

**Polycyclic Aromatics 의 수소화 가역반응을 위한
Biphenyl 과 Terphenyl 의 수소화 반응 연구**

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A study of hydrogenation of biphenyl and terphenyl for reversible hydrogenation of polycyclic aromatics

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Introduction

A few catalysts that would be promising for hydrogenation of aromatics were prepared and tested. Among these, we have chosen Pd-, Pt-containing catalysts on silica (in some cases alumina) and carbon-based (two types of activated charcoal and graphitized Sibunit) carrier systems. The porous characteristics of a Sibunit sample were close to those of the alumina carrier, which contained mostly mesopores with a minor content of micropores.

Experiment

1. Catalyst preparation

The oxide and carbon based catalysts were prepared by impregnation and ion exchange with anionic metal complexes like H_2PdCl_4 and H_2PtCl_6 . The disadvantage of this approach is the reduction of the anionic complexes in the course of ion exchange resulting in an uncontrolled deposition of reduced metal species, that is, the metal dispersion becomes poor and not uniform.

The following catalysts were prepared for hydrogenation- dehydrogenation reactions

1) 15%Pt/C, 2) 9%Pt/CKT-4, 3) 5%Pt/Sibunite, 4) 5%Pt/Sibunite-preoxidized, 5) 3%Pt/Sibunite-preoxidized, 6) 3%Pt-2%Pd/Sibunite-preoxidized, 7) 3%Pt-0.25%Pd/Sibunite-preoxidized, 8) 2%Pd/Sibunite, 9) 2%Pd/Sibunite-pre-oxidized, 10) 1%Pt/Sibunite, 11) 9%Pt/SiO₂, 12) 5%Pt/SiO₂, 13) 3%Pt-2%Pd/SiO₂, 14) 3%Pt/Al₂O₃

2. Catalytic tests in hydrogenation of solid polycyclic aromatics

For biphenyl and terphenyl hydrogenation, the sample of the catalyst (80 mg) and solid aromatic substrate (800 mg) were loaded at once in 4 glass ampoules (d=9 mm, h=50 mm). Then these were placed into an autoclave and hydrogen was purged. One ampoule was equipped with a thermocouple connected with a temperature controller.

Then the autoclave was heated up to 80 °C, of which temperature was increased stepwise (15 min-100 °C, 20 min-120 °C, 30 min-140 °C, 150 min-160 °C) up to the reaction temperature-160 °C and was kept for some more 2 hours. After that, the autoclave was cooled down to the room temperature and hydrogen was discharged. The test device is a model of the real fuel tank where the hydrogenation reaction is carried out in a thick layer of the substrate without stirring. The height of the reaction vessel is near 10 mm, where the catalyst occupies only 1/7-1/10 part at the bottom of the vessel.

We specially discontinue the experience, when the pressure of hydrogen in a system still drops. It was more convenient to compare the conversion of aromatic substrates. The conversions of biphenyl and terphenyl were measured using a chromatographic column SE-54 in the isothermal regime at 140 and 240°C. If the reactant is still solid, the probe was dissolved in benzene.

3. Characterization of catalysts

Most promising catalyst samples (Pt-systems) were characterized before the reaction by Diffuse-reflectance Fourier-transform spectroscopy (DRIFTS), X-ray Photoelectron Spectroscopy(XPS), adsorption of CO (as an IR probe molecule) in order to reveal the state of the supported metal and its dispersion. Among the systems the metal dispersion (D), estimated from CO adsorption, of the aerosil systems (D = 80-88%) and carbon materials (D = 83-93%) was very high (because of the low metal loading and gentle conditions of the calcinations and reduction), whereas that of alumina catalysts (D = 70-76%) was low.

Result and Discussion

1. Biphenyl hydrogenation at 160 °C

As shown Table 1 the selectivity of all tested samples in biphenyl hydrogenation is near 100% even at high temperature (160 °C).

