

## Spillover hydrogen effect on amorphous hydrocracking catalysts

A.M. Stumbo, P. Grange and B. Delmon

*Unité de Catalyse et Chimie des Matériaux Divisés, Université Catholique de Louvain,  
Place Croix du Sud 2/ Bte 17, B-1348 Louvain-la-Neuve, Belgium*

Received 15 August 1994; accepted 15 December 1994

This work is a contribution to the understanding of the effect of spillover hydrogen in hydrotreating catalysts. Mixtures of sulfided CoMo/SiO<sub>2</sub> and an amorphous silica–alumina were studied. The hydrocracking of diphenylmethane was used as a test reaction. The addition of CoMo/SiO<sub>2</sub> to silica–alumina strongly increases the hydrocracking rate (by a factor between 4.5 and 8) and the OH–OD exchange (by a factor between 2.5 and 10 after a 20 h experiment). This is interpreted by the spillover of dissociated H<sub>2</sub> (or D<sub>2</sub>) onto the silica–alumina, with spillover hydrogen forming Brønsted sites and spillover deuterium exchanging with OH.

**Keywords:** spillover (hydrogen); amorphous silica–alumina (acidity); mechanical mixtures; hydrocracking; isotopic exchange

### 1. Introduction

Spillover has been defined as the phenomenon that involves the transport of an active species sorbed or formed on a first phase onto another phase that, under the same conditions, does not sorb or form the species. The active or “spillover” species on the second phase may react in some way, either with another sorbed species or with the second phase itself; it may also activate this second phase by creating or modifying catalytic sites [1]. Spillover seems to be of frequent occurrence, at least with supported metal catalysts [2].

Hydrocracking is a hydrotreating process that is receiving increasing attention due to its flexibility and the high yields of good quality middle distillates that can be obtained [3,4]. Hydrocracking catalysts possess two functions; they consist in general of a hydrogenation–dehydrogenation component (noble metals or transition metal sulfides) and an acidic support (silica–aluminas or zeolites). The distribution of the products formed depends critically upon the balance between these two components. Catalysts with high hydrogenation activity favor the formation of higher boiling point products, whereas those with relatively low hydrogenation activity compared to acidity yield products with higher branched paraffins content and less saturation of aromatics [4].

In the mechanism generally accepted to explain the hydrocracking reaction (the so-called “ideal hydrocracking”), an alkane is initially dehydrogenated to an olefin on the metal phase and then adsorbed on an acidic site, where it is converted to an alkylcarbenium ion. This one, probably after a rearrangement to a more stable form, will be cracked via a  $\beta$ -scission mechanism, forming a lighter olefin and an ion that are hydrogenated to the corresponding paraffins [5].

It has already been demonstrated that spillover hydrogen (Hsp) is important in several kinds of reactions of industrial interest like methanol synthesis [6] and hydrodesulfurization [7,8]. Some references in the literature [9–13] suggest that this could also be the case of hydrocracking:

Becker and co-workers [9], analyzing hydrocracking pilot plant experiments in industrial conditions, suggested that Hsp could be responsible for the higher resistance to deactivation shown by a mechanical mixture of NiO–MoO<sub>3</sub>/alumino-silicate and HNaY zeolite when compared to a Ni–Pd/HNaY catalyst.

Fujimoto and co-workers [10–13] developed a new method for upgrading heavy oils, producing high quality middle distillates with small hydrogen consumption, named transfer hydrocracking. Most of the oil is thermally cracked. The asphaltenes are adsorbed on the support (silica–alumina or activated carbon) and cracked or dehydrogenated, forming coke and hydrogen atoms. These hydrogen atoms migrate on the surface (reverse spillover) to reach supported metal particles (Ni, Mo or Fe) where they react with olefins, free radicals or sulphur compounds, or recombine, forming H<sub>2</sub>, which is desorbed into the gas phase.

