ELSEVIER

Catalysis Today 45 (1998) 313–318

CATALYSIS TODAY

DRIFT study of temperature programmed desorption of NO adsorbed on Co–Mo/Al_2O_3 sulfided at high pressure

Naoto Koizumi*, Kazunori Takahashi, Masato Yamazaki, Muneyoshi Yamada

Department of Applied Chemistry, Graduate School of Engineering, Tohoku University, Aoba, Aramaki, Aoba-ku, Sendai 980-8579, Japan

Abstract

In order to make clear the coordinatively unsaturated sites (CUS) of Co–Mo/Al_2O_3 sulfided at high pressure, the temperature programmed desorption of NO adsorbed on Co–Mo/Al_2O_3 sulfided at high pressure was studied by DRIFT method. The intensity of two IR bands (1835 and 1785 cm^{-1}) of adsorbed NO on Co–Mo/Al_2O_3 decreased simultaneously up to 393 K. The higher frequency band disappeared at 393 K, while the lower frequency band remained even at 403 K. In the case of Mo/Al_2O_3, the intensities of two bands appeared at 298 K decreased monotonously with increasing temperature, and disappeared simultaneously over 433 K. In the case of Co/Al_2O_3, two bands disappeared simultaneously over 393 K. These results suggest that two kinds of nitrosyl species are formed on Co–Mo/Al_2O_3. One is dinitrosyl species adsorbed on CUS of Co, and the other is unidentified nitrosyl species. Comparing DRIFT spectra of Co–Mo/Al_2O_3 with those of a physical mixture of Mo/Al_2O_3 and Co/Al_2O_3, it is also suggested that the formation of the latter one correlates with the interaction between Co and Mo in Co–Mo/Al_2O_3. The unidentified nitrosyl species might be the key to explain the dependency of DRIFT spectrum of adsorbed NO on the pressure of sulfiding.

Keywords: High pressure sulfided Co-Mo/Al_2O_3; NO adsorption; Temperature programmed desorption; High pressure DRIFT

1. Introduction

Hydrotreating reactions, such as hydrodesulfurization (HDS), hydrodenitrogenation (HDN) and hydrodemetallization (HDM), etc., play an essential role in not only pretreating streams for other refinery processes but also preventing the environmental destruction. As concerns the latter, more severe environmental regulations will require higher performance of hydrotreating reactions in the future [1]. For these reasons, many efforts have been made to make clear the correlation between catalytic activity and the surface fine structure of the catalysts by means of both various spectroscopic techniques [1,2] and activity tests [1,3]. However, surface characterization results reported so far are limited to the catalysts sulfided at atmospheric pressure. In order to understand the catalysis under industrial reaction conditions, it is necessary to investigate the surface structure of the catalysts under high pressure conditions, at least to investigate in situ (without exposing the catalyst to the air) the surface structure of the catalysts sulfided at high pressure.

For these reasons, we have tried to investigate the surface fine structure of Co (or Ni)–Mo/Al_2O_3 sulfided at high pressure by means of in situ diffuse reflectance infrared fourier transform (DRIFT) measurements using NO as a probe molecule [4–7]. As a result, it

---

*Corresponding author.

PII: S0920-5861(98)00237-5

was found that the relative intensities of three IR bands of adsorbed NO clearly change depending on the catalyst sulfiding pressure. On the analogy of the IR band assignments of Millman and Hall [8], and Topsøe [9], the change was interpreted that higher pressure sulfiding effectively forms Co–Mo interaction species.

In the present work, in order to examine the above interpretation further, the assignment of IR bands of adsorbed NO was studied from a different point of view. Especially, it is important to make sure that there are only two types of adsorbed nitrosyl species (i.e. dinitrosyl species adsorbed on CUS of Co and those of Mo). Because no evidence has been reported on the presence of adsorbed dinitrosyl species in Co–Mo/Al_2O_3, although the presence of dinitrosyl species in Mo/Al_2O_3 has been reported by Millman and Hall [8]. If more than two types of adsorbed NO species coexist on the catalyst surface, it is expected to discriminate them depending on the strength of adsorption. For this purpose, the present work carries out DRIFT measurements of adsorbed NO combined with temperature programmed desorption (TPD).

