

# New molecularly modified noble metal catalysts for gas phase hydrogenation reactions

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A new approach for the molecularly modified promotion of noble metal catalysts (Pt, Pd, Au) for the hydrogenation of different compounds in the gas phase is described. After premodification of the catalysts in solution, using several amines, the degree of modification has been measured using UV-spectroscopy and temperature programmed oxidation (TPO). Most modified catalysts showed changes in catalyst activity and product selectivity. Furthermore, they gave sustained long term stability with time on line. These two factors together represent a sound basis on which to identify future applications of this new type of catalyst.

## Introduction

The design of heterogeneous catalysts remains central to the efficient operation of the chemical industry. Promoters, and their counterparts poisons, are two topics that have been studied extensively since heterogeneous catalysts have been used industrially. Commercial catalysts tend to involve multiple promoters to enhance the activity, selectivity lifetime and structural integrity.

The molecular nature of homogeneous catalysts enables these systems to be studied spectroscopically and consequently, these catalysts tend to be well defined in comparison to heterogeneous catalysts, that is the rate enhancement and enantioselectivity induced by addition of ligands has been exemplified in the titanium/tartrate based Sharpless epoxidation<sup>1</sup> and manganese/salen based epoxidation catalysts.<sup>2</sup> However, industry has preferred to use heterogeneous catalysts due to the ease with which product separation can be achieved. In addition, solid catalyst/gaseous reactant systems are preferred in industrial syntheses because they represent solventless processes, which have lower environmental impact. Besides the promotion of catalysts by incorporation of promoters during catalyst preparation,<sup>3</sup> the addition of molecular compounds to well-known catalysts represents a relatively simple route to change the properties of heterogeneous catalysts. Through the addition of different organic compounds to various metal catalysts (including Pt, Pd, Ni, Au, Cu),<sup>4–8</sup> significant changes in catalyst activity and increased chemo- and enantioselectivities have been achieved in previous studies. For some of these catalyst systems a reasonable understanding of the molecular processes on the catalyst surface has been gained.<sup>9,10</sup>

In the work presented here, we have built on these advances and developed new procedures to use molecularly modified

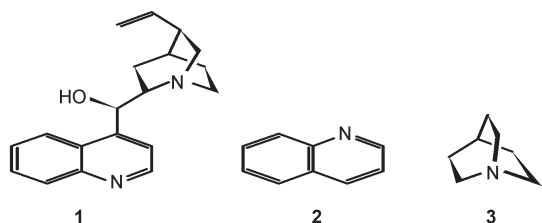
noble metal catalysts and evaluated them in several gas phase reactions. In these initial studies, cinchonidine **1**, quinoline **2**, and quinuclidine **3** have been investigated as modifiers.

## Experimental

All reactants, solvents and modifiers are commercially available and have been used without further purification. 5% Pt/Al<sub>2</sub>O<sub>3</sub>, 5% Pd/Al<sub>2</sub>O<sub>3</sub> and the pure Al<sub>2</sub>O<sub>3</sub> support were obtained from Johnson Matthey and have been used as received. 5% Au/ZnO has been prepared as described elsewhere.<sup>11</sup> For some experiments the Pt and Au catalysts have been reduced in a flow of hydrogen at 300 °C for 90 min prior to use. Au/ZnO catalysts have been selected for study, rather than Au/Al<sub>2</sub>O<sub>3</sub>, since Au/ZnO has been shown to be highly effective for the selective hydrogenation of crotonaldehyde in our earlier studies,<sup>7,11</sup> whereas Au/Al<sub>2</sub>O<sub>3</sub> is not so effective.

In a standard premodification procedure the catalyst (0.5 g) was stirred in CH<sub>2</sub>Cl<sub>2</sub> (10 ml) containing 0.1 to 2 molar equiv (related to the metal surface atoms at an estimated dispersion of 0.25) of the modifiers. After filtration the catalysts were dried under vacuum for 1 h and used within 1 week.

