

Determination of acidic centers on supported Mo₂C catalysts

László Óvári, Frigyes Solymosi *

*Institute of Solid State and Radiochemistry, University of Szeged and Reaction Kinetics Research
Group of the Hungarian Academy of Sciences, ¹ P.O. Box 168, H-6701 Szeged, Hungary*

Received 12 March 2003; accepted 9 June 2003

Abstract

The acidic properties of both HZSM-5 and SiO₂ supported MoO₃ and carburized MoO₃ have been investigated by FTIR spectroscopy. Deposition of Mo caused the consumption of Brønsted acidic OH groups of HZSM-5 as shown by the changes in the ν(OH) region of the spectra and also by pyridine and low temperature CO adsorption measurements. Carburization of the sample did not result in regeneration of acidic OH groups of the zeolite. Mo reacted with OH groups during its deposition on SiO₂. The results of both pyridine and CO adsorption measurements did not indicate the generation of Brønsted acidic sites on MoO₃/SiO₂ and carburized MoO₃/SiO₂. Lewis acid sites are formed, however, upon the deposition of Mo. Carburization led to stronger Lewis centers, which are probably the active sites—together with the carbide phase—in methane aromatization on MoO₃/SiO₂.

© 2003 Elsevier B.V. All rights reserved.

Keywords: Methane aromatization; FTIR spectroscopy; Molybdenum carbide; Pyridine and CO adsorption; Brønsted and Lewis acidic centers

1. Introduction

A great effort is being made to evaluate the elementary steps of the aromatization of methane over Mo₂C/ZSM-5 and to determine the active sites of the catalysts for this complex reaction [1–20]. It is generally accepted now that Mo₂C is responsible for the mild activation of methane, and the role of the ZSM-5 is to oligomerize and aromatize the ethylene on the Brønsted sites of zeolite. As regards elementary steps between the two main processes we know relatively little. Studies of the reactions of CH₃, CH₂ and C₂H₅ on Mo₂C/Mo(1 0 0) disclosed that the coupling of these hydrocarbon fragments formed in the primary step of the CH₄ dissociation may also occur on Mo₂C [17–20].

A surprising result obtained in an early study was that MoO₃/SiO₂ also catalyzed the aromatization of methane [2], although its catalytic performance was far behind that of Mo/ZSM-5. This finding was confirmed by Lunsford and co-workers [21]. As the carburization of MoO₃ also occurred on silica, we could assume that Mo₂C is the primary activator in this case, too, and we can count with the same

initial steps as on Mo₂C/ZSM-5, at least up to the formation of ethylene [3]. As silica contains no Brønsted sites, the question is as to how ethylene is converted into benzene on Mo₂C/SiO₂. Note that ethylene on unsupported Mo₂C undergoes only cracking, and produces no higher hydrocarbons and aromatics [22,23]. SiO₂ (either Cab-O-Sil or Aerosil) is very unreactive towards ethylene: no traces of benzene were detected even at 973–1073 K [22,23]. One of the possible explanations is that new acidic sites may be generated in the course of the conversion of MoO₃ into Mo₂C on silica or at the Mo/SiO₂ interface, which facilitates the aromatization of ethylene.

The primary aim of this work is to characterize the MoO₃/SiO₂ catalyst and to determine changes in the nature and the number of acidic centers in the course of carburization of MoO₃. In addition, some measurements are also carried out with MoO₃/ZSM-5, as different results have been found in the literature as concerns the acidic sites.

On the basis of H–D exchange results Iglesia and co-workers [24,25] claimed that Brønsted acid OH groups are regenerated during the induction period of the aromatization reaction concurrent with the carburization of (Mo₂O₅)²⁺ dimers leading to small (0.6–1 nm) MoC_x clusters as shown by EXAFS [26]. On the other hand, Su et al. [27] found no regeneration but some further consumption of acid sites during reaction with ¹H MAS NMR (773 K), and

* Corresponding author. Fax: +36-62-424-997.

E-mail address: fsolym@chem.u-szeged.hu (F. Solymosi).

¹ This laboratory is a part of the Center of Catalysis, Surface and Material Science at the University of the Szeged.

concluded that Mo remains in contact with lattice oxygen during carburization. Liu et al. [28] established a correlation between the number of Brønsted acid sites measured with pyridine adsorption on 4.5% MoO₃/ZSM-5 calcined at 773 K and the formation rate of C₆H₆ using zeolites with different Si/Al ratios. Both quantities showed a maximum at Si/Al = 80 while coke selectivity had a minimum. Liu et al. [28] observed that the reaction of methane with MoO₃/ZSM-5 at 973 K decreased the number of Brønsted acid sites and slightly increased that of Lewis acidic sites. Naccache and co-workers [29] registered a strong decrease of the 3622 cm⁻¹ IR band intensity of the MoO₃/HMCM-22 during calcination. Further reaction with CH₄ at 923 K resulted in an additional attenuation of this band.

