



# Deactivation Modes and Reactions of HZSM-5, AlPO<sub>4</sub>-5 and MnAPSO-5 in the Conversion of Cyclohexanol

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**Abstract**– Conversion of cyclohexanol has been used to investigate the deactivation modes of the HZSM-5, AlPO<sub>4</sub>-5 and MnAPSO-5. Conversion of cyclohexanol as a test reaction was used to evaluate the activity of these catalysts.

**Abstrak**– Penukaran sikloheksanol telah digunakan untuk mengkaji cara nyahaktif HZSM-5, AlPO<sub>4</sub>-5 dan MnAPSO-5. Penukaran sikloheksanol sebagai tindak balas uji telah digunakan untuk menilai keaktifan mangkin tersebut.

In our previous work [1, 2], it was found that the conversion of cyclohexanol is a good pointer to evaluate the Brønsted acidity from dehydration of cyclohexanol to cyclohexene and basicity from dehydrogenation of cyclohexanol to cyclohexanone of HZSM-5 and metal-substituted AlPO<sub>4</sub>-5. It was demonstrated that manganese-silicon-substituted AlPO<sub>4</sub>-5 (MnAPSO-5) was a potential catalyst for dehydration of alcohol [3]. In this work, the possible reaction of coke formation on HZSM-5 and MnAPSO-5 during the conversion of cyclohexanol is presented. The formation of coke in these catalysts was analysed by TGA, IR and GC-MS.

A more general definition of coke proposed by Karge [4] consists of

carbonaceous deposits which is deficient in hydrogen compared with the coke-forming reactant molecules. In this study, we have chosen the definition proposed by Guisnet and Magnoux [5]: Coke is a carbonaceous compounds (polyaromatic or nonpolyaromatic) formed during a reaction which is responsible for deactivation.

In this work, the activity, stability and lifetime of MnAPSO-5 in the conversion of cyclohexanol were also studied.

## **Experimental**

### ***Dehydration and Dehydrogenation of Cyclohexanol***

HZSM-5 was supplied by N. E. Chemcat

Corporation, Japan. MAS-NMR analysis shows that the Si/Al ratio is 38. The AlPO<sub>4</sub>-5 and MnAPSO-5 were prepared using the procedure given in [3]. All samples were calcined at 550°C for 20 hours in air before the reaction. Cyclohexanol (Riedel-de Haën) was used as purchased. The dehydration and dehydrogenation of cyclohexanol over the samples were carried out using a down flow, fixed bed, Pyrex reactor of 8 mm internal diameter at atmospheric pressure. The reactor was heated by a furnace. Oxygen was then passed through the catalytic bed. The reaction was carried out at 300°C, with a feed rate of 0.1 mL/min and 0.3 g of catalysts. The reaction mixture was fed from the top using a syringe pump. The water-cooled product was collected at the bottom. The unconverted cyclohexanol and the products were analysed by a Hewlett Packard Model 5880A gas chromatograph using Flame Ionisation Detector (FID). The products were analysed on Carbowax 20 M column. The column temperature was raised from 35°C to 210°C with a flow rate of 6°C/min. The activity of catalyst is expressed in terms of conversion (amount of transformed reactant per amount of inlet reactant) and selectivity (amount of desired product per amount of converted reactant).

For the optimisation of dehydration of cyclohexanol, the MnAPSO<sub>4</sub>-5 was used as the catalyst. The reaction was carried out in the temperature range of 100–400°C, with a feed rate of 0.05 mL/min and the amount of catalysts of 0.3 g.

