ELSEVIER

Journal of Molecular Catalysis A: Chemical 125 (1997) 47–52

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

Formation of bimetallic $RhCo_3$ clusters from monometallic carbonyl clusters on SiO_2 as probed by hydroformylation

Lin Huang [*]

State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, P.O. Box 110, 116023 Dalian, China

Received 31 July 1996; accepted 17 January 1997

Abstract

A bimetallic SiO_2-supported $RhCo_3$ cluster catalyst derived from $Rh_4(CO)_{12}$ and $Co_2(CO)_8$ by coimpregnation followed by decarbonylation under H_2 at 623 K has been probed by atmospheric ethylene hydroformylation at 423 K. The catalytic behavior is consistent with that of $RhCo_3/SiO_2$ derived from $RhCo_3(CO)_{12}$. At the same time, the corresponding binary catalysts prepared from inorganic rhodium and cobalt salts exhibit much lower activities than $RhCo_3/SiO_2$ and significantly enhanced activities compared to monometallic catalysts. The results suggest that the increase in catalytic activity by combination of rhodium and cobalt is attributed to the bimetallic catalysis by $RhCo_3$ clusters regardless of the synergistic catalysis by monometallic rhodium and cobalt sites. © 1997 Elsevier Science B.V.

Keywords: Silica-supported $RhCo_3$; $Rh_4(CO)_{12}$; $Co_2(CO)_8$; Coimpregnation; Hydroformylation

1. Introduction

For most of the heterogeneously catalyzed reactions, the enhancement of reaction rates by a combination of two different metals relative to the catalysis by one of the metals is probably ascribed to the bimetallic effect [1,2]. It is documented that many binary supported metallic catalysts which show considerably increased hydroformylation activity compared to monometallic catalysts virtually have the nature of bimetallic particles or bimetallic clusters [3–12]. In our recent studies, we discovered that the bimetallic carbonyl cluster $RhCo_3(CO)_{12}$ favorably gives the bimetallic $RhCo_3$ cluster on the SiO_2 surface after thermal decarbonylation under H_2 or under O_2, which brings about a 20-fold enhanced rate of formation of oxygenates in ethylene hydroformylation with respect to a monometallic catalyst Rh/SiO_2 [11–13]. IR spectroscopic evidence has been afforded that $RhCo_3(CO)_{12}/SiO_2$ is readily regenerated from $RhCo_3$ under catalytic conditions and is responsible for the strong catalysis [11]. Therefore, it appears likely that the increase in catalytic activity for hydroformylation depends on the content of bimetallic $RhCo_3$ clusters present on the surface in a binary supported rhodium and cobalt system. In the present paper, we report a similar observation concerning excellent catalytic performances in ethylene hydroformylation over a SiO_2-supported

---

[*] Tel. (+86-411) 4671991; Fax (+86-411) 4694447.

1381-1169/97/$17.00
PII S1381-1169(97)00035-6

catalyst derived from $Rh_4(CO)_{12}$ and $Co_2(CO)_8$ by coimpregnation, which suggests the same bimetallic effect. The catalytic data may be associated with the formation of bimetallic $RhCo_3$ clusters from the two monometallic clusters on SiO_2, by comparison with the catalytic behaviors of SiO_2-supported catalysts derived from $Rh_4(CO)_{12}$, $RhCo_3(CO)_{12}$, $[RhCl_3 + Co_2(CO)_8]$ and $[RhCl_3 + Co(NO_3)_2]$, etc.

2. Experimental

$RhCl_3 \cdot nH_2O$, $Co(NO_3)_2 \cdot 6H_2O$ and $Co_2(CO)_8$ were purchased commercially. $Rh_4(CO)_{12}$ and $RhCo_3(CO)_{12}$ were synthesized according to literature [14,15]. SiO_2 was a silica 'Aerosil' supplied by Degussa with a surface area of 380 m^2/g. n-hexane used as the solvent was distilled over P_2O_5 and stored under Ar over activated 5 A molecular sieves. The gases H_2, CO, C_2H_4 and Ar had a purity of 99.99%. Before introduction into a sample vessel and a reactor, they were further purified by passage through traps of activated 5 A molecular sieves and Mn/MnO.

