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n-PENTANE ISOMERIZATION IN A CONTINUOUS-FLOW REACTOR ON Pt/Al_2O_3 CATALYSTS MODIFIED BY ADSORBED BISMUTH AND PALLADIUM

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Isomerization of n-pentane has been studied in a continuous-flow reactor at atmospheric pressure on Pt/Al_2O_3 catalysts modified by adsorbed bismuth and palladium. Lower activity and higher selectivity have been obtained on a catalyst modified by bismuth. Both activity and selectivity have decreased on a catalyst modified by palladium. After oxygen treatment the $Pd-Pt/Al_2O_3$ catalyst showed the most pronounced change in catalytic properties and its stability was lower than that of the unmodified Pt/Al_2O_3 catalyst.

Изомеризация н-пентана была исследована в реакторе непрерывного потока, при атмосферном давлении и на катализаторе Pt/Al_2O_3, модифицированном адсорбированным висмутом и палладием. Пониженная активность и повышенная селективность наблюдались для катализатора, модифицированного висмутом. Как активность, так и селективность уменьшались в случае катализатора, модифицированного палладием. После обработки кислородом самые значительные изменения в каталических свойствах наблюдались для катализатора $Pd-Pt/Al_2O_3$ и его стабильность была меньше, чем для немодифицированного катализатора Pt/Al_2O_3.

INTRODUCTION

Bimetallic and multimetallic catalysts are generally prepared by impregnation of the support. However, bimetallic catalysts containing platinum can be prepared by adsorption of a second metal on platinum /1/. The adsorption of metal on platinum via ionization of adsorbed hydrogen allows the preparation of supported platinum catalysts modified by adsorbed metals /1-3/. Both the adsorption and catalytic properties of platinum are changed by adsorption of the second metal /4/. The modification of Pt/Al_2O_3 catalysts by metal adsorption may have a different effect on the properties of "fresh" and "used" catalysts and may affect also the stability of the catalysts. Therefore, parallel to our study using a pulse technique /5/, isomerization of n-pentane on Pt/Al_2O_3 catalysts modified by bismuth and palladium has also been studied in a continuous-flow reactor.

EXPERIMENTAL

Preparation and treatment of the Pt/Al_2O_3 catalyst as well as the modified $Bi-Pt/Al_2O_3$ and $Pd-Pt/Al_2O_3$ catalysts were carried out as described elsewhere /5/. The experiments were performed under atmospheric pressure in hydrogen stream. An electrically heated quartz reactor with an O. D. = 8 mm, was applied. The gas effluent from the reactor was connected to the G. C. via a six-way sample valve. 1.8 g catalyst (0.31-0.63 mm fraction) was used, n-pentane (puriss.) was purchased from Fluka. The hydrogen was deoxygenated on a Pt/Al_2O_3 catalyst at 400 °C. The hydrogen and oxygen used for regeneration were dried over Linde 4A molecular sieve. A gas mixture with a hydrogen to n-pentane ratio of 3:1 was used.

RESULTS AND DISCUSSION

The results obtained on different catalysts under selected experimental conditions (t = 400 °C, w = 1.0 g/g h) are shown in Fig. 1. As can be seen, there is a marked difference between modified and unmodified Pt/Al_2O_3 catalysts. The activity of Pt/Al_2O_3 and $Pd-Pt/Al_2O_3$ catalysts, naturally, exceeds the activity of $Bi-Pt/Al_2O_3$ catalyst, due to the effect of bismuth (catalyst poison) which diminishes catalytic activity /6/. Therefore, the Pt/Al_2O_3 catalyst modified by bismuth is often used in selective dehydrogenation of saturated hydrocarbons /7,8/.

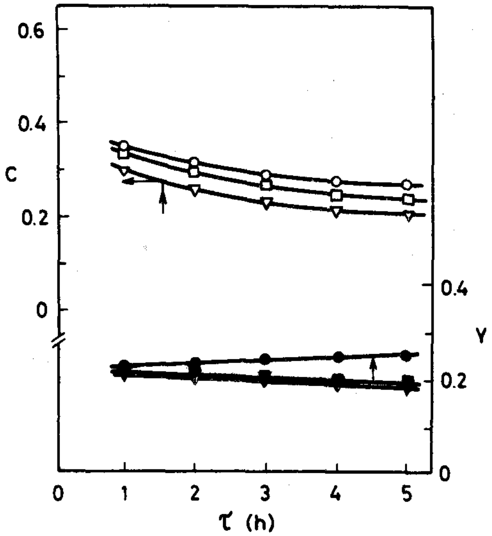

Fig. 1. Comparison of the Pt/Al_2O_3 and modified catalysts

The $Bi-Pt/Al_2O_3$ catalyst showed the highest selectivity to i-pentane formation. The high selectivity of the $Bi-Pt/Al_2O_3$ catalyst can be explained by the blocking of active sites due to hydrogenolysis on adsorbed bismuth. Thus, the extent of hydrogenolysis and coke formation on the metal component of the catalyst is lowered.

