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Regeneration, MDA, Mo carbide, zeolite, aromatic, coke

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Methane dehydro-aromatization (MDA) is a one-step conversion of methane to aromatics under non-oxidative condition in the presence of Mo-modified HZSM-5. The main drawback of MDA reaction is the rapid deactivation of the Mo carbide catalyst by coking. For catalyst stability and efficiency, a suitable and economical catalytic regeneration system is necessary. The present study investigates the regainability of catalyst activity by in-situ regeneration of spent 3wt% -Mo/HZSM-5 catalyst in air. Encouraging results is observed when 5% oxygen at a GHSV of 4800h^{-1} over 1 hour was used. The main drawback is coke is favored over aromatic product.

Keywords: Regeneration, MDA, Mo carbide, zeolite, aromatic, coke.

INTRODUCTION

One of the main sources of benzene (aromatic) in the world is produced via naphtha cracker or an ethylene cracker. For both the processes the main feedstock is crude oil. The present trend is to move away from crude oil. Natural gas shows promise. For aromatic production using natural gas, Methane dehydroaromatization (MDA) in the absence of oxygen can be an ideal choice. Regeneration of spent MDA catalyst has been least studied although the main catalyst deactivator is coke. Research groups like Liu et al (1998), Ohnishi et al (1999), Shu et al (2002) and Ma et al(2003) investigated catalyst stability for MDA reactions. These studies involve the effect of addition of small amounts of CO or CO_2 to mitigate coke build up during MDA reaction. Other groups like Liu et. al. (2002), Yuan et al. (1999) and Tan et. al (2002) include H_2 for the same purpose. They believed H_2 lowers rates of deactivation during the methane pyrolysis. Yuan et al (1999) and Tan et, al. (2002) studied the effect of adding O_2 and sometimes N_2O into the methane feed to prolong the catalyst life.

The main catalytic deactivation process for MDA reaction is due to coke build up in the pores and surface of the catalyst. Coke deposition occurs both at the pores and active sites present on the surface of the catalyst. It should also be noted the Mo precursors (MoO_3) are usually adsorbed on the external surface of the catalyst during impregnation. On calcination the migration of these MoO_3 species takes place over the external surface and some find its way into the pores to the Bronsted acid sites, which is the driving factor for migration of the MoO_3 species as indicated by Borry III et al (1999), Mestli et al (1998) and Zhang et al (1998). During carburization period the bulky MoO_3 precursor are converted to smaller and crystalline Mo_2C which are usually found in the pores, while others are found on the surface of the zeolite. For MDA reaction, Mo_2C are the active species. Deactivation of the catalyst result from coke deposition around the vicinity of these active species.

The main objective of the present study investigates the effect of in situ regeneration of spent 3wt% -Mo/HZSM-5 catalyst with air, the main source of oxygen. In-situ regeneration will be carried out at different GHSV between 1500 to 2400 h-1 and resident time between 0.5 to 1h. The regenerated catalyst will then be evaluated based in terms of conversion, yield and selectivity of products. Since the main deactivatant of the catalyst is coke, interference from NO formation during regeneration has not been indicated by Yuan et al (1999) and Tan et, al. (2002) in their regeneration studies.

EXPERIMENTAL

Fresh and Spent Catalyst Preparation

For the regeneration study, the 3wt% Mo modified HZSM-5 catalyst as described by Sinnathambi (2007) was prepared and used. Hereafter this catalyst will be designated as '3MoBM'. Approximately 5.0 gram of the freshly activated 3MoBM was subjected to MDA reaction in a quartz reactor tube at methane space velocity of 1500 h^{-1} over 48 hours at a temperature of 700°C using similar setup technique as used for calcination purposes as described by Sinnathambi (2007).

The coked catalyst was cooled under a flow of helium to room temperature, transferred to a drying oven at 120°C and left overnight. It was then cooled to room temperature in a dedicator without desiccant and stored for further testing. For all regeneration testing here after, the 3MoBM coked catalyst described above will be used, unless otherwise stated.

Catalyst Regeneration

The reactor setup for this experiment was similar to that described by Sinnathambi (2007). For each testing 0.2 gram of the coked catalyst was regenerated in-situ.

For the present study a couple of assumptions were made on the composition of compressed air: it is assumed that the oxygen content in air is 20 v/v% and the other components in the air mixture do not interfere with the regeneration process.

The regeneration process air was then blended with helium using Brooks mass flow controllers at various proportions to give an oxygen Regeneration mixture (ORM) of 2.5, 5 and 10 v/v %. Total flow rate was fixed at 8.0 ml/min which signifies GHSV of 1500h^{-1}. The coked catalyst was then heated to 650°C at a ramp rate of 10°C and maintained for an hour, cooled to room temperature under helium flow only. The O_2 regenerated catalyst is now ready for MDA reaction which follows the same procedure as described by Sinnathambi (2007).

