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Temperature-programmed reduction study of chromium oxide supported on zirconia and lanthana–zirconia

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Abstract

Temperature-programmed reduction (TPR) has been applied to study the reduction behavior of chromium oxide supported on pure zirconia and on lanthana-containing zirconia. The results revealed influences of support nature and chromium loading on the state of the supported chromium oxide. With catalysts containing lanthana and only low amounts of chromium, the decrease of the chromium oxidation state during TPR corresponded to the reduction of Cr^{6+} to Cr^{3+}. With lanthana-free catalysts, lower changes of oxidation state have been found, hinting on thermal instability of higher valent chromium species during thermal catalyst pretreatment. Chromium oxide supported on pure zirconia is reduced at temperatures between 340 and 370°C and is not quantitatively reoxidized by an oxygen treatment. Chromium oxide on lanthana–zirconia is reduced at higher temperatures between 370 and 415°C and is completely reoxidable at Cr loadings $\leq$4.0 wt.%. The results suggest that lanthana strengthens the interaction between the zirconia surface and chromium species and, therefore, stabilizes a dispersed state of chromium species. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Temperature-programmed reduction; Chromia; Chromia–zirconia; Lanthana; Reoxidation

1. Introduction

Chromia supported on alumina, silica or titania is known to catalyze a wide range of industrially important reactions, e.g. oxidation reactions, polymerizations, hydrogenation–dehydrogenation reactions, aromatization of C_{6+} paraffines or $DeNO_x$ [1–4]. Recently also, chromia supported on pure or modified zirconia has been investigated as catalysts, in particular, for the dehydrogenation and aromatization of hydrocarbons [4–7]. Lanthana proved to be a beneficial component in zirconia supported chromium oxide as a catalyst for the selective aromatization of C_{6+} paraffines [7]. One reason of the obvious versatility of supported chromium oxides as catalysts is certainly the variability of the chromium oxidation state and of the aggregation state of chromium species, with these properties being strongly dependent on Cr loading, treatment conditions as well as on the nature of the support [2,3]. Therefore, investigations of these properties are desirable. Besides spectroscopic methods [2,3], temperature-programmed reduction (TPR) has proved to be an useful technique for the study of the redox behavior of supported catalyst components [8]. TPR has already been applied for the study of chromia catalysts, too. However, most of the published TPR studies focus on unsupported chromia or on chromia supported on alumina, silica or titania [8–13], and not yet on chromia supported on zirconia.

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With our paper, we investigated the redox behavior of catalysts consisting of chromium oxide supported on pure zirconia and on lanthana modified zirconia by means of TPR, hoping that this method would deliver new insight into the state of chromium species and into the beneficial role of the lanthana component in the chromium oxide/lanthana–zirconia aromatization catalysts.

2. Experimental

2.1. Catalyst preparation

Catalyst samples were prepared by impregnating zirconium hydroxide based supports, i.e. amorphous zirconium hydroxide pure or doped with 7.0 wt.% La_2O_3 (MEL, UK) with an aqueous solution of $(NH_4)_2CrO_4$. The supports were dried in air at 120°C for 12 h and then immersed in solutions containing the appropriate amounts of $(NH_4)_2CrO_4$ to yield samples loaded with 0.5, 1.0, 4.0 and 8.0 wt.% Cr. By ammonia addition, the solution was kept at a pH of 10. Under stirring, the excess water was slowly evaporated at 50–60°C. The products obtained were dried at 120°C for 12 h and calcined in air at 600°C for 4 h, resulting in chromium oxide supported on zirconia (Z) (CrO_x/ZrO_2) and on lanthana–zirconia (LZ) ($CrO_x/La_2O_3–ZrO_2$). The catalyst samples were kept dry over zeolite till further use.

Below, the catalyst samples will be denominated by their Cr content and support nature. Thus, 0.5CZ and 0.5CLZ indicate 0.5% Cr on Z and 0.5% Cr on LZ support, respectively.

As reference substances, the chromium-free Z and LZ supports were dried and calcined under the above conditions, too.

