Oriental Journal of Chemistry Vol. **26**(1), 331-334 (2010)

Studies of some potential catalysts on the activity and deactivation process of low temperature co-conversion catalyst

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(Received: November 30, 2009; Accepted: January 10, 2010)

ABSTRACT

The present work embodies the investigation on some potential catalyst before and after used in Industry. In the fertilizer industries, the catalysts are mainly used to synthesis of gas for production of Ammonia, Ammonia is the basic Chemical for Nitrogenous fertilizer, for this purpose, different types of laboratory prepared and available commercial LT-CO Catalyst samples were taken. Collected samples such as fresh commercial, reduced or discharged condition form the plants were taken for comprehensive studies. In these analysis, the magnetic studies were taken as a base and some important physico-Chemical Parameters related to LT-CO catalyst such as, surface area, porosity, activity and deactivation were estimated form their magnetic data, which clarify the mechanism involved in their catalytic behaviours and observed value show that physico-chemical parameters of thermal shock catalysts were lower than to fresh commercial catalysts.

Key words: Thermal shock, Deactivation, Porosity, LT-CO shift catalysts, Activity of catalysts, magnetic susceptibility.

INTRODUCTION

Catalysts are chemical substance which increased the rate of reaction during the chemical reaction. Failure of any catalysts in a plant is costly it term of production loss. It is therefore, important to study and understand the cause of such failures, in the case of LT-CO shifts catalysts where generally CuO, ZnO, Al_2O_3, Fe_2O_3, NiO and Cr_2O_3 are the chemical components of catalysts which poisoning by sulphur, chlorine and Alkali are known to take place. Besides, a knowledge of chemical composition and structural properties. It may be useful to understand the nature of the active sities which may help to decide on the technique of preparation and also to optimize operating condition for higher efficiency of the catalysts. However, the data reported in literature mostly concern small quantities of the catalysts studied under laboratory condition and these may ot correspond exactly with the built catalysts in prolonged use and the changes that might have occurred in the structure is not known. It has been observed in Preliminary studies that ageing catalysts develop specific symptoms which can measured by magnetic and other technique and could possibly give guide line on the trend in catalysts deactivation. The present study is undertaken to establish a correlation, it exists between deactivations and electronic properties of catalysts.

MATERIAL AND METHODS

The different samples of LT-CO catalysts were collected from different sources such as laboratory and plant (fresh commercial samples D_1 to D_4 and E_1, Discharged samples from plant F_1 to F_5 and G_1, F_1 to F_5 were samples form different layers from top to bottom). The samples mentioned D_1 to D_4 and E_1 were subjected to an accelerated longevity test and represent the preliminary stage of deactivation which in turn and gives an idea about the expected stability of the catalysts in the plant. The Physico-Chemical parameters were studied regarding LT-CO shift catalysts. Porosity was measured using mercury porosimeter[1], surface area was measured by the conventional BET method[2] activity was measured by glass apparatus described by Sengupta et.al[3] and accelerated method[4] Magnetic susceptibility measured by magnetic balance using guoy apparatus[5] at room Temperature 25oC. The catalysts activity was determined by estimating carbon dioxide present in the exists gas. The percentage of carbon monoxide converted was calculated as given formula.

$$X=\frac{100[(CO_2)_E\text{-}(CO_2)_1\times100]}{100\text{-}(CO_2)_E\times(CO)l}$$

Where
X = Percentage CO Converted
$(CO_2)_E$ = Exist CO_2 Percentage
$(CO_2)_I$ = Inlet CO_2 Percentage
$(CO)_I$ = Inlet Co Percentage

RESULTS AND DISCUSSION

The chemical composition of fresh commercial catalysts samples are presented in table 1. The chemical parameters analysed in different samples such as surface area, porosity, phase compositions, activities, and Magnetic susceptibility are given in table 2.

