Probing palladium-cobalt/NaY catalysts by neopentane conversion

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Neopentane conversion in hydrogen was used as a catalytic probe for zeolite encaged PdCo particles. Activity and selectivity strongly depend on the pretreatment conditions. PdCo/NaY catalysts exhibit higher isomerization selectivity than Pd/NaY in conformity with previous results on SiO_2 supported Pd and PdCo. This is remarkable, because reduced Co/SiO_2 displays 100% selectivity for hydrogenolysis. The isomerization selectivity thus appears to be a useful measure for the extent of alloying between Pd and Co.

Keywords: PdCo/NaY; zeolite catalysts; bimetal catalysts; cobalt; palladium; neopentane conversion; catalytic isomerization of neopentane

1. Introduction

The location, ligancy, and reducibility of cobalt and palladium ions in zeolite NaY have been characterized by a variety of techniques, including UV-VIS diffuse reflectance spectroscopy, extended X-ray absorption fine structure (EXAFS), temperature-programmed reduction (TPR) and temperature-programmed oxidation (TPO) [1,2]. It was found that the reducibility of cobalt can be markedly enhanced by the presence of palladium, but the extent of this enhancement depends both on the type of cobalt precursor ($Co(H_2O)_6^{2+}$ or $Co(NH_3)_6^{3+}$) and on the temperature of calcination prior to reduction. These conditions control the relative locations of the palladium and cobalt ions. A close proximity between Pd and Co ions enhances the reducibility of the latter and is expected to favor the formation of bimetallic PdCo clusters.

Pd/NaY catalysts prepared by ion exchange are active catalysts for neopentane conversion. The activity depends on the concentration of protons in the zeolite, suggesting that electron-deficient metal-proton adducts are more active

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than neutral Pd particles [3,4]. With SiO_2 supported mono- and bimetallic Pd and Co catalysts, it was found that alloying of Co with Pd leads to a marked increase in isomerization selectivity above that of the monometallics [5].

In the present study NaY supported PdCo catalysts are probed with the same reaction in order to determine how activity, selectivity, and stability of such catalysts compare with their SiO_2 supported counterparts.

2. Experimental

a. CATALYSTS

Four catalysts were tested: (1) 5 wt% Pd/NaY, (2) 2.8 wt% Co/NaY, (3) (5.38 wt% Pd + 2.98 wt% Co)/NaY, and (4) (1.83 wt% Pd + 3.04 wt% Co)/NaY. These samples will be referred to as: (1) PdNaY; (2) CoNaY; (3) Pd9Co9NaY; (4) Pd3Co9NaY, respectively, where the numbers after the chemical symbols indicate the number of metal ions per unit cell. The samples were prepared from hexaaquocobalt (II) nitrate and tetraamminepalladium nitrate (both Alfa Chemicals). After ion exchange the samples were calcined at T_C in pure O_2 at a flow rate of 400 ml/min. Three calcination temperatures were applied: 250, 300 and 500°C. After calcination the samples were cooled in helium, reduced while the temperature increased at a 8°C/min to T_R, and then held at T_R for 20 min. After reaction the samples were reduced again up to 430°C and held at 430°C for 20 min before repeating the neopentane reaction.

b. KINETIC STUDIES

The reaction of neopentane with hydrogen was carried out at atmospheric pressure in a flow system with greaseless, glass stopcocks. A flow of neopentane premixed with hydrogen (1 : 9, Matheson) was diluted with helium (UHP, Linde) to obtain a neopentane partial pressure of 6 Torr. The overall flow rate was 76 ml/min. The reaction mixture was purified by passing it through MnO/SiO_2 and molecular sieve 5A traps. The latter trap efficiently removed any n-butane impurity from the reactant stream.

The reaction mixture flowed over the 0.3 g catalyst samples deposited in a U-tube with fritted disc; a thermocouple well was placed inside the catalyst bed. The effluent gas was analyzed by gas chromatography (HP 5790 with FID, 50 m cross-linked methyl silicone capillary column). Kinetic runs began at the lowest reaction temperature (usually ca. 220–230°C); when the conversion stabilized, the reactor temperature was increased by 10°C increments ("upwards"). After achieving conversions as high as 5–10% the temperature was lowered while additional data were collected ("downwards"). A typical kinetic run consisted of 10–12 experimental points.

