

SULFUR-RESISTANT BIMETALLIC NOBLE METAL CATALYSTS FOR AROMATIC HYDROGENATION OF DIESEL FUEL

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INTRODUCTION

It is recognized that high aromatic content will lower the cetane number of diesel fuel and contribute significantly to the formation of undesired emissions in exhaust gases. As a result of the stringent environmental regulations, lowering aromatic content in diesel fuel is one of important technologies. Aromatic hydrogenation, especially for monoaromatics, is more difficult than hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) on conventional sulfide catalysts (1). In addition to this, there is thermodynamic equilibrium limitation on aromatic hydrogenation within the normal operating range of hydrorefining. Therefore, the deep hydrodearomatization (HDA) is a formidable task by conventional hydrotreating technology using supported Ni(Co)Mo(W) sulfide catalysts.

Two-stage hydrotreating routes have been recommended to achieve low level of aromatics for its less investment in facilities and lower operating costs (2-5). In a two-stage process, a sulfide catalyst is used in the first stage where the sulfur and nitrogen are brought down, and a sulfur-tolerant noble metal catalyst is used in the second stage for aromatic hydrogenation. The key of the two-stage process is the development of high active noble metal catalyst with fine sulfur-resistance.

It has been generally acknowledged that the sulfur resistance of a noble metal can be enhanced by utilizing an acidic support, such as that of an acidic zeolite (6-14). Literatures on the sulfur resistance of bimetallic catalysts containing noble metals, except for Pt-Pd, are scarce (15). Y-zeolite supported noble metal catalysts, as important industrial catalysts for aromatics hydrogenation, have received increasing attention in recent years (16). Pd-M/Y bimetallic catalysts, where M are non-noble metal elements, were prepared to investigate the effects of the addition of a second metal in this study.

EXPERIMENTAL

70g NH₄Y (Na 1.2%, SiO₂/Al₂O₃=5) was mixed with 30g Al₂O₃, followed by kneading and extrudation, and finally calcined at 600°C for 2h.

The catalyst samples were prepared by incipient wetness impregnation technique. The Y zeolite support was brought in contact with a solution of Pd(NH₃)₄Cl₂ in deionized water, followed by drying at 120 °C for 2h and then calcining at 550 °C for 2h. The palladium-contained Y zeolite contacted with an aqueous solution of (NH₄)₂CrO₄, then dried and calcined as before. The Pd-Cr/Y catalyst has been prepared.

The other Pd-M/Y bimetallic catalysts were prepared following the same procedure with Pd-Cr/Y. The second metal precursors used for the preparation of the bimetallic catalysts are listed in Table 1. The metal contents, which were measured by inductively coupled plasma spectroscopy, are also listed in Table 1.

The sulfur resistance of catalyst was tested with a continuous down flow fixed-bed reactor. The reactor was packed with 1.0g catalyst (40-60 mesh) diluted with an inert 40-60 mesh ceramic in a ratio of 1:1. The upper and bottom part was filled with particles of a catalytically inactive ceramic material for preheating and preventing channel effects. The feed, toluene and n-hexane in a volume ratio of 1:1, was mixed with a certain amount of thiophene to prepare a feed of 300ppm sulfur content. Catalysts were firstly reduced at 300 °C under 600psig of pure hydrogen for 2h. After reduction, the catalytic reactions were carried out with a weight hourly space velocity (WHSV) of 4.0h⁻¹ and flowing hydrogen (400ml/min), under 600psig. Reaction products were analyzed by an on-line gas chromatography.

RESULTS AND DISCUSSION

The GC analysis results indicate that the main products of toluene hydrogenation on Pd-M/Y catalysts are methylcyclohexane(MCH) and 1,1-dimethyl cycloheptane (DMCH).

Fig.1 and Fig.2 show that hydrogenation activity of Pd-M/Y bimetallic catalysts are remarkably

different from Pd/Y catalyst, though the second metal-added was only 0.6%. This indicates that the sulfur resistance of Pd are remarkably affected by the second metal. The sulfur resistance of Y zeolite supported Pd catalyst is improved by Cr and W, but lowered by La, Mn, Mo, Ag.