#### **Characterisation of Coke in HZSM-5 and MnAPSO-5**

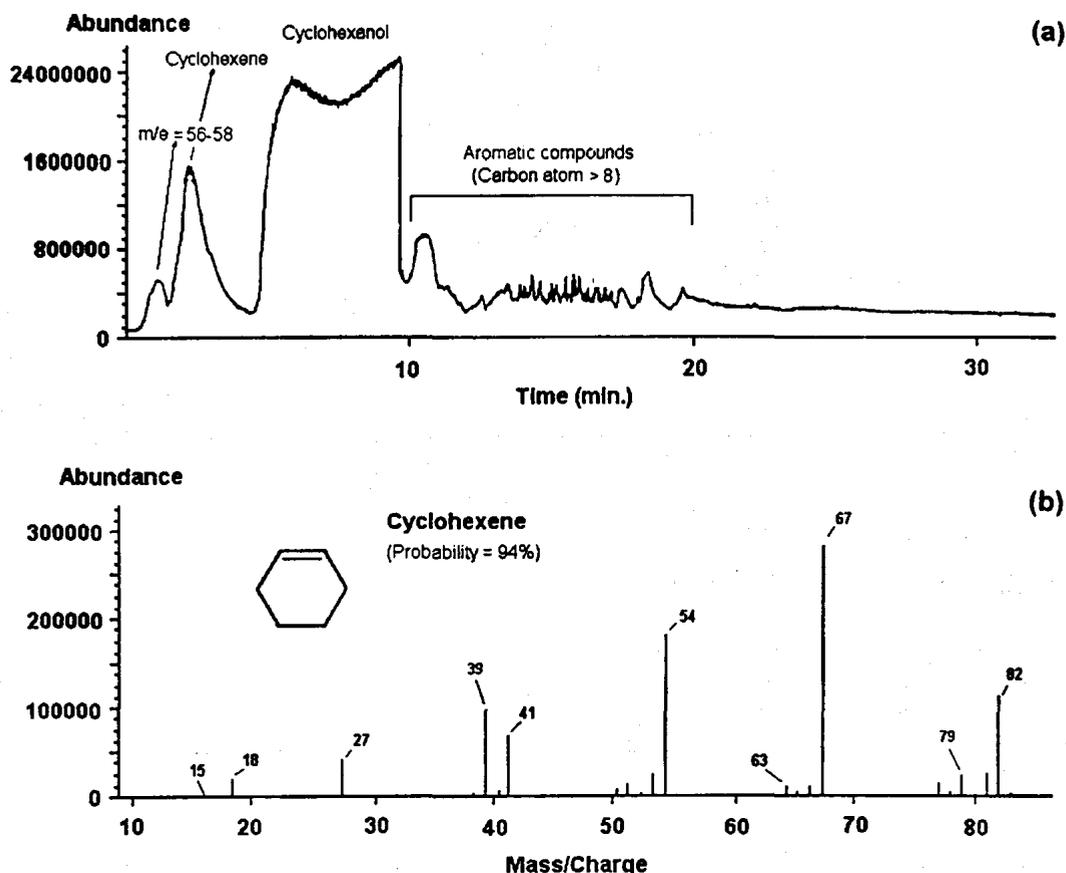
Differential thermogravimetry analysis (DTG) was performed in air using a Mettler TG50 with a scan rate of 10°C/min. GC-MS analysis was carried out using Hewlett Packard 5890 Series II gas chromatograph and Hewlett Packard 59827A mass spectrometer.

## **Results and Discussion**

As expected, AlPO<sub>4</sub>-5 did not show any catalytic activity due to the absence of Brønsted acidity. Cyclohexanol was converted to cyclohexene and cyclohexanone in the presence of MnAPSO-5 catalyst. Analysis of the products of cyclohexanol conversion over HZSM-5 by GC-MS indicated that cyclohexene was the major product followed by a light molecule (*m/e* = 56–58) and some aromatic compounds as the minor products (Figure 1).

Thermogravimetric analysis of HZSM-5 indicates two distinct weight losses as shown in Figure 2. Two temperature ranges representing the weight changes to two processes are observed: 100–250°C which corresponds to the removal of 'zeolitic' water, and 350–650°C which is typical of elimination of the coking products. In contrast, no significant peak is observed in DTG curve of AlPO<sub>4</sub>-5 and MnAPSO-5 samples after reaction, indicating that no coke was formed in these samples.

The composition of coke depends on four parameters [6]: (i) reaction conditions, (ii) nature of reactants and/or intermediates and/or products, (iii) pore structures and (iv) active sites. If parameters (i) and (ii) are assumed constant, two important aspects related to deactivation of HZSM-5 and AlPO<sub>4</sub>-5 based molecular sieves are delineated namely, pore structure and active sites. Pore structure and active sites are the main factors thought to determine the deactivation of a microporous material in a catalytic reaction. It is difficult to evaluate with precision the effect of the pore structure on the formation of coke since it is impossible to obtain the same acidity for molecular sieves of different pore structure [5, 7, 8]. However, it is obvious that the formation of coke is generally greater when there is more space available for its formation (e.g. in the cavities or at the channel intersection) and the intermediates to coke formation diffuse