The objective of this work is to investigate the influence of spillover phenomena on amorphous hydrocracking catalysts. In order to demonstrate the existence of spillover, the approach has been to use physically distinct phases, one carrying the generator of Hsp (or “donor”) and the other one the acidic component. Another originality of this work has been to use sulfide phases as donors, and an amorphous silica–alumina (instead of zeolites) as acidic phase. The donor was a CoMo/SiO<sub>2</sub> catalyst. Silica, a support with only a very weak acidity, has been chosen to avoid that the acidity of the support of the donor contribute significantly to total acidity and thus cause interferences with the reactions of the acidic phase. The Hsp effect will be revealed by the comparison between the activities of the pure phases and those measured for mechanical mixtures of both components in different proportions.

Diphenylmethane (DPM) has been chosen as a model molecule for the hydrocracking activity tests. The tests were performed in conditions representative of industrial hydrocracking: high temperature, high hydrogen pressure and presence of H<sub>2</sub>S.

Isotopic exchange (OH–OD) experiments, followed by FTIR measurements, were used to obtain direct evidence of the spillover phenomena. This technique had already been successfully used for this purpose in other systems like Pt mixed or supported on silica, alumina or zeolites [1]. Conner and co-workers [14] employed FTIR to follow the deuterium spillover from a point source (Pt/SiO<sub>2</sub>) situated at

the center of a silica disc. They observed a gradient of deuterium concentration as a function of the distance to the central point. The exchange was symmetrical around this point and the gradient decreased with time. If spillover phenomena were not involved, a gradientless exchange should have been observed.

## 2. Experimental

### 2.1. MATERIALS

The acidic phase was an amorphous commercial silica–alumina, Akzo LA-SHPV (surface area of 500 m<sup>2</sup>/g and pore volume of 1.3 ml/g), containing 12 wt% of Al<sub>2</sub>O<sub>3</sub>.

The precursors of the Hsp generator, a CoMo/SiO<sub>2</sub> catalyst containing 14 wt% of MoO<sub>3</sub> and 3% of CoO, was prepared by successive impregnation. Silica (Kali-Chimie AF-125, 130 m<sup>2</sup>/g) was first impregnated with an aqueous solution of cobalt acetate (Merck, ultra pure), followed by the impregnation with an aqueous solution of ammonium heptamolybdate (Merck, ultra pure). After each impregnation step the sample was dried overnight at 393 K and calcined at 673 K for 2 h.

### 2.2. PREPARATION OF THE MECHANICAL MIXTURES

A suspension in *n*-pentane (15 ml/g solid), containing both phases ground to sizes under 40 µm and mixed in the desired proportions was immersed in an ultrasonic bath for 5 min and submitted to vigorous mechanical agitation (3000 rpm) for 10 min. The *n*-pentane was evaporated at room temperature, under a flux of Ar and continuous magnetic stirring. After drying at 393 K overnight, the powder was pressed (10 ton/cm<sup>2</sup>), ground and sieved to obtain particles between 0.315 and 0.5 mm. The mechanical mixtures will be identified by their relative weight content of silica–alumina, named  $R_m$ , defined as

$$R_m = \frac{\text{wt\% SiO}_2\text{--Al}_2\text{O}_3}{\text{wt\% CoMo/SiO}_2 + \text{wt\% SiO}_2\text{--Al}_2\text{O}_3} \times 100.$$

### 2.3. CATALYTIC TESTS

The hydrocracking of diphenylmethane (DPM) was carried out in a continuous-flow tubular reactor. The liquid feed contained 29.5 wt% of DPM (Fluka, >99%), 70% of *n*-dodecane (Aldrich, >99%) and 0.5% of benzothiophene (Aldrich, 95%). The temperature was 673 K and the total pressure 50 bar. The liquid feed flowrate was 16.5 ml h<sup>-1</sup> and the H<sub>2</sub> flowrate 24 l h<sup>-1</sup> (STP). The catalytic bed consisted of 1.0 g of catalyst diluted with enough carborundum (Pro-labo, 0.34 mm) to reach a final volume of 4 cm<sup>3</sup>.

The catalysts were sulfided in situ before the catalytic tests with a mixture of  $\text{H}_2\text{S}$  (15 vol%) and  $\text{H}_2$  (100 ml/min) at 673 K for 2 h.

#### 2.4. H-D EXCHANGE

A Bruker IFS-88 Fourier-transform infrared spectrometer with a resolution of  $1\text{ cm}^{-1}$  was used to follow the isotopic exchange.