Fig.3 indicates that the second metal have no effect on the product selectivity of toluene hydrogenation on Pd bimetallic catalysts. The formation of isomer DMCH is related to the acidic properties of catalysts. The isomer selectivity doesn't change with the addition of the second metal. It could be deduced that the second metals have no effects on the acidic properties of Pd catalysts.

It can be observed from Fig.1 and Fig.2 that PdCr/Y and PdW/Y bimetallic catalysts exhibit better sulfur resistance than Pd/Y. This phenomena has not found to be reported yet. Since Y zeolite supported noble metal catalysts is important on industrial aspects, this discovery would have applied prospects for petroleum processing. From the aspects of isomer selectivity of toluene hydrogenation on Pd monometallic and bimetallic catalysts, the change of sulfur resistance of Pd catalysts was not caused by acidic properties. Nowadays, further studies on the mechanism that the second metal affects the sulfur resistance of Pd catalysts are carrying on in our laboratory.

CONCLUSIONS

The second metal has remarkable effects on the sulfur resistance of Y zeolite supported Pd catalysts. Among them, Cr and W improve the sulfur tolerance of Pd catalysts, but La, Mn, Mo and Ag make the sulfur resistance worse. For catalytic hydrogenation of toluene in presence of 3000ppm sulfur in feed on Pd/Y and Pd-M/Y, the second metals(M) have no obvious effects on product selectivity.

ACKNOWLEDGEMENTS

The support of Xiaohong Kang and Group 1508, Research Institute of Petroleum Processing are acknowledged.

Table 1. Summary of Catalyst Preparation and Composition

Catalyst	Precursor of Second metal	Pd content (wt%)	Second metal (wt%)
Pd	-	0.61	0
PdCr	(NH ₄) ₂ CrO ₄	0.59	0.61
PdW	(NH ₄) ₁₀ W ₁₂ O ₄₁ •11H ₂ O	0.59	0.59
PdLa	La(NO ₃) ₃	0.60	0.60
PdMn	Mn(NO ₃) ₂	0.60	0.60
PdMo	(NH ₄) ₂ MoO ₄	0.60	0.59
PdAg	AgNO ₃	0.61	0.61

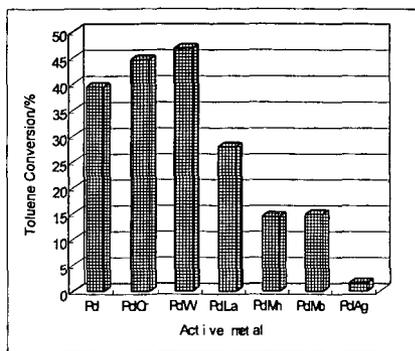


Fig.1 Toluene conversion on Pd bimetallic catalysts(T=280)

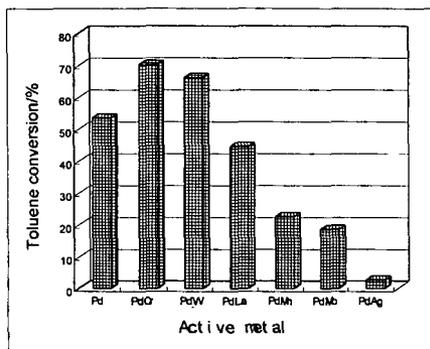


Fig.2 Toluene conversion on Pd bimetallic catalysts(T=300)

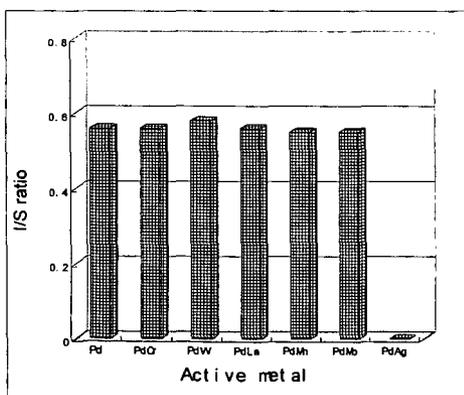


Fig.3 Isomerization selectivity(I/S ratio)
on Pd bimetallic catalysts
T=280°C

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