2. Experimental

2.1. Catalyst preparation

Home-made Co–Mo/Al_2O_3 (MoO_3: 15 wt%, CoO: 4.4 wt%), Mo/Al_2O_3 (MoO_3: 16 wt%) and Co/Al_2O_3 (CoO: 5.2 wt%) were used. Commercial Co-Mo/Al_2O_3 (supplied by Nippon Ketjen Co.) was also used. Home-made catalysts were prepared by conventional incipient wetness method, as described in our preceding paper [5,10,11].

2.2. DRIFT of adsorbed NO during TPD

Finely powdered catalysts were placed in situ DRIFT cell equipped with CaF_2 window, and then sulfided under flowing 5% H_2S/H_2 at 673 K for 1 h at the pressure of 1.1 MPa. After that, the catalyst was cooled to room temperature, then He flow was introduced into the DRIFT cell. NO adsorption was carried out in situ by pulse method [5,11]. After NO adsorption, He flow was replaced by 5% H_2S/H_2 flow at room temperature, and then the catalyst was heated up to 473 K.

FT-IR spectra of adsorbed NO were collected at intervals of 5 K from 298 to 473 K by means of diffuse reflectance method using FTS6000 (Bio-Rad) spectrometer. These spectra were converted into Kubelka–Munk functions by using background (KBr) spectra measured in a stream of 5% H_2S/H_2 at the corresponding temperature.

3. Results and discussion

3.1. DRIFT spectra of NO adsorbed on the catalysts sulfided at high pressure

In order to make clear the meaning of the present work with respect to our previous work [4–7], the effect of sulfiding pressure on DRIFT spectra of NO adsorbed on Co–Mo/Al_2O_3 is summarized as follows.

Fig. 1 shows DRIFT spectra of NO adsorbed on Co–Mo/Al_2O_3 sulfided at 0.1 and 1.1 MPa, respectively. DRIFT spectra of Mo/Al_2O_3 and Co/Al_2O_3 sulfided at 1.1 MPa are also shown in this figure, as

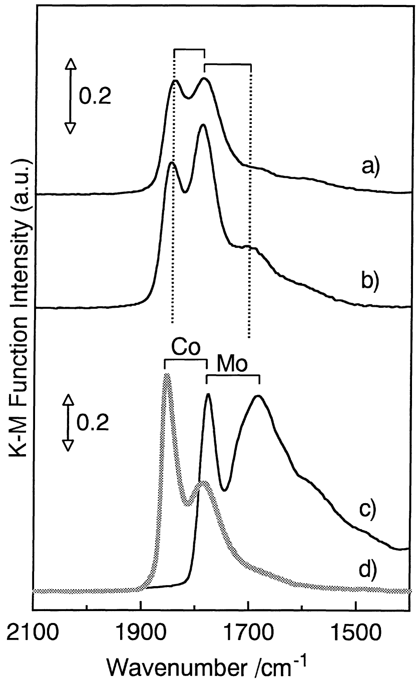

Fig. 1. DRIFT spectra of NO adsorbed on the catalysts: (a) Co–Mo/Al_2O_3 sulfided at 1.1 MPa, (b) Co–Mo/Al_2O_3 sulfided at 0.1 MPa, (c) Mo/Al_2O_3 sulfided at 1.1 MPa, and (d) Co/Al_2O_3 sulfided at 1.1 MPa.

