

Neopentane Reactions over Bimetallic Pt–Sn/Al₂O₃ and Pt–Au/SiO₂ Catalysts

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The reaction of 2,2-dimethylpropane (neopentane) with hydrogen was studied over two series of supported bimetallic catalysts containing platinum as the primary group VIII metal and either gold or tin as the second metallic component. In both catalyst series the platinum nominal loading was maintained constant at 1 wt%. The loading of the second metal component was varied. An effort has been made to better understand the reactivity trends in these catalysts, by bringing the neopentane reactivity data into context with previously obtained *n*-hexane reaction results and extensive catalyst characterization data. Small amounts of tin (1.0 Pt–0.1 Sn/Al₂O₃) caused the neopentane isomerization selectivity to drop in comparison to monometallic 1.0 Pt/Al₂O₃. However, further addition of tin up to 1.0 wt% caused the neopentane isomerization selectivity to increase above that of the monometallic 1.0 Pt/Al₂O₃ sample. On adding excess tin (5.0 wt%) the activity of the catalyst became prohibitively low. Hence, there seemed to be an optimum loading of tin giving desirable selectivity characteristics at reasonable activity levels. The differences in isomerization selectivity in the case of the Pt–Au/SiO₂ catalysts were not as significant as those observed for the Pt–Sn/Al₂O₃ catalysts. The trends in catalytic behavior were consistent with previously measured *n*-hexane reaction trends and could be interpreted on the basis of microstructural differences between the bimetallic catalysts. The effect of gold appeared to be mainly a geometric one, disrupting larger Pt ensembles. On the other hand, the role of tin appeared to go beyond a simple geometric effect. © 1991 Academic Press, Inc.

INTRODUCTION

Supported bimetallic catalysts consisting of platinum as the primary metal and a second metal like rhenium or tin have found extensive use in reforming reactions. Compared to monometallic Pt/Al₂O₃, bimetallic catalysts show better activity maintenance characteristics and higher selectivity for cyclization and isomerization products as opposed to hydrocracking products. This increases the octane number of the petroleum product (1). Gold is not used in industrial reforming catalysts but is of interest from a fundamental research point of view.

Another interesting property of these second metal additives is the extent of miscibility of Au and Sn with Pt in the bulk state. Au is only partially miscible with Pt in the bulk state and there is a distinct phase separation in the Pt–Au phase diagram (2). Sn, on the other hand, is miscible with Pt to a

greater extent in the bulk state and forms a whole range of solid solutions (3). Furthermore, Sn and the alumina support can form a so-called “Sn-aluminate” complex (4), but no such interaction between Au and the silica support has been noted. It is interesting to explore how these different bulk solubilities carry over into the realm of highly dispersed supported metallic particles. Pt/Al₂O₃ catalysts are said to be bifunctional in nature in hydrocarbon conversion reactions with Pt primarily being the seat of dehydrogenation and hydrogenation and Al₂O₃ being the seat of isomerization (5). The addition of Sn could have an effect on both Pt and the Al₂O₃ support and this could effect the activity and selectivity of the Pt–Sn/Al₂O₃ catalyst.

In the present study, 2,2-dimethylpropane (neopentane) was used as the probe hydrocarbon molecule. Neopentane is an attractive probe molecule because it is a very

stable hydrocarbon molecule, and there is no significant deactivation during neopentane reactions at moderate reaction temperatures, even on catalysts possessing strong acid sites. Neopentane does not readily form olefins or secondary or tertiary carbenium ions. Consequently, coke formation is suppressed and this preserves the catalyst in a state close to its original state at the start of the reaction (6, 7). Hence one can more easily correlate the reactivity of these catalysts with their surface composition and structure, allowing one to probe the effect of the second metal addition without significant contributions from coking (8). Another advantage of using neopentane as a reactant is that Pt is the primary seat of the hydrocarbon reactions (9). Hence the bifunctional nature of the catalyst is not evident when using this hydrocarbon molecule and one can better study the effect of the catalytic reactivity as a function of the Pt particle size.

Boudart *et al.* (10, 11) studied the reactions of neopentane on Pt catalysts. They found that the reactions of neopentane progressed via two parallel reactions. One was an isomerization reaction to give isopentane and the other was a hydrogenolysis reaction to give isobutane and methane. The reactions of neopentane on platinum were found to be "structure-sensitive" and the isomerization reactions occurred on the metal sites and not on the support. The nature of the support and the pretreatment protocol influenced the specific activity for the hydrogenolysis reactions to a much greater extent than for the isomerization.

On the basis of previous work (10-12), Foger and Anderson (9) proposed the existence of two parallel reaction pathways for neopentane reactions on Pt. Each pathway was proposed to have a different activation energy. The Pt particle size played a significant role in determining the relative amounts of neopentane reacting through each reaction pathway. Pathway 1 favoring neopentane isomerization reactions was said to involve one or both of the adsorbed

intermediates (9). These intermediates need an ensemble of more than one Pt atom. Pathway 2, which tends to steer the reaction toward a larger cracking selectivity, was said to occur more commonly on highly dispersed Pt particles. As the particle size increased, the amount of neopentane reacting via the pathway 2 tended to decrease. Foger and Anderson (9) proposed a model for pathway 2 in which only one surface Pt atom was involved and the reactions between hydrogen and the π -adsorbed intermediate would lead to cracking products, provided there were sufficient amounts of adsorbed hydrogen on the catalytic surface to react with the intermediate.

The above-mentioned interesting characteristics of the reactions of neopentane over supported Pt catalysts prompted us to use neopentane as the probe hydrocarbon molecule in our study of the reactivity behavior of the Pt-Sn/Al₂O₃ and the Pt-Au/SiO₂ catalytic systems. Our aim was to study the effect of the second metal on the reactivity of these catalysts.

EXPERIMENTAL

Two series of bimetallic catalysts containing Pt as the primary metallic component were studied. One series was the Pt-Sn/Al₂O₃ series in which the nominal Pt loading was kept constant at 1 wt% and the nominal Sn loading was increased from 0 to 5 wt%. The other series was Pt-Au/SiO₂ series where the nominal Pt loading was again kept constant at 1 wt% and the nominal Au loading was increased from 0 to 0.7 wt%. Catalysts containing only supported Sn and Au and the blank supports were also tested for any significant catalytic activity. Tables 1 and 2 give an overview of the catalysts investigated.