The gas phase hydrogenation reactions were carried out using a plug flow reactor (3.2 mm diameter; Cambridge Reactor Design, CRD 5000). Flow rates were controlled using mass flow controllers and lines to and from the reactor were heated. 1,3-Butadiene was mixed directly into the gas stream while crotonaldehyde and butyraldehyde were added by use of a saturator (usually at 0 °C). In a standard reaction the catalyst (particle size 200 µm, 25 mg) was treated first with a flow of He (50 ml min<sup>-1</sup> for 10 min), followed by the desired H<sub>2</sub>-He mixture (600 ml min<sup>-1</sup> for 10 min) before the reactant was cofed and the reaction started. The reactor temperature was held constant, usually at 25 °C. Conversions and selectivities were determined online with GC analysis using a Varian 3400 gas chromatograph fitted with a Chrompack CP Al<sub>2</sub>O<sub>3</sub>/KCl PLOT column for the 1,3-butadiene reaction and a Chrompack CP WAX 52 CB for the crotonaldehyde and butyraldehyde reactions. UV spectra were recorded on a Perkin Elmer Lambda 20 and for temperature programmed oxidations (TPO) a Micromeritics AutoChem 2910 was used.

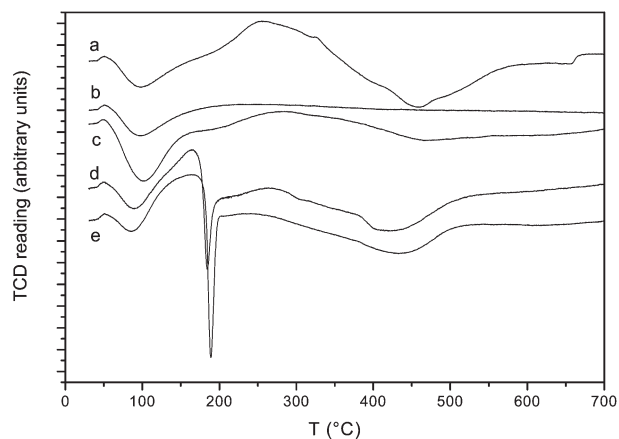


## Results

### Catalyst preparation and characterization

To make molecularly modified catalysts available for reactions at the solid/gas interface a procedure for premodification had to be developed. The very simple approach of stirring a defined amount of catalyst in a solution of the desired modifier in  $\text{CH}_2\text{Cl}_2$ , followed by filtration and drying of the catalyst under vacuum, proved to be successful. Several parameters such as modification time, modifier concentration, prereduction of the catalyst as well as the influence of washing the modified catalyst with pure solvent have been addressed. The adsorption behaviour of cinchonidine (CD) and quinoline on Pt, Pd and Au has been investigated by means of UV-spectroscopy of the solutions before and after contact with the catalysts. From the results presented in Table 1 it is clear that CD is almost completely adsorbed on all catalysts and the extent of adsorption is almost independent of the modifier concentration and catalyst prereduction. On Pt/ $\text{Al}_2\text{O}_3$  the adsorption is complete when the catalyst has been prereduced. Washing the catalyst with solvent resulted in only minor loss of modifier, indicating that it is strongly adsorbed. Quinoline, on the other hand, adsorbed on the catalysts much less effectively, independent of the metal used. Only 10–20% adsorbed on the catalysts while the rest remained in solution. Even though these findings provide interesting information on the adsorption behaviour of these modifiers on the catalysts used and show that premodification by this method is feasible, it was not clear how the modifiers were distributed between the support and the active metal surface, as it was found that, on pure  $\text{Al}_2\text{O}_3$ , the same amount of CD was adsorbed as on Pt/ $\text{Al}_2\text{O}_3$  and Pd/ $\text{Al}_2\text{O}_3$ .

Therefore, this problem was addressed by employing temperature programmed oxidation (TPO) to study the modified catalyst to provide an indication of whether the modifier is adsorbed on the metal nanocrystals. It was expected that the modifier adsorbed on the metal surface would be (at least partially) oxidized from the surface at relatively low temperature (lower than the thermal decomposition temperature). As the TCD detects the integral changes in the gas flow (changes of  $\text{O}_2$  concentration, formation of  $\text{CO}_2$ , CO and  $\text{C}_x\text{H}_y\text{O}_z$ , etc.) a detailed interpretation of the results is difficult. However, as exemplified for CD on Pt/ $\text{Al}_2\text{O}_3$  (Fig. 1) the comparison of the TPO of CD on  $\text{Al}_2\text{O}_3$  (trace a), pure  $\text{Al}_2\text{O}_3$  (trace b), Pt/ $\text{Al}_2\text{O}_3$  (trace c), CD on Pt/ $\text{Al}_2\text{O}_3$  (trace d) and CD on prereduced Pt/ $\text{Al}_2\text{O}_3$  (trace e), unambiguously showed that a significant amount of the modifier is adsorbed on the metal surface (negative signal at 189 °C). This signal is clearly distinct from the broad positive signal at 260 °C originating from CD