The carbonyl clusters $Rh_4(CO)_{12}$, $Co_2(CO)_8$ and $RhCo_3(CO)_{12}$ were employed to prepare a series of catalysts such as $Rh_6(CO)_{16}/SiO_2$ [16], $Co_4(CO)_{12}/SiO_2$ [17], $[Rh_6(CO)_{16} + Co_4(CO)_{12}]/SiO_2$ and $RhCo_3(CO)_{12}/SiO_2$. SiO_2 (60–80 mesh granule) was predehydroxylated under vacuum at 673 K for 5 h and impregnated or coimpregnated with the carbonyl clusters in dry n-hexane under Ar. The impregnated systems were subjected to 2 h of stirring. The solvent was removed by evacuation and the resulting solid samples were dried under vacuum at 1.3×10^{-3} kPa for 1 h. For preparing a binary SiO_2-supported catalyst from $RhCl_3$ and $Co_2(CO)_8$, SiO_2 was first impregnated with an aqueous solution of $RhCl_3 \cdot nH_2O$ followed by drying and calcination in air at 673 K for 5 h. Then the resulting sample was impregnated with a n-hexane solution of $Co_2(CO)_8$ followed by stirring and removal of the solvent. For preparing a conventional supported catalyst, SiO_2 was directly impregnated with an aqueous solution of $RhCl_3 \cdot nH_2O$ or of $[RhCl_3 \cdot nH_2O + Co(NO_3)_2 \cdot 6H_2O]$ followed by drying and calcination in air at 673 K for 5 h. Such oxidative calcination is believed to lead to a partial conversion of $RhCl_3$ to Rh_2O_3 [18] and a total conversion of $Co(NO_3)_2$ to Co_3O_4 [19,20]. All rhodium catalyst precursors prepared contained 1% Rh. The loading of cobalt in related catalysts was 1.7% at an atomic ratio of Co:Rh = 3:1. The catalyst precursors containing carbonyl clusters were transferred to the reactor under Ar prior to catalytic tests.

Hydroformylation of ethylene was conducted under atmospheric pressure at 423 K in a glass tubing flow reactor (i.d. = 7 mm) where 0.1 g of catalyst precursor was charged. The catalyst precursors were treated in flowing H_2 at 623 K for 2 h and subsequently H_2 was replaced by a mixture of C_2H_4, CO and H_2 (20:20:20 ml/min) at 443–473 K. Studies of temperature programmed reduction (TPR) have demonstrated that Rh_2O_3 (or $RhCl_3$) and Co_3O_4 are sufficiently completely reduced to Rh^0 and Co^0 at temperatures of 473 K [21,22] and 623 K [22–24], respectively. The total conversion of C_2H_4 was inferior to 15%. Data were taken 7 h after the initiation of reaction. Both hydrocarbon and oxygenated products were analyzed on line with gas chromatography, using a 2 m length column of Porapak R and a flame ionization detector.

The metal contents of the samples studied were determined by X-ray fluorescence spectroscopy.

3. Results and discussion

Table 1 summarizes the catalytic results of all the SiO_2-supported catalysts studied in ethylene hydroformylation under atmospheric pressure at 423 K. The monometallic rhodium catalysts derived from both $Rh_4(CO)_{12}$ and $RhCl_3$ presented lower activities and selectivities for the formation of propanal with no production of propanol. The monometallic cobalt catalyst derived from $Co_2(CO)_8$ exhibited undetectable activities for both hydroformylation and hydrogenation under the same conditions. In contrast, the $RhCo_3(CO)_{12}$-derived catalyst exhibited an incomparable catalytic performance in activity: the activity to oxygenates was increased by 20 times relative to the $Rh_4(CO)_{12}$-derived monometallic catalyst. Moreover it also exhibited an improved selectivity to oxygenates by 30%. The results are due to the bimetallic effect of $RhCo_3$ as we have concluded by spectroscopic and catalytic studies [11]. When a binary catalyst was obtained from $Rh_4(CO)_{12}$ and $Co_2(CO)_8$ by coimpregnation followed by decarbonylation under the same conditions, its catalytic behavior was quite similar to that of the $RhCo_3/SiO_2$ catalyst: after 7 h of reaction, the activities to oxygenates and to ethane were 6.10 and 3.32 mol/Rh mol/min respectively, which are close to those of $RhCo_3/SiO_2$ so that the selectivity to each product is much the same as that of $RhCo_3/SiO_2$, as shown in Table 1; after prolonged reaction, the catalyst was quite stable as shown in Fig. 1 and the activities are compatible with those of $RhCo_3/SiO_2$ [11] for the formations of both oxygenates and ethane within an experimental error. The catalytic results suggest that the coimpregnated catalyst possesses the bimetallic property rather than the binary monometallic property and probably involves the same bimetallic $RhCo_3$ clusters.