The details of catalyst preparation and characterization have been published previously (13, 14). In case of the Pt-Sn/Al₂O₃ catalytic series an additional catalyst, 1.0 Pt-0.5 Sn/Al₂O₃ (LC), was prepared using non-chlorine-containing precursors to compare its catalytic behavior with a conven-

TABLE 1

Catalyst Composition (Pt-Sn/Al₂O₃ Series)

Catalyst	Metal (wt%)	Sn (at.%)
1.0 Pt/Al ₂ O ₃	0.99	0
1.0 Pt-0.1 Sn/Al ₂ O ₃	1.10	19
1.0 Pt-0.5 Sn/Al ₂ O ₃	1.53	47
1.0 Pt-1.0 Sn/Al ₂ O ₃	1.88	65
1.0 Pt-5.0 Sn/Al ₂ O ₃	4.19	85
2.0 Sn/Al ₂ O ₃	1.90	100
1.0 Pt-0.5 Sn/Al ₂ O ₃ (LC)	1.50	51

tionally prepared 1.0 Pt-0.5 Sn/Al₂O₃ catalyst. The gases used in the neopentane reaction runs were: 2,2,-dimethylpropane (99% purity with *n*-butane as major impurity, Wiley Organics) and hydrogen (UHP grade, Air Products). The latter gas was purified by being passed through a Matheson palladium hydrogen purifier. In some cases, helium (high purity grade, Air Products), purified by being passed through a Matheson gas purifier, was used as a diluent.

The reaction was carried out in a Pyrex glass U-tube reactor. The catalyst powder was placed on top of a plug of Pyrex glass wool. A glass-sheathed thermocouple was placed at the center of the catalyst bed to measure the reaction temperature within ± 1 K. The reaction mixture was passed through the catalyst bed and the components in the product stream including the unreacted neopentane were identified by passing the mixture through a chromatographic column and then into the flame ionization detector of an HP 5890A gas chromatograph. The chromatographic column used in our study was obtained from Alltech Associates, Inc. The support in the column was Chrom P-AW-DMCS and squalane was the stationary phase. The column had a 0.125-in. o.d., 0.085-in. i.d., was 3-m long, and was made of stainless steel. It was operated at 303 K. The GC carrier gas used was He with a flow rate of 15 cc/min. The detector was operated at 393 K. The GC peaks were plotted and integrated using an HP 3396A integrator. Response factors were

obtained for the various hydrocarbon components using Scotty calibration mixtures.

The experimental protocol for the Pt-Sn/Al₂O₃ catalyst series consisted of weighing out 0.2 g of the calcined sample, inserting the sample into the glass U-tube, and reducing it in flowing hydrogen (15 SCCM/min) for 5 h at 673 K before cooling down to the reaction temperature in flowing hydrogen. The reaction mixture consisted of hydrogen (20 SCCM/min), and neopentane (1 SCCM/min). The hydrogen to neopentane molar ratio was 20/1 so as to prevent the poisoning of the catalytic surface by carbon deposits (15). The total gas flow rate was 21 SCCM/min. A data point was obtained after flowing the reactant mixture through the catalytic bed for 5 min. Then the neopentane flow was cut off, and the hydrogen stream was kept on as the sample was heated to a higher temperature, at which point we were ready to obtain the next data point. The total pressure in the reactor was close to 1 atm (1 atm = 1.013×10^5 Pa) during the reduction process and also during the reaction runs. The conversions of neopentane varied from ~ 0.5 to $\sim 10\%$ to maintain differential reactor conditions (16). To determine the amount of hydrocarbon impurities in the reactant stream, the reaction mixture was sent through a reactor bypass directly into the GC.

The same experimental protocol was used for the Pt-Au/SiO₂ catalysts to facilitate the comparison with the Pt-Sn/Al₂O₃ catalysts. In previous work, Foger and Anderson (9) studied the neopentane and hydrogen reaction over a 0.9 Pt/Aerosil SiO₂ catalyst hav-

TABLE 2

Catalyst Composition (Pt-Au/SiO₂ Series)

Catalyst	Metal (wt%)	Au (at.%)
1.0 Pt/SiO ₂	1.00	0
1.0 Pt-0.3 Au/SiO ₂	1.39	17
1.0 Pt-0.7 Au/SiO ₂	1.58	30
2.0 Au/SiO ₂	1.25	100

ing an average Pt particle size of 4.0 nm. The reactions were carried out in the temperature range 573–577 K. Their total neopentane rate equation was expressed as:

$$\text{Rate} \propto P_{\text{HC}}^x P_{\text{H}_2}^y$$

The exponents x and y in the rate equation were dependent on the partial pressures of neopentane and hydrogen, although the total pressure of the reaction mixture was 1 atm. The following values for x and y were found:

$$x = 0.7, \quad y = -0.9$$

$$\text{for } P_{\text{H}_2}, 60\text{--}100 \text{ kPa}; \quad P_{\text{HC}}, 1.3\text{--}12 \text{ kPa}$$

$$x = 0.04, \quad y = 0.3$$

$$\text{for } P_{\text{H}_2}, 20\text{--}50 \text{ kPa}; \quad P_{\text{HC}}, 1.8\text{--}6 \text{ kPa}.$$

The exponents x and y themselves consist of the sum of two other parameters as the total neopentane reaction could be broken up into two reactions, namely, isomerization and cracking. Foger and Anderson (9) came up with two other exponents n and m that could be substituted for x and y in the main rate expression so as to determine the individual rates for the isomerization and cracking reactions. The values of n and m were

$$\text{isomerization, } n \sim (x + 0.1),$$

$$m \sim (y - 0.1)$$

$$\text{cracking, } n \sim (x - 0.1),$$

$$m \sim (y + 0.1).$$

In a follow-up study, Foger and Anderson (15) conducted neopentane reactions over Pt–Au/SiO₂ bimetallic catalysts. However, in this case they restricted the study to the high-partial-pressure regime of hydrogen. Hence we decided to extend our experiments on Pt–Au/SiO₂ bimetallic catalysts into the as-yet unexplored low-pressure regime. These experiments required a slightly different experimental protocol, namely diluting the total gas stream with helium so as to lower the partial pressures of hydrogen and neopentane in the stream while keeping the hydrogen to neopentane molar ratio constant at 20/1. This modified experimental