2.2. Temperature-programmed reduction

The TPR experiments have been performed using a homemade gas flow system, including a fixed-bed quartz reactor and a gas analyzer unit. In this system, samples can be pretreated in several gas flows at desired conditions. The catalyst samples, with a particle size of 0.3–0.8 mm and calcined at 600°C for 4 h, were placed into the reactor and heated in an argon flow at 300°C for 1 h before the TPR experiment. After cooling the sample in an argon flow to 50°C, the first TPR run, TPR1, was carried out in 5.17% hydrogen in argon flow at a heating rate of 10 K/min and a gas flow rate of 15 ml/min. Optimum sample weights had been estimated according to the equation by Monti and Baiker [14]. TPR1 was finished by an isothermal period of 0.5 h at 750°C. Hydrogen consumed was monitored by a calibrated thermal conductivity detector (GOW-MAC Instruments). The samples, having been reduced during TPR1, were reoxidized in situ by 20% oxygen in helium flow at 600°C for 1 h. Afterwards, a second TPR run, TPR2, was carried out under the conditions of TPR1.

From the TPR signal intensities, changes of the oxidation state $(n - m)$, defined by

$$Cr^n + \left[\frac{n-m}{2}\right]H_2 \Leftrightarrow Cr^m + (n-m)H^+ \qquad (1)$$

have been calculated.

3. Results

3.1. TPR1 and TPR2 of CZ catalysts

TPR1 profiles of the CZ samples are shown in Fig. 1a. The TPR profile of the chromium-free support, Z, is shown, too. It demonstrates a hydrogen uptake of the zirconia support at 574°C. For the CZ catalysts, two resolved TPR signals can be observed, the first signal at $T_{max1} = 342–369°C$ and the second one at

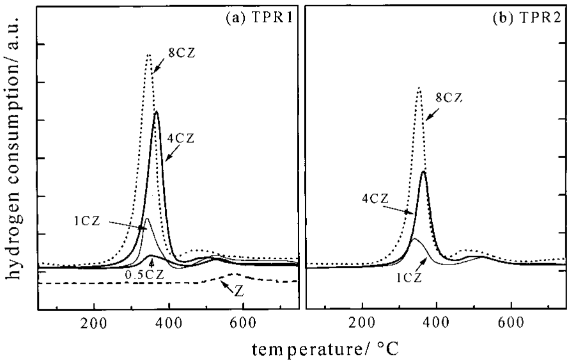

Fig. 1. TPR profiles of Cr/ZrO_2 (CZ) catalysts; (a) TPR1, (b) TPR2.

$T_{max2} = 473–533°C$. The intensity of the first peak increases with increasing Cr loading, that of the second peak remains almost unchanged. With CZ catalysts, a clear dependence of T_{max1} on the Cr content could not be observed. The position of T_{max2} is slightly shifted to lower temperatures with increasing Cr content.Reoxidation of 1CZ, 4CZ and 8CZ was followed by TPR2 experiments, the profiles of which are given in Fig. 1b. Apparently, the TPR2 profiles do not significantly differ from the TPR1 profiles and show TPR signals at almost the same temperatures, namely at $T_{max1} = 344–368°C$ and at $T_{max2} = 469–525°C$. As with TPR1, increasing Cr content only increases the intensity of the first TPR2 peak but not of the second one. Also, T_{max2} slightly shifts to lower values at higher Cr contents. As a further observation, the intensities of the first TPR2 peaks are significantly lower than those of the first TPR1 peaks. Fig. 2 depicts the dependence on the Cr content of hydrogen consumed within the first TPR1 and TPR2 peaks. As already mentioned, increasing Cr content only increases the intensity of the first TPR peaks, but leaves that of the second ones practically unchanged. Moreover, with Cr contents between 0 and 4.0 wt.%, a linear correlation between Cr loading and hydrogen consumption under the first TPR peaks is observed. The hydrogen consumptions are lower than expected for $(n - m) = 3$, which would correspond to a total reduction of Cr^{6+} to Cr^{3+}. Furthermore, Fig. 2 demonstrates that the deviations of the intensities of the first peak from a total reduction of Cr^{6+} to Cr^{3+} increase with higher Cr loading. Moreover, the hydrogen consumption under the first peak of TPR2 is always lower than that of TPR1.

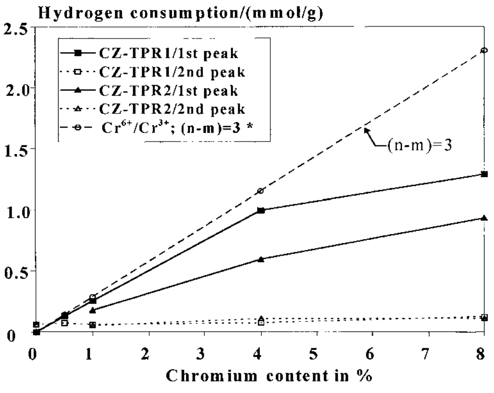

Fig. 2. Quantitative TPR results of CZ catalysts; (*) hydrogen consumption calculated according to Eq. (1) with $n = 6$ and $m = 3$.

