EFFECT OF CERIUM ON HYDRODESULFURIZATION CATALYST PERFORMANCE

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ABSTRACT

Effect of cerium on hydrodesulfurization catalysts performance have been investigated. The catalysts were Pt or Pt-Ce supported on zeolite. The Pt/Zeolite catalyst was prepared by wet impregnation method, while that of Pt-Ce/Zeolite catalyst was prepared using coimpregnation method both were followed by drying, calcination, oxidation and reduction. The catalysts activity test was performed in a micro reactor and products composition was determined using gas chromatography. The results showed that cerium enhanced catalyst performance especially catalyst lifetime. Therefore, the catalysts have higher tendency to remain active for longer period. Due to its function, cerium might be used as a promoter of hydrodesulfurization catalysts.

***Keywords**: Cerium, hydrodesulfurization, promoter, life time*

INTRODUCTION

Supported metal catalysts are generally comprised of small metal particles (1 – 100 nm in diameter) dispersed on high surface area carrier. Modern catalyst formulations often include an “active” metal (*e.g.* Pt, Pd, Ni) combined with other “less active” metals (*e.g.* Ru Au) [1,2]. The second metal can enhance catalyst performance in several ways, such as promote desired reactions, prevent undesirable side reactions, or enhance catalyst lifetime.

The addition of metal which by itself is catalytically inactive (e.g. Ce, Mo, W) to catalyst surface sometimes results in a quite considerable improvement of the catalyst effectiveness [2]. Such substances are called promoters.

Evaluation of deactivation kinetics of hydrodesulfurization catalysts involves two steps - a characterization step and a catalytic testing step. Much attention has historically been given to improved methods for catalyst preparation evaluation particularly with respect to addition of any metal to lengthen the hydrodesulfurization catalysts lifetime [3,4]. Proper simulation of the deactivation calculation is considerably important.

A kinetics deactivation model will be developed which combines catalyst and unit parameters to generate predicted equilibrium catalyst property distributions. These distributions can be approximated by bimetal catalyst at varying severities [3]. Catalyst deactivation rate calculation is essential to accurately predict catalyst performance.

There are two types of catalyst deactivation which occur in hydrodesulfurization systems - reversible and irreversible [1,5]. Reversible deactivation occurs due to coke deposition when the feed passes through the catalyst in a reactor, and is reversed by coke burning. Irreversible deactivation of the catalyst can be viewed as a combination of four separate mechanisms, but in correlation, i.e: zeolite dealumination, metal-zeolite decomposition, surface collapse, and contaminant effects. Zeolite dealumination, reduces the acid site density and, hence, the inherent activity per unit of catalyst. Metal-zeolite decomposition can be measured by dispersion, crystallinity or micropore surface area loss. Most of processes occur simultaneously in the catalytic hydrodesulfurization process [5,6]. Those are not independent, surface area collapse reduces activity by reducing catalytically active sites, as well as by reducing porosity of the particle, which can restrict accessibility of the catalyst. Contaminants such as sulfur also contribute to deactivation in various ways. The model presented here considers all of the mechanisms contribute catalyst deactivation.

The catalyst deactivation model most widely used for predicting activities is a first order decay type based on the following equation:

$$k = k_o \exp(-k\, t)$$

Where: k = spent catalyst activity; k_o = fresh catalyst activity; k = deactivation rate constant; and t = time on stream in unit, minutes. Because the above equation is only a model of activity, it can not be used to predict the catalyst property and selectivity changes. Conversion data are required to determine k, and laboratory measurement of k_o at zero time reaction is impossible. Therefore, extended reaction time is needed to indicate the initial rate to represent fresh catalyst activity. Based on the above equation, deactivation rate constant of thyophene hydrodesulfurization on the Pt/Zeolite and on Pt-Ce/Zeolite catalyst are calculated. The higher the deactivation rate constant, the lower the catalyst lifetime. Based on the deactivation rate constant, the effect of Ce on the catalyst is then evaluated.

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EXPERIMENTAL SECTION

Material

In this experiment the metal used for active component was platinum obtained from aqueous solution of H_2PtCl_6 (Merck), activated Indonesian natural zeolite (taken from Wonosari, Yogyakarta, Indonesia) was used as supporting agent and cerium oxide (CeO_2, Merck) as promoter.

