

# The effect on hydrogen transfer activity of catalytic cracking catalyst by heteropolyacid and heteropolyacid salt

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**Abstract:** To investigate the effect of heteropolyacid and heteropolyacid salt on catalyst cracking catalyst activity, selectivity and hydrogen transfer activity, different types of heteropolyacid and heteropolyacid salt were dispersed on the catalyst surface by dipping. The catalyst acidity was analyzed by in situ IR, the evaluation tests were carried out in fixed-fluidized bed and riser reactor, and the cracked gas composition was analyzed by on-line GC. The results showed that catalyst cracking activity and hydrogen transfer activity were improved by heteropolyacid and heteropolyacid salt. When heteropolyacid content is  $40\mu g/g$  feed, its acidity increased by 3 units, and the yield of light oil and total liquid enhanced by  $1.36\%(\omega)$  and  $2.24\%(\omega)$  respectively. When the mixture of heteropolyacid and heteropolyacid salt content content is  $40\mu g/g$ feed, the yield of light oil and total liquid enhanced by  $1.36\%(\omega)$  and  $2.24\%(\omega)$  respectively. When the mixture of heteropolyacid and heteropolyacid salt content content is  $40\mu g/g$ feed, the yield of light oil and total liquid enhanced by  $1.36\%(\omega)$ .

Keyword: catalytic cracking, hydrogen transfer, heteropolyacid, crack ability, acidity

#### **1** Introduction

The gasoline of fluid catalytic cracking(FCC) with high alkene content is favorable for increasing octane value, but alkene has negative effect on the engine deposit, the emission of harmful substance in the engine and the photochemical reaction activity of the tail gas. So the alkene content should be controlled within limits. FCC gasoline distillate contain high proportion of  $C_5 \sim C_{12}$ alkene, the chains of these alkene are relatively short, and their reaction activity is comparatively low. It is difficult for these alkene to undergo further  $\beta$ -scission reducing alkene content. But  $C_5 \sim C_{12}$  alkene are highly sensitive to hydrogen transfer reaction, so hydrogen transfer reaction can be utilized to reduce alkene content in FCC gasoline distillate.

Hydrogen transfer reaction is an important secondary reaction of molecular sieve catalytic cracking, and it plays a double role in catalytic cracking reaction. On the one hand, alkene act as hydrogen receptor to generate saturated hydrocarbon terminating alkene further cracking and retaining more products with high relative molecular weight, that is to increase gasoline and diesel yield and to reduce dry gas yield as well as to reduce alkene content in cracked products. On the other hand, alkene can be used as hydrogen donator to become carbonium ion or unsaturated substance, and after several times of hydrogen transfer, the alkene is even less hydrogen .The unsaturated arene, which is difficult to go on catalytic reaction, vigorously adsorb on the catalyst surface and condensate to generate coke <sup>[1]</sup>. The activity and selectivity of hydrogen transfer reaction are significantly affected by their adsorption mechanism<sup>[2,3]</sup>. Therefore the hydrogen transfer reaction activity of the catalyst greatly influences products distribution, products quality as well as the content of alkene, arene, and isomeric alkane in the cracked products. The optimum utilization of hydrogen transfer reaction can regulate the olefin content in the saturated products of bimolecular hydrogen transfer reaction, terminate cracking reaction, raise the isoalkane and arene content, and reduce olefin content in the cracked products while coke yield increasing slightly,

Owning the valence electron orbit structure of  $(n-1)d^{1-9}nS^{1-2}$ , transition elements have more vacancy orbits, their atoms and ions have the strong ability to form complex compound and heteropolyacid (salt), as

 $H_2[T_iF_6]$ ,  $[HV_{10}O_{28}]^{5-}$ ,  $N_{a2}[P(W_{12}O_{40})]$ ,  $[S_iW_{12}O_{40}]^{4-}$ , ect. The anion of heteropolyacid(salt) is volume biggish, symmetry high, and density of surface charge inferior, as a result, the proton inside of heteropolyacid(salt) molecule is legible to disentangle and to generate much stronger acidity than inorganic acid composed of central atoms or coordination atoms. Meanwhile, the resonance and polarization effect may occur between the vacancy orbits of transition elements and the Al-O-Si bond of molecular sieve, thus the mutual mobility of the proton may be enhanced, the catalyst acidity distribution may be improved and the B acid density and the B acid/L acid proportion may be improved as well, making heteropolyacid(salt) a bronsted acid reaction feature.

Utilizing the bronsted acid nature of heteropolyacid (salt) mixture, present paper reviewed their influence on the cracking activity, the selectivity and the hydrogen transfer activity of the solid acid catalyst by the way of passing the mixture and the feedstock through fixed-fluidized bed reactor and riser reactor.