**Fig. 1** TPO of : (a) CD on  $\text{Al}_2\text{O}_3$ , (b) pure  $\text{Al}_2\text{O}_3$ , (c) 5% Pt/ $\text{Al}_2\text{O}_3$ , (d) CD on 5% Pt/ $\text{Al}_2\text{O}_3$ , (e) CD on prereduced 5% Pt/ $\text{Al}_2\text{O}_3$ . Profiles are offset for clarity.

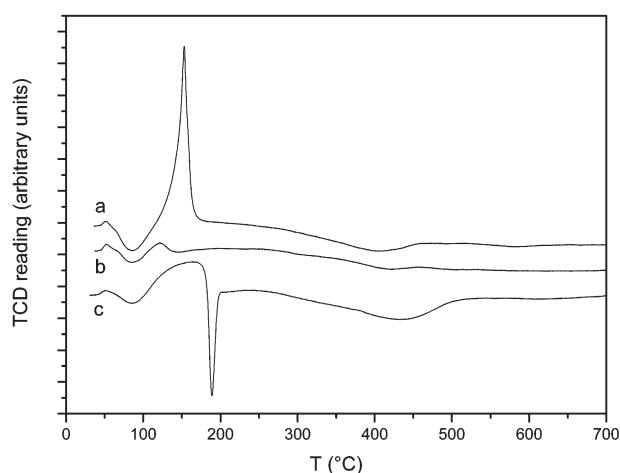
adsorbed on pure  $\text{Al}_2\text{O}_3$ . If the signal was due to an alternative effect resulting from oxidation of modifier adsorbed on the support, that is spillover of oxygen from the metal onto the support, then the signal could have been expected to be much broader, in line with the broad adsorption typically observed for the support alone. Since this is not the case and, furthermore, as we show below, the catalyst performance for hydrogenation is significantly affected, we conclude that this sharp signal is due to oxidation of the modifier adsorbed on the metal nanocrystals. The varying shift to lower temperature (compared to the decomposition temperature of CD: 296 °C) of these two signals is clear evidence for interactions of different strength between CD and the metal or  $\text{Al}_2\text{O}_3$  surfaces, respectively. The complete (trace e) and almost complete lack (trace d) of the positive signal in the TPO of the CD on noble metal-containing catalysts are a strong indication that CD is mainly adsorbed on the metal surface, not on the support, which agrees with the observed adsorption strengths. Prereduction of the catalyst seems to further shift the distribution in favour of the metal surface.

The comparison of the TPO of catalysts premodified with different modifiers is in agreement with the results obtained by UV-spectroscopy. In Fig. 2 the results for quinuclidine, quinoline and CD on 5% Pt/ $\text{Al}_2\text{O}_3$  are given as examples. Compared to CD, quinuclidine gave only a weak negative signal at ca. 150 °C, in line with the much lower adsorption coefficient

**Table 1** Adsorption of quinoline and cinchonidine on Pt, Pd and Au catalysts

Catalyst	Pre-reduction temp/°C	Modifier	Amount <sup>a</sup>	Adsorption coefficient <sup>b</sup>
5% Pt/ $\text{Al}_2\text{O}_3$	300	CD	0.5	1
5% Pt/ $\text{Al}_2\text{O}_3$	—	CD	0.5	0.98
5% Pt/ $\text{Al}_2\text{O}_3$	—	CD	0.5	0.98
5% Pt/ $\text{Al}_2\text{O}_3$	—	CD	0.5	0.97
5% Pt/ $\text{Al}_2\text{O}_3$	—	Quinoline	0.1	0.16
5% Pd/ $\text{Al}_2\text{O}_3$	—	CD	0.5	0.97
5% Pd/ $\text{Al}_2\text{O}_3$	—	Quinoline	0.5	0.21
5% Au/ $\text{ZnO}$	300	CD	0.2	0.95
5% Au/ $\text{ZnO}$	300	Quinoline	1	0.1
Pure $\text{Al}_2\text{O}_3$	—	CD	0.5 <sup>c</sup>	0.98

<sup>a</sup> Molar ratio of modifier/Ms (metal surface atoms) at a metal dispersion of 0.25. <sup>b</sup> A value of 1 corresponds to complete adsorption of the modifier on the catalyst. <sup>c</sup> Same amount as for 5% Pt/ $\text{Al}_2\text{O}_3$ .