a reference. All the spectra in this figure were normalized by the spectra taken before NO adsorption for the purpose of baseline correction. Three IR bands (1840, 1785 and 1700 cm^{-1}) appear in the spectrum of Co–Mo/Al_2O_3 sulfided at 0.1 MPa. This is consistent with the spectra reported earlier [9,11,12]. On the other hand, the spectrum of Co–Mo/Al_2O_3 sulfided at 1.1 MPa shows two bands at 1835 and 1785 cm^{-1}. The band at 1700 cm^{-1} cannot be discriminated distinctly in this spectrum. It is suggested that the distribution of CUS on Co–Mo/Al_2O_3 sulfided at 1.1 MPa is quite different from that on Co–Mo/Al_2O_3 sulfided at 0.1 MPa. For the assignment of IR bands on Co–Mo/Al_2O_3 sulfided at high pressure, the spectra of the reference catalysts are examined. Two bands appear in the spectra of Mo/Al_2O_3 and Co/Al_2O_3 sulfided at 1.1 MPa, respectively. It is well known that IR spectra of NO adsorbed on these catalysts sulfided at atmospheric pressure show the doublets. They are assigned to dinitrosyl species adsorbed on CUS of Mo and Co, respectively [8,9,13]. By analogy with the catalysts sulfided at atmospheric pressure, the bands of Mo/Al_2O_3 and Co/Al_2O_3 sulfided at high pressure are also assigned to the dinitrosyl species.

So far, IR spectrum of NO adsorbed on Co–Mo/Al_2O_3 sulfided at atmospheric pressure has been interpreted as superposition of two doublet bands, referring to the spectra of Mo/Al_2O_3 and Co/Al_2O_3. That is, the higher frequency band (1840 cm^{-1}) was assigned to the symmetric stretching vibration of dinitrosyl species adsorbed on CUS of Co, and the lower frequency band (1700 cm^{-1}) was assigned to the antisymmetric stretching vibration of dinitrosyl species adsorbed on CUS of Mo [9]. On the other hand, DRIFT spectrum of Co–Mo/Al_2O_3 sulfided at high pressure does not show the band in the same range as that of the lower frequency band of Mo/Al_2O_3 sulfided at 1.1 MPa. According to the above-mentioned assignments, two IR bands of Co–Mo/Al_2O_3 sulfided at 1.1 MPa are assigned to dinitrosyl species adsorbed on CUS of Co [4,5]. This means that CUS are selectively formed on Co when Co–Mo/Al_2O_3 is sulfided at high pressure. However, intensity ratio of two IR bands of Co–Mo/Al_2O_3 is quite different from that of Co/Al_2O_3. Therefore, it is possible that another nitrosyl species are formed on Co–Mo/Al_2O_3 sulfided at high pressure. Furthermore, no evidence that NO adsorbs as dinitrosyl on CUS of Co–Mo/Al_2O_3 sulfided at atmospheric pressure has been reported. Considering these matters, there are some questions in the above-mentioned assignments. For these reasons, the present work tries to make clear the features of NO adsorption on Co–Mo/Al_2O_3, especially on the catalyst sulfided at high pressure, by means of DRIFT measurements of adsorbed NO combined with TPD. Infrared spectroscopy combined with TPD has already been applied for the quantitation of MoO_3 layer on Mo/Al_2O_3 using CO as a probe molecule [14] and examination of the feature of thiophene adsorption on Al_2O_3 [15].

3.2. *DRIFT spectra of NO adsorbed on the catalysts during TPD*

3.2.1. *Mo/Al_2O_3 and Co/Al_2O_3*

First of all, the change of DRIFT spectra of NO adsorbed on Mo/Al_2O_3 and Co/Al_2O_3 sulfided at high pressure was observed during TPD, as a reference to Co–Mo/Al_2O_3.