protocol for the Pt–Au/SiO₂ catalyst series consisted of loading 75 mg of an air-dried sample into the glass U-tube reactor. The sample was then heated to 673 K in flowing hydrogen (15 SCCM/min) and reduced at that temperature for 14 h. Then the sample was cooled to the reaction temperature in flowing hydrogen. Before the commencement of the reaction runs the hydrogen flow was decreased to 6.8 SCCM/min. Then helium gas at a flow rate of 22.8 SCCM/min was turned on. Finally, the neopentane stream was added at a flow rate of 0.34 SCCM/min. The total gas flow rate was 30 SCCM/min and the hydrogen to neopentane molar ratio was 20/1. The reaction mixture was allowed to flow through the catalyst bed for 6 min before a reaction data point was obtained. Then the helium and hydrocarbon flows were cut off, the hydrogen flowrate was increased to 15 SCCM/min, and the catalyst sample was heated to a higher temperature so as to prepare for the next data point. The conversions of neopentane in case of the reaction runs over the Pt–Au/SiO₂ catalysts for this experimental protocol varied from <0.5% to ~26%, in order to examine the selectivity toward isomerization and hydrogenolysis for the different catalysts in this series, over a wide range of conversions, and to study subtle differences in reactivity behavior of these catalysts as a function of increasing Au content.

The total conversion (X), the rate of the reaction (R), the selectivity for isomerization (S_I), and the selectivity for cracking (S_{Cr}) were calculated using the method recommended by Ponc and Sachtler (17). A carbon balance was performed over the overall reaction of neopentane and then the overall conversion (X) was determined. The expression for X was

$$X = \frac{\left(\sum_{i=1}^n \sum_{j,j \neq k} i y_i^{(j)} \right)}{\left(\left(\sum_{i=1}^n \sum_{j,j \neq k} i y_i^{(j)} \right) + n y_n^{(k)} \right)}$$

Summation over j was performed over all the compounds that were detected, with y_i

representing the mole fraction of a hydrocarbon with i carbon atoms. The subscript (k) denotes the reactant hydrocarbon in the feed (neopentane). The values of the mole fractions of the components were obtained from their integrated GC peak areas and their GC response factors.

The selectivity for isomerization (S_I) is denoted by

$$S_I = \frac{\left(5 \sum_{j,j \neq k} y_5^{(j)}\right)}{\left(\sum_{j,j \neq k} \sum_{i=1}^n i y_i^{(j)}\right)}$$

The selectivity for cracking S_{Cr} is equal to

$$S_{Cr} = 1 - S_I$$

because the total selectivity must be equal to unity. The overall rate of the reaction (R) in units of $(\text{molec s}^{-1} \text{ g} \cdot \text{catalyst}^{-1})$ is defined as

$$R = (nXN)/W,$$

where n , number of mol/s of neopentane flowing; X , total conversion of neopentane; N , Avogadro's number; and W , catalyst weight in grams.

The products in the reaction of neopentane were: methane, ethane, propane, isobutane, n -butane, isopentane, and n -pentane. Out of these, isopentane and n -pentane constituted the isomerization products. These products had the same number of carbon atoms as the reactant molecule (neopentane) and were produced as a result of nondestructive hydrocarbon reactions. Methane, ethane, propane, isobutane, and normal butane had a lower number of carbon atoms than the reactant neopentane molecule. These components were cracking or hydrogenolysis products and were produced as a result of destructive hydrocarbon reactions.

RESULTS AND DISCUSSION

(a) Pt-Sn/Al₂O₃ Catalysts

The monometallic 2.0 Sn/Al₂O₃ sample and the blank Al₂O₃ support did not show

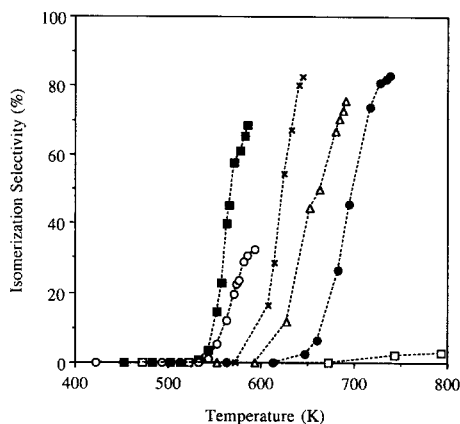


FIG. 1. Neopentane isomerization selectivity versus reaction temperature for catalysts of the Pt-Sn/Al₂O₃ series. (■) 1.0 Pt/Al₂O₃; (○) 1.0 Pt-0.1 Sn/Al₂O₃; (△) 1.0 Pt-0.5 Sn/Al₂O₃; (●) 1.0 Pt-1.0 Sn/Al₂O₃; (□) 1.0 Pt-5.0 Sn/Al₂O₃; and (×) 1.0 Pt-0.5 Sn/Al₂O₃ (LC).

measurable activity. On the monometallic Pt and the bimetallic Pt-Sn catalysts, the conversions of neopentane were confined to a range of ~0.3% to 10%. Figure 1 shows how the isomerization selectivity changed as a function of reaction temperature, while Fig. 2 shows how isomerization selectivity changed as a function of overall conversion of neopentane, the latter being modified by varying the reaction temperature. Ideally, one would prefer to control the conversion by adjusting the space velocity. The neopentane cylinder as supplied contained mainly a liquid phase with a gas-phase pressure of about 7 psig at room temperature. This neopentane pressure was too low to reliably control the neopentane flow rate by means of a mass flow controller. Instead, we had to set the flow rate by using a needle valve. This made it impractical to change the neopentane flowrate, and we decided to keep the neopentane flow rate constant for all the reaction runs. Once set, the flow rate remained very stable over the duration of a typical experimental run. We had to resort to the less desirable way of changing conversions by adjusting the reaction temperature.