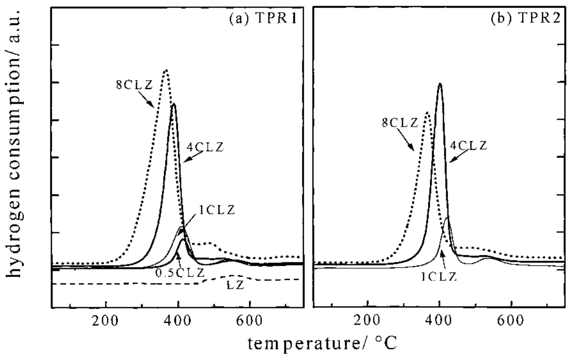

Fig. 3. TPR profiles of $Cr/La_2O_3–ZrO_2$ (CLZ) catalysts; (a) TPR1, (b) TPR2.

3.2. TPR1 and TPR2 of CLZ catalysts

Fig. 3a shows the TPR1 profiles of the lanthana-modified CLZ catalysts. As in the case of the CZ catalysts, the CLZ catalysts consume hydrogen under two TPR peaks and increasing Cr loading increases the intensities of the respective first peaks. Moreover, their T_{max1} shifts to lower values, in detail from 415 to 368°C. The second TPR1 peaks of 0.5CLZ and 1CLZ samples are found at 556 and 542°C, respectively. With 4CLZ and 8CLZ, their second TPR1 peaks are further shifted to lower temperatures and deformed at the same time, resulting in shoulders at 542 and 471°C. The TPR profile of the LZ support exhibits an hydrogen consumption peak in the same temperature range, at 554°C.

The TPR2 profiles of 1CZL, 4CLZ and 8CLZ are shown in Fig. 3b. The TPR2 spectra do not essentially differ from the TPR1 profiles in Fig. 3a. In Fig. 4, the amounts of hydrogen consumed under both the peaks measured by TPR1 and TPR2 are plotted versus the Cr loading. Analogously to the CZ catalysts, increasing Cr content increases the intensity of the first hydrogen consumption peaks, but leaves that of the second ones nearly unchanged. Also here, the amounts of hydrogen consumed deviate to some degree from those ones expected in case of a total reduction of Cr^{6+} to Cr^{3+}. Unlike the CZ catalysts, the TPR2 results on CLZ samples do not significantly differ from TPR1, except for the sample 8CLZ.

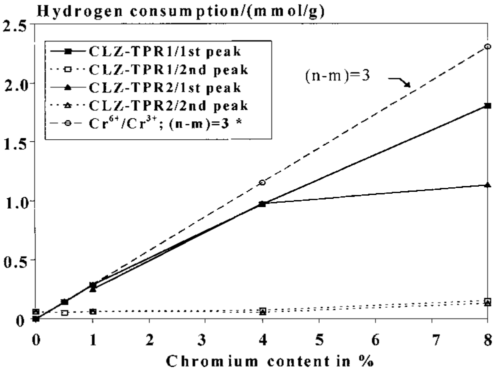

Fig. 4. Quantitative TPR results of CLZ catalysts; (*) hydrogen consumption calculated according to Eq. (1) with $n = 6$ and $m = 3$.

Quantitative results of TPR1 and TPR2 on the CZ and CLZ samples, consisting of T_{max} values, amount of hydrogen consumed under the first and second peak as well as $(n-m)$ values calculated from the first peak are summarized in Table 1.