Fig. 2(a) shows DRIFT spectra of NO adsorbed on Mo/Al_2O_3 sulfided at 1.1 MPa during TPD. The spectra collected at 298 K, 10 K intervals from 333 to 453 K, and 473 K are shown in this profile. Two IR bands (1780 and 1680 cm^{-1}) appear in the spectrum at 298 K. These bands disappear at 443 K. It is noted that all the spectra from 298 to 433 K show two IR bands. With increasing temperature, the intensity of both bands decreases simultaneously. That is, two IR bands of Mo/Al_2O_3 are strongly coupled, as was shown by Millman and Hall [8] using isotopic ^{15}NO. These results are consistent with the notion that NO adsorbs as dinitrosyl species on CUS of Mo. Fig. 2(b) shows DRIFT spectra of NO adsorbed on Co/Al_2O_3 sulfided at high pressure during TPD. This profile contains DRIFT spectra collected at 298 K, 10 K intervals from 333 to 413 K, and 473 K. The higher frequency bands (1840 and 1770 cm^{-1}) appear in the spectrum at 298 K. The intensity of each band decreases simultaneously, as well as Mo/Al_2O_3, and they disappear at 403 K. It is suggested that NO adsorbs as dinitrosyl species on CUS of Co.

3.2.2. *Co–Mo/Al_2O_3*

Based on the results of the reference catalysts, DRIFT spectra of NO adsorbed on Co–Mo/Al_2O_3

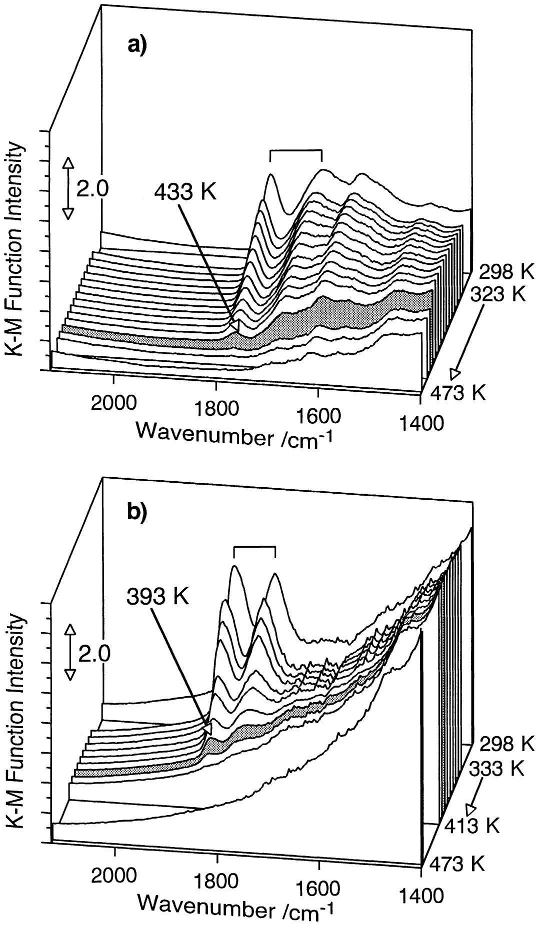

Fig. 2. DRIFT spectra of adsorbed NO during temperature programmed desorption: (a) Mo/Al_2O_3 sulfided at 1.1 MPa and (b) Co/Al_2O_3 sulfided at 1.1 MPa.

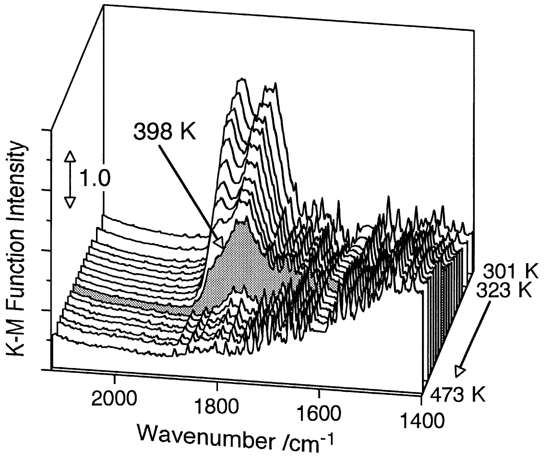

Fig. 3. DRIFT spectra of NO adsorbed on $Co–Mo/Al_2O_3$ sulfided at 1.1 MPa during temperature programmed desorption.