Table 3 summarizes the selectivity toward the various products of the neopentane reactions for the various catalysts at an overall

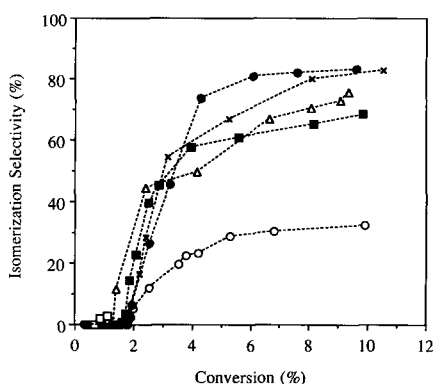


FIG. 2. Neopentane isomerization selectivity versus conversion for catalysts of the Pt-Sn/Al₂O₃ series. (■) 1.0 Pt/Al₂O₃; (○) 1.0 Pt-0.1 Sn/Al₂O₃; (△) 1.0 Pt-0.5 Sn/Al₂O₃; (●) 1.0 Pt-1.0 Sn/Al₂O₃; (□) 1.0 Pt-5.0 Sn/Al₂O₃; and (×) 1.0 Pt-0.5 Sn/Al₂O₃ (LC).

conversion of neopentane ~10%, and also displays the selectivity toward isomerization and cracking. Figure 3 shows the variation of the $\log_{10}(R)$ with changes in the inverse of the reaction temperature, where R denotes the overall rate of the neopentane reaction. Figure 1 shows that there was an absence of isomerization activity up to about 540 K. Further increases in reaction temperature caused a steep increase in isomerization selectivity within the temperature range studied. From Fig. 2 it is clear that isomerization selectivity increased with overall neopentane conversion up to ~10% conversion. There was a regime of low con-

version (0 to ~1.5%) where the isomerization selectivity was small as compared to the cracking selectivity. In fact, for very low conversions the cracking selectivity was 100%. Then there was a regime between ~1.5 and ~4% conversion, where there was a dramatic increase in isomerization selectivity with increasing conversion. Finally, between ~4 and ~10% conversion the isomerization selectivity increased more slowly.

Table 3 shows the amounts of various C₁ to C₅ products present at ~10% neopentane conversion. Regarding isomerization, the isopentane selectivity was significantly larger than the *n*-pentane selectivity. Among cracking products, the selectivities for methane, propane, and isobutane were usually quite large. There was also some normal butane produced except in case of the 1.0 Pt-0.5 Sn/Al₂O₃ (LC) catalyst. The selectivity for ethane production was quite small. In case of the high-loading tin catalyst, 1.0 Pt-5.0 Sn/Al₂O₃, there was such an excess of tin that the activity was very low in comparison to the other Pt-containing catalysts in this series, making it impossible to reach 10% conversion within a reasonable temperature range. Because of its lack of significant activity, this sample was not included in Table 3. There seems to be an optimal loading of Sn giving the desirable selectivity without allowing the parallel decrease in activity to become so significant that the use of the catalyst becomes prohibi-

TABLE 3

Product Selectivities at Total Conversion of Neopentane ~10% for Pt-Sn/Al₂O₃ Catalysts

Catalyst	Temperature (K)	Conversion (%)	Selectivity ^a (%)							
			M	E	P	i-B	n-B	i-P	n-P	S _{IS} ^b
1.0 Pt/Al ₂ O ₃	586	9.8	8.8	1.0	8.4	11.2	2.2	65.3	3.0	68.3
1.0 Pt-0.1 Sn/Al ₂ O ₃	593	9.9	16.0	2.7	11.1	34.4	3.5	31.7	0.6	32.3
1.0 Pt-0.5 Sn/Al ₂ O ₃	691	9.4	4.6	0.9	6.6	10.4	1.8	73.7	2.0	75.7
1.0 Pt-1.0 Sn/Al ₂ O ₃	738	9.6	2.4	0.4	4.2	6.9	3.1	80.7	2.4	83.1
1.0 Pt-5.0 Sn/Al ₂ O ₃ (LC)	645	10.5	3.2	0.6	8.1	5.4	—	75.5	7.2	82.7

^a M, methane; E, ethane; P, propane; i-B, isobutane; n-B, *n*-butane; i-P, isopentane; n-P, *n*-pentane.

^b Isomerization selectivity.

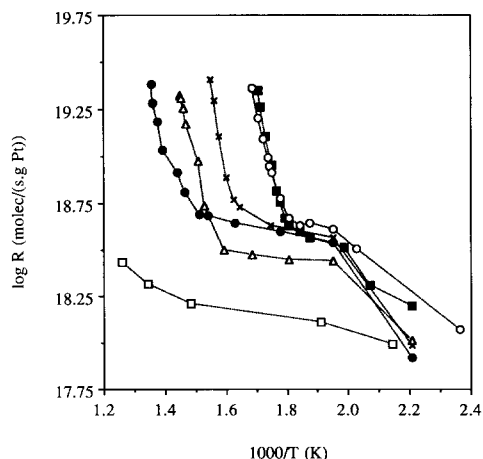


FIG. 3. \log_{10} (neopentane reaction rate) versus inverse of reaction temperature for catalysts of the Pt-Sn/Al₂O₃ series. (■) 1.0 Pt/Al₂O₃; (○) 1.0 Pt-0.1 Sn/Al₂O₃; (△) 1.0 Pt-0.5 Sn/Al₂O₃; (●) 1.0 Pt-1.0 Sn/Al₂O₃; (□) 1.0 Pt-5.0 Sn/Al₂O₃; and (×) 1.0 Pt-0.5 Sn/Al₂O₃ (LC).

tive. Similar observations were made previously on bimetallic catalysts with large loadings of the inactive second metal. For example, Clarke *et al.* (18) studied the reaction between neopentane and hydrogen over a monometallic 4% Pt/SiO₂ sample and over a bimetallic Pt-Au/SiO₂ sample with high Au loading (10% Pt-90% Au). They found that the monometallic Pt/SiO₂ catalyst displayed a significant isomerization selectivity in the reaction temperature range of 593-663 K. On the other hand, they had to reach at least a reaction temperature of 723 K in the case of the Au-containing catalyst before small levels of activity were detected. At temperatures of 693 K and lower this catalyst was totally inactive.

In our Pt-Sn catalyst series, there were subtle differences in product selectivity. For example, in both the 1.0 Pt-1.0 Sn/Al₂O₃ sample and the 1.0 Pt-0.5 Sn/Al₂O₃ (LC) sample the overall isomerization selectivities at ~10% conversion were quite similar at about 83%, but the *n*-pentane selectivity of the latter sample was three times larger (Table 3). The 1.0 Pt-0.1 Sn/Al₂O₃ sample

showed the largest selectivity for cracking products as compared to the other catalysts.

An examination of the isomerization selectivities (Table 3) shows that the monometallic 1.0 Pt/Al₂O₃ catalyst has a selectivity of 68.3%. When small amounts of tin were added (1.0 Pt-0.1 Sn/Al₂O₃), the isomerization selectivity dropped to 32.3%. With further addition of tin the isomerization selectivity went up to 75.7% for the 1.0 Pt-0.5 Sn/Al₂O₃ sample and then increased to 83.1% for the 1.0 Pt-1.0 Sn/Al₂O₃ sample. The 1.0 Pt-0.5 Sn/Al₂O₃ sample, which was prepared with non-chlorine-containing precursors, showed a slightly higher isomerization selectivity as compared to the 1.0 Pt-0.5 Sn/Al₂O₃ sample, which was prepared with chlorine containing precursors.