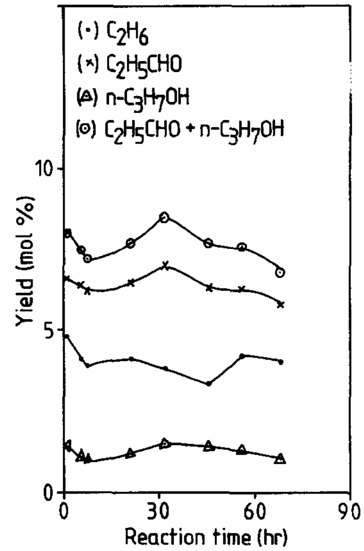

Fig. 1. Dynamic atmospheric ethylene hydroformylation (C_2H_4:CO:H_2 = 20:20:20 ml/min) at 423 K over a catalyst by 2 h of decarbonylation of $[Rh_6(CO)_{16} + Co_4(CO)_{12}]/SiO_2$ (1% Rh loading, Co:Rh = 3:1 atomic ratio) under H_2 at 623 K.

To put in evidence the existence of bimetallic $RhCo_3$ clusters in the coimpregnated catalyst, we performed an oxidative processing on the catalyst and investigated the catalytic properties of the catalyst thus treated. After 7 h of normal

Table 1
Catalytic properties of SiO_2-supported catalysts [a] in atmospheric ethylene hydroformylation (C_2H_4:CO:H_2 = 20:20:20 ml/min) at 423 K

Starting material	Co:Rh (atomic ratio)	Activity [b]		Selectivity (mol%)	
		C_2H_6	oxygenates [c]	oxygenates	$n-C_3H_7OH$
$Co_2(CO)_8$		0	0	—	—
$Rh_4(CO)_{12}$		0.62	0.31	34	0
$RhCl_3$		0.39	0.28	41	0
$RhCo_3(CO)_{12}$		3.63	6.56	64	6
$Rh_4(CO)_{12} + Co_2(CO)_8$	3:1	3.32	6.10	65	9
$[Rh_4(CO)_{12} + Co_2(CO)_8]$ [d]	3:1	2.16	4.69	69	5
$RhCl_3 + Co_2(CO)_8$	3:1	0.88	1.40	61	8
$RhCl_3 + Co(NO_3)_2$	3:1	0.35	0.96	74	9

[a] With 1% Rh and 1.7% Co loadings.

[b] Expressed by (mol/Co mol/min) for Co/SiO_2 and (mol/Rh mol/min) for Rh/SiO_2 and Rh-containing catalysts. Data were taken 7 h after the initiation of reaction.

[c] $C_2H_5CHO + n-C_3H_7OH$.

[d] The catalyst was treated under O_2 at 623 K for 2 h and flushed with Ar at 623 K for 1 h after 7 h of normal catalytic test, data were taken 1.5 h after the initiation of reaction.