2. Experimental

2.1. Methods

Infrared spectroscopic measurements were made in a vacuum IR cell (base pressure 5×10^{-6} Torr, 1 Torr = 133 Pa) using self-supporting wafers of catalyst powders (10 mg/cm²). The sample can be cooled by a copper block in contact with liquid nitrogen. Low temperature measurements were made in situ while, in high temperature measurements (above 300 K) the sample was cooled to room temperature before collecting spectra. A Bio-Rad (Digilaboratory Division) Fourier transform IR spectrometer FTS 155 was used. Typically, 128 scans were collected with 2 cm⁻¹ spectral resolution.

As the preparation of wafers of ZSM-5-based catalysts was difficult and sometimes resulted in samples of slightly different sizes, in order to be able to compare IR intensities, spectra were scaled with the intensity of the strong 1876 cm⁻¹ band of ZSM-5.

2.2. Materials

SiO₂ (Cab-O-Sil) and HZSM-5 were used as supports. The HZSM-5 support was obtained by five times repeated ion exchange of Na/ZSM-5 (Si/Al = 60). MoO₃/ZSM-5 and MoO₃/SiO₂ were prepared by impregnating the supports with a basic solution of ammonium heptamolybdate to yield a nominal 2 or 5 wt.% of MoO₃. The suspension was dried at 373 K and calcined—unless mentioned otherwise—at 873 K for 5 h.

Supported Mo₂C was prepared by the method of Lee et al. [30]. Briefly, about 0.5 g of MoO₃ was heated in 1:4 methane–H₂ mixture flowing at 300 ml (STP)/min in a quartz cell with two stopcocks. The preparation temperature was increased rapidly to 773 K and at 30 K/h between 773 and 1023 K, and maintained at 1023 K for 3 h. Following the suggestion of Lee et al. [30], the sample was deactivated at 300 K with air. As Mo₂C always contains excess carbon, the catalyst was treated with H₂ at 873 K before measure-

ments to remove this carbon species. In certain cases, the preparation of Mo₂C was made in situ, in the IR cell.

The gases used were of commercial purity (Linde): CH₄ (99.995%), H₂ (99.999%), Ar (99.999%), O₂ (99.995%), CO (99.97%). Pyridine (Reanal, spectroscopic grade) was purified by a freeze–pump–thaw method prior to use, and it was stored in a glass bulb containing activated molecular sieve (3A).

3. Results and discussion

3.1. MoO₃/ZSM-5

We felt worthwhile to perform some measurements on Mo/ZSM-5 sample, as the results concerning the alteration of acidic sites on Mo₂C/ZSM-5 are somewhat contradictory. Registering the IR spectra in the OH frequency range of pure ZSM-5 (Si/Al = 60) calcined at 673 K, we could detect bands at 3611, 3663 and 3746 cm⁻¹ (Fig. 1A). The first one is due to Brønsted acidic OH group, the second one is due to OH bonded to extra frame work Al and the third one to terminal Si–OH groups locating on external surface of zeolite lattice [31,32]. Annealing the sample the 3746 cm⁻¹ band remained unchanged, whereas the intensities of other two bands gradually decreased. When ZSM-5 contained 2% MoO₃, the band at 3746 cm⁻¹ seemed somewhat weaker. On the effect of calcination the attenuation of all bands was more expressed for MoO₃-containing sample due to the reaction of Mo on ZSM-5 with the different hydroxyls (Fig. 1A).

In the next experimental series the spectral changes have been followed in situ during the carburization of MoO₃/ZSM-5 at 973 K. Some characteristic spectra are displayed in Fig. 1B. The band at 3747 cm⁻¹ has been clearly reduced in intensity even after 30 min of reaction, which roughly corresponds to the end of induction period of the formation of benzene in the aromatization of methane [3,6]. With the progress of the reaction, the band became weaker but still detectable. At the same time the absorption in the range of 3500–3700 cm⁻¹ apparently did not change, but the bands at 3610 and 3660 cm⁻¹ were not so well resolved. This supports the observation that no regeneration of Brønsted acidic OH groups occurs during carburization [27–29].