Table 1 Results of catalysis of biphenyl hydrogenation without stirring (biphenyl/catalyst = 10)

Sample No	Catalyst	Pretreatment	Biphenyl conversion%	Product distribution, % wt.		
				C _{C12H22} , %	Intermediate, %	C _{C12H10} , %
1	15%Pt/C	Reduced	93,4	81,2	12,2	6,6
2	9%Pt/CKT-4	Reduced	86,0	38,2	47,8	14,0
3	5%Pt/Sibunite	Calcined	96,9	64,5	32,4	3,1
4	5%Pt/Sibunite-ox	Calcined	55,1	14,9	40,2	44,9
4-1	5%Pt/Sibunite-ox	Reduced	64,0	17,4	46,6	36,0
5	3%Pt/Sibunite-ox	Calcined	50,8	9,8	41,0	49,2
6	3%Pt-2%Pd/Sibunite-ox	Pt-Dried Pd-Cal	65,9	9,4	56,5	34,1
11	9%Pt/SiO ₂	Calcined	100	100,0	0	-
12	5%Pt/SiO ₂	Calcined	99,3	95,8	3,5	0,7
12-1	5%Pt/SiO ₂	Reduced	100	98,9	1,1	-
12-2	5%Pt/SiO ₂	Calcined	99,1	95,2	3,9	0,9
13	3%Pt-2%Pd/SiO ₂	Calcined	98,4	91,0	7,4	1,6
14	3%Pt/Al ₂ O ₃	Calcined	46,5	12,0	34,5	53,5
14-1	3%Pt/Al ₂ O ₃	Reduced	66,2	21,8	44,4	33,8

* The sample (No. 12-2) prepared by the impregnation method from an aqueous solution of [Pt(NH₃)₄]Cl₂.

we can see that unconverted biphenyl, bicyclohexene and some unidentified compound with the residual double bonds are present in the reaction mixture. For example, the biphenyl conversion for 15%Pt/C is 93.4%, moreover the reaction products contain near 12.2% of the compound with residual double bond /for example, 1-(2-) hydrobiphenyl. From Table 1 we can see that the biphenyl conversion for pre-reduced samples is in the sequence of 5%Pt/SiO₂ > 15%Pt/C > 9%Pt/CKT-4 > 3%Pt/Al₂O₃ > 5%Pt/Sibunite-ox. The reason of the low activity of the catalysts on carbon carriers and Al₂O₃ can be explained by poor distribution of the catalyst particles in biphenyl, unlike the light aerosol-based catalysts. The heavy-weight catalyst particles are located at the bottom. For Pt/SiO₂ (aerosil) catalysts, a good distribution of the small (light-weight) catalyst particles were observed in all the molten biphenyl with a high viscosity. It makes easier the diffusion of molecules and leads to increasing reaction rate. It should be noted that the order of carrier particles dispersion (SiO₂, C, and Al₂O₃) coincides with the order of catalyst activity.

2. Influence of Pt concentration on activity

Decrease of Pt loading of Pt/Sibunite-ox samples from 5 to 3% (Table 1, samples No. 4, 5) leads to some diminution of the catalysts activity in terms of the biphenyl conversion. The same effect was observed in the case of Pt/SiO₂ catalysts (Table 1, samples No. 11, 12).

3. Influence of preliminary activation on activity

For Pt-containing catalysts on different supports, the samples were activated in hydrogen or in air atmosphere on their catalytic properties (Table 1, samples No. 4 and 4-1; N0. 12 and 12-1; No. 14 and 14-1). We can see that the activity of the preliminary activated catalysts, supported on Sibunite, SiO₂ and Al₂O₃, somewhat increased.

4. Influence of catalysts preparation method on activity

For Pt/SiO₂ we can see (Table 1, samples No. 12 and 12-1) that the activity of the calcined sample, prepared from H₂PtCl₆, is somewhat higher than that of the catalyst prepared from {Pt(NH₃)₄}Cl₂. On a large scale, this effect was observed in the case of Pt-containing catalysts prepared on the basis of Sibunite and Sibunite-ox (Table 1, samples No. 3 and 4). It should be mentioned that the catalysts preparation method by Sibunite impregnation from H₂PtCl₆ is essentially simpler than that one by ion exchange of {Pt(NH₃)₆}Cl₂ with active oxygen-containing groups on the surface of modified Sibunite-ox.

