the equation $E_{ads} = E_{system} - (E_{cluster} + E_{adsorbate})$.
The adsorption energy of CO on dealuminated ZSM-5 was calculated as -4.83 kilo calorie and on dealuminated zeolite was calculated as -1.30 kilo calorie. It confirmed that the CO adsorption ability of dealuminated zeolite was lesser than that of CO adsorption ability of zeolite.

S2 BET ANALYSIS OF DAZMS, $MnCo_2O_4$ SYNTHESIZED WITHOUT THE PRESENCE OF DAZMS and $MnCo_2O_4$/DAZMS

BET analysis of DAZMS revealed that it possess a surface area of 10.12 m^2/g. The BET isotherm is shown in Figure S2-1. The MnCo2O4 prepared in the absence of DAZMS possessed the least surface area of 5.48 m^2/g as noted from Figure S2-2. But $MnCo_2O_4$/DAZMS had a very high surface area of 137.65 m^2/g , The BET isotherm is shown in Figure S2-3.

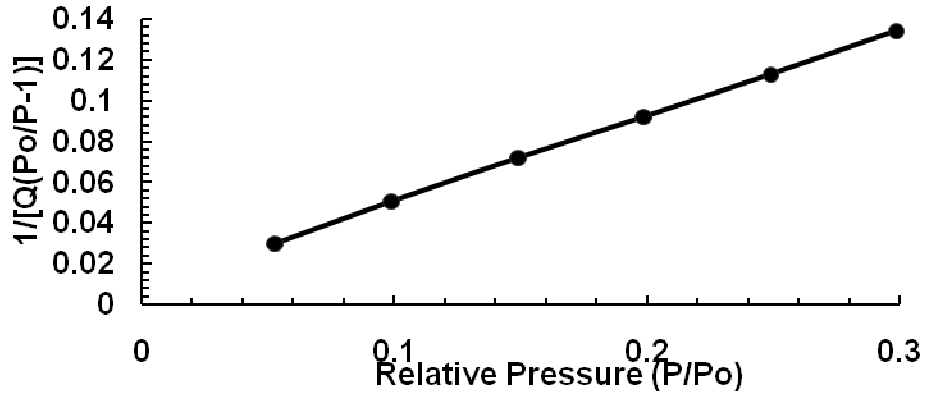


Figure S2-1 BET isotherm for DAZMS

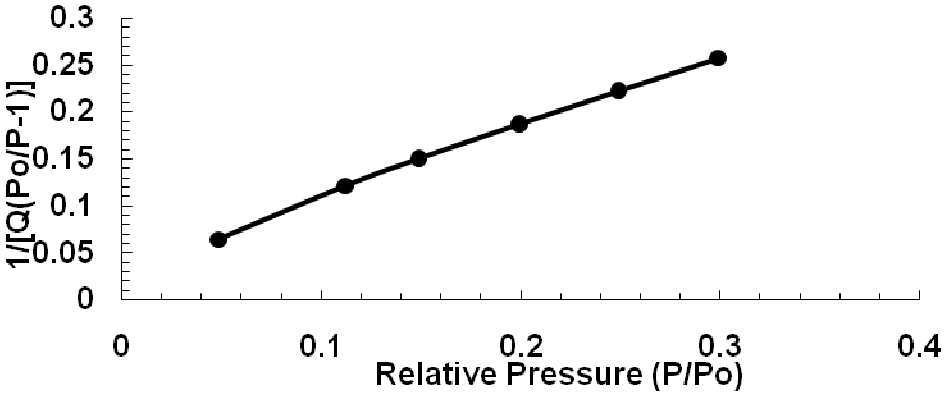


Figure S2-2 BET isotherm for $MnCo_2O_4$ synthesized in the absence of DAZMS

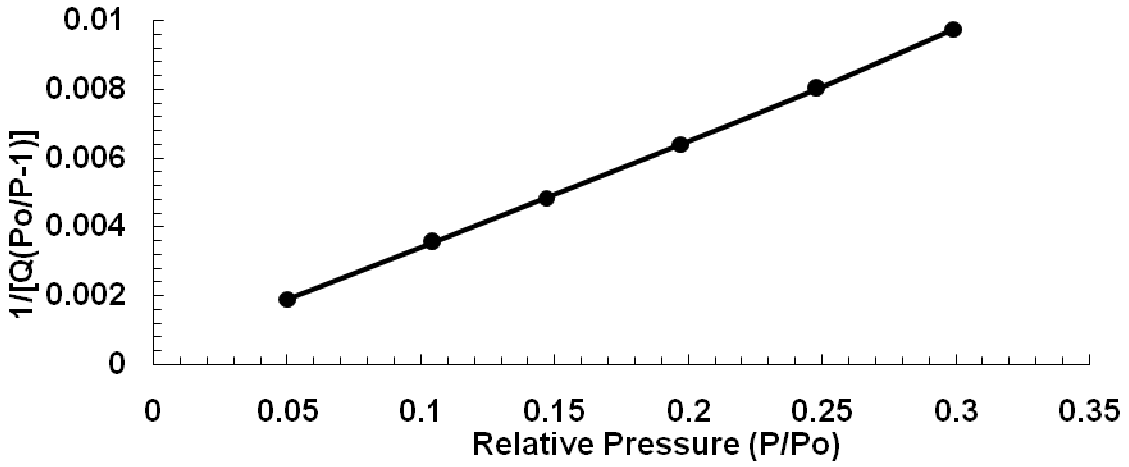


Figure S2-3 BET isotherm for $MnCo_2O_4$/DAZMS

S3 ENGINE OPERATIONAL CONDITIONS DURING CATALYTIC ACTIVITY ANALYSIS

Performance of the catalyst was analyzed using a four stroke diesel engine of ATUL Group of industries, India. The engine specifications are shown in S3-Table 1. A CO gas analyzer manufactured by Nevco Engineers Pvt. Ltd., model KM900PLUS was also used. The DAZMS supported $MnCo_2O_4$ catalyst was filled in an iron pipe and then fitted the catalyst chamber along with the exhaust of the actual engine. The performance was monitored continuously and intermittently under actual and under simulated conditions. The exhaust line of the engine was connected with a 5m long iron pipe and the catalyst chamber was connected at the end. A cooling water supply system was provided around some portions of the exhaust line such that a parallel flow of cooling water occurred along the direction of the exhaust. A rotameter was connected to the cooling water supply to control the water flow. The other portion of the exhaust line could be heated by means of a furnace. The operating conditions at the all catalytic efficiency analysis were following.

S3-Table1 Engine Specifications

Bore	85mm
Stroke	110mm
Swept volume	553 cm3
Clearance volume	36.87cm3
Rated Output	3.7kw at 1500 rpm
Orifice diameter	15mm
Rated Speed	1500 rpm

S3 a. Operating conditions for the efficiency analysis of $MnCo_2O_4$/DAZMS as a function of time in hours