#### **2** Experimental

#### 2.1 Feedstock

The feedstock is LuNing oil: 30%VR+70%VGO. The properties of the feedstock are tabulated in Table 1.

Density(20°C)/g.m <sup>-3</sup>	0.9097
Carbon residue / %	4.07
Total sulfur / %	0.63
Alkali nitride/ µg.g <sup>-1</sup>	1104
C/ %	86.82
H/ %	12.88
$< 500$ °C quantity/ $\omega$ %	55.5

Table 1 Properties of feedstock

# 2.2 Catalyst

Commercial equilibrium CC-20D catalyst. The properties of the catalyst are tabulated in Table 2.

Table 2. Catalyst properties

Name	CC-20D
Chemical composition, $\omega$ %	

Al <sub>2</sub> O <sub>3</sub>	45.2
Na <sub>2</sub> O	0.59
RE <sub>2</sub> O <sub>3</sub>	0.41
Surface area/m <sup>2</sup> .g <sup>-1</sup>	129
Pore volume/ml.g <sup>-1</sup>	0.40
Apparent bulk density/g.cm <sup>-3</sup>	0.79
Particle size distribution, $\omega\%$	
0~20 μm	0.4
20~40 µm	3.2
40~80 µm	53.1
>80 µm	43.3
$\omega$ (Metal)/ µg.g <sup>-1</sup>	
Ni	9700
V	2060
Fe	3700
Na	2600
Micro-activity/%	64.9

# 2.3 Characterization and evaluation

Three kinds of test units were used for evaluation. The market available Xytel ACE Model R test unit is a fixed-fluidized bed bench scale unit, operated in a continuously reaction-regeneration recycling mood. Catalyst loading and oil infection rate were 10 g and 2g/min, respectively. Two other kind of test units are a micro-scale fixed bed reactor and a bench-scale fixed bed (FFB) reactor. The reaction effluence was separated into gaseous and liquid products by the cooling-separation system. The cracked gas composition was analyzed by an on-line GC(HP4890). The liquid product is analyzed by an off-line GC (HP5890), followed by ASTM D-2887 simulated distillation. CO in the flue gas was completely converted into CO<sub>2</sub> in a catalytic converter. The coke yield was calculated by a computer after analyzing the CO<sub>2</sub> in flue gas through an on-line IR .Then the whole mass balance was worked out.

The commercial equilibrium catalyst dipping by heteropolyacid A and heteropolyacid salt on different concentration. The acidity of B acid were are tabulated in Table 3

The cracking tests for researching the effects of different concentration dipping catalyst on the hydrogen transfer reaction were conducted on the FFB unit under the conditions of 500 °C, n(c)/n(o)=5 and MHSV=12h<sup>-1</sup>.



#### 2.4 Heteropolyacid(salt)

Sample A: mixture of heteropolyacid Sample C: mixture of heteropolyacid and heteropolyacid salt

## **3 Result and discussion**

#### 3.1 Change of catalyst acidity

Under a certain catalyst/feedstock ratio, the flow rate of the feedstock, which may react with per recycling equilibrium catalyst in the reaction can be calculated. On base of this feedstock flow rate, the additive amount is calculated. Dissolve the additive in 80~120°C petroleum ether. Then disperse additive on the surface of equilibrium catalyst uniformly, then dry them under 150°C and measure the acidity.

 Table 3
 B acidity of equilibrium catalyst on heteropolyacids<sup>[4]</sup>

Heteropo	lyacids concentration <sup>1</sup>	0	20	40	60	80
А,	B acid/µmol.g <sup>-1</sup>	34.21	35.67	37.52	38.26	39.41
С,	B acid/µmol.g <sup>-1</sup>	34.21	35.07	36.14	37.30	38.24

※ Pyridine adsorption in situ infrared analysis

As shown in the table 3, all the B acidity are enhanced with the adding of additive A and C. Under the same dose, the acidity of the equilibrium catalyst containing pure mixture of heteropolyacid A is enhanced much higher than the one containing mixture of heteropolyacid and heteropolyacid salt which has buffer effect. This perfectly illustrates the system of heteropolyacid and heteropolyacid salt owns some buffer effect resembling the Hac-NaAc system, so the attenuation of catalyst cracking activity is retarded.

#### 3.2 Change of cracking activity

The heropolyacid (salt) mixed with feedstock are pumped into Middle-scale Riser reactor test unit for dynamic evaluation.