sulfided at 1.1 MPa during TPD was examined (Fig. 3). DRIFT spectra were taken at 301 K, and 10 K intervals from 323 to 373 K, 5 K intervals from 383 to 403, and 10 K intervals from 413 to 473 K. Two IR bands at 1835 and 1785 cm^{-1} appear in the spectrum of $Co–Mo/Al_2O_3$ at 301 K, and disappear at 413 K. It is noted that the intensity of each band decreases simultaneously in the range from 301 to 393 K, indicating the desorption of dinitrosyl species. It is also noted that IR band positions of $Co–Mo/Al_2O_3$ (1835 and 1785 cm^{-1}) are quite similar to those of Co/Al_2O_3 (1840 and 1770 cm^{-1}). Consequently, it is suggested that (a part of) NO adsorbs as dinitrosyl species on CUS of Co in $Co–Mo/Al_2O_3$. On the other hand, higher frequency band disappears at 398 K, and lower frequency band (1785 cm^{-1}) only appears in the spectra at 398 and 403 K. It is noted that DRIFT spectra of Mo/Al_2O_3 and Co/Al_2O_3 show doublet, not singlet band (Fig. 2(a) and (b)).

The band at 1785 cm^{-1} has not been reported in IR spectra of NO adsorbed on $Co–Mo/Al_2O_3$. In other words, this band does not appear in the spectrum without heating $Co–Mo/Al_2O_3$ after NO adsorption. This leads to the possibility that the surface reaction of adsorbed NO during heating of the catalyst causes the singlet band at 1785 cm^{-1}. In order to examine this possibility, the following experiment was carried out. That is, $Co–Mo/Al_2O_3$ was heated up to 353 K after NO adsorption in a stream of H_2S/H_2, and then cooled to room temperature. After that, NO adsorption was carried out again. The results are shown in Fig. 4. All the spectra in Fig. 4 were taken when $Co–Mo/Al_2O_3$ was in a stream of He, at room temperature. Fig. 4(b) shows a band at 1785 cm^{-1}, indicating that adsorbed species derived from the band at 1785 cm^{-1} in DRIFT spectra during TPD remain on the surface of $Co–Mo/Al_2O_3$. After NO readsorption, the intensity of the band at 1785 cm^{-1} grows up, and the band at 1840 cm^{-1} appears again, as is shown in Fig. 4(c). Comparing Fig. 4(c) with Fig. 4(a), it is noted that, although the intensity of each band in Fig. 4(c) larger than that in Fig. 4(a), the intensity ratio of the bands is

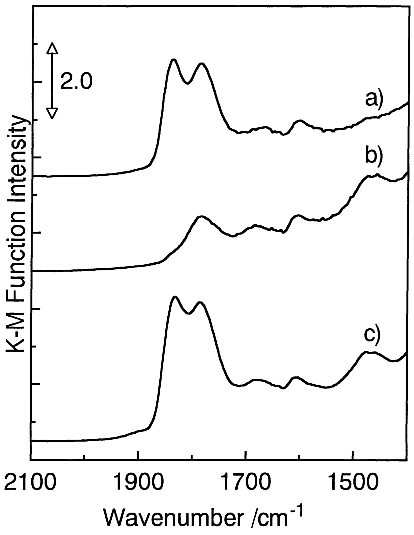

Fig. 4. DRIFT spectra of NO adsorbed on Co–Mo/Al_2O_3 sulfided at 1.1 MPa: (a) before heating, (b) after heating up to 353 K, and (c) successive NO adsorption.

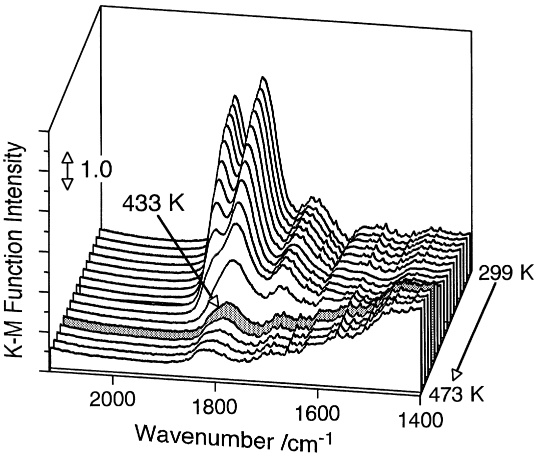

Fig. 5. DRIFT spectra of NO adsorbed on Co–Mo/Al_2O_3 sulfided at 0.1 MPa during temperature programmed desorption.