catalytic test, the catalyst was flushed with Ar at 423 K for 1 h and then Ar was replaced by O_2 at 423 K. The catalyst was oxidatively treated in flowing O_2 at 623 K for 2 h and flushed with Ar at 623 K for 1 h. Finally Ar was replaced by the reaction gas mixture at 423 K to start the reaction. After 1.5 h of reaction, the activities to oxygenates and to ethane were 4.69 and 2.16 mol/Rh mol/min respectively, which are still appreciably high. Moreover there was no significant difference in product selectivity compared to the initial catalyst. These observed activities are certainly not attributed to the catalysis by monometallic rhodium particles, Rh^+ and Rh_2O_3 (or $RhCl_3$), etc. supported on SiO_2. In a very recent work, we demonstrated the preservation of bimetallic $RhCo_3$ clusters derived from $RhCo_3(CO)_{12}/SiO_2$ by decarbonylation under O_2 at 623 K by hydroformylation probing; we also illustrated the oxidation of a binary SiO_2-supported rhodium and cobalt system derived from $Rh_4(CO)_{12}$ and $Co_2(CO)_8$ after decarbonylation under O_2 at 623 K, which resulted in almost no catalytic activity for ethylene hydroformylation. Consistent with the stability of bimetallic $RhCo_3$ cluster in $RhCo_3(CO)_{12}/SiO_2$ under O_2 at high temperatures, the catalytic behavior of the coimpregnated catalyst following thermal treatment under O_2 in the present case suggests that bimetallic $RhCo_3$ clusters are effectively formed from $[Rh_6(CO)_{16} + Co_4(CO)_{12}]/SiO_2$ (Co:Rh = 3:1 atomic ratio) by decarbonylation under H_2 at 623 K and can be retained intact on the SiO_2 surface without oxidative decomposition during oxidative treatment under O_2 at 623 K. It is necessary to mention that monometallic rhodium and cobalt particles, if produced by thermal decarbonylation of supported monometallic clusters under H_2 can be fully oxidized to Rh^+, Rh_2O_3 and Co_3O_4 on SiO_2 upon treatment under O_2 at 623 K [18–21] and that the resulting monometallic rhodium and cobalt oxides are impossibly transformed to bimetallic Rh–Co particles under a H_2-containing hydroformylation atmosphere at 423 K, as indicated by our another study [12]. Following oxidative processing, the systematic slight decrease in the activities to oxygenates and to ethane may result from the sintering of $RhCo_3$ on the surface caused by additional heating at a high temperature.

The above catalytic data provide cardinal evidence for the presence of bimetallic $RhCo_3$ clusters on the SiO_2 surface in the coimpregnated system. On the other hand, the synergistic catalysis by two heteronuclear monometallic sites with the mechanism of dinuclear elimination toward hydroformylation especially heterogeneous hydroformylation is poorly understood. Previous findings regarding the remarkable enhancement of catalytic activity in hydroformylation by combination of various noble metals with cobalt with respect to monometallic catalysts [25–31], led us to verify the possible synergistic effect resulting in strongly increased hydroformylation activity with monometallic rhodium and cobalt sites on SiO_2.

Apart from coimpregnation with $Rh_4(CO)_{12}$ and $Co_2(CO)_8$, we adopted alternative combinations such as $[RhCl_3 + Co_2(CO)_8]$ and $[RhCl_3 + Co(NO_3)_2]$ as starting materials in the preparation of binary SiO_2-supported catalysts with the equivalent composition. As shown in Table 1, interesting observations were made:

First, the $RhCl_3$-derived Rh/SiO_2 catalyst had comparable activity and relatively good selectivity for ethylene hydroformylation to the $Rh_4(CO)_{12}$-derived Rh/SiO_2 catalyst.

Second, addition of cobalt to the $RhCl_3$-derived Rh/SiO_2 led to obvious increases in activity and selectivity toward hydroformylation, showing significantly the promoting effects of cobalt on the catalysis.

Third, $RhCl_3$ was not able to play the same role as $Rh_4(CO)_{12}$ in the enhancement of hydroformylation activity by combination with $Co_2(CO)_8$ although the hydroformylation activity of the corresponding binary catalyst was 4 times higher than that of the $RhCl_3$-derived Rh/SiO_2 catalyst.

We thus reckon that the catalytic behavior of a $Co_2(CO)_8$-derived binary rhodium and cobalt system would not rely to appreciable extent on the choice of rhodium precursors if the synergistic hydrogenolysis step forming propanal via dinuclear reductive elimination occurred between a cobalt acyl and rhodium hydride. It is generally difficult to prepare highly active metallic catalysts from inorganic salts. It has long been known that both monometallic and binary supported catalysts derived from organometallic complexes are of great advantage over those prepared from inorganic compounds for many reactions. The observed apparent difference in catalytic activity due to the different precursors in the present work suggests that the hydroformylation activity of a binary rhodium and cobalt catalyst depends on the degree of formation of bimetallic $RhCo_3$ clusters on SiO_2. The formation of $RhCo_3$ seems to be remarkably influenced by the use of precursors. The combination of the carbonyl clusters $Rh_4(CO)_{12}$ and $Co_2(CO)_8$ may be the best, which favorably yields $RhCo_3$ clusters on the surface by thermal decarbonylation under H_2, whereas the use of the inorganic salts $RhCl_3$ and $Co(NO_3)_2$ results in the formation of $RhCo_3$ clusters on the surface only to a very small extent. In this regard, a detailed spectroscopic characterization on the formation of $RhCo_3$ clusters from different rhodium and cobalt precursors for hydroformylation catalysts is now in progress.