RESULT AND DISCUSSION

Effect of Oxygen Content in Regeneration Mixture

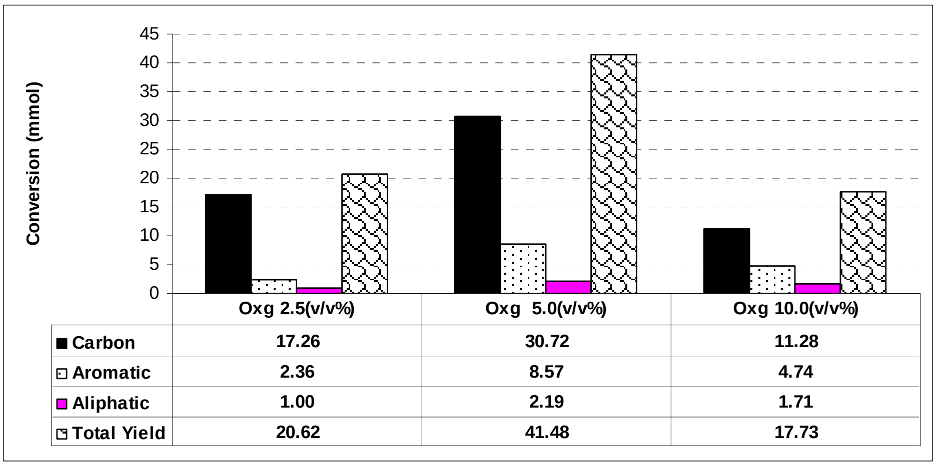
Visual color inspections on all three fresh regenerated catalysts were also done. The 2.5% regenerated catalyst was black; indicating incomplete regeneration while the 10% regenerated catalyst was white reflecting complete or over regenerated. The 5% regenerated catalyst was grey overall. It should be noted that coke is an active ingredient for MDA reaction.

Figure 1 shows the yield (mmols) distribution of the product from MDA resulting from ORM studies over 20 hours TOS. From the same figure it can be seen that 5v/v% oxygen gives the most promising results of the three ORM studied. Apart from having a high catalytic activity it also has the highest aromatic yield. Since 5 % O_2 regenerated catalyst (ORC) proves to be the most effective, it was used for further studies hereafter. Liu et, al. (2002) recommended that a high flow rate and reasonably low oxygen dosing are most favored for regeneration studies .

The gas hourly space velocity (GHSV) was then carried out between 2400 to 7200 h^{-1}. Based on this 2400, 4800 and 7200 h^{-1} was selected. The regeneration dwell periods was fixed at 0.5 hours and 1 hour.

Methane Conversion and GHSV Studies

Table 1 shows the average methane conversion (% conversion of C per gram catalyst) for the freshly 5% (ORC) with different GHSV and dwell time. For tagging purposes GHSV 2400 and dwell time of 0.5 h is represented as R2400(0.5h) similar tagging techniques are applied to the others. Table is divided into three parts, one representing the average: 1st 10 hours TOS, the 2nd 10 hours (11th to 20th hour TOS) and the overall average over 20 hours TOS. The control used and stated hereafter refers to the carbon conversion derived from freshly activated 3MoBM catalyst which has not undergone any regeneration process. From the data obtained in Table 1, it can be seen that R 7200(0.5h) shows poor results and will not be discussed hereafter. As for GHSV 2400 and 4800h^{-1} type it can be seen that increases in regeneration dwell time increases in methane conversion. Furthermore the overall methane conversion is not significantly affected by GHSV between the 2 ranges namely 2400 to 4800h^{-1}. Although both R24800 (1h) and R4800 (1h) start at a higher average methane conversion (8% to 11% higher than control) during the 1st 10 hours this advantage reduces with increase in TOS.



	Oxg 2.5(v/v%)	Oxg 5.0(v/v%)	Oxg 10.0(v/v%)
■ Carbon	17.26	30.72	11.28
□ Aromatic	2.36	8.57	4.74
■ Aliphatic	1.00	2.19	1.71
▨ Total Yield	20.62	41.48	17.73

Fig 1. Effect of Oxygen Content in Regeneration Mixture

Table 1. Regeneration Study and Methane Conversion

	Methane Conversion in % C/g cat					
	Control	R2400 (0.5h)	R4800 (0.5h)	R7200 (0.5h)	R2400 (1.0h)	R4800 (1.0h)
1st 10 h	6.24	6.62	6.11	2.77	6.76	6.95
2nd 10h	5.49	4.51	4.97	-	5.18	4.98
Average	5.86	5.57	5.54	-	5.97	5.96

Product Yield

Table 2 compares the yield and selectivity of the product in mmols obtained from the GSV studies for the four 5% OR catalysts as against the control over 20 hours TOS. The data in brackets represent the selectivity (%) of the MDA products from the same studies.

From the Table 2 it can be seen that for all the regenerated catalyst the coke yield is much higher than the control. Aliphatic content on the other hand is lower than the control. It increases slightly with increase in GHSV and dwell time for the OR catalysts.