Next, the samples were characterized by the adsorption of pyridine and CO. In order to avoid the presence of the weakly bonded pyridine, the sample was degassed at 423 K after adsorption. As shown in Fig. 2A, for pure ZSM-5 we obtained bands at 1456, 1491, 1547, 1624 and 1636 cm⁻¹. The 1456 and 1624 cm⁻¹ bands are attributed to Lewis, and the 1547 and 1636 cm⁻¹ bands to the Brønsted acidic centers [33]. The band at 1491 cm⁻¹ is composed of both. The 1547 and 1456 cm⁻¹ bands are most commonly used in the literature to estimate changes in the number of Brønsted and Lewis acidic sites, as they are well-separated from other modes. Deposition of MoO₃ on ZSM-5 led to the decrease

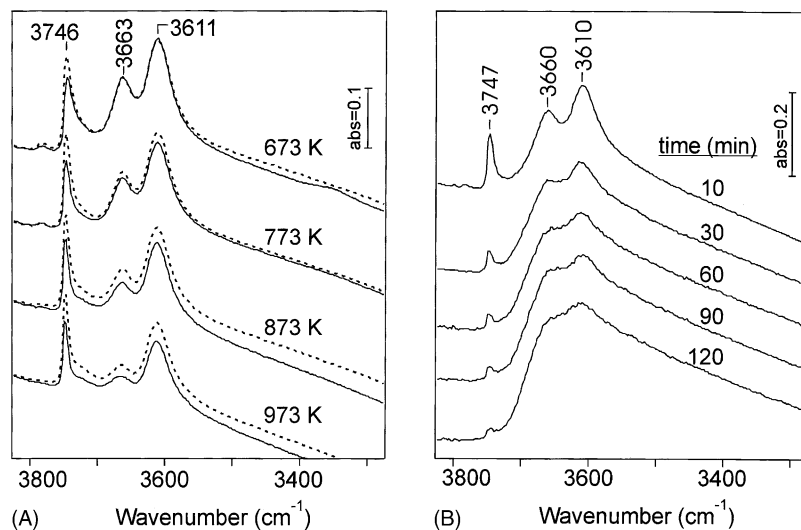


Fig. 1. (A) FTIR spectra of the $\nu(\text{OH})$ region of ZSM-5 (dashed line) and 2% $\text{MoO}_3/\text{ZSM-5}$ (solid line) after evacuation for 45 min at different temperatures. (B) FTIR spectra of 2% $\text{MoO}_3/\text{ZSM-5}$ after reaction with a 10% $\text{CH}_4 + 90\%$ Ar gas mixture at 973 K for different times. The flow rate was 12 ml/min.

of the band at 1547 cm^{-1} and to the increase of the Lewis sites at 1456 cm^{-1} . The latter band became more intense for the $\text{Mo}_2\text{C}/\text{ZSM-5}$ (Fig. 2A). These measurements suggest that the number of Brønsted sites remained unaltered as a result of carburization, while the number of Lewis sites somewhat increased.

The adsorption of CO was performed at 153 K. At low CO pressure (0.02 Torr) a band appeared at 2220 cm^{-1} on ZSM-5, the intensity of which did not increase with the CO pressure. This band is due to CO attached to Lewis centers. Another band developed at 2174 cm^{-1} in 0.1 Torr of CO which is attributed to CO bonded to Brønsted acidic OH group [34]. Further increase in the CO pressure to 1 Torr induced a third band at 2137 cm^{-1} (Fig. 2B) which became

very intense at 10 Torr of CO. This spectral feature belongs to physisorbed CO.

In the OH stretching region the adsorption of CO caused the diminution of the band at 3611 cm^{-1} due to Brønsted acidic OH and the appearance of a new broad feature at 3306 cm^{-1} assigned to acidic OH groups interacting with CO (not shown). The strong acidity of ZSM-5 explains this large wavenumber shift. When 2% MoO_3 was deposited on ZSM-5, the band at 2174 cm^{-1} clearly diminished (Fig. 2B). Carburization of MoO_3 did not alter much the intensity of the 2174 cm^{-1} band, whereas it led to the slight enhancement of the 2220 cm^{-1} feature. These results are in harmony with those obtained from the adsorption of pyridine.