In the current work, the chlorine-containing inorganic compound $RhCl_3$ was used as a precursor instead of $Rh(NO_3)_3$ to prepare a Rh/SiO_2 and some $(Rh + Co)/SiO_2$ catalysts. The presence of chlorine in Rh/SiO_2 catalysts is known to exert an important detrimental influence on the catalytic properties toward oxygenated products from CO hydrogenation and olefin hydroformylation [32,33]. According to a recent study of Gloor et al. by EXAFS, a Rh/SiO_2 catalyst prepared from $[Rh(NH_3)_5Cl]Cl_2$ via calcination and reduction at 673 K is still not free of chlorine yet and the remaining chlorine atoms are in contact with Rh atoms [18]. Similarly, not all chlorine atoms could be removed despite that our catalysts prepared from $RhCl_3$ have undergone calcination at 673 for 5 h and reduction at 623 K for 2 h. However, this vestige of chlorine seems to play a negligible role in diminishing the hydroformylation activity of Rh/SiO_2, by comparison of the catalytic results of the catalysts derived from $Rh_4(CO)_{12}$ and prepared from $RhCl_3$ in Table 1. Also these two catalysts have much the same dispersion of metallic rhodium particles on SiO_2 [34]. When $Rh_4(CO)_{12}$ was chosen in place of $RhCl_3$ to make $[Rh_4(CO)_{12} + Co(NO_3)_2)/SiO_2$, the resulting catalyst only exhibited a very slight increase in hydroformylation activity compared to the $[RhCl_3 + Co(NO_3)_2]$-derived catalyst [35]. In addition, we observed that coimpregnation of chlorine-containing $[Rh(CO)_2Cl]_2$ and $Co_2(CO)_8$ on SiO_2 followed by reduction at 623 K led to equivalent excellent catalytic performances to those of the bimetallic catalyst $RhCo_3/SiO_2$ derived from $RhCo_3(CO)_{12}$ [35]. There was no negative effect on both the activity and the selectivity of $RhCo_3/SiO_2$ in ethylene hydroformylation by use of $[Rh(CO)_2Cl]_2$. These findings could allow us to account for the nature and significance of the enhanced hydroformylation activities to different extent over the binary rhodium and cobalt catalysts studied. The different behaviors of metal carbonyls and metal salts on the surfaces with respect to the formation of supported bimetallic catalysts, are far from being understood and deserve to be explored.

In summary, this work has shown a successful preparative approach to bimetallic supported $RhCo_3$ cluster catalysts from monometallic carbonyl clusters by coimpregnation, based on the similarity of the catalytic properties in ethylene hydroformylation with those of the $RhCo_3(CO)_{12}$-derived $RhCo_3/SiO_2$ catalyst. The observed considerably high catalytic activities suggest that bimetallic $RhCo_3$ clusters can be effectively obtained from monometallic rhodium and cobalt carbonyls as well as from $RhCo_3(CO)_{12}$ on SiO_2 by thermal decarbonylation under H_2. Up to date, there is no success which appears concerning the production of a bimetallic cluster from two monometallic clusters on inorganic surfaces. By contrast, although binary SiO_2-supported catalysts prepared from inorganic rhodium and cobalt salts display significantly increased activity and improved selectivity compared to monometallic catalysts, the activity is much lower than that of the coimpregnated catalyst. This appears highly related to the slight formation of $RhCo_3$ in binary catalysts prepared from inorganic salts. The obtained catalytic results suggest that the enhancement in activity in hydroformylation relative to monometallic catalysts is ascribed to the bimetallic catalysis by $RhCo_3$ clusters rather than to the synergistic catalysis via dinuclear elimination by monometallic rhodium and cobalt sites.

Acknowledgements

The author is grateful to the Chinese Academy of Sciences for supporting this research project.