Table 4 Product	distributing	on Heterop	olvacids(ω%)
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Heteropolyacids			А			С	
μg.g <sup>-1</sup>	0	20	40	60	20	40	60
dry gas	4.43	4.21	3.67	4.48	4.16	3.59	3.89

liquefied petro- leum gas	20.55	20.87	21.43	21.00	20.17	21.05	21.27
gasoline	39.59	40.30	40.92	40.51	40.03	40.54	40.61
diesel	23.24	23.45	23.27	23.18	24.10	24.19	23.54
slurry	4.97	4.08	3.91	3.84	3.98	3.90	3.87
coke	7.22	7.09	6.80	6.99	7.02	6.73	6.84
conversion/ %	71.79	72.47	72.82	72.98	71.92	71.91	72.59
light oil yield / %	62.83	63.75	64.19	63.69	64.13	64.73	64.15
total liquid yield/ %	83.28	84.62	85.62	84.69	84.84	85.78	85.42

XAverage data of 48 hours

As can be seen from table 3 and 4, with the amount of additive A and C increasing, the B acidity increase obviously on equilibrium catalyst. The reason is that, after the adding of acidity additive, one part of additive can neutralize the alkaline nitrogen to avoid B acid and L acid loss from catalyst surface, while the bronsted acid in the other part of the additive can be adsorbed on the catalyst surface to enhance B acid. Correspondingly, the equilibrium catalyst cracking activity is enhanced, the conversion is improved and the selectivity is increased as well. When the acid additive adsorbed and enrichmented on equilibrium catalyst exceed a certain value, dry gas and coke yield may rise because of the high catalyst activity. Meanwhile, coke as one of the reaction products may continuously deposit and cover on the active surface of the cracking catalyst and induce a change to the acidity structure and approachability of the catalyst activity center, as a result, the cracking activity and selectivity may decrease. But the additive C, which has buffer effect, owns stronger ability to keep equilibrium catalyst acidity stabilize from the position of the nozzle to the exit of the riser than additive A does. Therefore the activity decrease speed is slowed down, consequently thermal cracking reaction may be repressed at the end of the riser, fluid catalytic cracking reaction may be promoted and finally the selectivity for light distillate and coke may be improved.

With the amount of additive A and C increasing, the same results are shown in table 5,6.

In the middle, rear of the riser reactor, the deposit and cover of coke on the active surface of the catalyst may induce a poor approachability to the activity center and a catalyst activity descending and less conversion and selectivity. While this can be compensated for by the technology of molecular sieve crystal size<sup>[5,6]</sup>, the technology</sup> of infusing terminating agent into riser, and the riser rapid separating technology, and so on. The additive C, which is composed by the mixture of heteropolyacid and heteropolyacid salt, also shows some advantage in this aspect. As it is comparatively shown in table 3 and table 4, the acidity of the equilibrium catalyst with additive A added is obviously higher than the one of the equilibrium catalyst with additive C in low additive content level, but the relation of the final conversion and light distillate yield for the two contradicts each other. In the front of the riser, additive A has an equivalent effect with additive C to improve catalyst activity. While in the middle and rear of the riser, coke deposit may induce an activity drop for the equilibrium catalyst with additive A, but for the additive C, which has buffer effect, owns stronger ability to keep equilibrium catalyst acidity stabilize from the position of the nozzle to the exit of the riser than additive A does. Then the activity decrease speed is slowed down, thus thermal cracking reaction may be repressed at the end of the riser, and fluid catalytic cracking reaction is promoted, finally the selectivity for light distillate and coke is improved.

# **3.3** Change of hydrogen transfer reaction Activity

Bimolecular hydrogen transfer reaction is carried out on base of the intermediate of suitable carbonium ion, and the reaction needs active center with high acidity and suitable special structure and acid density<sup>[7]</sup>. The directional adsorption and deposit of transition elements on molecular sieve catalyst can increase activity center density, which is favorable for suitable carbonium ion to form, and thus to promote hydrogen transfer reaction occurring among hydrocarbon molecules and to enhance the reaction activity as well. As is clearly shown in table 5, the olefin in the cracked gas is reduced while the alkane is increased.

Table 5.Activity change on hydrogen transfer reaction



Heteropolyacids concentration µg.g <sup>-1</sup>	0	20	40	60	80
HTC(A)	0.39	0.42	0.57	0.69	0.80
HTC(C)	0.39	0.43	0.60	0.71	0.78

#### 3.4 Change of FCC gasoline composition

Hydrogen transfer reaction includes the bimolecular reaction between alkene and cycloalkane, the bimolecular reaction between alkene and alkene, the bimolecular reaction between cycloalkene and cycloalkene and the bimolecular reaction between coke forehand and coke forehand. The reaction equation is shown as follow:

 $3C_nH_{2n}(alkene)+C_mH_{2m}(cycloalkane)\rightarrow 3C_nH_{2n+2}(alkane)+C_mH_{2m-6}(arene)$ 

 $4C_nH_{2n}(alkene) \rightarrow 3C_nH_{2n+2}(alkane) + C_nH_{2n-6}(arene)$ 

 $3C_mH_{2m-2}(cycloalkene) \rightarrow 2C_mH_{2m}(cycloalkane) + C_mH_{2m-6}(arene)$ 