The observed values of fresh commercial, plant discharged and overheated samples respectively data indicate. It is well known that copper oxide when dispersed over aluminium oxide or a combination of both the mixed oxide system after reduction works as a catalysts for Co-conversion shift reduction as lower temperature to defect centers in Cu-Cu_2O as was observed. However, in a highly deactivated condition, the Cu^{2+} species will convert into bulk copper metal form and the number of dispersed defect centre are expected to decrease to a large extents. For discharge samples collected form different layers' of the some convert indicated an interesting trend. It was observed that a rough correlation between the residual activity and the spin density, the greater the spin density higher was activity, the rate of disappearance of defects may provide a means to predict the residual activity and life of catalysts.

The stability and activity of the catalysts were evaluated by observed data, which indicate that catalysts E_1 has highest fall (37.6) in activity while others were relatively more stable, samples D_1 seems to be quite stable but probable defect in the catalysts in very low CuO percentage, when it put on carrier will give higher dispersion and simultaneously copper aluminates type surface species formation may lead to higher magnetic susceptibility and higher stability and less affected by thermal shocks. But as CuO percentage is quite low, activity is only 66 percent in initial stage. This drawback can be removed probably by increasing copper concentration in the catalysts, sample D_4 has 69 percent activity but its stability is good.

Table 1: Chemical composition of fresh commercial catalysts % (W/W)

Catalysts		CuO	ZnO	Al_2O_3	Fe_2O_3	TiO_2	L.O.I. at 700°C
1.	D_1	11.25	25.61	25.81	ND	1.56	11.96
2.	D_2	33.00	67.00	28.00	2.21	ND	2.21
3.	D_3	26.31	29.51	27.90	3.10	4.00	12.61
4.	D_4	34.00	63.50	ND	1.98	3.10	4.10
5.	E_1	37.68	44.21	11.08	ND	1.21	9.53

Table 2: Observed Physico-Chemical parameters of fresh commercial, discharge and shock treated catalysts samples

Catalysts	Physico-Chemical Parameter							
samples Point	Surface Area M^2/g	Porosity Co/100°C	Phase	Composition %	Activity after thermal shock	Activity activity (Stability)	% fall in susceptibility in C.G.S. Units$\times 10^{-6}$	Magnetic
1.	D_1	115.4	61.7	ZnO, CuO, Al_2O_3	66	56	13.9	+ 3.89
2.	D_2	19.8	59.8	ZnO, CuO	76	52	32.0	+ 4.41
3.	D_3	85.5	50.9	ZnO, CuO, á Al_2 $O_3.H_2O$, Fe_2O_3, TiO_2	75	60	22.7	+ 7.79
4.	D_4	36.8	65.9	ZnO, CuO, Fe_2O_3	69	53	23.2	+ 8.49
5.	E_1	106.0	54.1	ZnO, CuO, á Al_2O_3	80	50	37.6	+ 11.80
6.	F_1	11.44	45.8	ZnO, CuO, Cu_2O, Cu	13.14	ND	ND	+ 17.80
7.	F_2	20.16	43.4	ZnO, CuO, Cu_2O	19.5	41	ND	+ 12.6
8.	F_3	30.14	49.5	ZnO, CuO, Cu_2O, Cu	46.0	43	ND	+ 15.3
9.	F_4	16.5	44.6	ZnO, CuO, CU_2O, Fe_2O_3	64.1	47	10.3	+ 16.4
10.	F_5	10.8	47.8	ZnO, CuO, Cu_2O, Fe_2O_3	51.3	ND	11.2	+ 22.4
11.	G_1	27.3	54.3	ZnO, CuO, Cu_2O, Al_2O_3	26.3	ND	ND	+ 14.8

CONCLUSION

The result of the investigation suggest that the different type of catalysts before and after used in industries, physicochemical parameters indicated that the discharged catalysts from industries contain lower catalytic behaviour than to fresh catalysts and more affected the their structure related to Active centre which increased the rate of the reaction. It is therefore suggested that there should be periodical investigation of the failure of catalysts which effect the production quantity.

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