Once the engine was started it was run for half an hour's for getting a stable exhaust condition and the activity was analysed. The CO conversion ability of the catalyst was monitored for 15 hours continuously. The average concentration of NOx was 98 ppm and average concentration of HC was 36 ppm. The engine was run under no load condition with 1500 rpm speed. The average temperature was maintained at 155 ^{0}C as monitored by using the rotameter system.

S3 b. Operating conditions for the efficiency analysis of $MnCo_2O_4$/DAZMS as a function of time in month

In order to find the ageing of the catalyst as a function of time it was kept in the automobile engine for 7 months. The engine was run an average of 6 hours per day at loaded and no loaded condition continuously. It worked like an ordinary automobile engine. But at the time of data acquisition the operating condition was same at no load condition viz: average exhaust temperature: 155^0C with 1500 rpm speed and the average CO inlet concentration was 243 ppm.

S3 c. Operating conditions for the efficiency analysis of $MnCo_2O_4$/DAZMS as a function of CO concentration

The concentration of CO was increased by applying different load to the engine while speed of the engine was kept constant at 1500 rpm by governing mechanism. The temperature was kept at an average temperature of 165^0C by adjusting the flow of cooling water.

S3 d. Operating conditions for the efficiency analysis of $MnCo_2O_4$/DAZMS as a function of temperature

The temperature of the exhaust was increased by means of a furnace prior to its entry into the catalyst chamber. The average exhaust concentration was 240 ppm under no load condition and the speed of the engine was 1500 rpm.

S4 THE CO OXIDATION SELECTIVITY OF THE PRESENT CATALYST IN PRESENCE OF NOX AND HC

CO oxidation ability of the catalyst along with change in concentration of NOx and HC was studied by applying different loads to the engine (The average exhaust temperature was 165^0C and the engine speed was 1500 rpm). Under these conditions the average HC concentration was found to vary from 36 to 55 ppm. But the catalyst showed no significant change in its activity while the concentration of NOx and HC got varied. This observation confirmed that the $MnCo_2O_4$/DAZMS catalyst was more selective to CO rather than NO_X and HC. The figure shows the selectivity of CO oxidation in presence of NOx.

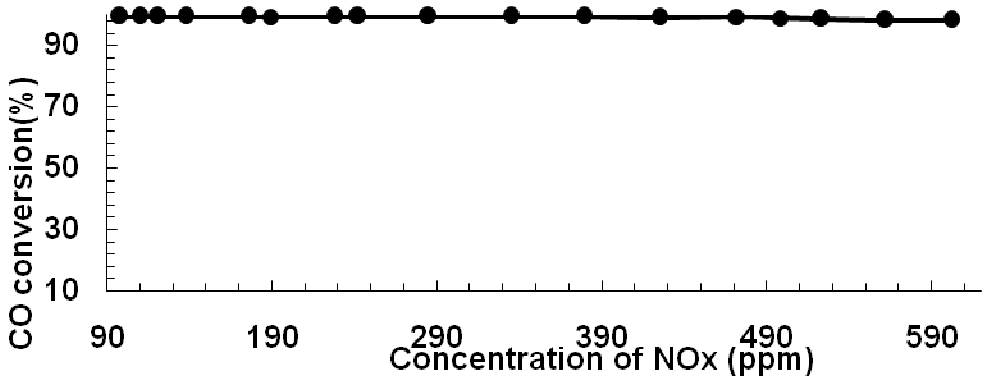


Figure S4-1 Percentage of CO oxidized in presence of different concentration of NO_x at an average exhaust temperature of 165^0C, at 1500 rpm speed at this condition HC concentration was varied from 36 to 55 ppm.