The main observations to be taken from Figs. 1–4 and Table 1 are the following:

- The chromium-free supports, Z and LZ, cause hydrogen uptake signals at 574 and 554°C, respectively.
- Both the CZ and CLZ catalysts give two separate TPR signals. With CZ, these signals appear at $T_{max1} = 340$–$370°C$ and $T_{max2} = 470$–$533°C$, with CLZ at $T_{max1} = 370$–$415°C$ and $T_{max2} = 490$–$556°C$. The temperature maxima shift more or less to lower temperatures as the Cr loading is increased. Increasing Cr content increases the intensity of the first TPR peak, but does not significantly influence the intensity of the second one.
- The oxidation state change $(n-m)$ reaches values near 3 with catalysts of low chromium content and in the presence of lanthana. With higher chromium loading and in the absence of lanthana, considerable deviations of $(n-m)$ from the value 3 were observed.
- With the lanthanum-free CZ catalysts, the hydrogen consumption during the second TPR run TPR2, i.e. after reoxidation, has been generally lower than the hydrogen consumption during the

Table 1
Summarized TPR results on CZ and CLZ catalysts

Catalysts	%Cr	T_{max1} (°C)	H_2 consumption, 1st peak (mmol/g)	$n-m$[a]	T_{max2} (°C)	H_2 consumption, 2nd peak (mmol/g)
TPR1						
Z	0				574	0.0605
CZ	0.5	350	0.1310	2.72	533	0.0628
	1.0	342	0.2574	2.68	523	0.0594
	4.0	369	0.9971	2.59	503	0.0758
	8.0	350	1.2933	1.68	473	0.1263
LZ	0				554	0.0558
CLZ	0.5	415	0.1423	2.96	556	0.0532
	1.0	410	0.2874	2.99	542	0.0621
	4.0	390	0.9697	2.52	522	0.0691
	8.0	368	1.8063	2.35	487	0.1546
TPR2						
CZ	1.0	344	0.1796	1.87	525	0.0523
	4.0	367	0.596	1.55	505	0.11
	8.0	350	0.9353	1.22	469	0.1118
CLZ	1.0	420	0.2352	2.63	537	0.0641
	4.0	403	0.9749	2.53	522	0.053
	8.0	368	1.1353	1.48	500	0.1317

[a] The $(n-m)$ values were calculated from hydrogen consumed under the first TPR peak.

foregoing TPR1 run. With the lanthana-containing CLZ catalysts, except 8CLZ, the TPR2 hydrogen consumptions do not significantly differ from TPR1.
- With identical Cr contents, $T_{\max 1}$ of CLZ catalysts is always higher than $T_{\max 1}$ of CZ catalysts.

4. Discussion

In literature, the redox behavior of supported chromium has been found to depend on the Cr loading, on the support nature as well as on treatment conditions [2,3]. For zirconia supported chromia, the existence of Cr^{6+} and Cr^{5+} as well as of some Cr_2O_3 has been detected after calcination at 550–800°C by several methods [2–6,15–18]. The higher valent Cr species are believed to be anchored by esterification with support surface hydroxyl groups, resulting in real surface species. Beyond a saturation coverage with such surface species, i.e. beyond a certain chromium content, which is determined by the nature of the support, excess chromium species are converted to bulky Cr_2O_3 by calcination at high temperature. By treating at 120–600°C with a reducing agent, chromium oxidation states of +6 or +5 have been reported to be reduced mainly to Cr^{3+} [2–6,15–18], but partly also to Cr^{4+} [5] or to Cr^{2+} [4,15].

Our aim was to investigate the catalyst system $CrO_x/La_2O_3–ZrO_2$, which had proved to be an interesting and very selective dehydrocyclization catalyst [7], by means of TPR, looking for insight in the oxidation and dispersion state of the chromium oxide component as well as on the role of lanthana within this catalyst system.

TPR spectra can give, by the $T_{\max}$ positions of their hydrogen consumption signals, qualitative information on the reduction behavior of the sample under investigation and, by the intensity of the signals, quantitative information on the amount of reducible species. In case of supported substances, the results can allow to calculate the change of the oxidation state of a supported species during its reduction. If TPR experiments are included into the investigations with samples reoxidized after a first TPR run and experiments with varying content of the supported species, the results can give valuable information on changes of the chemical state or of the dispersion state during the reduction and can allow to differentiate between hydrogen consumption of a reducible species or of the support, respectively.