The samples were pressed in the form of wafers of about 13 mm diameter and sulfided in the same way as for the catalytic tests, followed by 2 h of heating at 673 K under vacuum (about  $10^{-3}\text{ Pa}$ ). The samples were cooled down to room temperature and kept under vacuum overnight. The temperature was then raised to 423 K and 80 kPa of deuterium (Air Liquide, N28) was admitted into the cell. Several spectra were taken at regular intervals. Before each measurement the sample was cooled down to room temperature.

The extent of exchange was measured by the total area of the OD bands situated between 2800 and  $2100\text{ cm}^{-1}$ . Corrections have been made to take into account the differences in weight and surface of the wafers.

### 3. Results and discussion

Fig. 1 shows the DPM conversion as a function of the silica–alumina content after 1 h of reaction and at the steady-state. The dashed lines represent the sum of the properly weighted individual contributions of the pure phases ( $\text{CoMo}/\text{SiO}_2$  and silica–alumina), calculated supposing a zero order reaction and the absence of

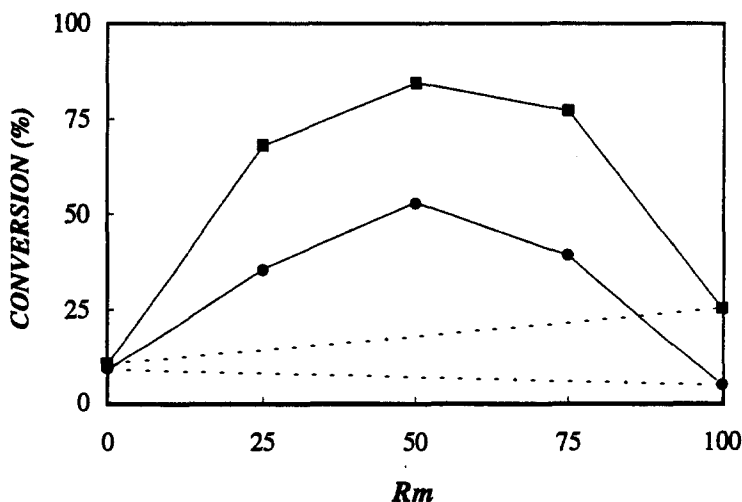


Fig. 1. Diphenylmethane conversion as a function of mechanical mixture composition, after 1 h (■) and at the steady-state (●).

interactions of any kind between these phases. A very important synergetic effect is observed. The hydrocracking activity of all mechanical mixtures is higher than these calculated values by a factor of about 4.5, 8 and 7 for the mixtures containing 25%, 50% and 75 wt% of silica–alumina, respectively (values at the steady-state). The maximum of conversion is situated around 50 wt% of silica–alumina. Benzene and toluene are the main reaction products. Small amounts of polymerized by-products have been found but no cyclohexane or partially hydrogenated compounds (like cyclohexylphenylmethane) have been detected.

Hattori and co-workers [15], studying DPM hydrocracking over a large variety of catalysts, found three possible routes for this reaction: (i) via carbocation intermediates, formed on acidic sites, producing benzene and toluene (and diphenylethane as polymerization by-product); (ii) through hydrogenation of both aromatic rings, which is followed by the cleavage of the C–C bond, producing cyclohexane and methylcyclohexane, which undergo further cracking to produce methane; (iii) via simple cleavage of the C–C bond, forming benzene and toluene. The main products of Mo/SiO<sub>2</sub> and Ni–Mo/Al<sub>2</sub>O<sub>3</sub> catalysts, tested under high temperature (673 K), moderate H<sub>2</sub> pressure (0.1 MPa) and presence of H<sub>2</sub>S (3 vol%) were benzene and toluene, with traces of polymerized products. No methane or hydrogenated products have been found. A silica–alumina, tested under similar conditions (673 K and 2–4 MPa), but in the absence of H<sub>2</sub>S, produced benzene and toluene and large amounts of polymerized products. Shimada and co-workers [16,17] studied DPM hydrocracking on sulfided supported Mo/SiO<sub>2</sub> catalysts (673 K and 6.9 MPa) and found mainly benzene and toluene and very small amounts of hydrogenated products.