 $xC_nH_{2n}(alkene)$ +cokeforehand $\rightarrow xC_nH_{2n+2}(alkane)$ +coke

When alkene is saturated by hydrogen transfer reaction, alkane and arene are generated at the same time. But with the hydrogen transfer reaction progress, coke yield rate presents the increasing trend. Therefore, in order to reduce gasoline alkene content and keep gasoline octane value and repress coke producing, the selectivity of hydrogen transfer reaction between alkene and cycloalkane and the selectivity of hydrogen transfer reaction between alkene should be improved , meanwhile the hydrogen transfer reaction between alkene and coke forehand also should be avoided. That is to adjust and control the hydrogen transfer reaction strength in the FCC process, to promote the selective and controllable hydrogen transfer reaction, and to depress the deep hydrogen transfer reaction.

The characteristic of arene and cycloalkene have great difference with alkane, alkene and cycloalkene in hydrogen transfer reaction system. Arene and cycloalkene have strong ability to be adsorbed on the acidity active center , but their reaction activity is relatively weak. They may continue to release negative hydrogen ion ,then saturate other alkene molecule to generate more alkane, and finally convert into polycyclic arometic hy-



drocarbon, coke forehand and even coke in themselves. Base on arene desorption, hydrogen transfer reaction is categorized into two types<sup>[8]</sup>:

Type I:



Type II:



Type I hydrogen transfer reaction convert alkene into the intended alkane and arene, and the selectivity is well. While in type II reaction arene and cycloalkene are hard to desorb, the reaction here is deep hydrogen transfer reaction ,and the reaction products are coke and coke forehand.

Transition elements own strong polarization effect, and they can polarize much more protons and increase the proton mutual mobility. So suitable amount of transition elements depositing on molecular sieve is helpful to form strong acid spot on molecular sieve, to increase B acid/L acid proportion and to improve the density of acid center in Y type molecular sieve. The ability for middle distillate conversion is enhanced, at the same time, both the reaction speed and the reaction selectivity are improved. Consequently, as can be seen from table 6, alkene content in gasoline is reduced, arene and iso-alkane content is raised, and gasoline octane value is kept nearly around a certain level. Mixture C of heteropolyacid and heteropolyacid salt can increase the hydrogen transfer reaction rate much more than what mixture A of heteropolyacid can do, so the former is much easier to enhance reaction selectivity than the latter.

The depositing and enrichment of transition elements can increase arene being adsorbed on molecular sieve activity center, and this can educe type II hydrogen transfer reaction, so coke yield appears a little increasing. In order to keep a better coke selectivity and to control the reaction intensity, transition elements content should be suitable, as is shown in table 6.

Table 6 Change of FCC gasoline composition (500°C,C/O 5, MHSV 12h<sup>-1</sup> $\omega$ %)

	<i>n</i> -alkane	<i>i</i> -alkane	Olefin	Naphthene	Aromatic	RON
B acid A/C (0μg.g <sup>-1</sup> )	7.23	26.47	38.54	5.09	21.47	91.3
$\begin{array}{c} B \text{ acid } A \\ (40 \mu g.g^{\text{-1}}) \end{array}$	6.47	28.91	36.82	5.76	22.04	91.2
$\begin{array}{c} B \text{ acid } C \\ (40 \mu g.g^{\text{-1}}) \end{array}$	5.33	29.77	33.17	7.71	24.02	91.2

## 4 Conclusions

(1) The oil-soluable additive, which is composed of the mixture of transition elements heteropolyacid (salt), can optimize FCC reaction condition and improve catalyst dynamic activity. Suitable amount of transition elements depositing on molecular sieve is favor of forming strong acid site on molecular sieve, increasing B acid/L acid proportion and improving the density of acid center in Y type molecular sieve. The hydrogen transfer reaction rate is increased, and the reaction selectivity is improved. Consequently, Both FCC conversion rate and FCC light distillate yield rate are increased, while alkene content in gasoline is reduced, the content of arene and iso-alkane is raised, and gasoline octane value is remained.

(2) Mixture C of heteropolyacid and heteropolyacid salt can increase the hydrogen transfer reaction rate much more than mixture A of heteropolyacid, especially for the former, the reaction selectivity increases distinctly.

<sup>(3)</sup>Heteropolyacid and heteropolyacid salt can regulate catalyst acidity and improve catalyst activity, meanwhile, improve hydrogen transfer reaction selectivity and increase FCC conversion, liquid yield and reduce gasoline alkene content. Further research is needed for the theory and mechanism of this technology, especially for the buffer effect of Heteropolyacid and heteropolyacid salt system has very important theoretical and industrial application value.

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