The aromatic yield is also higher for the control the OR catalysts. The selectivity and yield for the OR catalysts increases with increase in GHSV and dwell time. From the present study, R4800 (1h) shows the best results when compared to the rest of the regenerated catalyst. Although this regenerated catalyst is inferior to the control in terms of aromatic and aliphatic yield and selectivity, the catalytic activity on the other hand is higher than the control. This higher yield is unfortunately is favored towards coke production.

Table 2. Regeneration Studies – MDA Product Yield

	Yield in mmol over 20 hours TOS				
	Control	R2400(0.5h)	R2400(1h)	R4800(0.5h)	R4800(1h)
Coke	29.66 (41%)	55.91 (82%)	55.96 (76%)	47.32 (70%)	49.36 (67%)
Aromatic	36.95 (52%)	8.96 (13%)	12.96 (18%)	16.18 (24%)	18.74 (26%)
Aliphatic	5.27 (7%)	3.27 (5%)	4.31 (6%)	4.44 (6%)	4.99 (7%)
Total	71.88	68.14	73.23	67.94	73.09

Table 3. Regeneration Studies and Surface Area Measurements

		BET Surface Area		External Surface Area	
		BET (m2/g cat)	Loss (%)	Ext. (m2/g cat)	Loss (%)
Regen Stock	Coked Cat	189.2	-50.0	35.07	-75.0
R4800(0.5h)	Regenerated	316.8	-16.0	118.3	-15.0
	Spend	205.2	-46.0	40.89	-71.0
R4800(1h)	Regenerated	352.1	-8.0	120.4	-13.0
	Spend	209.7	-46.0	42.16	-70.0
Control	Activated	381.0		138.8	
	Spend	204.6	-46.0	49.7	-64.0

Catalyst Characterization and Surface Area

The catalyst characterization for the surface properties, in particular the BET and external surface areas were carried out using the surface analyzer ASAP 2000, as described by Sinnathambi (2007) and is presented in Table 2 and 3. The most promising GHSV from the regeneration studies is R4800 (0.5h) and R4800 (1h) as compared to R2400 (0.5h) and R2400 (1h). As a result R4800 will be further analyzed based on it dwell time. In Table 3 the regen stock refers to the spent catalyst prepared as described in experimental section of this study. Taking the freshly activated value for BET and external SA of the control as base, the % loss was calculated for all the regenerated catalyst.

From these observations in Table 3, it can be seen that the BET and external SA can be quite easily regained at high GHSV. This may explain the increased catalytic activity for these regenerated catalysts. Increase in dwell time shows an additional gain in BET and external surface area by 8 and 2 % for R4800 (1h) and R4800(0.5h) respectively.

From Table 2 it can be observed that for R 4800(1h) has an increase of about 5 % more catalytic activity than R 4800(0.5h). The extra increase in catalytic activity is a result of increase yield for coke (2 %), aromatic (2.5%) and aliphatic (0.5%). Although coke yield for R4800 (1h) is higher than R4800 (0.5h) its selectivity is much lower due to increase in aromatic and aliphatic yield.

From the above observation it can be seen that although the regenerated catalyst is able to regain almost 84 to 92% of its initial active catalyst BET surface area and 85 to 87 % of its external surface area, its main drawback is in terms of reduced aromatic at the expense of increased coke yield and selectivity.

CONCLUSIONS

From the above process conditions, observation and evaluation, it can be seen that it is possible for the regenerated catalyst to regain its initial catalytic activity, but the product selectivity is favored more towards the coke formation rather than the favored aromatic yield and selectivity.

REFERENCES

Borry III, R.W., Kim, Y.H, Huffsmit, A.,Reimer, J.A. and Iglesia, E., J Phys. Chem. B (1999) 103, 5787.

Liu, S., Don, Q., Ohnishi, R., and Ichikawa, M., Chem. Commun, (1998) 1217

Liu, Z., Nutt, M.A., and Iglesia, E., Catal. Lett. 81 (2002) 271

Ma, H., Ohnishi, R., and Ichikawa, M., Catal. Letts. 89 (2003) 143

Mestl, G., and Knozinger, H., Langmuir (1998) 14 3964

Ohnishi, R., Liu, S.T., Dong, Q., Wang, L.S., and Ichikawa, M.,

J. Catal.182 (1999) 92

Tan, P.L., Leung, Y.L., Lai, S.Y., and Au, C.T., Catal. Lett. 78 (2002) 251

Shu, Y., Ohnishi, R., and Ichikawa, M., J. Catal. 206 (2002) 134

Sinnathambi C.M., Somche (2007)

Yuan, S., Li, J., Hao, Z., Feng, Z., Xin, Q., Ying, P., and Li, C., Catal. Letts. 63 (1999) 73

Zhang, J.Z., Long, M.A, Howe, R.F., Catal Today 44 (1998) 293