Because CoNaY was found to be totally inactive, the catalytic activities of PdCo/NaY samples were calculated as rates per Pd atom per second. Based on EXAFS results suggesting a 100% metal dispersion, these rates are equal to the turnover frequencies (TOF). Selectivities were calculated as the carbon percentage of neopentane converted to a designated product (methane, ethane, propane, i- and n-butane, i- and n-pentane).

3. Results and discussion

a. ACTIVITY

CoNaY samples tested in four kinetic runs after various pretreatments ($T_C = 250°C$, $T_R = 350°C$ and $T_R = 430°C$; $T_C = 500°C$, $T_R = 350°C$, and $T_R = 430°C$) failed to display any activity at temperatures up to 340–350°C. This is not surprising; previously it was found that no reduction of Co/NaY takes place below 750°C [1]. PdNaY, Pd9Co9NaY and Pd3Co9NaY were active catalysts; rate data were collected between 220 and 290°C. Independent runs with three PdNaY and two Pd9Co9NaY samples agreed within ±15%.

Turnover frequencies, selectivities, and activation energies are presented in tables 1 and 2. Most products are primary products, but some n-butane formed at higher temperature resulted from secondary reactions such as hydrogenolysis of isopentane.

Fig. 1 shows Arrhenius plots for PdNaY, Pd9Co9NaY and Pd3Co9NaY after various pretreatments. For the majority of samples the experimental points collected "upwards" (open symbols) and "downwards" (filled symbols) produced good straight lines. Exceptions were: PdNaY, after calcination at 500°C and reduction at 350°C (not shown), and two bimetallic samples reduced at 430°C (fig. 1d).

The activation energies depend more on the pretreatment than on the Pd/Co ratio (tables 1 and 2). They are higher (ca. 65 kcal/mole) for samples calcined at 250°C than for $T_C = 300$ or 500°C (45–54 kcal/mole). The difference between $T_C = 250°C$ and $T_C = 300°C$ is more critical than the difference between $T_C = 300°C$ and $T_C = 500°C$, respectively.

In previous work it has been established that the temperature interval of 250°C and 300°C is critical for the location and the ligancy of Pd ions [6]. At $T_C = 250°C$ deammination of $Pd(NH_3)_4^{2+}$ ion is incomplete, the ion remains in the supercage and retains two ammine ligands. At $T_C = 300°C$ deammination is virtually complete, and the Pd^{2+} ions are located in sodalite cages and hexagonal prisms. For samples calcined at 250°C the protons formed during reduction are neutralized by the liberated NH_3 molecules; whereas for samples calcined at 300°C the protons are available as Brønsted sites and for the formation of adducts $[Pd_n - H_x]^{x+}$. Therefore, the data for the monometallic Pd/NaY

Table 1
Neopentane conversion over PdCoNaY after reduction at 350°C: product distributions, reaction rates and activation energies.

Catalyst	Calcination temp. (°C)	Reaction temp. (°C)	Product distribution (%)							Reaction rate [a]	Activation energy (kcal/mole)
			Me	Et	Pr	iB	nB	iP	nP		
PdNaY	250	250	19.3	–	–	51.8	4.9	23.9	–	$2.70 * 10^{-5}$	67.5 ± 3.1
		260.5	20.9	–	–	52.0	9.5	13.3	–	$7.85 * 10^{-5}$	
	300	230	17.5	–	–	57.7	5.9	18.9	–	$5.57 * 10^{-5}$	47.4 ± 1.1
		244	21.1	–	3.5	61.7	6.0	7.6	–	$2.01 * 10^{-4}$	
	500	230	20.7	–	–	53.2	11.2	14.9	–	$3.23 * 10^{-5}$	see [b]
		247	22.5	–	8.2	53.5	10.4	5.5	–	$8.42 * 10^{-5}$	
Pd9Co9NaY	250	237	19.3	–	–	67.0	–	13.7	–	$2.99 * 10^{-5}$	63.6 ± 3.6
		251	21.1	–	2.8	65.3	4.1	6.7	–	$1.23 * 10^{-4}$	
	300	228.5	13.3	–	–	35.0	–	51.7	–	$1.90 * 10^{-5}$	48.1 ± 0.6
		240.5	14.9	–	–	46.5	5.3	33.3	–	$6.45 * 10^{-5}$	
	500	229	17.3	–	–	46.9	–	35.7	–	$3.02 * 10^{-5}$	48.4 ± 1.1
		245	19.1	–	1.9	57.0	6.8	15.3	–	$1.29 * 10^{-4}$	
Pd3Co9NaY	250	275	14.7	–	–	35.3	8.9	41.1	–	$8.73 * 10^{-5}$	67.9 ± 0.8
		291	19.5	–	5.1	42.8	12.9	19.6	–	$4.67 * 10^{-4}$	
	300	269.5	17.4	–	–	47.5	4.9	30.2	–	$8.85 * 10^{-5}$	54.0 ± 2.8
		280	19.0	–	4.2	49.0	7.6	20.2	–	$2.41 * 10^{-4}$	
	500	254	20.0	–	–	52.4	6.8	20.9	–	$8.15 * 10^{-5}$	48.9 ± 1.5
		268	22.2	–	5.9	59.9	5.4	6.5	–	$2.58 * 10^{-4}$	

