Spent Residue Fluid Cracking Catalyst- Temperature programmed oxidation studies using Mass spectroscopy

Tony Joseph*, Gnana Pragasam Singaravel, Abdul Majed Al Katheeri

ADNOC Refining Research Centre, Abu Dhabi Oil Refining Company, P O Box 3593, Abu Dhabi, United Arab Emirates

**Corresponding author: tkjoseph@adnoc.ae*

Abstract: Temperature programmed oxidation (TPO) studies were conducted on fresh, laboratory deactivated Ecat and Residue fluid catalytic cracking (RFCC) commercial unit spent Ecat. The cracking reactions were carried out using ACE unit to find the nature of deposited coke and compared with Ecat from refinery. Simultaneous measurement of carbon monoxide and carbon dioxide on chemisorption unit connected with MS analyzer has been carried out . The ratio of carbon monoxide to carbon dioxide from TPO varied with the type of coke deposition.

Keywords: RFCC catalysts, Coke, Temperature programmed oxidation (TPO)

1. Introduction

Residue fluid catalytic cracking (RFCC) is an important conversion process in modern refineries. RFCC equilibrium catalyst (Ecat) coke characterization is important to know the nature of response for the catalyst for a typical feed [1]. It is well documented that other than operating parameters like catalyst to oil ratio, metal contaminants in the feed influence the coke content and its type. Different types of coke are identified viz. catalytic coke, contaminant coke, catalyst coke, residual coke. There were many studies including TPO describe in detail the nature and types of coke formed in RFCC reactions [2].

In this study spent catalysts from cracking reactions with fresh, lab deactivated Ecat prepared with spiked nickel and vanadium metal organic contaminants using cyclic deactivation unit (CDU) and then tested in Advanced Cracking Evaluation (ACE) test unit were utilized for TPO studies. RFCC Ecat from refinery used for cracking reactions was also utilized for TPO studies for the comparison purpose. The results of the TPO study will be discussed in detail.

2. Experimental

RFCC Ecats are prepared in cyclic deactivation unit according to the protocol developed by ADNOC Refining. The required nickel and vanadium content were deposited on the catalyst by spiking the metal naphthenates into HVGO feed and used it for cracking, regeneration cycles. Laboratory Ecats as well as commercial refinery e-cat were used in ACE unit for coke evaluation by varying catalyst to oil ratios, metal content etc., and the spent catalyst without regeneration was withdrawn from the system were used in this study. Coke content of these spent catalyst are measured by combustion method (Carbon & sulfur, D 144, LECO) and Thermo gravimetric measurements as well. Chemisorption unit (Micromeritics AutoChem II ASAP 2920 coupled with CIRRUS 2 MS) was used for TPO study. In a typical experiment 15- 30 mg of spent catalyst used for TPO studies. Helium was used as diluent for oxygen and also as purge gas to drive out the evolved gases from the catalyst. TPO was connected to an MS after the gases exit from TCD. MS was calibrated for CO and CO2 using calcium oxalate monohydrate and CO2 gas. TPO was conducted in “U” tube, filled with the catalyst in between quartz wool. The catalyst was heated up to 900 ^{o}C with a temperature ramp of 5-10 ^{o}C/min.

3. Results and discussion

Calcium oxalate monohydrate decomposition is well known in literature for its stepwise evolution of water, carbon monoxide and carbon dioxide [3]. TPO with MS was calibrated using calcium oxalate and carbon dioxide gas dosing. There was good agreement while using both the calibrants. TPO of a typical fresh catalyst with helium purge flow mass spectra is given Figure 1. It is evident that carbon monoxide and carbon dioxide peak appears almost at same time and the amounts were calculated from calibration data. The properties of the fresh and spent Ecat catalysts are given in Table 1.

Figure1. Typical TPO of spent catalyst from fresh catalyst used in ACE testing

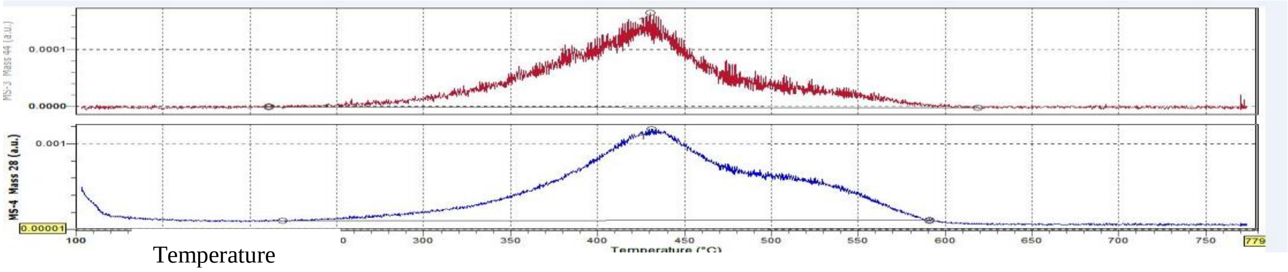

Table 1. Catalyst properties and TPO results

	Reaction temperature, ^{o}C	Coke content wt%	CO2 Mole%	CO Mole%
Fresh Catalyst	550	2.55	56	44
	540	1.77	53	47
	530	1.58	58	42
Lab Deactivated Ecat 1(Ni+V, 8600ppm)	540	1.43	67	33
Lab Deactivated Ecat 2(Ni+V, 5600ppm)	540	0.930	36	64
Lab Deactivated Ecat 3(Ni+V, 4500ppm)	540	0.720	42	58
Refinery Ecat (Ni+V, 2800ppm)	550	1.99	35	65
	540	1.28	27	73
	530	0.89	36	64

The experimental data reveals that fresh catalyst, the cracking activity is higher than equilibrium catalyst which in turn showed higher amount of coke. It is expected that coke content decreases with the cracking reaction temperature for a given catalyst to oil ratio. However we could observe the type of coke deposition was different between fresh and equilibrium catalysts prepared from laboratory and obtained from commercial refinery unit. Since equilibrium catalyst is partially deactivated and it contains nickel and vanadium deposits its activity pattern and nature of coke is different [3]. Coke deposition could be on the catalyst surface or with in the pores. It is noted that spent equilibrium catalyst coke burn is harder than fresh catalysts. The amount of carbon monoxide formation tendency for spent equilibrium catalyst was also higher which could be due to poly aromatic coke deposition is happening with equilibrium catalysts [5]. However, when metal contaminant concentration increases partial hydrogenation could make coke richer in hydrogen, which could oxidize easily. A detailed study is in progress on our lab to gather more information in this area. The results of study have applications in refinery for catalyst regeneration process.

4. Conclusions

RFCC spent catalysts TPO of coke can be studied well with the use of mass detector. Utilizing MS detector avoids complicated set up and ambiguity in converting the primary product CO to methane using methanator. The nature of catalyst decides the type of coke and its oxidation properties. Spent equilibrium catalysts coke removal with metal deposits is relatively tougher than fresh catalysts.

References

1. S.Haito, D. Zhijian, Z Yuxia, T. Huiping, Catal. Commun. 16(2011) 70-74
2. S. Gnana Pragasam, Abdul Majed Al Katheeri, Tony Joseph, FEZA Int. conf. Leipzig, Germany (2014)
3. O. Bayraktar, E.L. Kurgler, Applied catalysis A:General 233(2002) 35-41
4. S. Gnana Pragasam, Tony Joseph, Abdul Majed Al Katheeri, JPI Conference, Asahikawa, Japan (2014)
5. O. Bayraktar, E.L. Kurgler, J.Therm.Anal. Calorimetry, 71 (2003) 867-874