identical with each other. The intensity change of DRIFT spectra accompanied by heating is recovered by NO readsorption. Considering this reversibility, it is not likely that the surface reaction of adsorbed NO species occurs during heating of the catalyst. In other words, it is suggested that the singlet band at 1785 cm^{-1} is not originated from the surface reaction during TPD.

Based on the results of Figs. 2–4, DRIFT spectra of NO adsorbed on Co–Mo/Al_2O_3 during TPD can be interpreted as the desorption of two kinds of nitrosyl species. One is the dinitrosyl species adsorbed on CUS of Co, and the other is nitrosyl species which cannot be assigned. This indicates the formation of unidentified CUS on Co–Mo/Al_2O_3 sulfided at high pressure. Furthermore, DRIFT spectra of Co–Mo/Al_2O_3 sulfided at atmospheric pressure showed the singlet band during TPD (Fig. 5). Therefore, it is suggested that the unidentified CUS are formed by atmospheric pressure sulfiding as well as high pressure sulfiding.

3.2.3. *Physical mixture of Mo/Al_2O_3 and Co/Al_2O_3*

Authors have already reported that DRIFT spectra of NO adsorbed on Co–Mo/Al_2O_3 cannot be expressed by the linear combination of those on Mo/Al_2O_3 and Co/Al_2O_3. On the other hand, the spectra of a physical mixture of Mo/Al_2O_3 and Co/Al_2O_3 can be expressed by the linear combination of those on Mo/Al_2O_3 and Co/Al_2O_3 [7]. Based on these results, authors proposed the formation of CUS on Co interacted with Mo (Co–Mo interaction species) in Co–Mo/Al_2O_3 by sulfiding. In the present work, it was found that the unidentified CUS were formed on Co–Mo/Al_2O_3. Considering these results, it is suggested that the unidentified CUS correspond to the CUS on Co–Mo interaction species. According to this notion, DRIFT spectra of NO adsorbed on the physical mixture during TPD would not show the singlet band.

Finally, this point was examined. Fig. 6 shows DRIFT spectra of NO adsorbed on the physical mixture of Mo/Al_2O_3 and Co/Al_2O_3 (Co/Mo ratio: 0.56 mol/mol) at 10 K intervals from 333 to 433 K, and 473 K. Three IR bands appear at 1840, 1780 and 1680 cm^{-1} in the spectra from 333 to 393 K, while two bands (1780 and 1680 cm^{-1}) appear at 403 and 413 K. It is noted that these spectra can be expressed by the linear combination of those of Mo/Al_2O_3 and Co/Al_2O_3 (Fig. 2(a) and (b)). This clearly indicates that DRIFT spectra of the physical mixture does not include the singlet band at 1785 cm^{-1}. In other words, Fig. 6 supports the notion that the singlet band at 1785 cm^{-1} is assigned to NO adsorbed on the CUS of Co–Mo interaction species.

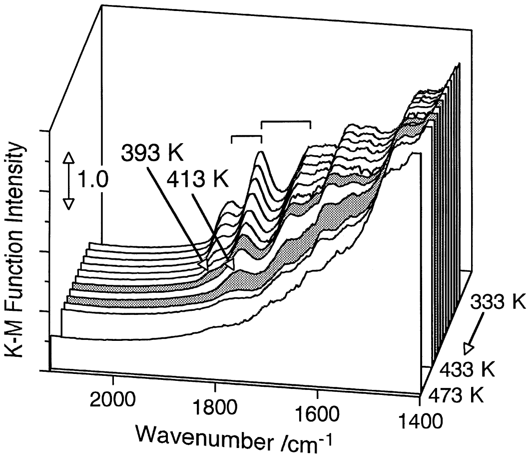

Fig. 6. DRIFT spectra of NO adsorbed on the physical mixture of Mo/Al_2O_3 and Co/Al_2O_3 during temperature programmed desorption.

