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Activity and selectivity of PtNi / TiO_2 catalysts for hydrogenation of crotonaldehyde

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The hydrogenation of crotonaldehyde over a series of titania supported PtNi catalysts was investigated. Pt/TiO_2 had the highest activity to hydrogenate the C=O bond of crotonaldehyde. With the addition of Ni to Pt the activity for carbonyl group hydrogenation decreased, while that for the C=C bond hydrogenation increased. Two different types of sites were established to be active for C=O bond hydrogenation, located at (i) the Pt–TiO_2 interface and (ii) the PtNi bimetallic phase. For the Pt–TiO_2 interface the presence of accessible Ti^{x+} cations in close distance to Pt and for the PtNi phase a slightly positively charged Ni on the surface of these alloy particles were concluded to be responsible for the enhanced selectivity to crotylalcohol. The hydrogenation of the C=C bond occurs mainly on the "clean" metal surfaces of Ni and Pt.

Keywords: Selective hydrogenation; PtNi/TiO_2; bimetallic catalysts

1. Introduction

Over most group VIII metal catalysts the hydrogenation of α, β-unsaturated aldehydes proceeds mainly to the saturated aldehyde [1]. Only Os was found to be highly selective in the formation of unsaturated alcohols from crotonaldehyde, acrolein and cinnamaldehyde [2]. The modification of the catalytic properties of supported platinum by other metals like Sn [3,4], Fe [5,6], and Ni [7] led to an improvement of the selectivity to unsaturated alcohol. In these cases the increased activity for the hydrogenation of the carbonyl group was attributed to the properties of the bimetallic particles, in which the less noble constituent was speculated not to be completely reduced under reaction conditions.

Considering the enhancement of the rates for C≡O hydrogenation over TiO_2 supported group VIII metals (e.g. refs. [8,9]) and the improvement of activity for hydrogenation of the carbonyl bond [10] the question arises, how interactions between bimetallic PtNi particles and TiO_2 modify the selectivity of the hydrogenation of crotonaldehyde. Recently, we reported an increased selectivity to crotylalcohol for PtNi supported on silica compared to either Pt/SiO$_2$ or Ni/SiO$_2$ [7]. In this communication we report on the role of these Pt/Ni particles supported on titania for selective hydrogenation of the carbonyl bond.

2. Experimental

2.1. CATALYSTS

A series of titania (Degussa TiO$_2$ P25) supported PtNi bimetallic catalysts with a constant metal loading of 0.4×10^{-3} mol per gram support was prepared by coimpregnation of the support with aqueous solutions of the metal chlorides (PtCl$_4$, 99.98%, NiCl$_2 \cdot 6H_2O$, 99.9985%, both from Ventron). Typically, a ratio of 1 ml of solution per gram of titania was used. The precursors were dried in air at 373 K for 12 h before they were stored.

2.2. HYDROGEN CHEMISORPTION

Hydrogen chemisorption was measured in an all glass system with PTFE valves, connected to an oil diffusion pump, which was equipped with a liquid N$_2$ baffle and capable of evacuating the system to pressures lower than 10^{-2} Pa. Between 0.5 and 1.5 g of precursor were placed between two quartz wool plugs in a glass tube and heated in flowing H$_2$ (200 ml min^{-1} at 10 K/min up to 673 K. After reduction at 673 K for 2 to 4 h, the reactor was evacuated for 2 h at the same temperature.