Those results suggest that the previous hydrogenation of the aromatic rings is not necessary to DPM hydrocracking and that route (i), i.e., carbocation formation on acidic sites, is the main reaction pathway.

Some previous works have shown that protonic acidic sites can be generated on many kinds of solids by the action of Hsp, enhancing their activity for a variety of acid catalyzed reactions:

Teichner and co-workers [18], studying the hydroconversion of *n*-heptane on H-erionite, have shown that the spillover activation of that zeolite by a Pt/Al<sub>2</sub>O<sub>3</sub> catalyst (withdrawn after the activation) increases substantially its activity without changing the selectivity (propane and *n*-butane are produced in similar proportions), probably through an increase of the number of acid and hydrogenating sites. When the Hsp is continuously supplied by mechanically mixed or impregnated platinum, the selectivity is modified and propane becomes the major product. It has been demonstrated that this is related to the Hsp action and not merely to the presence of platinum.

Teichner and co-workers [19] also observed the generation of acidic sites on silica. After being treated with hydrogen at 400°C, in the presence of Pt/Al<sub>2</sub>O<sub>3</sub>, silica showed catalytic activity for benzene cracking and cyclohexadiene hydrogenolysis, two typical acid catalyzed reactions.

Hattori [20] observed an enhancement of the butane skeletal isomerization over  $\text{Pt}/\text{SO}_4^{2-}\text{-ZrO}_2$  under different hydrogen pressures. This has been explained by the spillover of H atoms from metallic platinum onto the support. An H atom releases an electron to a Lewis site and the  $\text{H}^+$  formed, stabilized by the oxygen atom near this site, can act as an active site for the reaction. IR spectra of adsorbed pyridine showed that Brønsted sites are created on heating in the presence of hydrogen, with a concomitant decrease in the amount of Lewis sites.

Nakamura and co-workers [21] found that mechanical mixtures of  $\text{CoMo}/\text{Al}_2\text{O}_3$  and Fe-HY showed high toluene disproportionation activity, in the presence of  $\text{H}_2\text{S}$  and high hydrogen pressure, while the isolated components showed low activity. Their interpretation was that Hsp, generated on the metals present in both components, migrates to the zeolite surface as a proton and promotes the acid catalyzed reaction. They have also found that Fe-HY showed higher activity for the hydrocracking of a heavy oil (Kuwait atmospheric residue) than a conventional HDS catalyst or a USY zeolite alone.

Likewise, the ability of the unsupported or supported transition metal sulfides to adsorb and dissociate molecular hydrogen from the gas phase is well known (refs. [7,8,22–25] and references therein). The species thus formed could then migrate (spillover) from the sulfides to the silica–alumina and create new protonic acidic sites, increasing the hydrocracking activity.

Another notorious effect of the Hsp is the capacity to diminish the deactivation caused by coke deposition via some reaction with its precursors, very likely a hydrogenolysis [26–28].

As shown in fig. 2, the pure silica–alumina, where there is no source of Hsp, loses about 80% of its activity before reaching the steady-state, which takes approximately 6 h. The mechanical mixtures reach the same condition after about 16 h,

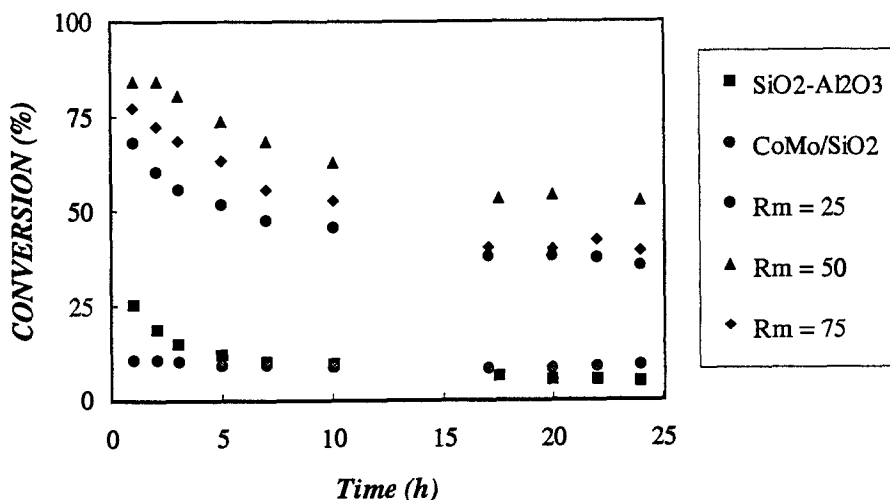


Fig. 2. Diphenylmethane conversion as a function of time.