[a] Reaction rate expressed in moles of neopentane converted per mole of palladium per second.
[b] Sample experienced some deactivation in time-on-stream.

catalyst confirm our previous conclusion that the activation energy for neopentane conversion is lower for electron-deficient $[Pd_n - H_x]^{x+}$ adducts than for Pd_n clusters.

For the bimetal catalysts additional phenomena must be considered. First, reduction of Co produces additional protons; their concentration thus depends on the Pd^0/Co^0 ratio and the temperature at which the Pd precursor was deamminated. Further, the reducibility of Co in the presence of Pd depends on the calcination temperature, as mentioned above; Pd ions in the supercages are of little help to reduce Co ions, but after jumping into small cages at $T_C = 300°C$ their proximity to Co leads to a marked reduction of the latter element. Consequently, samples calcined at $T_C = 300°C$ contain more Co^0 after reduction than those which had been calcined at $T_C = 250°C$. Therefore, the higher activity of samples calcined at $T_C = 300°C$, over those calcined at $T_C = 250°C$ might be due to the higher concentration of Co^0 in the bimetal catalysts.

Both phenomena, proton adduct and alloy formation, could be responsible for the lower activation energy of samples calcined at $T_C > 250°C$. There is,

Table 2
Neopentane conversion over PdCoNaY after reduction at 430°C: product distributions, reaction rates and activation energies.

Catalyst	Calcination temp., °C	Reaction temp., °C	Product distribution, %							Reaction rate [a]	Activation energy, (kcal/mole)
			Me	Et	Pr	iB	nB	iP	nP		
PdNaY	250	240.5	22.4	–	–	54.0	–	23.6	–	$1.57*10^{-5}$	62.7 ± 1.9
		261	21.1	–	5.7	54.6	8.4	10.2	–	$1.15*10^{-4}$	
	300	228.5	14.3	–	–	41.6	4.9	39.2	–	$3.98*10^{-5}$	47.8 ± 3.8
		244	18.7	–	2.7	51.0	9.7	17.8	–	$1.39*10^{-4}$	
	500	241	14.2	–	–	40.4	–	45.4	–	$2.97*10^{-5}$	48.0 ± 2.5
		260	18.4	–	3.2	50.1	9.9	18.4	–	$1.35*10^{-4}$	
Pd9CoNaY	250	255	16.0	–	–	45.4	–	38.6	–	$4.22*10^{-5}$	50.9 ± 1.0
		270.5	17.8	–	2.1	49.8	6.9	23.4	–	$1.77*10^{-4}$	
	300	237.5	8.1	–	–	22.4	–	69.5	–	$3.70*10^{-5}$	see [b]
		255	11.0	–	2.2	31.7	7.0	45.0	2.1	$9.66*10^{-5}$	
	500	242.5	7.3	–	–	18.4	–	74.3	–	$4.78*10^{-5}$	see [b]
		258.5	9.6	–	2.5	23.1	4.7	58.1	1.9	$1.00*10^{-4}$	
Pd3Co9NaY	250	271	–	–	–	28.9	–	71.1	–	$3.68*10^{-5}$	71.0 ± 2.5
		281	10.6	–	–	27.0	5.1	57.4	–	$1.19*10^{-4}$	
	300	269.5	10.1	–	–	21.8	–	68.1	–	$7.43*10^{-5}$	see [b]
		287.5	12.6	–	2.0	31.8	10.2	41.8	1.6	$2.68*10^{-4}$	
	500	259	7.2	–	–	15.2	–	77.6	–	$7.66*10^{-5}$	45.1 ± 2.7
		269	5.0	–	–	17.4	6.5	71.1	–	$1.40*10^{-4}$	