By examining previously obtained chemisorption data on the Pt-Sn/Al₂O₃ samples one can better understand the trends in reactivity behavior. Hydrogen chemisorption experiments at room temperature (14) showed that the 1.0 Pt-0.1 Sn/Al₂O₃ sample adsorbed more hydrogen than the monometallic 1.0 Pt/Al₂O₃ sample (0.300 cc STP/g catalyst compared to 0.200 cc STP/g catalyst). This means that the H/Pt_t ratio was larger for the low-tin-loading bimetallic sample as compared to the monometallic sample. Now in case of the 1.0 Pt-0.5 Sn/Al₂O₃ sample the hydrogen uptake value at room temperature was 0.227 cc STP/g catalyst and the H/Pt_t ratio had dropped to a value closer to the H/Pt_t value of the 1.0 Pt/Al₂O₃ sample. On further addition of tin (1.0 Pt-1.0 Sn/Al₂O₃) sample the hydrogen uptake value dropped further to 0.182 cc STP/g catalyst. The H/Pt_t value for this sample was very close to the H/Pt_t value of the monometallic 1.0 Pt/Al₂O₃ sample. The H/Pt_t value is usually termed as the dispersion value in the case of monometallic Pt/Al₂O₃ and Pt/SiO₂ samples. Dispersion is defined as Pt_s/Pt_t, where Pt_s is the number of surface atoms of Pt on the catalyst and Pt_t is the total number of atoms of Pt in the catalyst. In case of the supported monometallic Pt samples an assumption of a chemi-

sorption stoichiometry of one hydrogen atom adsorbed per surface Pt atom is usually correct. In the case of the bimetallic samples, however, this assumption may not always be correct. Some of the possible reasons for this are: (a) change in the chemisorption stoichiometry of hydrogen on platinum due to the influence of the second metal, (b) simultaneous adsorption of hydrogen on the second metal under the existing conditions of temperature and pressure, and (c) possible spillover of atomic hydrogen from Pt sites to the nearby sites of the second metal. Hence one should be aware of the inherent limitations of assuming that the H/Pt_t value is equal to the Pt dispersion in bimetallic catalysts. In spite of the ambiguities regarding the exact H/Pt stoichiometry, the H/Pt_t ratio can still serve as an indicator for general trends in Pt dispersion. We believe that the 1.0 Pt–0.1 Sn/ Al_2O_3 catalyst had a higher dispersion of Pt than the monometallic 1.0 Pt/ Al_2O_3 sample.

Foger and Anderson (9) conducted a detailed study on supported Pt samples to observe the effect of Pt particle size on the isomerization selectivity during neopentane reactions. They found that with increasing Pt dispersion (decreasing average Pt particle size) the neopentane isomerization selectivity tended to decrease for Pt average particle sizes lying in the range of less than 20 nm. This change was more drastic for Pt average particle sizes less than 1.5 nm. They found that the trends in the variation of isomerization selectivity with average Pt particle size were similar to the trends in the variation of the number of surface Pt atoms in (111) facets with average Pt particle size. Hence they concluded that with more surface Pt atoms in (111) facets there would be an increase in isomerization selectivity during neopentane reactions. They also noted that with increasing Pt dispersion (i.e., decreasing average Pt particle size) the overall activation energy for the neopentane reaction tended to increase. Based on temperature-programmed desorption of hydrogen (TPD), Foger and Anderson (9) concluded that adsorbed hy-

drogen, rather than gas-phase hydrogen, played a significant role in converting one of the intermediates during the neopentane reaction to cracking products.

Hence one could say with some justification that the decrease in isomerization selectivity from 68.3% (1.0 Pt/ Al_2O_3 sample) to 32.3% (1.0 Pt–0.1 Sn/ Al_2O_3 sample) in the neopentane reactions can be attributed partially to a dispersion effect. The higher nominal Pt dispersion of the low-tin-loading bimetallic sample as compared to the monometallic Pt/ Al_2O_3 sample could have played a role in lowering the isomerization selectivity. On the 1.0 Pt–0.5 Sn/ Al_2O_3 catalyst, the neopentane isomerization selectivity at a conversion of $\sim 10\%$ increased to 75.7%, a value slightly higher than that obtained on the monometallic 1.0 Pt/ Al_2O_3 sample. Nevertheless, the nominal dispersion of this catalyst was still slightly higher than that of the monometallic Pt catalyst. Comparing the 1.0 Pt–0.5 Sn/ Al_2O_3 sample with the monometallic 1.0 Pt/ Al_2O_3 sample we see that in this case one cannot attribute the increased isomerization selectivity of the bimetallic sample simply to a dispersion effect.

On further addition of tin (1.0 Pt–1.0 Sn/ Al_2O_3) the neopentane isomerization selectivity increased to 83.1%. The H/Pt_t ratio for this sample was still slightly larger than that of the monometallic Pt/ Al_2O_3 catalyst, but lower than that of the 1.0 Pt–0.5 Sn/ Al_2O_3 sample. Excess tin addition is likely to lead to a decrease in the number of sites for hydrogen adsorption. Since adsorbed hydrogen plays an important role in cracking reactions (15), a decrease in hydrogen adsorption sites could cause an increase in the isomerization selectivity. One must be aware, though, that the hydrogenolysis pathway is strongly affected by the hydrogen surface coverage, which of course will change as a function of temperature. One cannot draw definitive conclusions about the hydrogen surface coverage under reaction conditions from hydrogen chemisorption data obtained at room temperature.

Juszczyk and Karpinski (19) found that the alloying of Pd with Ag caused the neopentane isomerization selectivity to be enhanced although the overall rate of the reaction was lowered. In our case X-ray photoelectron spectroscopy (XPS) results (14) did not indicate the presence of any zero-valent Sn species in the reduced Pt-Sn/Al₂O₃ samples, hence there was no definite proof that Pt-Sn alloys existed on the surface of our catalysts. But there could still be some interaction between zero-valent Pt and oxidized Sn species stabilized by the Al₂O₃ support.