losing only 40–50% of their activity. Likewise, the pure CoMo/SiO<sub>2</sub> catalyst, where the spillover source is closer to the few active (weak acid) sites present on SiO<sub>2</sub>, is deactivated only very slowly and loses no more than 15% of its activity within the same period.

The reproducibility of the isotopic exchange experiments has been checked. Fig. 3 shows the results obtained in four different experiments with the same mechanical mixture (50 wt% silica–alumina). There is no significant variation between the four series, showing that the quantitative measurements of the OD bands are quite reliable.

Fig. 4 shows the intensities of the OD bands plotted against the composition of the mechanical mixtures. There is a striking similitude with fig. 1: as in the catalytic tests with DPM reactant, the intensities of the OD bands of the mechanical mixtures are significantly higher (by a factor between 2.5 and 10, after 20 h) than the sum of the individual contributions of the pure phases when investigated separately.

The interpretation of the deuterium exchange results needs some care. Indeed, species like HDO or D<sub>2</sub>O may be responsible for a non-spillover exchange mechanism [29]. It has also been proposed that they could be formed by the reaction between oxygen traces and deuterium, in the presence of metals, but no experimental proof has been shown that this reaction could take place in the test conditions. One possibility, in the present work, is therefore that these species, present in the deuterium as impurities, could be responsible for the observed exchange. If we accept this explanation, we should also observe an exchange in the case of pure silica–alumina, where there is no Hsp source. This is not the case: practically no deuterium is detected on the surface. We must therefore conclude that there is no or only negligible direct exchange through the gas phase. An additional argument is that no IR bands corresponding to these oxygenated species (1445 and 1218 cm<sup>-1</sup>

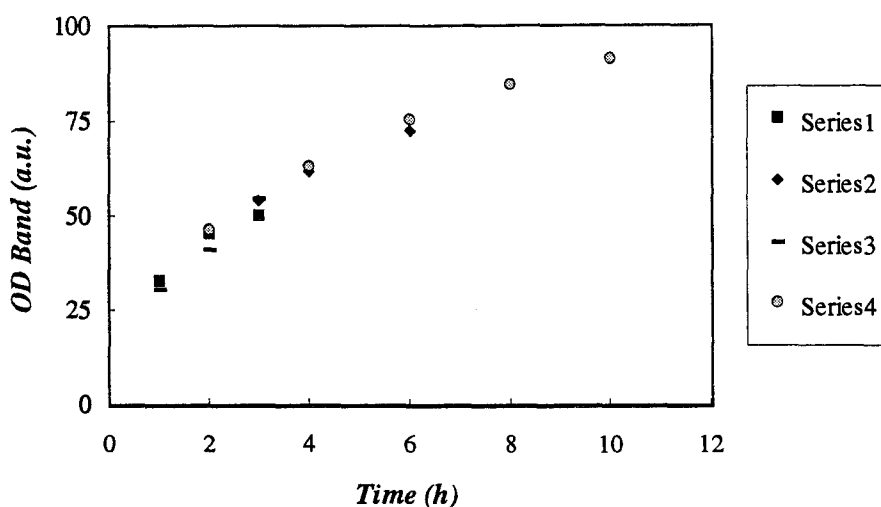


Fig. 3. Reproducibility of isotopic exchange results.

