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Vapour phase dehydrogenation of cyclohexanol over alumina-supported Pt–Co bimetallic catalysts *

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$Pt/\gamma\text{-}Al_2O_3$, $Co/\gamma\text{-}Al_2O_3$ and $Pt\text{–}Co/\gamma\text{-}Al_2O_3$ with different Pt : Co atomic ratios have been prepared with a total metal content of 10 wt% and characterised by hydrogen chemisorption. The activities of the prereduced catalysts were studied for the reaction of cyclohexanol at 523 K and WHSV of 4.82 and 7.7 h^{-1}. The $Pt\text{–}Co/\gamma\text{-}Al_2O_3$ catalyst with 1 : 1 Pt : Co atomic ratio shows typical high metal dispersion and cyclohexanone selectivity.

Keywords: bimetallic, selectivity, active sites

1. Introduction

Industrially, bimetallic catalysts are of great significance for their high stability and activity [1], modified selectivity [2] and lifetime [3,4] in several reactions as in naphtha reforming over Pt–Re and Pt–Ir, in selective hydrogenation over Pd–Cu and Pd–Ag, in cyclization and hydrogenolysis over Pt–Sn [5], in CO hydrogenation for alcohols over Pt–Co [6,7], in hydrogenation skeletal rearrangement over Pt–Co, Pt–Ru and Ir–Co [8], in gasoline reforming and in the hydrogenation of phenol to cyclohexanone over Pt–Cr [4,9]. Catalytic transformation of cyclohexanol over unsupported Os, Co, Fe, Re and Ru mainly yields cyclohexanone; on the other hand, on Pt, Pd and Ni further dehydrogenation of cyclohexanone occurs to give mainly aromatics [10,11]. The mechanism of deactivation and formation of carbonaceous deposits and their influence on the activity of unsupported platinum and platinum bimetallics are subject of recent interest [12–15]. In this communication we report the selective dehydrogenation of cyclohexanol to cyclohexanone over bimetallic Pt–Co supported on $\gamma\text{-}Al_2O_3$ at typical conditions of reaction and composition of Pt–Co.

2. Experimental

A series of $Pt\text{–}Co/\gamma\text{-}Al_2O_3$ catalysts were prepared by co-impregnating Harshaw $\gamma\text{-}Al_2O_3$ support (BET surface area 205 $m^2\,g^{-1}$, pore volume 0.6 ml g^{-1} and particle size, 0.5 mm) with aqueous solution containing H_2PtCl_6 (Fluka) and cobalt nitrate (Fluka) so as to give 10 wt% of total metal content. The relative metal content of either Pt or Co varied from 0 to 100%. The ratios referred to in the text for bimetallic catalysts are atomic ratios of Pt : Co. The catalysts were air-dried at 393 K for 24 h and then calcined at 773 K for 5 h in air. These catalysts were characterised for their BET surface areas using N_2 adsorption at 77 K in an all-glass volumetric high-vacuum system. The same high-vacuum system was used to determine hydrogen chemisorption capacities of the catalysts at 298 K. Prior to a chemisorption experiment the catalyst (250 mg) was reduced at 673 K for 4 h in flowing hydrogen (30 ml min^{-1}) and then evacuated (10^{-6} Torr) for 1 h followed by cooling to the (ambient) temperature of chemisorption [13].

A fixed-bed micro-catalytic reactor was employed to carry out the cyclohexanol conversion reaction. Prior to the activity test the catalyst sample (500 mg) was reduced in H_2 flow (30 ml min^{-1}) for 5 h at 673 K followed by cooling to reaction temperature. The reactant cyclohexanol along with nitrogen as carrier gas (35 ml min^{-1}) was fed into the reactor using a micro-processor-controlled Secura (B. Bruan, Germany) syringe pump for pumping the reactant. The reaction was studied at 523 K at a WHSV of 4.82 h^{-1}. The reaction products were collected each hour and analysed by gas chromatography using 10% carbowax 20M on a chromosorb W column (2 m). The main products of the reaction are cyclohexanone, cyclohexane, cyclohexene, benzene and phenol. The conversion and product selectivities reported here are the steady-state values.