It would be interesting at this juncture to compare the previously determined *n*-hexane conversion data on these Pt-Sn/Al₂O₃ catalysts (20) with the neopentane conversion data. In case of *n*-hexane reactions the products consisted of cracking products (C₁ to C₅ *n*-alkanes), isomerization products (2-methylpentane and 3-methylpentane), and cyclization products (methylcyclopentane and benzene). At ~10% total conversion of *n*-hexane, the monometallic 1.0 Pt/Al₂O₃ sample had a cyclization selectivity of 13.1%, an isomerization selectivity of 35.2%, and a cracking selectivity of 51.7%. On adding small amounts of tin (1.0 Pt-0.1 Sn/Al₂O₃), the cyclization selectivity remained almost the same while there was a small increase in isomerization selectivity (from 35.2 to 39%). On adding more tin (1.0 Pt-0.5 Sn/Al₂O₃), the isomerization selectivity did not change much (39.6%), but the cyclization selectivity went up significantly (31.0%) and the cracking selectivity dropped to 29.4%. The 1.0 Pt-1.0 Sn/Al₂O₃ sample, on the other hand, showed mainly an isomerization selectivity (95.5%). The 1.0 Pt-0.5 Sn/Al₂O₃ (LC) catalyst gave a cracking selectivity (20.7%) lower than that of the 1.0 Pt-0.5 Sn/Al₂O₃ sample (29.4%), a trend similar to that obtained with neopentane.

In the case of the neopentane reactions the data analysis is simpler than in the *n*-hexane reaction analysis because there are no cyclical products formed and one must

deal only with isomerization and cracking products. For the neopentane reactions it was found that except in the case of the low-tin-loading bimetallic catalyst (1.0 Pt-0.1 Sn/Al₂O₃) there was a decrease in cracking selectivity with increasing amounts of tin. A similar result was obtained in case of the *n*-hexane reaction runs (20) although the low-tin-loading sample did not behave like it did for the neopentane reaction runs. These results illustrate the fact that although overall reaction trends may show similarity one can still observe some differences in reaction behavior for the catalysts in a catalytic series depending on the type of hydrocarbon probe molecule used in the study. One of the reasons for this is that different hydrocarbons adsorb in different modes on the catalytic surface and may require different ensemble sizes and different geometries of surface Pt adsorption sites and this could have an influence on the product selectivities.

In Fig. 3 one can observe that in a low-temperature regime, the rate of the neopentane reaction increased at a fairly rapid rate with increasing temperature, followed by an intermediate temperature regime where the rate of increase was relatively slow, and finally there was a third regime where the rate increased very steeply with increasing temperature. The third regime shifted to higher temperatures with increasing tin content. The highest temperature data points shown on Fig. 3 were obtained at ~10% conversion for all catalysts except for the 1.0 Pt-5.0 Sn/Al₂O₃ catalyst, which displayed such low activity that it was not feasible to reach that level of conversion. Another interesting point to note is that the intermediate regime, where the rate of the reaction increased slowly with temperature, stretched over a larger temperature range with increasing tin content.

Careful inspection of the raw data for the neopentane reactions over the various catalysts showed that the first regime in Fig. 3 corresponded to a total neopentane conversion (*X*) lying in the range of <0.5% to

TABLE 4

Product Selectivities at Total Conversion of Neopentane ~10% for Pt–Au/SiO₂ Catalysts
(Feedstream Not Diluted with Helium)

Catalyst	Temperature (K)	Conversion (%)	Selectivity ^a (%)							
			M	E	P	i-B	n-B	i-P	n-P	S _{IS} ^b
1.0 Pt/SiO ₂	613	10.4	1.9	0.3	9.6	3.7	—	78.0	6.6	84.6
1.0 Pt–0.3 Au/SiO ₂	604	10.5	3.6	0.3	9.5	4.5	—	78.7	3.3	82.0
1.0 Pt–0.7 Au/SiO ₂	587	9.9	4.6	0.6	10.4	8.0	—	74.5	1.9	76.4

^a M, methane; E, ethane; P, propane; i-B, isobutane; n-B, *n*-butane; i-P, isopentane; n-P, *n*-pentane.

^b Isomerization selectivity.

~1.5%. During this stage of the reaction the cracking selectivity was 100%. The second regime shown in Fig. 3 corresponded to *X* lying between ~1.5 and ~2%. During most of this stage only cracking products were present, but toward the high-temperature end of this stage isomerization products started to appear. Hence this regime appears to be a transition stage before isomerization reactions started to dominate. Once the threshold temperature for the isomerization reactions was exceeded, the rate of the overall neopentane reaction increased sharply and the reaction entered the third regime. This sharp increase in the rate started within 20 K of the onset of the isomerization reactions and continued up to ~10% conversion, the highest conversion investigated. Clearly, the mechanisms for the cracking and isomerization reactions must be quite different.

(b) Pt–Au/SiO₂ Catalysts

The activity of the 2.0 Au/SiO₂ sample and the blank SiO₂ was insignificant in comparison to the Pt containing samples. On the bimetallic Pt–Au catalysts, the reaction between neopentane and hydrogen was studied first under conditions similar to those used for the Pt–Sn/Al₂O₃ catalysts. Table 4 summarizes the product selectivities at a total neopentane conversion of about 10%. In contrast to Sn, addition of Au did not decrease the activity of the catalyst, but

instead the 10% conversion level was achieved at progressively lower temperatures with increasing gold content. This observation was in agreement with previous results on *n*-hexane conversion at 673 K, where the gold-containing samples showed higher conversion as compared to the monometallic Pt catalyst (21). In the *n*-hexane reaction runs, the monometallic Pt catalyst and the two bimetallic Pt–Au catalysts showed some deactivation during 10 h on stream, but there was no significant difference in the rate of deactivation as a function of gold content. Consequently, one can rule out that the higher activity of the gold-containing catalysts was simply due to better activity maintenance. The results on the Pt–Au catalysts were in striking contrast to those on Pt–Sn, where Sn addition lowered the activity, while improving the activity maintenance (20).

A comparison of product selectivities for the neopentane reaction over the Pt–Au/SiO₂ catalyst series at approximately 10% conversion (Table 4) did not reveal significant differences, taking the effects of conversion and temperature on selectivity into account (Figs. 4 and 5). The Pt–Sn catalysts, on the other hand, showed more pronounced differences in isomerization selectivity (Figs. 1 and 2). These differences between Pt–Sn and Pt–Au were further illustrated by comparing the overall reaction rates as a function of inverse temperature (Figs. 3 and 6). Again, the data for Pt–Sn

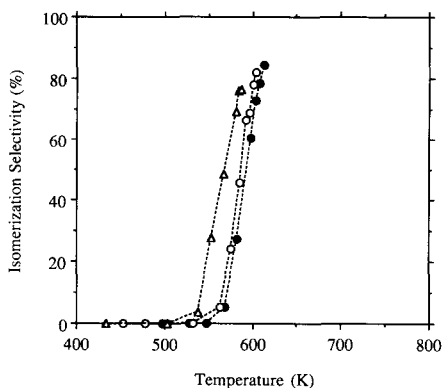


FIG. 4. Neopentane isomerization selectivity versus reaction temperature for catalysts of the Pt-Au/SiO₂ series (feedstream not diluted with helium). (●) 1.0 Pt/SiO₂; (○) 1.0 Pt-0.3 Au/SiO₂; and (△) 1.0 Pt-0.7 Au/SiO₂.