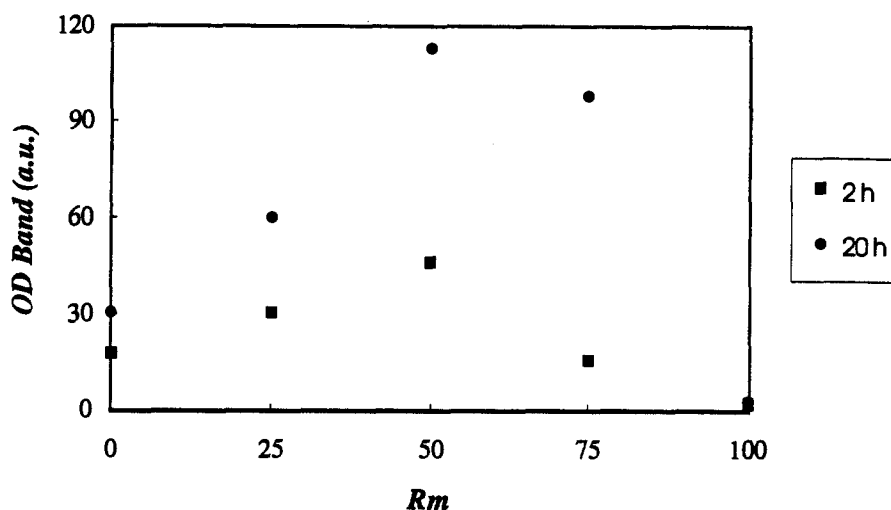


Fig. 4. OD band surface as a function of sample composition.

for HDO and D<sub>2</sub>O, respectively [30]) have been detected on the pure phases or mechanical mixtures. One can of course argue that these species exist but are below the sensitivity limit of IR. We admit that further experiments with still more drastically purified deuterium would be advisable to fully clarify the role that those species could play in the exchange mechanism, since some authors consider that they could also act as co-catalysts for spillover (ref. [1] and references therein). It seems, however, doubtful that this supposed effect could be the only explanation of the effect observed. This would imply that extremely small amounts, not detectable in IR, could bring about an extremely intense effect. We must conclude that our results most likely represent a direct evidence for the existence of spillover phenomena in that system.

The shape of the curves in fig. 4 is similar to those of the catalytic tests. This strongly suggests that the magnitude of the synergy in catalytic activity is related to the Hsp generation. The maximum found in both cases (catalytic tests and isotopic exchange) corresponds to a situation where there is an ideal balance between the activity of the donor (supported metal sulfides) to produce Hsp and the acceptor (silica–alumina) capability to exchange with Hsp. Below 50%, the growth reflects the increase in the number of active sites that can be generated, namely the increasing silica–alumina content. When this content is superior to 50%, the donor is not any more able to produce enough Hsp to activate the acidic phase as much as it could be possible. This explains the decrease observed beyond 50%.

#### 4. Conclusions

A very important synergy effect is observed when particles of a sulfided CoMo/SiO<sub>2</sub> catalyst are mixed with particles of an amorphous silica–alumina in



the cracking of diphenylmethane in the presence of hydrogen. This can be attributed to the action of spillover hydrogen. Isotopic experiments, showing that the presence of CoMo/SiO<sub>2</sub> bring about the exchange of deuterium with the hydroxyls of the silica–alumina, constitute a direct evidence of this phenomenon.

## Acknowledgement

The silica–alumina sample was kindly supplied by Akzo Chemicals BV. One of the authors (AMS) thanks the CNPq (National Council for Scientific and Technological Development, Brazil) for financial support. This work is part of a series carried out on the role of spillover hydrogen and remote control in hydrotreating catalysts with the financial support of the Federal Science Policy Office of Belgium, through the Interuniversity Pole of Attraction (IPA Program) “Katalyse”.