Selectivity and activity are lower in the case of a $Pd-Pt/Al_2O_3$ catalyst treated in hydrogen, than for an unmodified Pt/Al_2O_3 catalyst, whereas these values are in agreement with the results obtained on a $Pd-Pt/Al_2O_3$ catalyst prepared by impregnation /9,10/ and on a Pd–Pt alloy film catalyst /11/. The extent of side reactions (1–S) (viz. hydrogenolysis, coke formation) is higher on a $Pd-Pt/Al_2O_3$ than on a Pt/Al_2O_3 catalyst. This can be explained by the increase in activity towards dehydrogenation /12/ and by the increase in hydrogenolysis selectivity /9,11/ due to the palladium content. Formation of methane was especially extensive on "fresh" catalysts /9/.

The results of our further experiments are summerized in Table 1. No change could be observed in the trend of the results when the spece velocity was altered. Comparison of the data in Fig. 1 and Table 1 show that a 50% decrease in space velocity results in a 50% increase in conversion and i-pentane yield. For all three catalysts, the selectivity was increased slightly. After regeneration with oxygen, the Pd–Pt/Al_2O_3 catalyst showed the most significant change in catalytic properties, both the conversion and yield of i-pentane increased, whereas the selectivity was lower. The same phenomenon, although not so pronounced, could be observed using a Bi–Pt/Al_2O_3 catalyst.

If the reaction temperature was raised to 450 °C after 1 hour of reaction, the conversion was lower than at 400 °C. Because of the faster aging process, a decrease in i-pentane yield and selectivity could also be obtained. If the catalyst was modified by bismuth, however, not only the selectivity but also the yield was higher than on an unmodidied Pt/Al_2O_3 catalyst. This can be explained probably by the fact that the desorption of bismuth (in the form of BiH_3) is more pronounced during pretreatment at 450 °C than at 400 °C /13/. In this case the activity of the modified Bi–Pt/Al_2O_3 catalyst approached the activity of the unmodified Pt/Al_2O_3 catalyst. The lower activity towards hydrogenolysis and coke formation may be attributed to the residual amount of bismuth on the modified catalyst. Even in experiments carried out at 450 °C, the effect of oxygen regeneration resulted in a much higher conversion, higher yields of i-pentane as well as higher selectivities. The yield and selectivity appeared to be most substantial on the Bi–Pt/Al_2O_3 catalyst, while the extent of side reactions was highest on the Pd–Pt/Al_2O_3 catalyst.

Based on our experimental data, it may be concluded that modification of the Pt/Al_2O_3 catalyst by adsorption of bismuth and palladium followed by hydrogen treatment resulted in only minor changes in catalyst stability. The aging process on Pd–Pt/Al_2O_3 was found to be faster than on the unmodified Pt/Al_2O_3 catalyst. After pretreatment by an oxidation-reduction procedure, the change in catalytic

Table 1

Test of different catalysts in the isomerization of n-pentane in a continuous-flow reactor

	Parameters		Catalysts				
	t (°C)	w (g/g h)	τ(h)		Pt	Bi–Pt	Pd–Pt
1	400	0.5	1	C	0.51	0.36	0.45
				Y	0.39	0.30	0.31
				S	0.78	0.83	0.69
			5	C	0.41	0.29	0.34
				Y	0.40	0.28	0.29
				S	0.93	0.97	0.85
2[a]			1	C	0.46	0.44	0.62
				Y	0.36	0.35	0.39
				S	0.78	0.80	0.63
			5	C	0.42	0.39	0.56
				Y	0.41	0.37	0.45
				S	0.98	0.97	0.80
3[b]	450	1.0	1	C	0.38	0.38	
				Y	0.08	0.13	
				S	0.21	0.34	
4[a,b]			1	C	0.60	0.52	0.57
				Y	0.33	0.32	0.22
				S	0.55	0.62	0.39

Pt: Pt/Al_2O_3, Bi–Pt/Al_2O_3, Pd–Pt/Al_2O_3

C – conversion, Y – yield of i-pentane, S – selectivity (S=Y/C),

[a] After regeneration, [b] After 1 h reaction time

properties was more pronounced on the Pd–Pt/Al_2O_3 catalyst. This behavior of the Pd–Pt/Al_2O_3 catalyst can be attributed to a change in the composition and dispersity of the metal as a consequence of segregation in the platinum and palladium components /14/. This segregation phenomenon is probably due to oxygen treatment, which may also be involved in the change of the catalytic properties.

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