Procedure

Pt/Zeolite catalyst was prepared using impregnation method, activated zeolite was immersed in the platinum solution followed by filtration, drying, calcination, oxidation and reduction. The calcination, oxidation and reduction steps were done at temperature between of 400 °C. Pt-Ce/Zeolite catalyst was prepared using coimpregnation method, activated zeolite was immersed in the platinum-cerium solution followed by filtration, drying, calcination, oxidation and reduction. The characterization of catalysts consists of metal content using atomic absorption spectroscopy (AAS), platinum dispersion by CO adsorption, surface area, porosity, pore size distribution by gas sorption analyzer NOVA 1000 and surface morphology using transmission electron micrograph (TEM).

The hydrodesulfurization of thiophene was carried out in a differential reactor 25 cm long and 0.25 cm ID stainless steel tubing equipped with thermocouple connected to an instrulab 2000 data logger for continuously measuring reaction temperature. Feed for this reactor was a mixture of thiophene and hydrogen at total flow rate of 20 cc min^{-1}. One gram catalyst (0.7 cc) was placed in the reactor between glass wool on the top as well as on the bottom of the catalyst batch. Reactor temperature was 350 °C monitored by a thermocouple. Catalyst activity presented in this paper was thiophene conversion after reactions proceed for 15, 30, 45, 60 and 75 min, at the regulated temperature.

RESULT AND DISCUSSION

Catalysts Characterization

The result of catalysts characterization showed that the metal impregnated was only about 70 %, therefore, the amount of the metal impregnated was less than the metal added into the solution. Thirty percent of the metal in the solution was still in the solution and released during filtration. However, the dispersion of metal on the catalyst surface is good as shown by CO adsorption. Characters of the catalysts developed are summarized in Table 1.

Table 1. Characters of developed catalysts in the laboratory

Catalyst	Surface area (m^2/g)	Average pore diameter (Å)	Pore volume (10^{-3}cc/g)	Metal content (%)		Pt Dispersion (%)		
				Pt	Ce	fresh	spent	61
Zeolite	97.31	15.73	54.62	-	-			
Pt/zeolite	88.56	18.22	51.83	0.35	-	63	21	
Pt-Ce/Zeolit	84.74	19.91	49.77	0.35	0.46	61	37	

From the surface area measurement, metal loading on the zeolite decreased the surface area of zeolite. It can be explained that the metal particles are dispersed close to the pore mouth and prefer to be adsorbed in the small pores. This statement is supported by lowering catalyst pore volume due to impregnation. From these data, it can be concluded that some of the metal particles blocked the pore, so the surface area decreased. Platinum content in Pt/zeolite and in Pt-Ce/zeolite catalysts are designed equal to 0.35 wt.%. The addition of cerium onto the zeolite reduced the Pt dispersion from 63% becomes 61%. This phenomena indicated that addition of Ce did not affect the number of catalyst active sites.

Catalyst Testing

Hydrodesulfurization reaction carried out using Pt-Ce/zeolite at 350 °C showed that the conversion decreased slowly as follow, 4.49, 3.32, 2.66, 2.25 and 2.06 % at reaction time of 15, 30, 45, 60 and 75 min, respectively. At the same reaction temperature, the reaction on Pt/zeolite showed similar tendency on conversion, decreased slightly faster from 5.04, 3.41, 2.26, 2.01 and 1.86 % at reaction time of 15, 30, 45, 60 and 75 min, respectively. The values of the corresponding rate constant are written in Table 2.

Table 2 showed that the rate constant of thyophene hydrodesulfurization decreased with time on stream. Catalytic activity of Pt-Ce/zeolite decreased to about 1/3 for 60 min. In the same periode, catalytic activity of Pt/zeolite activity decreased to about 1/5. This data indicated that the reduction of rate constant using the catalyst without Ce is twice to that of the catalyst with Ce addition. Thus, the addition of Ce lengthened the catalyst lifetime.

Fig 1 showed the prediction of deactivation curves for both catalysts. The shapes are quite similar. It was showed that using Pt-Ce/zeolite catalyst, the activity response was more stable.

