SIIC033

CATALYST DEACTIVATION ANALYSIS ON Cu/Zn/Al/Zr CATALYST IN METHANOL SYNTHESIS VIA CO_2 HYDROGENATION REACTION

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Abstract:
Global warming issue had become most challenging issue which believe due to the increasing of greenhouses gases mainly CO_2 that gradually increase the global temperature. Hence, the conversion of CO_2 gases to value-added chemical and fuel received a significant attention. In this regard, the hydrogenation of CO_2 in methanol synthesis was one of the effective strategies in utilization of CO_2 emission. Though, due to the complexities that associated with CO_2 high stability, the stability/activation of CO_2 into methanol becomes one of challenging issues. Also, the loss over time of catalytic activity of heterogeneous catalyst had been a significant concern in operation plant and has been studied for many industrial catalytic applications. Thereby, this research highlights the recent effective investigation in prepare and characterize a single formulation of multi-metallic Cu/Zn/Al/Zr catalyst. Also, to evaluate the deactivation behavior of Cu/Zn/Al/Zr catalyst during methanol synthesis via CO_2 hydrogenation reaction. The deactivation behavior of co-precipitated Cu/Zn/Al/Zr catalysts has been studied over 48h of reaction that associated to their performance in methanol by CO_2 hydrogenation reaction. In synthesis of methanol process, the conventional Cu/Zn/Al/Zr catalyst system typically prone to the sintering and coking. Nevertheless, the prove of this deactivation behavior was presented based on the chemical and physical characterization of these catalyst system. The characterization of the fresh and spent catalyst using BET indicated that the Cu particles sites been blocked which decreased surface area of the catalyst sample after the performance testing. Next, TPR analysis shows that the spent catalyst reduction peak area was shifts to a higher temperature which 354.21 ^oC, it is mainly illustrated the Cu reducibility becomes weaken which decrease of the Cu dispersion and H_2 consumption after the reaction takes place. Thus, the result shows that coking is the predominant cause of deactivation of catalyst. In addition, based on the mechanism reaction hydrogenation of CO_2, the catalyst system proved that it undergone a deactivation process by carbon deposition.

***Keywords*:**
CO_2 hydrogenation, Methanol synthesis, Catalyst Deactivation, Cu/Zn/Al,Zr

Objectives:

- To prepare and characterize a single formulation of a multi-metallic Cu/Zn/Al/Zr catalyst.
- To evaluate the deactivation behavior of Cu/Zn/Al/Zr catalyst during methanol synthesis via CO_2 hydrogenation reactions.

Methodology:

Figure 1 illustrates the process flow on the catalyst deactivation of Cu/Zn/Al/Zr catalyst in methanol synthesis via hydrogenation of CO_2.

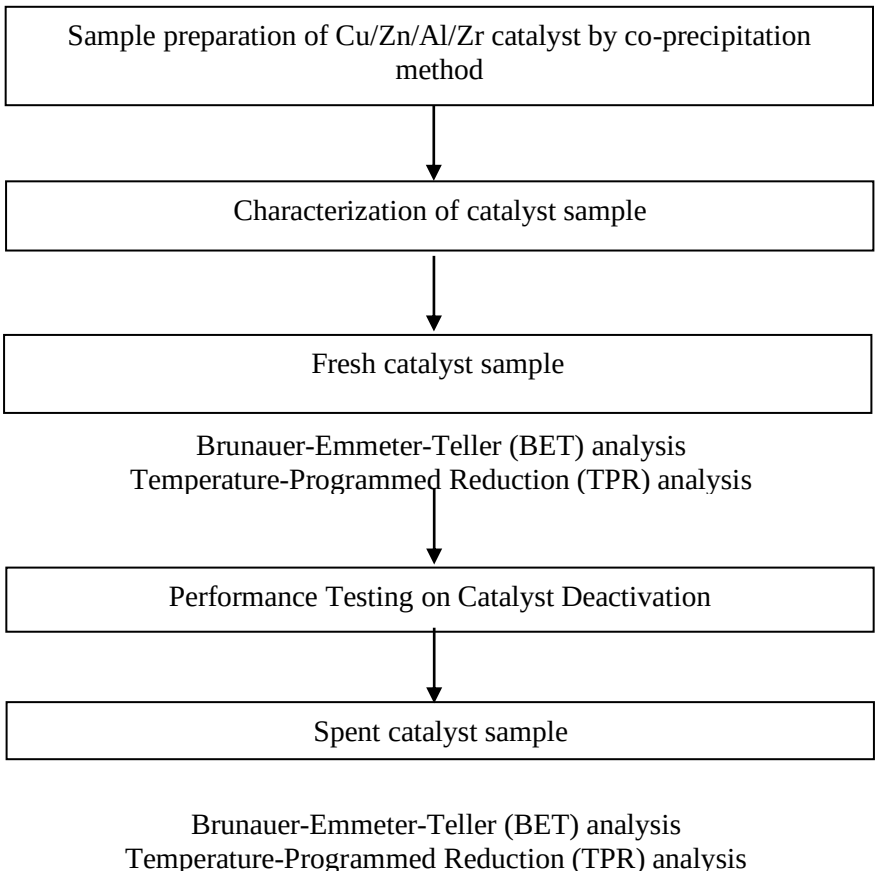

Figure 1 Process Flow of Project.