3. Results and discussion

The catalyst composition, BET surface areas, cyclohexanol conversion and product distribution of various catalysts are presented in table 1. The H_2 uptake, cyclohexanol conversion and cyclohexanone selectivity stud-

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Table 1
Cyclohexanol conversion and product selectivities of Pt/γ-Al_2O_3, Co/γ-Al_2O_3 and Pt–Co/γ-Al_2O_3 catalysts at reaction temperature of 523 K and WHSV of 4.82 h^{-1}

Catalyst	Catalyst composition (%)			BET surface area ($m^2\,g^{-1}$)	Cyclohexanol conv. (%)	Selectivity (%)				
	Pt	Co	γ-Al_2O_3			cyclohexane	cyclohexene	benzene	cyclohexanone	phenol
Al_2O_3	0	0	100	205	35.0	100.0				
PCA-1	10	0	90	155	80.0	28.4	trace	55.5	8.4	7.5
PCA-3	7	3	90	164	63.5	12.4	trace	2.0	79.0	6.5
PCA-5	5	5	90	134	62.4	3.0	1	trace	92.0	3.5
PCA-7	3	7	90	167	65.1	10.7	6	trace	80.0	3.0
PCA-10	0	10	90	150	60.5	–	87	–	13.0	–

ied over a series of γ-Al_2O_3-supported Pt–Co catalysts at 523 K and 4.82 h^{-1} WHSV are shown in figure 1. It is clear from the figure that at 100% Pt the cyclohexanol conversion is maximum and decreased with decreasing Pt content. However, a steady activity is observed on systems with 70 to 30% Pt. This steady activity slightly decreased when Pt content decreased further to 0% (100% Co). A typical selectivity pattern towards cyclohexanone is observed over this series. It is minimum at 100% Pt and 100% Co and touching a maximum of 92% at 1 : 1 ratio of Pt : Co. The H_2 uptake over these catalysts also follows the same trend as that of cyclohexanone selectivity. For a further understanding, the cyclohexanol reaction is studied for a period of 10 h at 523 K using 4.82 and 7.7 h^{-1} WHSV over 1 : 1 Pt–Co/γ-Al_2O_3 catalyst (figure 2).

At high residence time the initial activity is decreased at a faster rate and steady activity is obtained from the third hour of the reaction and steady selectivity from the fourth hour. With a decrease in residence time the initial activity is decreased at a slower rate and steady activity is reached at the sixth hour of the reaction and the steady selectivity to cyclohexanone in the seventh hour. Selective dehydrogenation of cyclohexanol to cyclohexanone over 1 : 1 Pt : Co may be attributed to the formation of a Pt–Co bimetallic system, which has been evidenced from TPR studies of these catalysts [16]. TPR profiles of these catalysts are shown in figure 3. Shifting of the low-temperature reduction peak on PCA-1 (100% Pt) from 435 K to 563 K on PCA-7 (30% Pt + 70% Co) and of the high-temperature reduction peak on PCA-10 (100% Co) from 655 K to 503 K on PCA-3 (70% Pt + 30% Co) and overlapping of these two (Pt and Co) peaks on PCA-5 (50% Pt + 50% Co) in the temperature region of 441–511 K with maximum H_2 consumption indicate the possible association of platinum with cobalt forming a bimetallic in 1 : 1 Pt–Co/γ-Al_2O_3 [6] with maximum metal dispersion. Addition of cobalt appears to modify the dehydrogenation functionality of the Pt/γ-Al_2O_3 to produce selectively cyclohexanone.

The results in table 1 demonstrate the variation of the product distribution of the monometallic and bime-

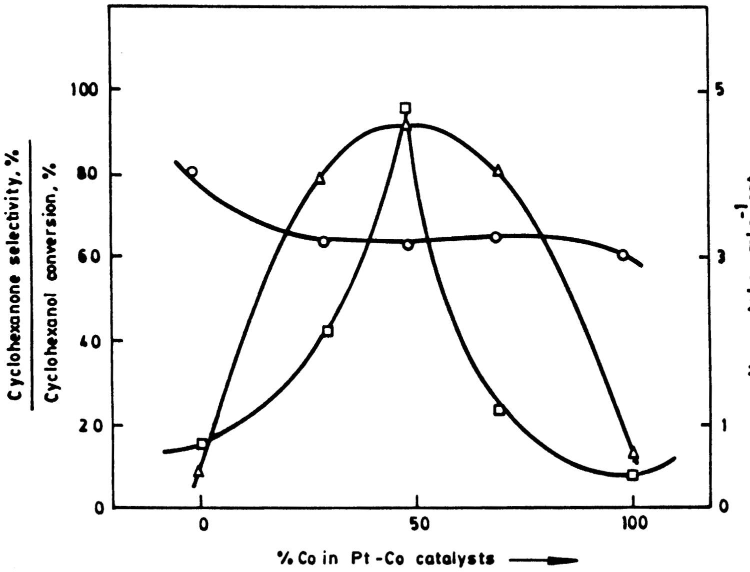

Figure 1. Cyclohexanol conversion, cyclohexanone selectivity and hydrogen uptake as a function of catalyst composition: WHSV, 4.82 h^{-1}, (○) cyclohexanol conversion, (△) cyclohexanone selectivity, (□) H_2 uptake.