**Figure 1.** Chromatogram (a) and an example MS spectrum (b) of product of cyclohexanol conversion over HZSM-5.

more slowly into the gas phase [5]. If we look into the pore and channel network of HZSM-5 and  $\text{AlPO}_4\text{-5}$  based molecular sieves in more detail, it is observed that the HZSM-5 consists of interconnecting channels and  $\text{AlPO}_4\text{-5}$  has non-interconnecting channel network (see Figure 3). From this point of view, it is suggested that the channel in  $\text{AlPO}_4\text{-5}$  molecular sieves are more likely to be blocked by coke formation rather than HZSM-5. However, the accessible cages in HZSM-5 are much larger than in AlPOs. As a result, the transition state for formation of coke is more easily formed in HZSM-5 than in AlPOs. Furthermore, note that the size of apertures of the framework structures

for HZSM-5 and AlPOs are different. The size of aperture of HZSM-5 is  $0.54 \times 0.56 \text{ \AA}$  and for  $\text{AlPO}_4\text{-5s}$  is  $7.3 \text{ \AA}$ . It was found that the most strongly acidic sites as found in HZSM-5 lead to detrimental irreversible adsorption, coking, and deactivation of catalyst [9].

The acidic sites in HZSM-5 are strong at high temperatures. Being a superacid, it is capable of protonating paraffins and thereby initiating catalytic cracking [10]. Gates [10] described that catalytic cracking involves many complicated side reactions which disturbs the formation of carbenium ions. These ions decompose to give hydrogen and carbenium ions, which may deprotonate and undergo isomerisation,

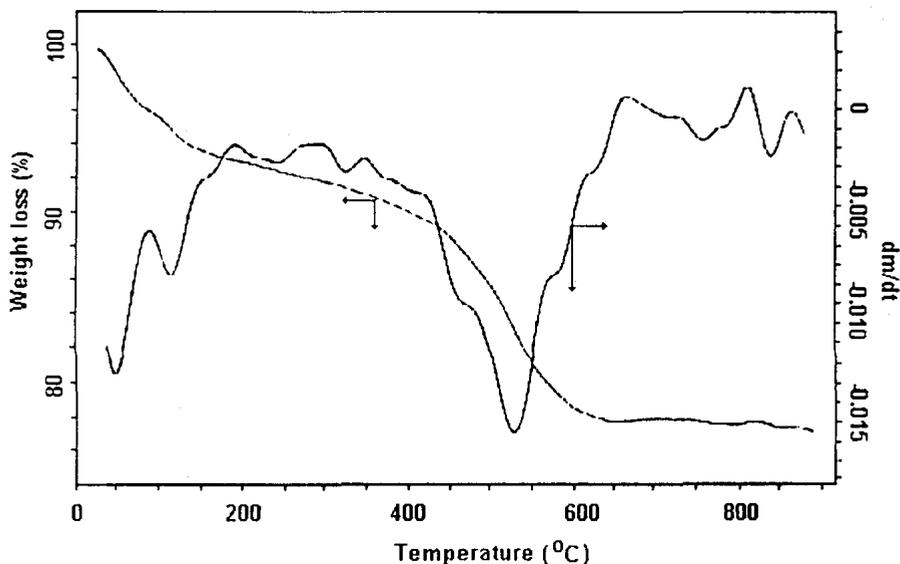


Figure 2. The TG and DTG patterns of HZSM-5 after cyclohexanol conversion.

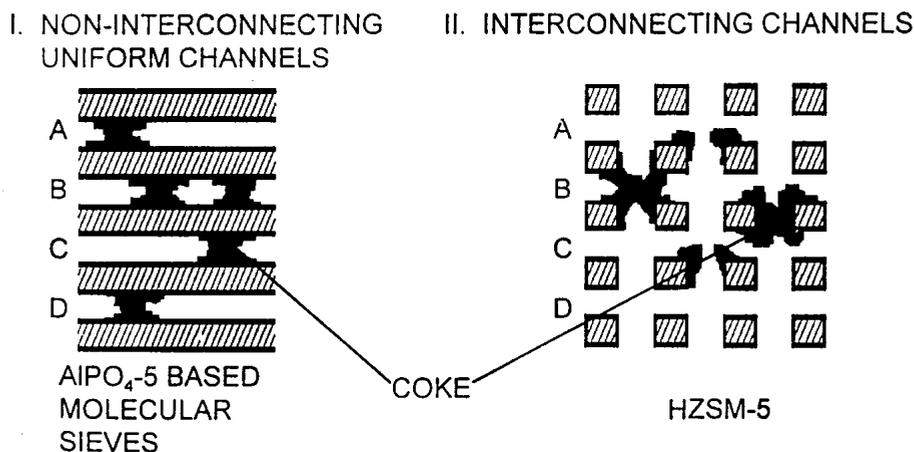


Figure 3. Types of pore channel networks in zeolites.