**Fig. 2** TPO of (a) quinuclidine, (b) quinoline and (c) cinchonidine on 5% Pt/ $\text{Al}_2\text{O}_3$  at identical modifier loading. Profiles are offset for clarity.

observed by UV-spectroscopy (see Table 1). Nevertheless, this signal is a clear indication of quinoline being adsorbed on the Pt surface. Quinuclidine on the other hand gave a strong positive signal at 153 °C. In analogy to the positive signal observed for CD on pure  $\text{Al}_2\text{O}_3$ , we assume this signal to correspond to the adsorption of quinuclidine on  $\text{Al}_2\text{O}_3$ , which is favoured over adsorption on the metal surface.

### Hydrogenation reactions at solid/gas interface

The performance of the catalysts, modified and characterized as described above, have been investigated in the hydrogenation of three different reactants (containing C=C double bonds, aldehyde C=O double bonds and combinations thereof). The startup procedure for the reactions proved to be a critical factor. Reproducible conversions and selectivities were obtained only if the catalyst bed (modified or unmodified) was treated first with a flow of  $\text{H}_2$ , followed by the desired  $\text{H}_2$ -He mixture, before the reactant was cofed and the reaction started.

With all reactants and catalysts the conversion showed a typical profile with time on line. After a decrease in the initial phase of the reaction, constant or only slightly decreasing conversion has been achieved after 20 to 60 min, depending on the reactant. Fig. 3 shows typical examples for the hydrogenation of 1,3-butadiene and crotonaldehyde. It can be seen that with both reactants the conversion was decreased (compared to the unmodified reference catalyst) for the whole reaction time when using the premodified catalyst. This is an indication that the premodified catalysts are stable and that the adsorbed modifier is not removed from the catalyst surface by coadsorption of hydrogen, reactant or product during reaction. For some reactant catalyst combinations an increased resistance to the poisoning of the catalyst with time on line could be achieved by using premodified catalysts (see profiles of crotonaldehyde hydrogenation in Fig. 3). In a few reactions this led to higher conversions of the premodified catalysts (compared to the reference catalyst) after several hours of reaction time.

However, not all catalyst modifier combinations led to changes in catalyst activity. An overview of the activities of some catalysts tested in the hydrogenation of 1,3-butadiene is given in Table 2. Using quinoline or quinuclidine on Pt or Pd did not affect the reaction rate at all. Within the error limits no change in conversion was observed during the whole time on line. With CD however, the activity was decreased for both metals. On Pt the effect was smaller (but still significant) when using prerduced catalysts. The observed effect tends to be greater with increasing modifier loading, as can be seen from

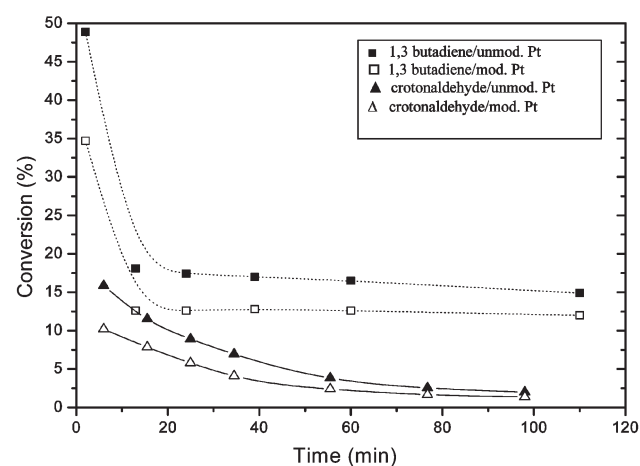


Fig. 3 Typical profiles of conversion with time on line for the hydrogenation of 1,3-butadiene and crotonaldehyde on modified and unmodified 5%  $\text{Pt}/\text{Al}_2\text{O}_3$ .