At initial rate of reaction, 15 min, reaction proceed rapidly and then decreased considerably followed by

Table 2. Rate constants for reaction on Pt-Ce/Zeolite and on Pt/Zeolite catalysts at 350^{o}C at various reaction time (Time on Stream)

Time on Stream (min)	Rate constant (k. min)	
	Pt-Ce/zeolite	Pt/zeolite
15	1.55	1.63
30	1.04	1.16
45	0.80	0.87
60	0.69	0.49
75	0.58	0.38

Table 3. Thyophene percent conversion after 75 min. reaction (at 350^{o}C)

Catalyst	Zeolite	Pt/zeolite	Pt-Ce/zeolite
Conversion	undetected	14.58 %	14.78 %

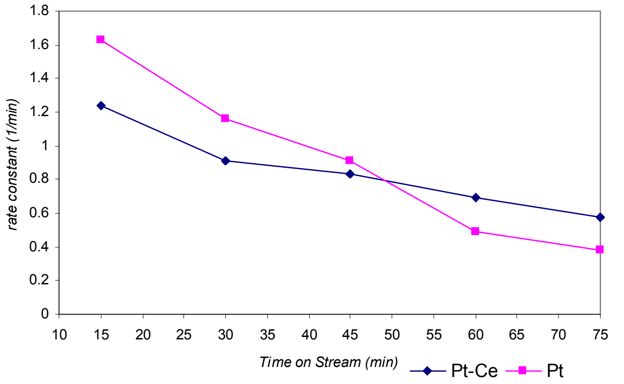

Fig 1. Reaction rate constant vs Time on Stream (ToS) for both catalysts used in this experiment

Table 4. Relative rate constants (k/k$_0$) for reaction on the Pt-Ce/zeolite and Pt/zeolite catalysts at 350^{o}C at various reaction time (Time on Stream)

t^{o}S/ min.	(k/k$_o$) (Pt-Ce/zeolite)	ln (k/k$_o$) (Pt-Ce/zeolite)	(k/ko) (Pt/zeolite)	ln (k/k$_o$) (Pt/zeolite)
15	1	0	1	0
30	0.73	-0.31	0.71	-0.34
45	0.67	-0.49	0.56	-0.56
60	0.56	-0.58	0.29	-1.22
75	0.47	-0.76	0.23	-1.46

fairly stable conversion down to 75 min. These behaviors occurred on both catalysts. The change in catalytic activity can be an effect of one or several processes. There are probably many mechanisms of catalyst deactivation occured in this reaction. When the unwanted, harmful components are accumulated on the catalysts surface and slowly poison the catalyst. When coke formation occurred, carbonaceous residues cover the active surface sites and decreased the active site of catalyst. The amount of coke might be increased by the increase of time on stream. Therefore, the kinetics and performances of catalyst deactivation is a function of time on stream.

The catalysts performance of the hydrodesulfurization of thyophene at 350 ^{o}C after 75 min. reaction are summarized in Table 3. At first, it was checked that no reaction occurs in the absence of the catalyst. Therefore, thermal hydrodesulfurization of thyophene was not able to proceed. Using zeolite, the reaction occurred very slowly, the thyophene conversion can not be measured.

Table 3 showed the slightly difference of activity between the catalysts with and without platinum. The Pt-Ce/zeolite showed slightly higher activity than that of the Pt/zeolite. The slightly higher active catalyst is caused by double impacts metal active sites of platinum and cerium. On the other hand, zeolite which is active for several reaction showed very low activity for hydrodesulfurization. Table 1 showed that small difference on physical characters of catalysts given quite difference in activity. Since the change of physical properties of Pt/zeolite and Pt-Ce/zeolite was not significantly large, therefore those factors would not have any effect to the catalytic activity. Based on the catalyst testing data, the activity of Pt-Ce/zeolite is only slightly higher than that of the Pt/zeolite. From this activity point of view, it is predicted that the difference in activity was due to the electronic effect towards the platinum active sites resulted by addition of cerium.