disproportionation and alkylation. As shown in Figure 4, from GC-MS analysis, many complicated products may be formed. HZSM-5, having smaller pores, are proved to be blocked than the larger pores in AlPOs.

As stated above, zeolites exhibit a high catalytic activity for the formation of coke over the temperature range of 300–600°C. The mechanism of coke formation is rather

complex and involves several reaction steps. It is generally accepted that coke formation over acidic solids is derived from extensive dehydrogenation of fused ring aromatics [4, 11, 12]. Experimentally, if we check the type of coke that is formed using IR, we arrived at different conclusions. IR spectroscopy was one of the first techniques employed to investigate the nature of carbonaceous deposits laid down



generation of cyclohexanol compared to the other metal-substituted AlPO<sub>4</sub>-5. Since MnAPSO-5 only generates a weak basicity, it only produces a small amount of cyclohexanone as the product of dehydrogenation of cyclohexanol. Because of that, dehydration of cyclohexanol was chosen in order to investigate the activity, regenerability and lifetime of the catalyst.

Figure 6 shows that conversion of cyclohexanol at 100°C was not observed. Knowing that the boiling point of cyclohexanol is 161°C; at 100°C the reaction was expected to take place in the liquid phase. This means that the activity of the catalyst for this reaction depends on whether the reactant exists as a gas phase or a liquid phase. It shows that the MnAPSO-5 was active at a temperature higher than the boiling point of cyclohexanol. In addition, the viscosity of reactant also affects the degree of conversion, since a viscous liquid is difficult to diffuse through unidimensional channel of AlPOs. Figure 7 shows that the viscosity decreases when the temperature increases [14].

As shown in Figure 8, the conversion of cyclohexanol decreased from 78% to 7% after 10 hours. After this period the catalyst was activated at 550°C for 4 hours in order to remove the species or coke which could possibly block the active sites. The catalyst was used again and the result

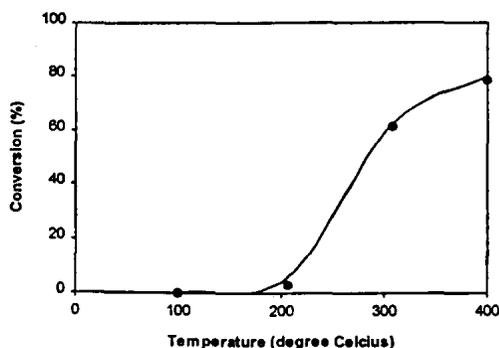


Figure 6. Conversion of cyclohexanol function of temperature.

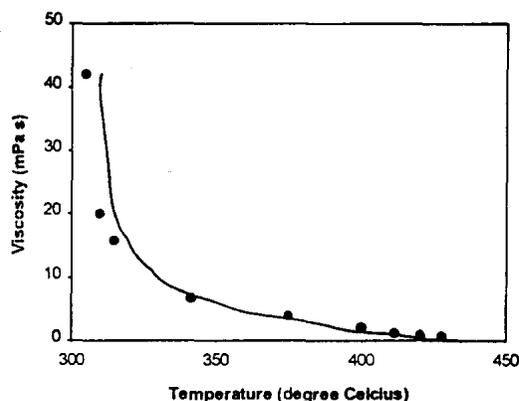


Figure 7. Viscosity of cyclohexanol as function of temperature (modified from ref. [14]).