Table 2 Catalyst activity in the hydrogenation of 1,3-butadiene

Catalyst	Pre-reduction temp./°C	Modifier	Amount <sup>a</sup>	% Conversion <sup>b</sup>	±% Error
5% $\text{Pt}/\text{Al}_2\text{O}_3$	—	—	—	17.4	1
5% $\text{Pt}/\text{Al}_2\text{O}_3$	300	—	—	14.3	1
5% $\text{Pt}/\text{Al}_2\text{O}_3$	300	CD	0.5	12.7	1
5% $\text{Pt}/\text{Al}_2\text{O}_3$	—	CD	0.5	12.6	1
5% $\text{Pt}/\text{Al}_2\text{O}_3$	—	CD	0.25	14.4	1
5% $\text{Pt}/\text{Al}_2\text{O}_3$	—	CD	1	13.3	1
5% $\text{Pt}/\text{Al}_2\text{O}_3$	—	Quinoline	0.5	18.2	1
5% $\text{Pt}/\text{Al}_2\text{O}_3$	—	Quinuclidine	0.5	16.8	1
5% $\text{Pd}/\text{Al}_2\text{O}_3$	—	—	—	57.0	4
5% $\text{Pd}/\text{Al}_2\text{O}_3$	—	CD	0.5	43.5	4
5% $\text{Pd}/\text{Al}_2\text{O}_3$	—	Quinoline	0.5	54.1	4
5% $\text{Pd}/\text{Al}_2\text{O}_3$	—	Quinuclidine	0.5	56.2	4
5% $\text{Au}/\text{ZnO}$	300	—	—	2.7	0.3
5% $\text{Au}/\text{ZnO}$	300	CD	0.5	1.6	0.3
5% $\text{Au}/\text{ZnO}$	300	Quinoline	0.5	1.3	0.3
5% $\text{Au}/\text{ZnO}$	300	Quinuclidine	0.5	1.0	0.3

<sup>a</sup> Molar ratio of modifier/Ms (metal surface atoms) at a metal dispersion of 0.25. <sup>b</sup> After 30 min of reaction time.

the results obtained on Pt. On Au, reasonable activities were observed only using prerduced catalysts. In contrast to Pd and Pt, with Au, the reaction rate decreased for all modifiers used. Furthermore, quinoline and especially quinuclidine, which showed no effect on Pt and Pd, had even a stronger poisoning effect on Au than CD. Even though conversions were obviously affected by changing the amount of catalysts, by using different reactant or hydrogen concentrations, or by changing space velocity or reaction temperature, the general picture presented in Table 2 remained valid.

The observed effects are not limited to the hydrogenation of 1,3-butadiene. As shown in Table 3, CD on Pt had once again a poisoning effect on the hydrogenation of crotonaldehyde and butyraldehyde, independent of catalyst prerduction and modifier loading. Even at very low CD loading there was a small but distinct poisoning.

Concomitant with the decrease in reaction rate, changes in the chemoselectivity have been observed for the hydrogenation of 1,3-butadiene and crotonaldehyde. The modifiers, therefore, not only block active surface sites but change the chemical environment at the catalyst surface, which affects the product selectivity for the reaction. In the hydrogenation of 1,3-butadiene for instance, the cis/trans selectivity of the 2-butenes was affected by most catalysts that exhibited a change in conversion after modification (Table 2, Fig. 4). On Au the selectivity as well as the conversion were affected by all modifiers. On Pt, only CD led to a change in the selectivity, while on Pd none of the modifiers had an influence on the chemoselectivity, not even CD, which affected the reaction rate. In addition, the alkene/alkane as well as the 1-butene/2-butene selectivity were affected by some of the modified catalysts. In one case,

Table 3 Activity of CD modified  $\text{Pt}/\text{Al}_2\text{O}_3$  in the hydrogenation of crotonaldehyde and butyraldehyde

Reactant	Pre-reduction temp./°C	Modifier	Amount <sup>a</sup>	% Conversion <sup>b</sup>
Crotonaldehyde	—	—	—	8.0
Crotonaldehyde	—	CD	0.5	6.1
Crotonaldehyde	300	—	—	7.0
Crotonaldehyde	300	CD	0.5	4.2
Butyraldehyde	—	—	—	2.6
Butyraldehyde	—	CD	0.05	2.2
Butyraldehyde	—	CD	0.25	1.7

<sup>a</sup> Molar ratio of modifier/Ms (metal surface atoms) at a metal dispersion of 0.25. <sup>b</sup> After 50 min of reaction time.