## References

- [1] W.C. Conner Jr., G.M. Pajonk and S.J. Teichner, *Adv. Catal.* 34 (1986) 1.
- [2] S.J. Teichner, in: *New Aspects of Spillover Effect in Catalysis*, eds. T. Inui et al. (Elsevier, Amsterdam, 1993) p. 27.
- [3] *The Petroleum Handbook*, eds. Royal Dutch/Shell Group (Elsevier, Amsterdam, 1983) p. 294.
- [4] R.F. Sullivan and J.A. Meyer, *ACS Symp. Ser.* 20 (1975) 28.
- [5] J.A. Martens, P.A. Jacobs and J. Weitkamp, *Appl. Catal.* 20 (1986) 283.
- [6] R. Burch, S.E. Golunski and M.S. Spencer, *J. Chem. Soc. Faraday Trans.* 86 (1990) 2683.
- [7] M. Karroua, H. Matralis, P. Grange and B. Delmon, *J. Catal.* 139 (1993) 371.
- [8] S. Giraldo, P. Grange and B. Delmon, in: *New Aspects of Spillover Effect in Catalysis*, eds. T. Inui et al. (Elsevier, Amsterdam, 1993) p. 345.
- [9] K. Becker, K.-H. Steinberg and H. Spindler, in: *2nd Conf. on Spillover*, Leipzig 1989, ed. K.-H. Steinberg, p. 204.
- [10] I. Nakamura, K. Aimoto and K. Fujimoto, in: *New Aspects of Spillover Effect in Catalysis*, eds. T. Inui et al. (Elsevier, Amsterdam, 1993) p. 361.
- [11] I. Nakamura, K. Aimoto, K. Fujimoto and H. Tominaga, *Chem. Lett.* (1988) 437.
- [12] I. Nakamura, K. Fujimoto and H. Tominaga, *Chem. Lett.* (1988) 167.
- [13] I. Nakamura, K. Aimoto and K. Fujimoto, *AIChE Symp. Ser.* 85 (1989) 15.
- [14] W.C. Conner, J.F. Cevallos-Candau, N. Shah and V. Haensel, in: *Spillover of Adsorbed Species*, eds. G.M. Pajonk et al. (Elsevier, Amsterdam, 1983) p. 31.
- [15] H. Hattori, K. Yamashita, T. Tanabe and K. Tanabe, in: *Proc. 9th Int. Congr. on Catalysis*, Calgary 1988, eds. M.J. Phillips and M. Ternan (Chem. Inst. of Canada, Ottawa, 1988) p. 27.
- [16] H. Shimada, M. Kurita, T. Sato, Y. Yoshimura, T. Hirata, T. Konakahara, K. Sato and A. Nishijima, *Chem. Lett.* (1984) 1861.
- [17] H. Shimada, T. Sato, Y. Yoshimura, J. Hiraishi and A. Nishijima, *J. Catal.* 110 (1988) 275.
- [18] A. El Tanamy, G.M. Pajonk, K.-H. Steinberg and S.J. Teichner, *Appl. Catal.* 39 (1988) 89.
- [19] M. Lacroix, G.M. Pajonk and S.J. Teichner, *Bull. Soc. Chim. France* (1981) 265.
- [20] H. Hattori, in: *New Aspects of Spillover Effect in Catalysis*, eds. T. Inui et al. (Elsevier, Amsterdam, 1993) p. 69.
- [21] I. Nakamura, R. Iwamoto and A. Iino, in: *New Aspects of Spillover Effect in Catalysis*, eds. T. Inui et al. (Elsevier, Amsterdam, 1993) p. 77.

- [22] S. Kasztelan and G.B. McGarvey, J. Catal. 147 (1994) 476.
- [23] X. Chu and L.D. Schmidt, J. Catal. 144 (1993) 77.
- [24] N.M. Rodriguez and R.T.K. Baker, J. Catal. 140 (1993) 287.
- [25] L. Jalowiecki, J. Grimblot and J.P. Bonelle, J. Catal. 126 (1990) 101.
- [26] G.M. Pajonk, in: *2nd Conf. on Spillover*, Leipzig 1989, ed. K.-H. Steinberg, p. 1.
- [27] D.M. Bibby, N.B. Milestone, J.E. Patterson and L.P. Aldridge, J. Catal. 97 (1986) 493.
- [28] I. Nakamura, K. Fujimoto and H. Tominaga, Chem. Lett. (1988) 167.
- [29] D. Bianchi, D. Maret, G.M. Pajonk and S.J. Teichner, in: *Spillover of Adsorbed Species*, eds. G.M. Pajonk et al. (Elsevier, Amsterdam, 1983) p. 45.
- [30] E. Baumgarten and E. Denecke, J. Catal. 95 (1985) 296.