5. Terphenyl hydrogenation at 160°C

The results of the promising catalysts in terphenyl hydrogenation at 160°C without stirring and terphenyl/catalyst = 10 are presented in Table 2.

Table 2 Results of pre-reduced catalysts in terphenyl hydrogenation

No	Catalyst	Terphenyl conversion, %	Product distribution, % wt		
			C _{C18H32} , %	Intermediate, %	C _{C18H14} , %
1	15%Pt/C	66,9	36,7	30,2	33,1
2	9%Pt/CKT-4	63,6	23,8	40,8	36,4
3	5%Pt/Sibunite-ox	47,9	16,6	31,3	52,1
12-1	5%Pt/SiO ₂	70,1	40,2	29,9	29,9
14-1	3%Pt/Al ₂ O ₃	45,8	16,0	29,8	54,2

In catalytic hydrogenation of terphenyl and biphenyl of Tables 1, 2 at the same reaction conditions (160°C, contact time - 4 hours) the activity of catalysts in terphenyl hydrogenation is somewhat lower. It can be explained only by the lower reactivity of a more complex and heavy molecule such as terphenyl.

Also, as in biphenyl hydrogenation, the reaction products of per-phenyl hydrogenation contain nearly 30-40% of intermediate product with residual double bonds. In biphenyl hydrogenation at the same conditions, the concentration of incompletely hydrogenated products did not exceed 3-12%. The maximum concentration of completely hydrogenated products was observed for the 5%Pt/Sibunite sample. The order of catalysts activity in terphenyl hydrogenation is 5%Pt/SiO₂ > 15%Pt/C > 9%Pt/CKT-4 > 3%Pt/Al₂O₃ = 5%Pt/Sibunite-ox, which is the same as in the case of biphenyl hydrogenation. It confirms that in hydrogenation of molten polycyclic aromatics without stirring the light supports particles in Pt/SiO₂ catalysts in all the reaction volume are more effective than the more heavy particles in other catalysts even on the basis of activated coal or moreover other oxide carriers.

Conclusion

We found that the carrier exhibits a pronounced effect on the activity and effectiveness of Pt-based catalysts in hydrogenation without stirring. For the high reactivity to hydrogenation, lower hydrogenation temperature and higher hydrogen solubility the stirring of CCM is unusable to resolve the hydrogen charging problem of CCM. The experiments on hydrogenation of polycyclic aromatics (biphenyl and terphenyl) over Pt and Pt-Pd-based catalysts supported on high dispersed carrier (pounded SiO₂) showed that these systems exhibit a number of advantages over other catalytic systems (even over Pt/C and Pt/Sibunite catalysts on the basis of a granular carrier), in particular, in terms of the activity at low metal content.

The heavy-weight particles of the catalyst are located only on the bottom of the reaction vessel. We observed the good distribution of the small (light-weight) Pt/SiO₂ catalyst particles in all the volume of molten biphenyl and terphenyl with high viscosity. However, it is obvious that the most active catalysts (Pt/SiO₂) in hydrogenation of heavy molten aromatic without stirring is essentially lower than the stirring conditions. For example, the hydrogen charging of CCM without stirring takes 3-5 times more time than that under stirring with 300-500 rpm. This problem can be solved by changing the geometry of the reactor.

There should be easier in the case of hydrogen release (with and without stirring) because of the high reaction temperature (near 280-320°C) natural stirring occurs due to convection of aromatic and naphthalene substrates. It should be noted that the selectivity for all the used catalysts in terphenyl and biphenyl hydrogenation is near 100%. At the high temperature, particularly during the dehydrogenation stage, a cracking of large polycyclic aromatic molecules is quite possible and it makes some catalysts unusable for hydrogen storage. So, the goal of our further investigation will be a preliminary evaluation of selectivity and stability of the more effective different catalyst in dehydrogenation reactions at high temperatures.