All the TPR1 profiles of CZ and CLZ catalysts shown in Figs. 1 and 3 exhibit two hydrogen consumption stages appearing as two peaks. As shown in Table 1 and Figs. 2 and 4, only the intensities of the first TPR peak, but not of the second one, depend on the Cr loading. This should mean that only the first TPR peak can be assigned to the reduction of supported Cr species. Hence, one should exclude that the second peak is due to a further reduction of Cr^{3+} formed under the first peak into Cr^{2+} [9,19,20] or to a separate reduction of another higher valent Cr species at higher temperature [4,10,15]. The range of the $T_{\max 2}$ temperatures is near the hydrogen uptake temperature of the pure zirconia Z. Hence, with high probability the second peak is to be assigned to a hydrogen uptake of the zirconia support, already observed with pure zirconia [21–23]. The second peak shifts towards lower $T_{\max 2}$ values with increasing chromium content. This can perhaps be explained by an activation of hydrogen by chromium oxide species, facilitating the hydrogen uptake of the zirconia supports.

With the catalysts containing only 0.5 or 1 wt.% Cr, especially with the samples additionally containing lanthana, the amounts of hydrogen consumed within the first TPR peak, which is assigned to chromium reduction, correspond to $(n - m)$ values near 3. This is most probably explained by the assumption that the initial Cr oxidation state had been predominantly Cr^{6+}, which is reduced to Cr^{3+} during TPR. At higher chromium contents, the $(n - m)$ values of both the CZ and CLZ catalysts are more or less lower than 3, i.e. lower than expected for a total reduction of Cr^{6+} to Cr^{3+}. This deviation could be a hint on an incomplete reduction of Cr^{6+} [18]. More probably, however, this can be explained by the assumption mentioned above that an excess part of Cr^{6+}, which could not be chemically stabilized on the support surface, is converted into lower valent chromium already by the preceding calcination at 500–600°C, i.e. before TPR [3,6,18].

The $(n - m)$ values of the CLZ samples are generally higher than those of the CZ samples, see Table 1. This can most clearly be seen by comparing the samples 8CZ and 8CLZ. In terms of the above model of the co-existence of stabilized surface species and thermally instable bulky excess species before the reduction, this finding indicates that the surface of the LZ support contains a higher number of the stabilizing surface groups, leading to a higher capacity for the more stable chromium surface species. The shift of $T_{\max 1}$ to lower temperatures with increasing Cr loading can be explained by means of this model, too. Increasing chromium content leads beyond the saturation limit to more bulky and non-stabilized chromium species which are reduced at lower temperatures.

A feature distinguishing the TPR1 profiles of the CLZ catalysts from those of the CZ catalysts are the $T_{\max 1}$ values. The values of the CLZ samples are always higher than the corresponding values of the CZ samples (with the same Cr loading). This suggests that not only a higher number of Cr^{6+} species can be stabilized on the lanthana containing support, but that lanthana also strengthens the interaction between higher valent chromium species and the support surface. Such a stronger interaction means a stabilization of Cr^{6+} species and results in higher reduction temperatures. The more detailed mode of action of the lanthana addition is not yet clear.

According to former works, Cr^{3+} species formed on supports after reduction proved to be reoxidable to Cr^{6+} to some extent [3,13,18]. This behavior may be of interest, if, for example, an oxidative regeneration of Cr based catalysts is necessary, as is usual with hydrocarbon conversion reactions, or if such catalysts shall be applied in deep oxidation reactions, which require a steady oxidation–reduction cycle of the catalytically active element [24]. However, on different supports different types of supported Cr can exist [2,10], which differ in their degree of reoxidability. Therefore, it was of interest to investigate this problem also with our catalysts, taking the TPR2 experiments as an appropriate tool.

With the TPR2 profiles of the CZ catalysts, Fig. 1b, Fig. 2 and Table 1, the intensities of the first TPR peak have been always lower than with the corresponding TPR1 spectra. But, in case of the CLZ samples, Fig. 3 as well as Fig. 4 and Table 1, the intensities of the first TPR peak are almost identical with TPR2 and TPR1, with the exception of the high chromium content sample 8CLZ. This indicates that the reduction of the lanthanum-containing CLZ catalysts preferably results in Cr^{3+} species, the nature of which enables a reoxidation. Having in mind that the TPR1 results on the lanthanum-containing CLZ samples are best explained by a lanthana induced stabilization of Cr^{6+} species, which are surface dispersed on a molecular level, the reoxidable Cr^{3+} should be of high dispersion. This is in line with the picture that high chromium content and low chromium-support interaction (CZ samples) result in bulky chromia already during high temperature calcination. According to the results by Zaki et al. for alumina supported chromia [15], those chromium species, which can reversibly be reduced and reoxidized, may be polychromates. The anchoring of polychromate species on zirconia was actually evidenced by UV–VIS diffuse reflectance spectroscopy and Raman spectroscopy [2,3,17].