Adsorption was carried out at 298 K and initial pressures between 5×10^4 and 7×10^4 Pa. At the initial pressure the catalyst was permitted to equilibrate for 12 h before measuring the first hydrogen uptake. The adsorption isotherms were obtained by subsequently decreasing the pressure to 3×10^3 Pa and equilibrating for 1 h between all further data points. The total amount of absorbed hydrogen extrapolated to zero pressure was used to calculate the number of accessible metal

Table 1
H$_2$ chemisorption results at 298 K on PtNi/TiO$_2$ reduced at 673 K

Catalyst	Ni (at%)	wt% metal (Pt+Ni)	H$_2$ ads. (μmol/g)	Accessible metal (atoms/g$_{(cat)}$ $\times 10^{19}$)	Dispersion H$_{(ads)}$/M (%)
Pt	0	7.2	13.4	1.61	7
Ni10Pt90	10	6.8	9.5	1.15	5
Ni30Pt70	30	5.8	7.6	0.92	4
Ni50Pt50	50	4.8	12.0	1.45	6
Ni70Pt30	70	3.8	13.0	1.65	7
Ni90Pt10	90	2.8	8.0	0.99	4
Ni	100	2.3	5.5	0.68	3

atoms. The hydrogen used was of 99.9990 vol% purity and was used without further purification.

The chemical composition of the catalysts and the results from hydrogen chemisorption after reduction of the precursors at 673 K for 2 h are compiled in table 1. The amount of hydrogen adsorbed per gram was quite low on all catalysts and the dispersion of the metallic phase was below 10% for all samples. Note, that this might be indicative of the so-called strong metal–support interaction, for which suppression of H_2 chemisorption is expected [11,12].

2.3. HYDROGENATION OF CROTONALDEHYDE

The gas phase hydrogenation of crotonaldehyde (2-butene-1-al from Aldrich, purity $>99.5\%$, used without further purification) was carried out in a quartz glass tubular reactor under atmospheric pressure. Typically, between 1 and 10 mg of the chloride precursor were placed in the reactor. In order to obtain a suitable catalyst bed and to avoid temperature gradients, the catalyst was highly diluted with quartz beads (i.e. to 2–4 wt% catalyst). The reactor temperature was measured outside the catalyst bed at the reactor wall. Crotonaldehyde was introduced into the H_2 stream by means of a saturator. Catalytic measurements were performed between 353 and 413 K at partial pressure of 60 and 953 mbar of the aldehyde and hydrogen, respectively. Total reactant flow rates were typically 2.5×10^{-5} mol/s. The conversion was kept below 20%.

The reactor effluent was analyzed by means of a HP5890 gaschromatograph, equipped with a 30 m J&W DB-WAX capillary column and a flame ionization detector. Catalysts were reduced in situ under hydrogen by increasing the temperature from 353 to 673 K at 10 K/min. The reduction was carried out for another 2 h at 673 K. Subsequently, the catalysts were allowed to cool to reaction temperature under hydrogen before the aldehyde was added.

Catalytic activities are reported as rate per gram metal and as turnover frequencies (TOF), i.e. number of crotonaldehyde molecules converted per exposed metal atom per second. The concentration of exposed metal atoms was determined from hydrogen chemisorption at 298 K as described above.

3. Results

Hydrogenation of crotonaldehyde

Table 2 lists the overall activities for the gas phase hydrogenation of crotonaldehyde. It should be noted that all catalysts deactivated significantly. Typically, a decrease of 20–30% of the overall conversion within the first 60 min on stream was observed. Additionally, the reactions leading to butyraldehyde and crotylalcohol showed different rates of deactivation over the catalysts investigated. Because

Table 2
Catalytic activity of PtNi/TiO$_2$ catalysts at 353 K after 1 h on stream (conversion < 10%)

Catalyst	Ni (at%)	Rate (10^4 mol/g(met) s)	TOF (molec./$H_{(ads)}$ s)	E_a(app) (kJ/mol)
Pt	0	1.04	0.29	28
Ni10Pt90	10	1.23	0.49	29
Ni30Pt70	30	2.43	0.94	39
Ni50Pt50	50	4.03	0.84	27
Ni70Pt30	70	8.59	1.22	53
Ni90Pt10	90	7.29	1.32	54
Ni	100	0.91	0.21	74

deactivation was observed in every experiment, the catalytic data are compared after 1 h of time on stream.