tallic catalyst systems at different Pt : Co compositions in the cyclohexanol reaction at 523 K and 4.82 h^{-1}. On γ-Al_2O_3 alone cyclohexanol conversion was 35% with total selectivity towards cyclohexene. On Pt/Al_2O_3 the product distribution shows that cyclohexanol dehydrogenates not only to cyclohexanone but also to phenol. Further, significant quantities of benzene and cyclohexane are formed. The formation of benzene and cyclohexane may have occurred through the initial dehydration of cyclohexanol to cyclohexene on the acidic sites of the catalyst followed by dehydrogenation to benzene or hydrogenation to cyclohexane. If cyclohexene is the starting material, the conversion is 5% and the product selectivities are 65% for benzene and 35% for cyclohexane on Pt/γ-Al_2O_3. The product pattern is changed to 74% of cyclohexane and 26% benzene on cobalt-added catalysts. Benzene and cyclohexane may also be formed through hydrogenolytic splitting of phenol and cyclohexanol respectively. PCA-10 (Co/γ-Al_2O_3) effects cyclohexanol dehydration as the major reaction with minor dehydrogenation activity as it is difficult to reduce Co completely to its zero-valent state over this system because of the possible formation of cobalt surface phase [6]. Dehydration and deeper dehydrogenation activity decreased on PCA-3 (Pt : Co = 7 : 3), PCA-5 (Pt : Co = 5 : 5) and PCA-7 (Pt : Co = 3 : 7) showing typically cyclohexanone as the major product of the reaction (figure 1).

From figure 2 it is clear that the same level of steady-state activity and selectivity is attained for both the space velocities studied, the difference being the time required to reach the steady-state activity. During the first few hours of the reaction, the formation of aromatics is more and with time on stream the activity decreased and reached a steady-state value forming cyclohexanone as the major product of dehydrogenation. The steady activity of cyclohexanol transformation at 523 K shows not only the presence of typical sites but also indicates a unique higher dispersion on 1 : 1 Pt–Co/γ-Al_2O_3 compared to other compositions, as has been evident from H_2 chemisorption data. Such dispersed systems are also liable for less coking resulting in steady activity [17]. In order to ascertain whether there is coking in the initial hours of reaction, carbon analysis has been done (LECO gas analyser) on fresh PCA-5 and PCA-5 after 4 and 8 h of reaction. While the fresh catalyst does not contain any carbon, the samples after 4 and 8 h of reaction show 4.98 and 5.05% of carbon respectively. It appears that, initially, coke is depositing on the stronger acidic sites of the catalyst making them less effective for the dehydration reaction.

In our Pt–Co/γ-Al_2O_3 system it is shown that the H_2 uptake is maximum when Pt : Co atomic ratio is 1 : 1. At this composition the hydrogen chemisorption is almost five times more than on monometallic systems. The H_2 uptakes for Pt-rich and Co-rich systems lie in between, although the Pt-rich system shows a somewhat higher

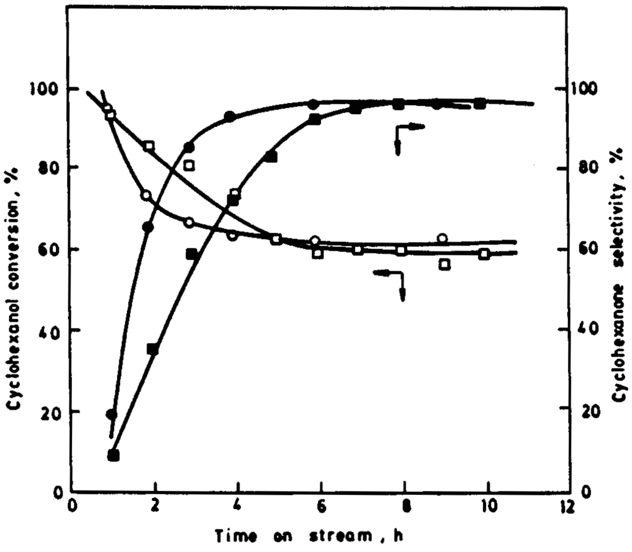

Figure 2. Cyclohexanol conversion and cyclohexanone selectivity as a function of time on stream over 1 : 1 Pt–Co/γ-Al_2O_3 catalyst: WHSV, 4.82 h^{-1} and 7.70 h^{-1}. (○) Conversion at WHSV, 4.82 h^{-1}; (□) conversion at WHSV, 7.70 h^{-1}; (●) selectivity of WHSV, 4.82 h^{-1}; (■) selectivity at WHSV, 7.70 h^{-1}.