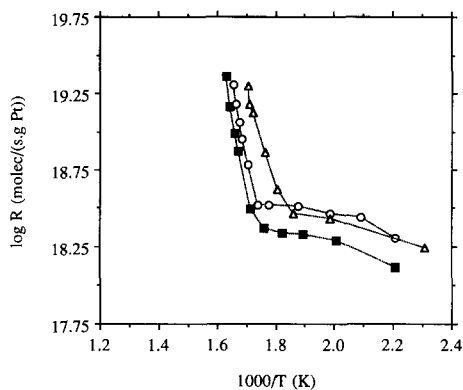


FIG. 6. Log₁₀(neopentane reaction rate) versus inverse of reaction temperature for catalysts of the Pt-Au/SiO₂ series (feedstream not diluted with helium). (■) 1.0 Pt/SiO₂; (○) 1.0 Pt-0.3 Au/SiO₂; and (△) 1.0 Pt-0.7 Au/SiO₂.

were much more spread out as compared to the Pt-Au catalysts. It is well known that gold acts mainly as a geometric diluent, breaking up Pt ensembles. The different behavior of the Pt-Sn catalysts indicates that the role of tin goes beyond a simple geometric diluent effect.

To explore additional regions of the parameter space, a second series of neopentane reaction runs were conducted over Pt-Au/SiO₂ catalysts. For these experi-

ments, a modified protocol was used in which helium was used as a diluent, as explained in the experimental section. The overall conversions of neopentane varied from ~0.4 to ~26%. Figure 7 shows how the isomerization selectivity changed with increasing reaction temperature, while Fig. 8 indicates the nature of variation of isomerization selectivity with increasing total conversion of neopentane. Table 5 summarizes the values of selectivity toward isomeriza-

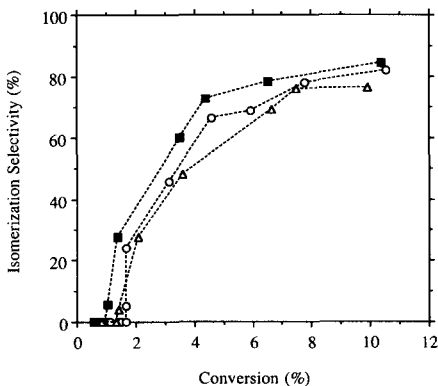


FIG. 5. Neopentane isomerization selectivity versus conversion for catalysts of the Pt-Au/SiO₂ series (feedstream not diluted with helium). (■) 1.0 Pt/SiO₂; (○) 1.0 Pt-0.3 Au/SiO₂; and (△) 1.0 Pt-0.7 Au/SiO₂.

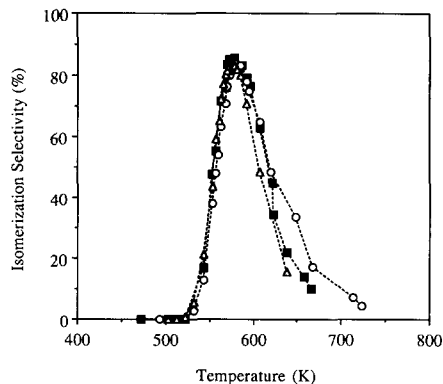


FIG. 7. Neopentane isomerization selectivity versus reaction temperature for catalysts of the Pt-Au/SiO₂ series (feedstream diluted with helium). (■) 1.0 Pt/SiO₂; (○) 1.0 Pt-0.3 Au/SiO₂; and (△) 1.0 Pt-0.7 Au/SiO₂.

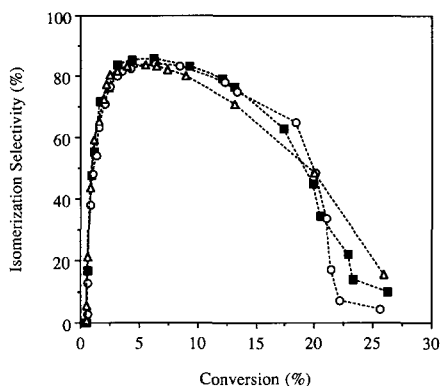


FIG. 8. Neopentane isomerization selectivity versus conversion for catalysts of the Pt-Au/SiO₂ series (feed-stream diluted with helium). (■) 1.0 Pt/SiO₂; (○) 1.0 Pt-0.3 Au/SiO₂; and (△) 1.0 Pt-0.7 Au/SiO₂.

tion and cracking for the three catalysts at three different values of total conversion of neopentane, namely, 0.6, 4, and 26%.

From Fig. 7 it is evident that with increasing temperature the isomerization selectivity increased from 0% to a maximum of more than 80%, followed by a decrease with further increase in temperature. A likely reason for the decrease is the onset of secondary hydrogenolysis of isopentane at higher conversions. One can also observe that although the curves for the three catalysts are very close to each other up to the maximum value of isomerization selectivity, on the way down they tend to get slightly separated from each other. Figure 8 indicates that the isomerization selectivity goes through a maximum at about 4–5% conversion, decreasing at higher conversions. Hence, depending on which side of the maximum one operates in, there can be either an increase or decrease in selectivity with increasing temperature or conversion. The differences in selectivities for the three catalysts can be better understood from Table 5. At the low and the high values of total neopentane conversion, the 1.0 Pt-0.7 Au/SiO₂ catalyst showed the highest isomerization selectivity, while the 1.0 Pt-0.3 Au/SiO₂ catalyst had the lowest isomerization selectivity. At intermediate conversions of about 4%, all

catalysts displayed very similar isomerization selectivities.