4. Conclusion

DRIFT spectra of NO adsorbed on the catalysts sulfided at high pressure was studied by a temperature programmed desorption method. It was found that two kinds of nitrosyl species were formed on Co–Mo/Al_2O_3. One is dinitrosyl species adsorbed on CUS of Co (doublet band at 1835 and 1785 cm^{-1}), and the other is unidentified nitrosyl species (singlet band at 1785 cm^{-1}). The singlet band also appeared in DRIFT spectra of Co-Mo/Al_2O_3 sulfided at atmospheric pressure. So far, IR spectrum of NO adsorbed on sulfided Co–Mo/Al_2O_3 has been interpreted as superposition of two doublet bands. But the results obtained in the present work indicate that such an interpretation is not adequate.

Comparing DRIFT spectra of Co–Mo/Al_2O_3 with those of the physical mixture of Mo/Al_2O_3 and Co/Al_2O_3, it was suggested that the singlet band was assigned to NO adsorbed on the CUS of Co–Mo interaction species. As concerns the effect of sulfiding pressure, it is noted that the relative intensity of the singlet band in the spectrum of Co–Mo/Al_2O_3 sulfided at high pressure seems to be different from that of Co–Mo/Al_2O_3 sulfided at atmospheric pressure. Therefore, it is possible that the formation of Co–Mo interaction species depends on the pressure of sulfiding. This might be the reason for the difference between DRIFT spectrum of NO adsorbed on Co–Mo/Al_2O_3 sulfided at high pressure and that on Co–Mo/Al_2O_3 sulfided at atmospheric pressure.

Acknowledgements

This work was partly supported by a grant-in-aid for Scientific Research from the Ministry of Education, Science and Culture of Japan.

References

[1] B.S. Clausen, H. Topsøe, F.E. Massoth, in: J.A.R. Anderson, M. Boudart (Eds.), Catalysis – Science and Technology, vol. 11, Springer, Berlin, 1996, p. 1.
[2] R. Prins, V.H.J. de Beer, G.A. Somorjai, Catal. Rev. -Sci. Eng. 31(1)(2) (1989) 1.
[3] B. Delmon, G.F. Froment, Catal. Rev. -Sci. Eng. 38(1) (1996) 69.
[4] N. Koizumi, M. Iijima, S. Kasahara, M. Yamada, Chem. Lett. (1996) 815.
[5] N. Koizumi, M. Iijima, T. Mochizuki, M. Yamada, Stud. Surf. Sci. Catal. 106 (1997) 255.
[6] N. Koizumi, M. Yamazaki, M. Iijima, M. Yamada, Appl. Surf. Sci. 121 122 (1997) 429.
[7] N. Koizumi, M. Yamazaki, S. Hatanaka, M. Yamada, Catal. Today 39 (1997) 33.
[8] W.S. Millman, W.K. Hall, J. Phys. Chem. 83 (1979) 427.
[9] N.-Y. Topsøe, H. Topsøe, J. Catal. 84 (1983) 386.
[10] S. Kasahara, N. Koizumi, J. Iwahashi, M. Yamada, Sekiyu Gakkaishi 38 (1995) 345.
[11] S. Kasahara, N. Koizumi, M. Yamada, Y. Udagawa, Sekiyu Gakkaishi 38 (1995) 439.
[12] L. Portela, P. Grange, B. Delmon, Catal. Rev. -Sci. Eng. 37(4) (1995) 699.
[13] A. Kazusaka, R.F. Howe, J. Catal. 63 (1980) 447.
[14] A.L. Diaz, M.E. Bussel, J. Phys. Chem. 97 (1993) 470.
[15] W.W.C. Quigley, H.D. Yamamoto, P.A. Aegerter, G.J. Simpson, M.E. Bussel, Langmuir 12 (1996) 1500.