The overall activity increased approximately one order of magnitude from the Pt to the Ni90Pt10 catalyst (see table 2). The TOF for Ni/TiO$_2$ was lower than expected from this trend. In fig. 1 the rates of formation of *n*-butyraldehyde (BuHO) and crotylalcohol (CrOH) versus the catalyst composition are plotted. The rates over the silica supported catalysts (values taken from ref. [7]) are added for comparison. Over Pt/TiO$_2$ both products were formed with similar rates. With increasing Ni concentration the rate of BuHO formation increased while that of formation of CrOH decreased.

The selectivities of the various catalysts at 353 K are compiled in table 3. BuHO was the main reaction product over all catalysts. Considerable amounts of

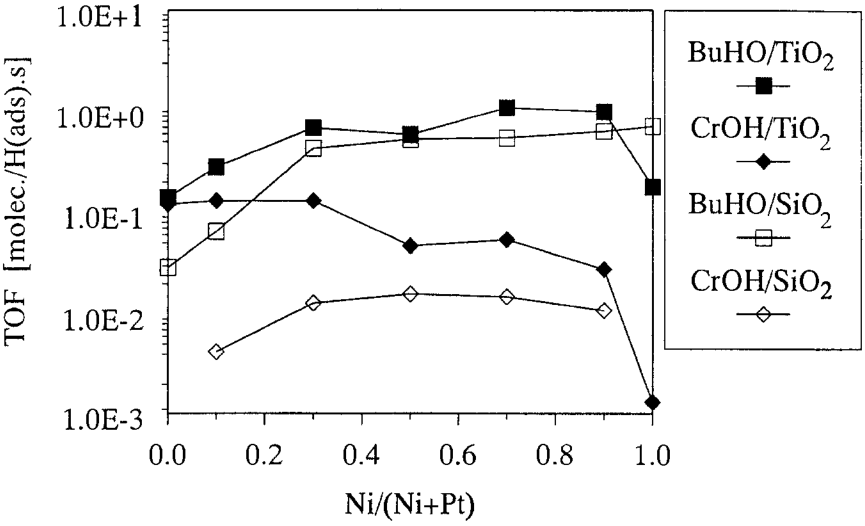

Fig. 1. Rates of product formation in crotonaldehyde hydrogenation over PtNi catalysts supported on TiO$_2$ and SiO$_2$ at 353 K (p(CrHO) = 60 mbar, $p(H_2)$ = 953 mbar).

Table 3
Selectivity at 353 K and 5% overall conversion and apparent energies of activation of PtNi/TiO$_2$ for crotonaldehyde hydrogenation

Catalyst	Ni (at%)	Selectivity (mol%)				E_a(app) (kJ/mol)		
		butane	BuHO	BuOH	CrOH	BuHO	BuOH	CrOH
Pt	0	0.9	46.1	6.7	46.3	29	38	25
Ni10Pt90	10	2.5	61.6	5.3	30.6	30	45	27
Ni30Pt70	30	1.3	79.9	3.8	14.9	41	48	30
Ni50Pt50	50	0.7	88.1	3.0	8.2	23	24	14
Ni70Pt30	70	0.4	93.1	2.1	4.5	52	76	16
Ni90Pt10	90	0.4	95.1	1.9	2.5	67	73	20
Ni	100	1.9	95.6	2.2	0.3	75		

CrOH were formed over Pt and the Pt-rich catalysts. The selectivity at 373 K to CrOH was 46% over Pt/TiO$_2$ and decreased rapidly upon addition of Ni (see table 3). Over Ni/TiO$_2$, the selectivity to CrOH was very low at 353 K ($<0.5\%$), but was higher at temperatures above 393 K. The selectivity to *n*-butanol (BuOH) was approximately 7 mol% over Pt/TiO$_2$, but decreased with increasing Ni content. Additionally, small amounts of *n*-butane were also observed.