Deactivation Kinetics

The catalyst activity usually decreases as a consequence of encapsulating coke formation. Given that, at the operating conditions used, part of the encapsulating coke formed can be eliminated in situ by hydrogen present in the reaction. The deactivation kinetic is first order, the rate is expressed in terms of :

$$k = k_o \exp(-k\, t)$$

$$\ln (k/k_o) = -k\, t$$

Plot of ln (k/k$_o$) vs t will produce straight line with slope of -*k*

Due to the fact that measuring the activity of the zero time reaction is impossible, the k$_o$ is taken when the activity was measured at the first time (ToS = 15 min). The result of relative rate constant obtained from

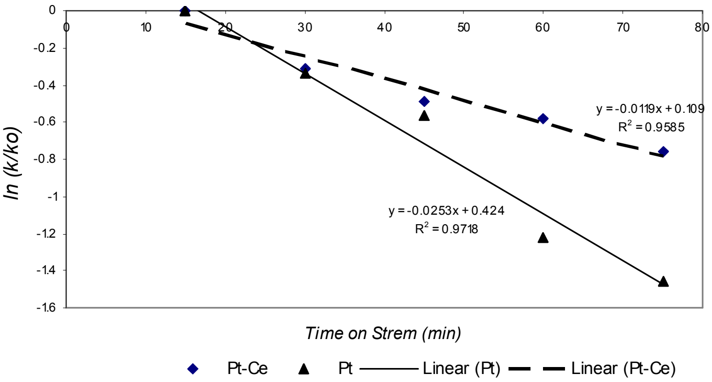

Fig 2. Ln relative rate constants (k/k_0) for reaction on the Pt-Ce/zeolite and Pt/zeolite catalysts at 350 °C vs Time on Stream

a series of reactions conducted at 350 °C are summarized in Table 4.

Based on the line equation written in Fig 2, deactivation rate constant on the catalyst of Pt/zeolite was 2.53×10^{-2} min^{-1}, while that of on Pt-Ce/zeolite was 1.19×10^{-2} min^{-1}. Therefore, cerium lengthens the catalyst life time by factor of 2.216. The addition of small amount of cerium drastically influenced the catalyst life time. This phenomenon may be due to stable dispersion of the active species on the support. Moreover, this stable dispersion was influenced by the surface composition of the active sites and could be associated with a specific interaction between Pt and hydroxyl groups of the zeolite promoted by cerium.

CONCLUSION

Attempting to investigate the effect of cerium on hydrodesulfurization catalyst performance, preparation and characterization of Pt/Zeolite and Pt-Ce/Zeolite catalyst was carried out and their properties in the hydrodesulfurization of thiophene were evaluated. The results obtained in this work are : The loading of Pt and/or Ce metal onto the zeolite decreased the surface area of zeolite. The Pt-Ce/Zeolite catalyst showed slightly higher activity than that of the Pt/Zeolite catalyst. Deactivation rate constant of the Pt/Zeolite catalyst was 2.53×10^{-2} min^{-1} while that of Pt-Ce/Zeolite catalyst was 1.19×10^{-2} min^{-1}. Therefore, cerium lengthens the catalyst life time by factor of 2.216. The addition of small amount of cerium drastically enhanced the catalyst life time.

The characterization results suggested that the length of Pt-Ce catalyst lifetime was due to stable dispersion of the active species on the support. Moreover, this stable dispersion was influenced by the surface composition of the active sites and could be associated with a specific interaction between Pt and hydroxyl groups of the zeolite promoted by cerium.

REFFERENCES

1. Ponec, V., and Bond, G.C., 1995. *Catalysis by Metals and Alloys: Studies in Surface Science and Catalysis*, 95, Elsevier, Amsterdam.
2. Braunstein, P., and Rose, J., 1988, *Heterometallic Clusters in Catalysis*: *Stereochemistry of Organometallic and Inorganic Compounds*, 3, Elsevier, Amsterdam,
3. Song, L. F., Hu, J. Y., Ong, S. L., Lee, Y. H. Wang, J. G. and Zhao, R. Y., 2005, *J. Energy Conv. & Man.* , 46, 1, 1-9
4. Pinzón, M.H, Centeno, A and Giraldo, S.A., 2006, *Appl. Catal. A: General*, *302, 1*, 118-126
5. Kanda, Y, Kobayashi, T, Uemichi, Y, Namba, S and Sugioka, M., 2007, *Appl. Catal. A: General*, 308, 111-118
6. Yasuharu, K, Takao, H, Yoshio, U and Masatoshi, S., 2006, *J. Jpn. Pet. Inst*, 49, 2, 49-56