Results:

Table 1 The BET analysis data for fresh Cu/Zn/Al/Zr catalyst.

Surface Area (Fresh)	
Single point surface area at P/Po = 0.300690297:(Fresh)	129.0966 m²/g
Single point surface area at P/Po = 0.300690297:(Spent)	56.4511 m²/g

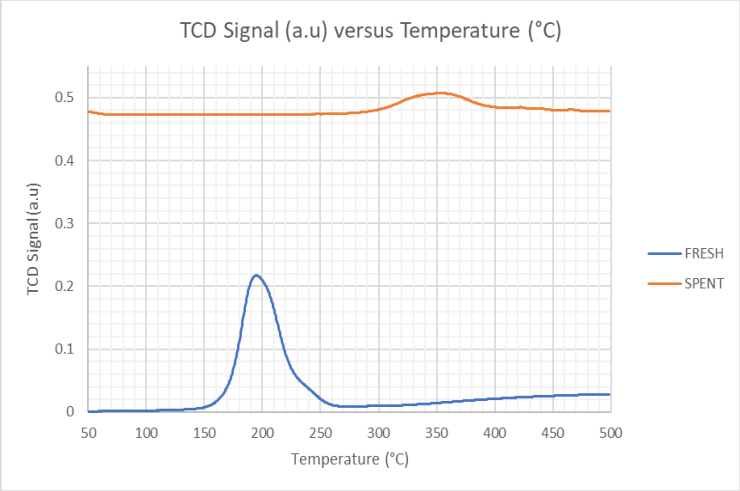

Figure 2 TPR Profile for fresh and spent Cu/Zn/Al/Zr catalyst sample

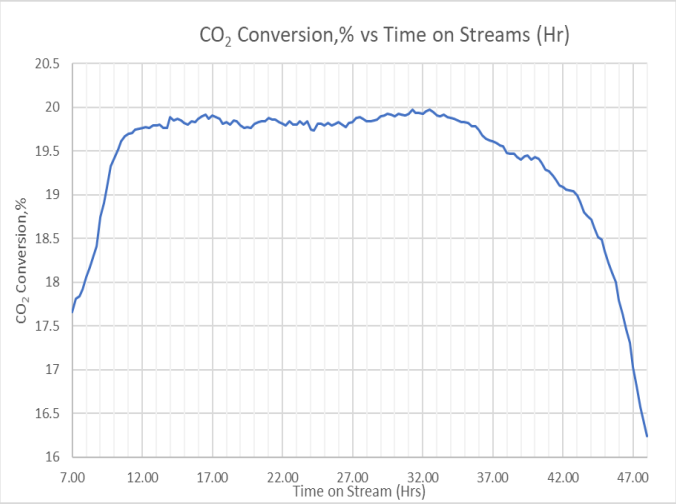

Figure 3 The Deactivation Trend on 47h of Reaction

Table 2 Catalytic performance of CO2 hydrogenation

CO^2 conversion (%)	Selectivity (%)				STY
	MeOH	CH^4	H_2O	CO	
20.1%	8.0%	0.1%	16.5%	75.4%	0.452966

Conclusion:

The Cu/An/Al/Zr catalyst with the ratio 4:3:1.5:1.5 successfully prepared by using co-precipitation method. The BET surface area results prove that as the reaction takes place, there are decreasing of BET surface area attribute to the active sites of the catalyst decrease. The decrease of the number of active site lead to the principle of deactivation. In addition, the TPR profile illustrated that the temperature shifts to the higher temperature indicating the lower reducibility capacity and low H2 consumption. The catalytic activity or performance was evaluated out in commercial customized Microactivity Reference, PID Eng&Tech bench plant which operating in a high pressure fixed-bed tubular reactor at operating condition of 230oC, 40 bar and 10000 GHSV. The CO2 conversion shown a fair value as it achieved 20.1% and the methanol yield produced about 8% while the undesired CO is 75.4%. Subsequently, the deactivation behavior of Cu/Zn/Al/Zr catalyst was evaluated by performing cumulative reaction data for 47 h at 230ºC and 40 bar. The result prove that the deactivation starts to occur at 33h after the reaction. The mechanism of deactivation only proven by possible reaction in CO2 hydrogenation reaction which is coking.