Over freshly reduced samples changes in selectivity were observed in addition to the deactivation. The typical deactivation behavior for the Pt and Ni50Pt50 catalyst is presented in fig. 2, in which the rates of BuHO and CrOH formation have been normalized to their initial values (i.e. rates observed after 20 min) and plotted versus the number of turnovers per exposed metal atom (TON). Note that after a

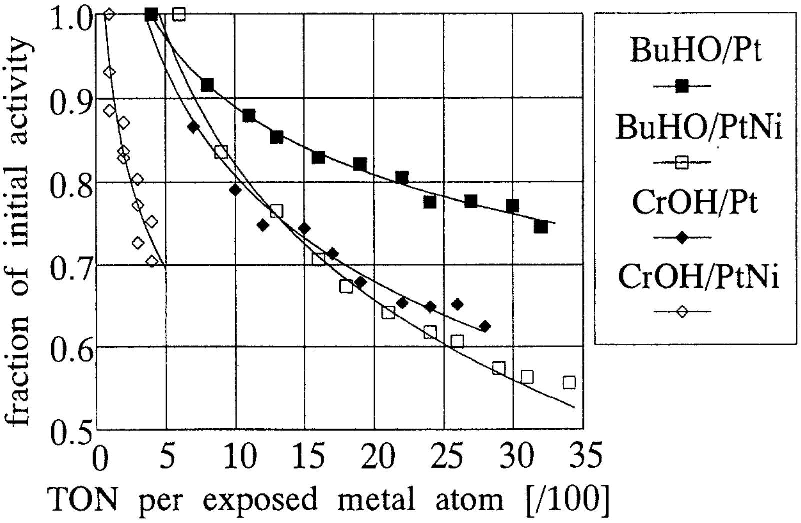

Fig. 2. Deactivation behavior of Pt/TiO$_2$ and Ni50Pt50/TiO$_2$ catalysts as a function of turnover number (TON). The last value in all curves corresponds to 180 min time on stream at 353 K (p(CrHO) = 60 mbar, p(H$_2$) = 953 mbar).

TON of 1000 the rate of BuHO formation over Pt/TiO$_2$ decreased approximately 12%, that of CrOH formation approximately 20% (see fig. 2). Addition of Ni to Pt led to an increased deactivation for both BuHO and CrOH formation. For Ni50Pt50 fig. 2 reveals an almost 20% deactivation of BuHO formation after 1000 TON. That for CrOH can only be extrapolated, but appears to be almost 50%. Tentatively, this behavior is explained with the different contribution of the phases to the overall reaction rate. The rate of butyraldehyde formation (the "pure" phases of Pt and Ni catalyze this reaction) is concluded to decrease more rapidly with time on stream over Ni and PtNi phases than over Pt. In the hydrogenation of the carbonyl group Pt/TiO$_2$ seems to have a higher stability than the PtNi phase.

Assuming different catalytically active sites, the apparent energies of activation for BuHO and CrOH were calculated. For hydrogenation to BuHO a continuous increase of the apparent energy of activation from Pt (29 kJ/mol) to Ni (75 kJ/mol) was observed (see table 3). A similar trend was observed for hydrogenation to BuOH (38 kJ/mol over Pt, 73 kJ/mol over Ni90Pt10). Over the Ni-rich catalysts the apparent energies of activation for hydrogenation to CrOH were significantly lower than those for hydrogenation to BuHO. They did not change substantially from Pt to Ni (25 kJ/mol for Pt, 20 kJ/mol for Ni90Pt10; see table 3).

Table 4
Influence of reduction temperature on activity and selectivity of PtNi/TiO$_2$ in crotonaldehyde hydrogenation at 353 K