5. Conclusions

- The results of the TPR study on chromium oxide/zirconia and chromium oxide/lanthana–zirconia can be explained in terms of a model, which assumes the stabilization of Cr^{6+} species on the surface of the zirconia support and, beyond a saturation coverage, a co-existence of such surface stabilized and therefore molecularly dispersed Cr^{6+} with non-stabilized bulky Cr^{6+} species. The stabilized Cr^{6+} species are reduced at relatively high temperature to dispersed Cr^{3+} species, which are reoxidable. A part of the non-stabilized species can already thermally decompose during calcination, resulting in bulky and non-reoxidable chromia. The rest of them is reduced at lower temperatures resulting in Cr^{3+} species, which are not quantitatively reoxidable.
- Lanthana increases the capacity of the support for the formation of surface stabilized Cr^{6+}, leading to a larger portion of highly dispersed Cr^{3+} during reduction. This ability of lanthana might be one of the reasons for its beneficial role in chromium oxide/lanthana–zirconia aromatization catalysts.

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References

[1] Ch.P. Poole Jr., D.S. McIver, Adv. Catal. 17 (1967) 223.

[2] B.M. Weckhuysen, I.E. Wachs, R.A. Schoonheydt, Chem. Rev. 96 (1996) 3327.

[3] B.M. Weckhuysen, R.A. Schoonheydt, Catal. Today 51 (1999) 223.

[4] V. Indovina, Catal. Today 41 (1998) 95.

[5] K. Arata, M. Hino, H. Matsuhashi, Appl. Catal. 100 (1993) 19.

[6] J.R. Sohn, S.G. Ryu, H.W. Kim, J. Mol. Catal. 135 (1998) 99.

[7] H. Lieske, D.L. Hoang, German patent DE-OS 196 12 000.

[8] N.W. Hurst, S.J. Gentry, A. Jones, B.D. McNicol, Catal. Rev. 24 (1982) 23.

[9] W. Grünert, W. Saffert, R. Feldhaus, K. Anders, J. Catal. 99 (1986) 149.

[10] M.I. Zaki, N.E. Fouad, G.C. Bond, S.F. Tahir, Thermochim. Acta 285 (1996) 176.

[11] J. Engweiler, J. Nickl, A. Baiker, K. Köhler, C.W. Schläpfer, A. von Zelewsky, J. Catal. 145 (1994) 141.

[12] L.I. Ilieva, D.H. Andreeva, Thermochim. Acta 265 (1995) 223.

[13] M.I. Zaki, M.A. Hassan, N.E. Fouad, Appl. Catal. A: General 171 (1998) 315.

[14] D.A.M. Monti, A. Baiker, J. Catal. 83 (1983) 323.

[15] A. Cimino, D. Cordischi, S. de Rossi, G Ferraris, D. Gazzoli, V. Indovina, M. Occhiuzzi, M. Valigi, J. Catal. 127 (1991) 761.

[16] T. Yamaguchi, M. Tan-no, K. Tanabe, in: G. Poncelet, P.A. Jacobs, P. Grange, B. Delmon (Eds.), Preparation of Catalysts V, Elsevier, Amsterdam, 1991, pp. 567–574.

[17] D.S. Kim, I.E. Wachs, J. Catal. 141 (1993) 166.

[18] J.R. Sohn, S.G. Ryu, Langmuir 9 (1993) 126.

[19] A. Hakuli, M.E. Harlin, L.B. Backman, A.O.I. Krause, J. Catal. 184 (1999) 349.

[20] B.M. Weckhuysen, R.A. Schoonheydt, J.-M. Jehng, I.E. Wachs, S.J. Cho, R. Ryoo, S. Kijistra, E. Poels, J. Chem. Soc. Faraday Trans. 91(18) (1995) 3245.

[21] C. Dall′Agno, A. Gervasini, F. Morazzoni, F. Pina, G. Strukul, L. Zanderighi, J. Catal. 96 (1985) 106.

[22] W.K. Jozwiak, React. Kinet. Catal. Lett. 30(2) (1986) 245.

[23] D.L. Hoang, H. Lieske, Catal. Lett. 27 (1994) 33.

[24] R. Prasad, L.A. Kenedy, A.E. Ruckenstein, Catal. Rev.-Sci. Eng. 26(1) (1984) 1.