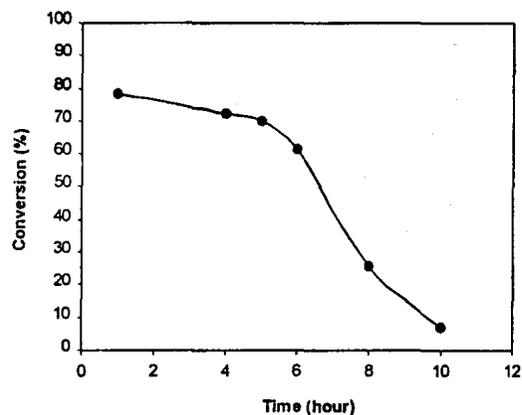
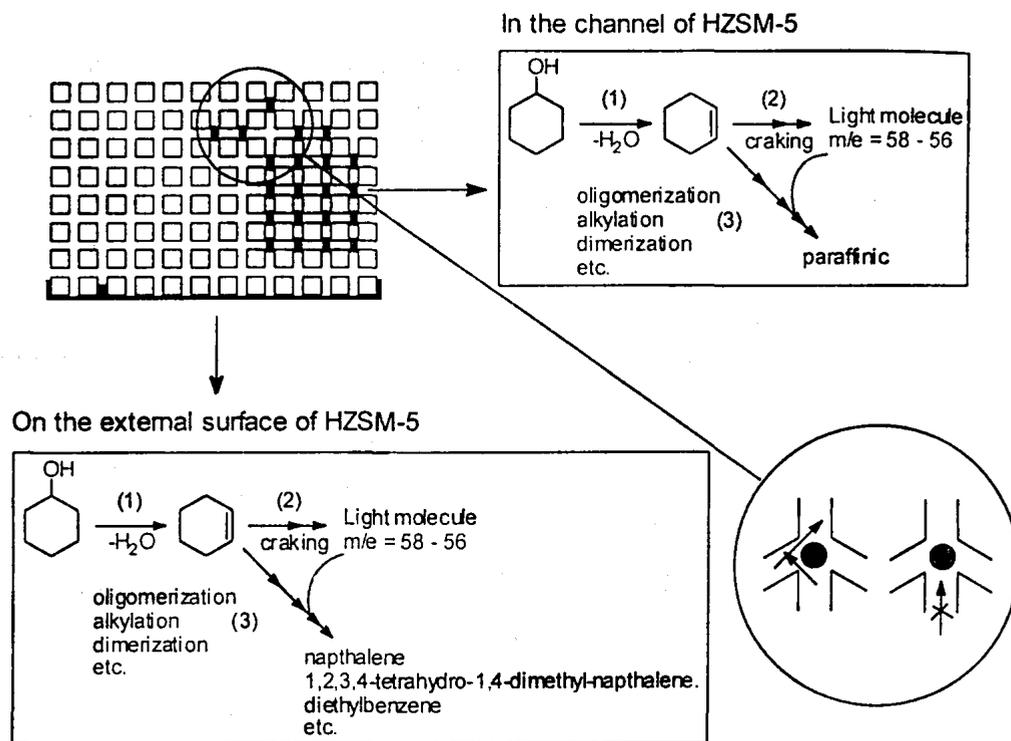


Figure 8. Conversion of cyclohexanol as function of time.

indicated that the activity was increased to 75%. After repeating the process for three times, the catalyst was still active, suggesting that its structure did not collapse during reaction and upon heat treatment.

## Conclusions

It is concluded that the type of coke formed in the channel of HZSM-5 after conversion of cyclohexanol is paraffinic. The sites on the outer zeolitic surface contribute to the production of polyaromatic hydrocarbon which was also considered for coke



**Figure 9.** Schematic of cyclohexanol reaction, coke formation and modes of deactivation over HZSM-5 catalyst.

formation of HZSM-5. The size of the polyaromatic hydrocarbon is larger than the pore size of HZSM-5 and is considered being the cause of the pore blocking on the outer zeolitic surface as shown in Figure 9. The coke molecules located on the outer surface of the crystallites can block the access to the sites of channel intersection where there are no coke molecules. The formation of polyaromatic in the channel of HZSM-5 is prevented by steric constrains in HZSM-5. The results of the cyclohexanol reaction over HZSM-5 are summarized in Figure 9. Step 1 is not "demanding" and is accelerated by the presence of acid centers of different nature and strength. Step 2 and 3 occur only on strong acid sites. Cyclohexanol conversion was terminated at step 1 over MnAPSO-5.

Temperature is an important factor

which influences the conversion of cyclohexanol over MnAPSO-5 catalyst. The conversion of cyclohexanol takes place above the boiling point of cyclohexanol ( $> 161^\circ\text{C}$ ).

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*Deactivation Modes and Reactions of HZSM-5, AlPO<sub>4</sub>-5 and MnAPSO-5 in the Conversion of Cyclohexanol*

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