Catalyst	Treatment	Overall rate (mol/mol s)	Selectivity (mol%)		
			BuHO	BuOH	CrOH
Ni	A precursor/1st red. at 673 K	1.0×10^{-2}	98.0	1.5	0.5
	B ox. at 573 K/2nd red. at 673 K	1.1×10^{-2}	98.4	1.6	0.0
	B/A	1.1	1.0	1.0	0
	A precursor/1st red. at 673 K	1.0×10^{-2}	98.2	1.8	0.0
	C ox. at 573 K/2nd red. at 473 K	3.2×10^{-2}	99.0	1.0	0.0
	C/A	3.2	1.0	0.6	
Ni50Pt50	A precursor/1st red. at 673 K	6.7×10^{-2}	89.6	3.2	6.9
	B ox. at 573 K/2nd red. at 673 K	9.5×10^{-2}	90.1	3.2	6.4
	B/A	1.4	1.0	1.0	0.93
	A precursor/1st red. at 673 K	6.7×10^{-2}	88.4	2.7	8.5
	C ox. at 573 K/2nd red. at 473 K	4.7×10^{-2}	89.3	2.8	7.4
	C/A	0.69	1.0	1.03	0.88
Pt	A precursor/1st red. at 673 K	2.9×10^{-2}	47.2	7.9	43.6
	B ox. at 573 K/2nd red. at 673 K	3.4×10^{-2}	38.1	7.9	52.6
	B/A	1.2	0.81	1.01	1.2
	A precursor/1st red. at 673 K	2.9×10^{-2}	50.6	5.0	43.3
	C ox. at 573 K/2nd red. at 473 K	3.0×10^{-2}	28.0	7.2	64.1
	C/A	1.0	0.55	1.4	1.5

Because TiO_2 is known as a partially reducible support we investigated also the influence of two different reduction temperatures upon activity and selectivity. Three catalysts, i.e. Ni, Ni50Pt50 and Pt were exposed to a reduction (–reaction)–oxidation–reduction(–reaction) cycle for which two different temperatures were chosen for the second reduction (673 and 473 K). A comparison of the overall rate and selectivity after each reduction step is given in table 4. The second reduction at 673 K of the Ni catalyst following oxidation in 30% O_2/Ar at 573 K neither affected the overall activity nor the selectivity. When the second reduction was performed at 473 K, the rate of hydrogenation of CrHO increased by a factor of 3. Over the Ni50Pt50 catalyst the observed changes in activity were much smaller than over Ni. The second reduction at 673 K increased the overall rate of CrHO hydrogenation by 40%, while it did not affect the selectivity. Upon reduction at 473 K the overall activity decreased, but the selectivity remained the same as found after reduction at 673 K. Over Pt only a small change in overall activity was observed between the two reduction steps, while the selectivity changed significantly upon a second reduction (see table 4). After the second reduction at 673 K as well as at 473 K, selectivity to CrOH increased, while that to BuHO decreased.

4. Discussion

Over silica supported PtNi catalysts the catalytic activity for hydrogenation of crotonaldehyde was attributed to three different metallic phases, i.e., Ni, Pt and PtNi, which were found to be present after reduction. The sequence $Pt \ll PtNi < Ni$ was established for the overall hydrogenation activity of PtNi/SiO_2 catalysts.

Fig. 3 gives a comparison of the overall rate of CrHO hydrogenation for PtNi supported on SiO_2 (from ref. [7]) and TiO_2. The TOFs obtained with PtNi catalysts supported on titania were generally higher than those of PtNi supported on silica (except for Ni). The same trend as with silica supported samples, i.e. an increase of the TOF with increasing Ni concentration was observed. Pt/TiO_2 was approximately one order of magnitude more active than Pt/SiO_2, but the differences in overall activity decreased to a factor of 2 for Ni concentrations higher than 30 at%. The increase in activity with increasing Ni concentration is followed by the increase of the apparent energy of activation for the overall reaction, i.e. from 28 kJ/mol on Pt to 75 kJ/mol on Ni. The results for Pt/TiO_2 are in good agreement with those of Vannice and Sen [10] who reported an apparent activation energy between 23 and 37 kJ/mol (for the overall reaction). The increasing apparent energy of activation suggests that the increase in the rates is probably due to an increase of the preexponential factor of the rate constant. The apparent activation energies for the formation of CrOH are very similar to those for BuHO over the catalysts containing more than 50 at% Pt. This indicates that the reaction paths leading either to BuHO or CrOH are energetically not too different for these catalysts.