References

[1] J.H. Sinfelt, J. Catal. 23 (1973) 308.
[2] R.M. Laine, J. Mol. Catal. 14 (1982) 137.
[3] M. Ichikawa, J. Catal. 59 (1979) 67.
[4] M. Ichikawa, Proc. 5th Int. Symp. on Relations between Homogeneous and Heterogeneous Catalysis, 1986, p. 819.
[5] A. Fukuoka, L.-F. Rao, N. Kosugi, H. Kuroda, M. Ichikawa, Appl. Catal. 50 (1989) 295.
[6] A. Fukuoka, T. Kimuru, N. Kosugi, H. Kuroda, Y. Minai, Y. Sakai, T. Tominaga, M. Ichikawa, J. Catal. 126 (1990) 434.
[7] A. Trunschke, H.-C. Bottcher, A. Fukuoka, M. Ichikawa, H. Miessner, Catal. Lett. 8 (1991) 221.
[8] L. Alvila, T.A. Pakkanen, T.T. Pakkanen, O. Krause, J. Mol. Catal. 75 (1992) 333.
[9] T. Shido, T. Okazaki, N.A. Ulla, T. Fujimoto, M. Ichikawa, Catal. Lett. 17 (1993) 97.
[10] F.-S. Xiao, M. Ichikawa, J. Catal. 147 (1994) 578.
[11] L. Huang, A. Liu, Y. Xu, J. Mol. Catal. A, in press.
[12] L. Huang, Y. Xu, Catal. Lett. 40 (1996) 203.
[13] L. Huang, J. Mol. Catal. A 112 (1996) 69.
[14] S. Martinengo, G. Giordano, P. Chini, Inorg. Synth. 20 (1980) 209.
[15] S. Martinengo, P. Chini, V.G. Albano, F. Cariati, J. Organomet. Chem. 59 (1973) 379.
[16] A. Theolier, A.K. Smith, M. Leconte, J.M. Basset, G.M. Zanderighi, R. Psaro, R. Ugo, J. Organomet. Chem. 191 (1980) 201.
[17] R.L. Schneider, R.F. Howe, K.L. Watters, Inorg. Chem. 23 (1984) 4593.
[18] A.P. Gloor, R. Prins, J. Am. Chem. Soc. 98 (1994) 9865.
[19] H. Ming, B.G. Baker, Appl. Catal. A: General 123 (1995) 23.
[20] M.K. Niemela, A.O.I. Krause, T. Vaara, J. Lahtinen, Topics. Catal. 2 (1995) 45.
[21] H.F.J. van't Blik, J.M. Niemantsverdriet, Appl. Catal. 10 (1984) 155.
[22] L. Huang, Y. Xu, Kinet. React Catal. Lett., in press.
[23] D.G. Gastner, P.R. Watson, I.Y. Chan, J. Phys. Chem. 94 (1990) 819.
[24] A. Lapidus, A. Krylova, V. Kazanskii, V. Borovkov, A. Zaitsev, J. Rathousky, A. Zukal, M. Jancalkova, Appl. Catal. 73 (1991) 65.
[25] D.L. Hunter, S.E. Moore, P.E. Garrou, R.A. Dubois, Appl. Catal. 199 (1992) 281.
[26] M. Marchionna, G. Longoni, J. Mol. Catal. 35 (1986) 107.
[27] M. Hidai, A. Fukuoka, Y. Koyasu, Y. Uchida, J. Mol. Catal. 35 (1986) 29.
[28] P. Andrianary, G. Jenner, J. Organomet. Chem. 322 (1987) 89.
[29] Y. Ichii, M. Sato, H. Matsuzaka, M. Hidai, J. Mol. Catal. 54 (1989) L13.
[30] L. Alvila, T.A. Pakkanen, T.T. Pakkanen, O. Krause, J. Mol. Catal. 71 (1992) 281.
[31] K. Takeuchi, T.-a. Hanaoka, T. Matsuzaki, Y. Sugi, S. Ogasawara, Y. Abe, T. Misono, Catal. Today 20 (1994) 423.
[32] B.J. Kip, F.W.A. Dirne, J. van Grondelle, R. Prins, Appl. Catal. 25 (1986) 43.
[33] S.S.C. Chuang, G. Srinivas, A. Mukherjee, J. Catal. 139 (1993) 490.
[34] L. Huang, unpublished result.
[35] L. Huang, J. Mol. Catal. A, submitted for publication.