[a] Reaction rate expressed in moles of neopentane converted per mole of palladium per second.
[b] Sample experienced some deactivation in time-on-stream.

however, independent evidence suggesting that alloying small amounts of Co with Pd will cause an increase in activity. Consider the activity sequences displayed in fig. 1. After calcination at 250°C and reduction at 350°C when certainly only a very small fraction of the cobalt in the bimetal catalyst is reduced, the highest activity is found for Pd9Co9NaY. Under all other conditions, higher T_C and or higher T_R, all bimetal catalysts display a lower activity than Pd. Moreover, the activity further decreases with increasing Co/Pd ratio. These data suggest that small additions of Co to Pd enhance the catalytic activity, which passes through a maximum at larger ratios of Co^0/Pd^0.

b. SELECTIVITY

Selectivity data are given in fig. 2. The isomerization selectivity for PdNaY depends to some extent on the pretreatment, varying between 20 and 40%. More importantly, alloying of Co with Pd clearly enhances the selectivity for

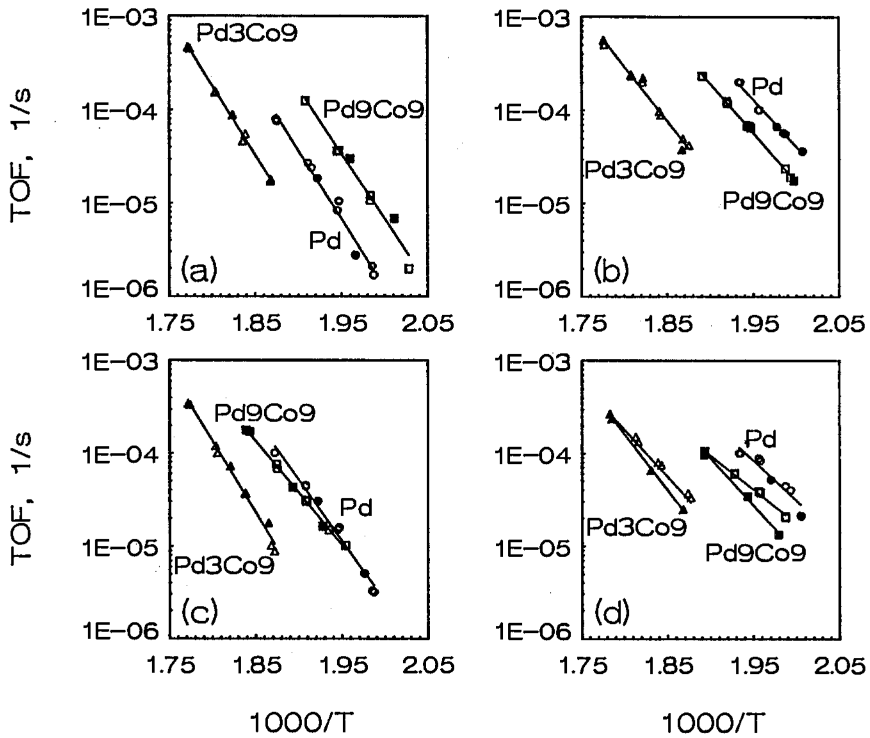

Fig. 1. Examples of Arrhenius plots for the reaction of neopentane with hydrogen on PdNaY (Pd), Pd9Co9NaY (Pd9Co9) and Pd3Co9NaY (Pd3Co9) after various calcination/reduction pretreatments: (a) calc. 250°C/red. 350°C, (b) calc. 300°C/red. 350°C, (c) calc. 250°C/red. 430°C, (d) calc. 300°C/red. 430°C, where open/filled points represent kinetic data collected by increasing/lowering the reaction temperature, respectively.