Based on the temperatures needed to reach the highest levels of conversion (~26%) (Table 5), the bimetallic 1.0 Pt-0.7 Au/SiO₂ sample was more active than the monometallic 1.0 Pt/SiO₂ sample, which in turn was more active than the bimetallic 1.0 Pt-0.3 Au/SiO₂ sample. From the trends evident in both the selectivity and activity of the three catalysts it is clear that the bimetallic 1.0 Pt-0.7 Au/SiO₂ sample was a better catalyst for the isomerization reactions of neopentane than the monometallic 1.0 Pt/SiO₂ sample, which in turn was superior to the other bimetallic sample (1.0 Pt-0.3 Au/SiO₂). One would have generally expected that with increasing Au content of the catalyst the trends in reactivity for the catalysts would follow a sequential pattern, but we found a deviation from this pattern.

Foger and Anderson (15) conducted a detailed neopentane reaction study on a series of Pt-Au/SiO₂ catalysts. They found that the isomerization selectivity increased initially with increasing gold content of the catalyst, reached a maximum, and then started to decrease once the gold content was increased beyond a certain point. The reason given for this trend in reaction behavior was that in the case of the monometallic Pt/SiO₂ there was a predominance of large surface ensembles of Pt and the reaction pathway consisting of the diadsorbed or the triadsorbed intermediate was more prevalent. As gold was added this led to a decrease in the amount of adsorbed hydrogen on the catalyst. This, in turn, led to an increase in isomerization selectivity due to the fact that a decrease in adsorbed hydrogen lowered the extent of cracking. As more and more Au was added to the catalytic surface beyond a certain optimal value, a new reaction pathway with enhanced cracking selectivity became more and more dominant. Hence after this point the isomerization selectivity started dropping (15). But in our study the situation appears to be more complicated, as one needs to take into account the distinct

TABLE 5

Selectivities at Conversions of Neopentane ~0.6, 4, and 26% for Pt–Au/SiO₂ Catalysts
(Feedstream Diluted with Helium)

Catalyst	Temperature (K)	Conversion (%)	Selectivity (%)	
			Isomerization	Cracking
1.0 Pt/SiO ₂	543	0.7	16.7	83.3
	573	4.4	85.2	14.8
	666	26.2	8.2	91.8
1.0 Pt–0.3 Au/SiO ₂	543	0.6	12.7	87.3
	577	4.3	82.6	17.3
	714	25.6	4.3	95.7
1.0 Pt–0.7 Au/SiO ₂	543	0.6	21.3	78.7
	573	4.0	83.2	16.8
	638	25.9	15.5	84.5

differences in microstructure and morphology of the catalysts. The differences between the catalysts are better illustrated in a study of *n*-hexane reactions with our Pt–Au/SiO₂ catalysts (22).

A detailed experimental analysis including temperature-programmed reduction (TPR), high-resolution transmission electron microscopy (HRTEM), and analytical electron microscopy (AEM) had to be performed before the reasons in these unexpected reactivity trends could be better understood (22). Reactions of *n*-hexane on our Pt–Au/SiO₂ catalysts at 550 K (22) showed that the bimetallic 1.0 Pt–0.7 Au/SiO₂ gave an isomerization selectivity significantly higher than that of the monometallic 1.0 Pt/SiO₂ catalyst. But the trends in cracking selectivity showed that the bimetallic 1.0 Pt–0.3 Au/SiO₂ sample gave a higher cracking selectivity than the monometallic 1.0 Pt/SiO₂ sample, while the 1.0 Pt–0.7 Au/SiO₂ sample displayed the lowest cracking selectivity. The TPR and microscopy results (22) showed that there was evidence of a closer interaction between Pt and Au in the case of the bimetallic 1.0 Pt–0.7 Au/SiO₂ sample in comparison with the bimetallic 1.0 Pt–0.3 Au/SiO₂ sample. This interaction in case of the 1.0 Pt–0.7 Au/SiO₂ catalyst was due either to the formation of the Au₃Pt alloy,

which is the only known alloy for the Pt–Au system, or due to the formation of bimetallic Au–Pt clusters. In either case one would expect a decrease in the average ensemble size of Pt due to its closer interaction with Au atoms. Now it is known that for the reactions of *n*-hexane a large ensemble size of Pt favors the cracking reactions while smaller ensembles of Pt enhance the isomerization reactions. Hence in the case of the 1.0 Pt–0.7 Au/SiO₂, where the Pt ensemble size was small due to interactions with Au, the cracking selectivity was low while the isomerization selectivity was high. In the case of the 1.0 Pt–0.3 Au/SiO₂ sample, Pt and Au were segregated from each other, and the average ensemble sizes of Pt tended to be larger, thereby favoring cracking. Hence one can see that there were distinct differences in the particle compositions and in the type of interactions existing between Au and Pt for the various catalysts in the Pt–Au/SiO₂ series. It would be reasonable to expect that these differences in reactivity observed for *n*-hexane reactions would also manifest themselves when neopentane was used as the probe hydrocarbon molecule.

CONCLUSIONS

Neopentane proved to be an interesting hydrocarbon probe molecule with which to

study the reactivity of Pt–Sn/Al₂O₃ and Pt–Au/SiO₂ catalysts, bringing out subtle differences in reactivity between the catalysts. Small amounts of tin (1.0 Pt–0.1 Sn/Al₂O₃) caused the neopentane isomerization selectivity to drop in comparison to the monometallic 1.0 Pt/Al₂O₃ catalyst. However, further addition of tin (1.0 Pt–0.5 Sn/Al₂O₃ and 1.0 Pt–1.0 Sn/Al₂O₃) caused the neopentane isomerization selectivity to increase above that of the monometallic 1.0 Pt/Al₂O₃ sample. On adding excess tin (1.0 Pt–5.0 Sn/Al₂O₃) the activity of the catalyst became prohibitively low. Hence, there seemed to be an optimum loading of tin that gave desirable selectivity characteristics without sacrificing too much activity.

The 1.0 Pt–0.7 Au/SiO₂ catalyst displayed better catalytic activity trends than the monometallic 1.0 Pt/SiO₂ catalyst. In the case of the 1.0 Pt–0.3 Au/SiO₂ sample, the differences between the bimetallic and the monometallic 1.0 Pt/SiO₂ sample were less pronounced. The differences in isomerization selectivity were not as significant as those observed in the case of Pt–Sn catalysts. The trends in catalytic behavior were consistent with previously measured *n*-hexane reaction trends and could be interpreted on the basis of microstructural differences between the bimetallic catalysts (22). The effect of gold appeared to be mainly a geometric one, disrupting larger Pt ensembles. In contrast to gold, the role of tin appeared to go beyond a simple geometric effect.

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