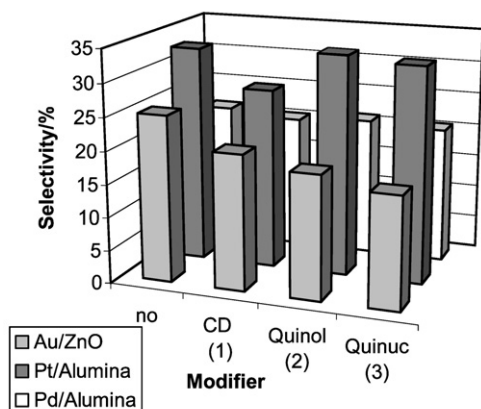


Fig. 4 cis/trans selectivity of the 2-butenes in the hydrogenation of 1,3-butadiene over modified and unmodified Pt, Pd and Au catalysts. Selectivity (%) =  $100 \cdot [\text{cis}/(\text{cis} + \text{trans})]$ .

with quinoline modified Pt, a slight change in product selectivity (alkene/alkane selectivity) was observed even though the reaction rate was not affected.

Once again, these observations are not limited to the gas phase hydrogenation of 1,3-butadiene. In the hydrogenation of crotonaldehyde, the selectivity of crotyl alcohol formation was affected in a similar manner.

## Discussion

The application of TPO to premodified catalysts provides an interesting and very simple new tool for the investigation of molecularly promoted catalysts. The results in Figs. 1 and 2 illustrate that a qualitative distinction between modifiers adsorbed on the support and the metal surface can be made. Furthermore, the small but distinct differences (different intensity and slight shift of the signal at 189 °C) occurring with CD modified Pt/Al<sub>2</sub>O<sub>3</sub>, depending on the prereduction of the catalyst (see traces d and e in Fig. 1), illustrate that this method is sensitive to small changes in the surface characteristics of the metal or the adsorption geometry of the modifier. We assume that the observed differences are indeed due to a change in adsorption geometry of CD, as it is known that in enantioselective hydrogenation of ethyl pyruvate in solution, higher enantioselectivities are obtained after prereduction of the catalyst, because it affects the Pt particle size and as a consequence favours an adsorption mode of CD beneficial for enantioselection.<sup>12</sup>

The differences in the adsorption behaviour of CD and quinoline on all metals are surprising. Both, UV-spectroscopy and TPO confirm that quinoline is adsorbed on the metal surface to a much lower extent (see Table 1 and Fig. 2). However, based on the work of several groups in the field of enantioselective hydrogenation over cinchona modified Pt and Pd, it has been concluded that the quinoline part of CD is responsible for the adsorption of the molecule onto the surface in a predominantly flat adsorption mode of the  $\pi$ -system of the

aromatic ring.<sup>13–15</sup> In this respect, it is not clear why the absorption coefficients observed for CD and quinoline are different by a factor of 5 to 10. These results imply that the other structural parts of CD (*i.e.*, the quinuclidine moiety, OH group and vinyl group) have considerable influence on its adsorption strength and that the simplification of CD to the quinoline part may not be valid under all circumstances even if it is the most crucial part for the geometry of adsorption. This difference is reflected also in the performance of the catalysts where quinoline modified Pt and Pd showed no change in reaction rate, while CD affected all metals significantly.

In contrast to the rate enhancement observed with CD modified Pt in liquid phase ethyl pyruvate hydrogenation<sup>4,9</sup> or with other molecularly modified hydrogenation catalysts,<sup>6,7</sup> the use of our premodified catalysts in the reactions described above led to a poisoning effect. However, the changes in product selectivity observed with some catalysts indicate that the modifiers not only block the active sites, but also change the chemical environment at the metal surface. This is a very promising finding as it is, together with the long term stability observed, a crucial requirement for possible future applications. Amine modified Au and CD modified Pt and Pd catalysts, premodified in the way described above, represent the most promising candidates for new applications in environmentally friendly gas phase catalysis. Future testing of different reactions, including reactants with potentially strong intermolecular interactions with the modifier, may lead to even more pronounced effects on product selectivity and hopefully induce rate enhancement.

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