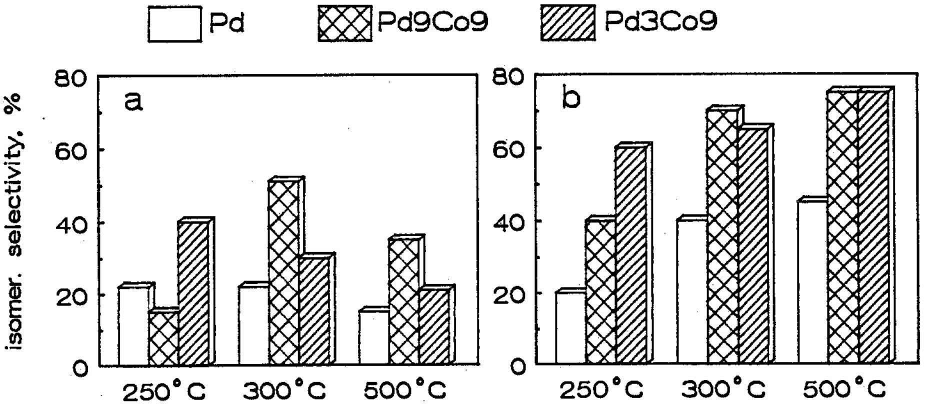

Fig. 2. Selectivity for neopentane isomerization (conversion = 1%) on PdNaY and PdCoNaY catalysts after reduction at 350 (a) and 430°C (b). The effect of calcination temperature (250, 300, and 500°C).

Table 3
Estimated Co^0/Pd^0 ratios for Pd9Co9NaY (Pd3Co9NaY)

$T_R \backslash T_C$ (°C)	250	300	500
350	0.03	0.46	0.45 (0.32)
430	0.12	0.63	0.60 (0.48)

isomerization and lowers the selectivity for hydrogenolysis. This is similar to the selectivity pattern found previously for SiO_2 supported Pd, Co and Pd-Co catalysts. The result is particularly remarkable when recalling that reduced Co/SiO_2 exhibits 100% selectivity for hydrogenolysis, viz., zero selectivity for isomerization [5].

Fig. 2 also shows that more severe calcination/reduction conditions result in higher isomerization selectivities. Selectivities up to 70–75% have been achieved for Pd9Co9NaY and Pd3Co9NaY after calcination at $T_C = 300°$ or 500°C and reduction at 430°C. Previous TPR data [1] were used to estimate the Co^0/Pd^0 ratios for the Pd9Co9NaY samples used in the present study. The results are shown in table 3. For Pd3Co9NaY, less complete TPR data are available and the results are given in brackets. On the basis of these estimates a comparison of the isomerization selectivities of the present zeolite supported catalysts with those of the SiO_2 supported samples can be attempted. Fig. 3 shows that within experimental error the data for the NaY supported samples, reduced at 430°C, and those for the SiO_2 supported catalysts are located on the same curve. Lower selectivities are, however, found for the zeolite supported samples after reduc-

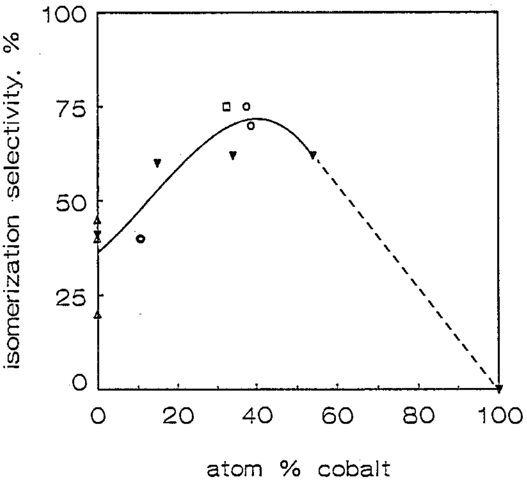

Fig. 3. Selectivity for neopentane isomerization over PdCoNaY and 10 wt% $PdCo/SiO_2$. The kinetic data for $PdCo/SiO_2$ taken from ref. [5]; the surface composition of silica-supported Pd-Co alloys was calculated from unpublished data [9]. PdNaY–open triangles, Pd9Co9NaY–circles, Pd3Co9NaY–square, 10wt% $PdCo/SiO_2$–filled triangles.

tion at 350°C, suggesting that alloying is less complete in NaY at 350°C than 430°C.

c. STABILITY AGAINST DEACTIVATION

Another indication for more extensive alloying of Co with Pd after high temperature calcination/ reduction is provided by the rather distinct deactivation of PdCoNaY samples with time-on-stream. Deactivation is faster for samples calcined at 500°C and reduced at 430°C than those reduced at 350°C. As Co catalysts are known to give extensive self-poisoning in hydrocarbon conversion reactions [7,8], we tentatively attribute the higher deactivation rate of the catalysts with high Co^0/Pd^0 ratio to the deposition of carbonaceous residues.

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