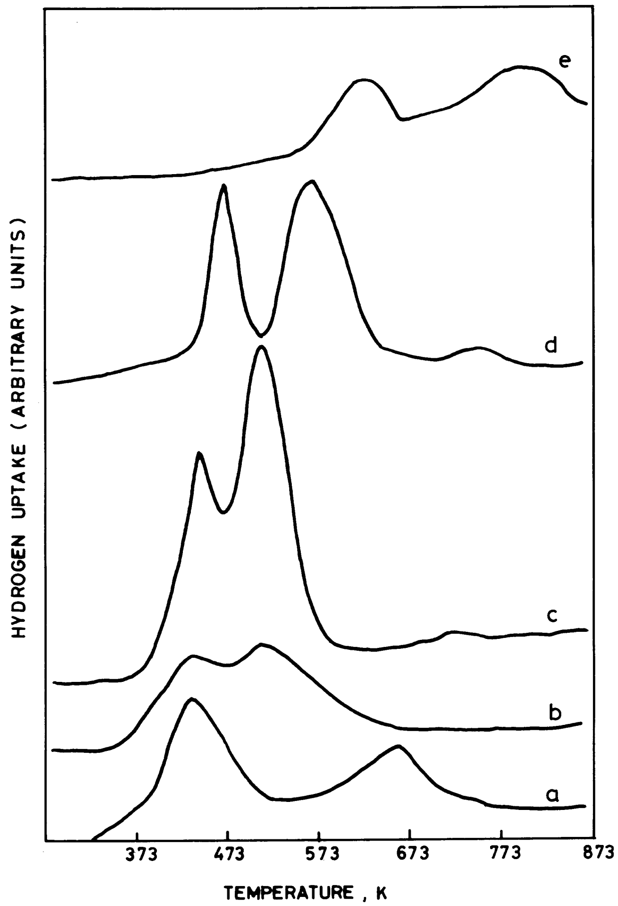

Figure 3. TPR profiles of Pt–Co/γ-Al_2O_3 catalysts. Pt : Co ratios of 0 : 100 (a), 30 : 70 (b), 70 : 30 (d) and 100 : 0 (e).

value than the Co-rich system. The remarkable differences in hydrogen uptake on Pt/γ-Al_2O_3 and Co/γ-Al_2O_3 on one hand and Pt–Co/γ-Al_2O_3 on the other hand may be due to the addition of Co, which increases the dispersion of the Pt–Co catalyst to a composition of 1 : 1 and then decreases thereafter because of the enrichment of Co on the surface which has a lower surface energy [18]. In X-ray diffraction patterns, the interference between the diffraction patterns of the metal and the metal and the support is observed, as was reported earlier [13]. It has been shown from TPR that the reduction temperature shifts to a lower value in the bimetallic Pt–Co/γ-Al_2O_3 catalysts compared to monometallic Co/γ-Al_2O_3 catalysts [5,6,19]. At 1 : 1 composition it appears that the platinum–cobalt interaction is optimum affecting the strength of bonding between reactant and products facilitating maximum cyclohexanone selectivity. Srinivas and Kanta Rao [9] have recently reported preferential selectivity to cyclohexanone on a Pt–Cr/C bimetallic system compared to that on Pt/C in the hydrogenation of phenol. They have further shown that a second metal (Cr, V, Zr) in addition to platinum on the carbon-supported bimetallic system has a profound effect on the product selectivity in the hydrogenation of phenol [20].

The higher level of selectivity to cyclohexanone may be additionally due to the neutralization of acidic sites of the alumina support due to initial coke formation. The original activity, selectivity and stability of the bimetallic Pt : Co at 1 : 1 composition are restored after air treatment of the used catalyst at 673 K followed by reduction at the same temperature.

4. Conclusions

Addition of cobalt to platinum or vice-versa (30–70%) generates sites for the selective dehydrogenation of cyclohexanol to cyclohexanone ($>$ 80% selectivity), which sites can be titrated by H_2 chemisorption. The bimetallic Pt–Co/γ-Al_2O_3 system with Pt : Co atomic ratio of 1 : 1 appears to be unique; on this catalyst the cyclohexanol selectively converted to cyclohexanone. Coke formation has perhaps an additional beneficial effect on these bimetallic catalyst systems in stabilizing the catalyst.

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