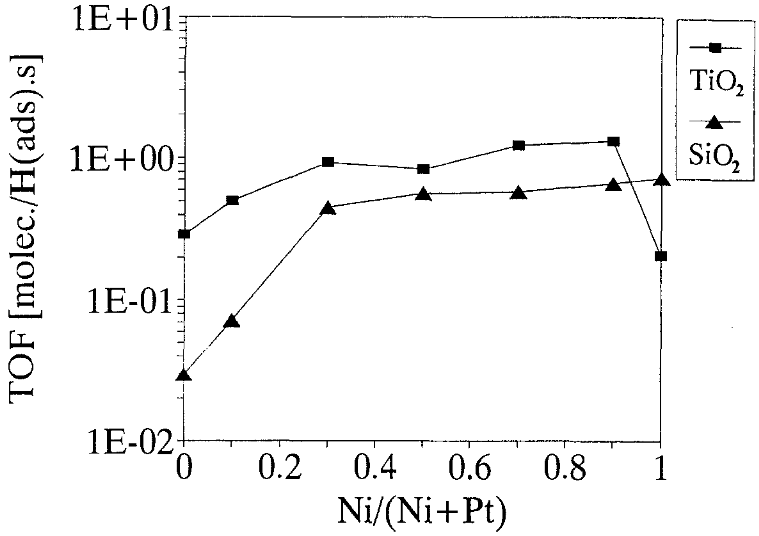

Fig. 3. Overall reaction rates of crotonaldehyde hydrogenation over PtNi/TiO_2 and PtNi/SiO_2 at 353 K (p(CrHO) = 60 mbar, $p(H_2)$ = 953 mbar).

From fig. 1 it can be seen that TiO_2 as support modifies primarily the hydrogenation of the carbonyl group, which occurs several orders of magnitude faster on Pt/TiO_2 than on Pt/SiO_2 (where CrOH formation was not observed). The addition of Ni to Pt up to 30 at% enhances mainly the rate of C=C double bond hydrogenation, while it does hardly affect the rate of C=O group hydrogenation. From a Ni content higher than 30 at% the TOF values for the formation of BuHO and CrOH show a similar trend on the titania as well as the silica supported samples. However, the formation of CrOH over the TiO_2 supported catalysts proceeds approximately five times faster than over silica supported PtNi. Over PtNi on silica a slightly positively charged Ni on the surface of the bimetallic phase was suggested to increase the polarization of the carbonyl oxygen and, thus, to enhance the hydrogenation of this functional group [13]. Such a promoting effect of a less noble metal on the carbonyl group hydrogenation activity of Pt was previously also reported by several authors (e.g., [3,5,14,15]).

Thus, surface polarity should also play a key role for the selective hydrogenation of α, β-unsaturated aldehydes over titania supported catalysts. It suggests that sites capable of hydrogenating the carbonyl group must be oxygen vacancies of the TiO_2 support, leading to accessible Ti^{x+} cations at the Pt/TiO_2 interface. These sites might already be created by reduction below 773 K. The adsorption of crotonaldehyde could then be visualized with the carbonyl oxygen coordinated to Ti^{x+} and the carbon atom bound to Pt. If these speculations were correct, one would expect a substantial sensitivity of the rate of C=O group hydrogenation on the reduction process. This was indeed observed (see table 4). For the Pt catalyst a second reduction step at 673 K after exposing the reduced catalyst to 30% O_2/Ar at 573 K increased the rate of CrOH formation by 40%. That of BuHO formation decreased by 10% compared to the rate after the initial reduction of the precursor at 673 K. This effect was even more significant when the catalyst was rereduced at 473 instead of 673 K (table 4). In both cases additional sites preferentially hydrogenating the C=O group of crotonaldehyde were created during the oxidation–reduction treatment. Because the overall rate remained approximately constant, we conclude that some sites which were active for C=C bond hydrogenation were converted into sites active for carbonyl group hydrogenation. This could be achieved by redispersion of Pt particles or redispersion of the TiO_x phase on top of the metal particles. Our data do not allow to differentiate between these two possibilities.

It is interesting to note that in the presence of Ni such subtle changes in selectivity were not observed. After the Ni50Pt50 catalyst was treated accordingly, only the overall rate of CrHO hydrogenation changed, while the selectivity was hardly affected (table 4). This suggests that the ratio of sites active in hydrogenating the C=C and C=O groups is constant and that the decrease in the overall rate after reduction at 473 K is due to a variation of the concentration of the exposed metal atoms.

For PtNi/SiO_2 it was shown that the activity to the selective hydrogenation of the carbonyl group of crotonaldehyde was directly proportional to the concentration of the PtNi phase [7]. Thus, for PtNi catalysts supported on titania one should not only consider the contribution of the sites at the Pt–TiO_2 interface but also the specific activity of the PtNi phase. The additive contribution of Pt/TiO_x sites and of PtNi sites not located at the interface (the activity of these sites equal to that of

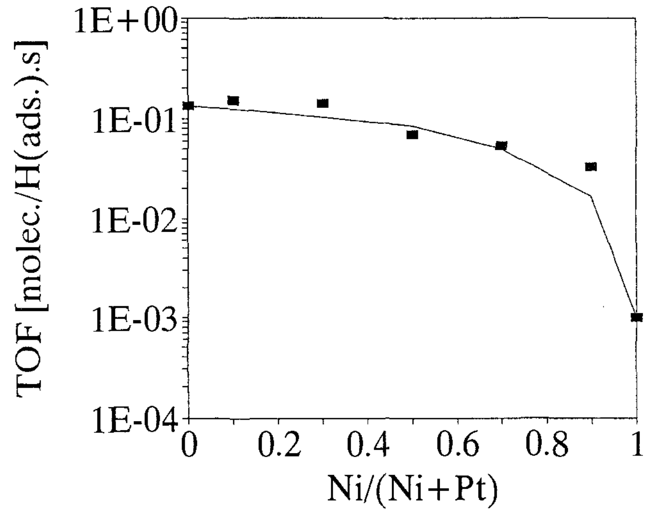

Fig. 4. Rates of crotylalcohol formation over PtNi/TiO_2 catalysts at 353 K. The points correspond to the rates measured. The solid line corresponds to an additive contribution of Pt–Ni, Pt–TiO_x and Ni–TiO_x sites to the overall rates of hydrogenation of CrHO to CrOH.

the silica supported stoichiometric PtNi compound) describes the observed reactivity and selectivity adequately (see fig. 4). The slightly higher values of the experimental results suggest that the dispersion of the Pt particles, respectively the PtNi particles, is higher than that of Ni. Alternatively one might propose a higher surface concentration of Pt than expected from the bulk values.

On the Ni catalyst different reduction temperatures affected only the overall activity. The threefold increase of the rate of CrHO hydrogenation after an oxidation–reduction treatment is explained with redispersion of the metal. However, changes at the Ni–TiO_2 interface leading to an increase of CrOH formation were not observed.

5. Conclusions

The use of TiO_2 as support significantly increased the rate of hydrogenation of the carbonyl group of crotonaldehyde to crotylalcohol as compared to SiO_2. Pt/TiO_2 exhibited the highest activity for this reaction. It decreased with increasing Ni content. In comparison to silica supported catalysts it was shown that mainly the rate of C=O bond hydrogenation is enhanced, while differences in specific activities of C=C bond hydrogenation were significantly smaller. Two types of sites are proposed to be active for C=O group hydrogenation, i.e. (i) the PtNi bimetallic phase and (ii) the Pt–Ti interface, which was found to be approximately five times as active as the PtNi sites. For both sites the polarity is suggested to be responsible for the activation of the carbonyl group. The formation of butyraldehyde, i.e. the hydrogenation of the C=C bond occurs mainly on the "pure" surface (Pt, Ni and PtNi).

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