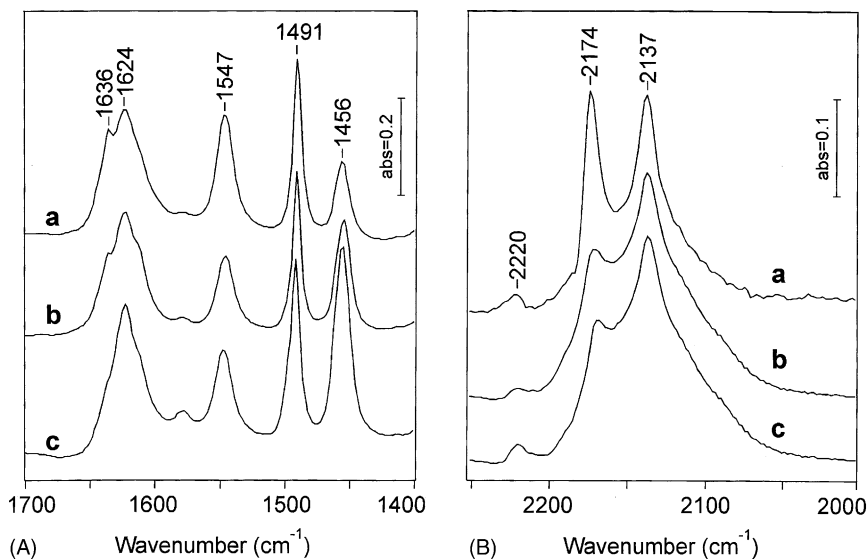


Fig. 2. FTIR spectra of (A) pyridine adsorbed at room temperature and evacuated at 423 K and (B) in the presence of 1 Torr of CO at 153 K on (a) ZSM-5; (b) 2% $\text{MoO}_3/\text{ZSM-5}$ and (c) carburized 2% $\text{MoO}_3/\text{ZSM-5}$. The spectra recorded before adsorption (and that of the gas phase) were subtracted.

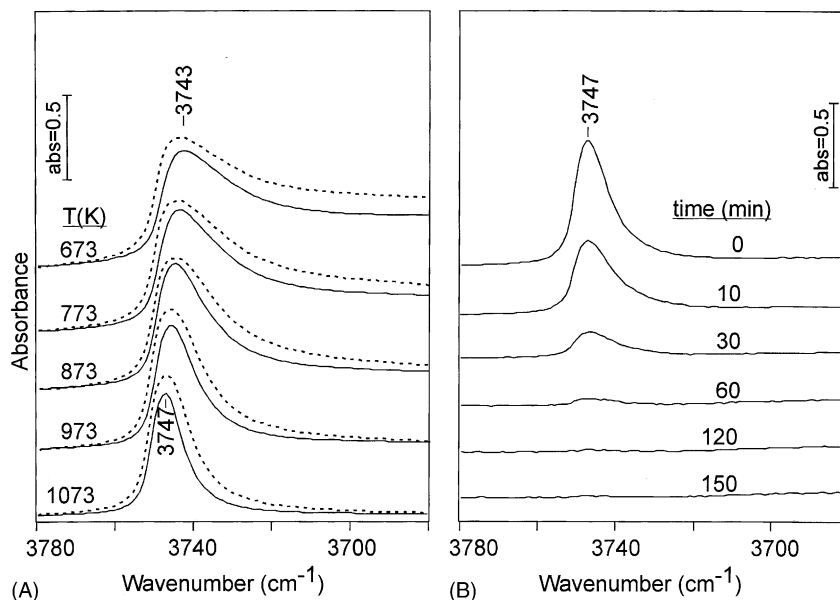


Fig. 3. (A) FTIR spectra of the $\nu(\text{OH})$ region of SiO₂ (dashed line) and 2% MoO₃/SiO₂ (solid line) after evacuation for 45 min at different temperatures. For (B) FTIR spectra of 2% MoO₃/SiO₂ after reaction with a 10% CH₄ + 90% Ar gas mixture at 973 K for different times. The flow rate was 12 ml/min.

3.2. MoO₃/SiO₂

Same kind of measurements have been performed with SiO₂ and 2% MoO₃/SiO₂. Fig. 3A shows the IR spectra of SiO₂ (calcined at 673 K) in the range of OH stretching mode as a function of annealing. We obtained a broad band at 3743 cm⁻¹, which became narrower and smaller with the increase of the evacuation temperature. In the case of 2% MoO₃/SiO₂ this change became more explicit (Fig. 3A), very likely due to the reaction between SiO₂ and MoO₃. This absorption band underwent a drastic reduction during the reaction of CH₄ with MoO₃ at 973 K (Fig. 3B). The band almost disappeared after 2 h of reaction. Taking into

account the previous XPS measurement [3], this feature can be attributed to the partial formation of Mo-oxy-carbide. Treating this sample with H₂ at 873 K did not cause any spectral changes.

In the next experimental series, pyridine was adsorbed on above samples at 300 K. Adsorbed pyridine on pure SiO₂ calcined at 973 K produced absorption bands at 1446, 1455, 1495, 1580, 1597 and 1621 cm⁻¹ (Fig. 4A). From these bands 1455, 1495 and 1621 cm⁻¹ belong to weak Lewis acidic centers [35]. These bands with the other ones disappeared even after heating the sample to 373 K under continuous evacuation. When the SiO₂ contained 2% MoO₃ the bands due to Lewis centers became more intense and slightly

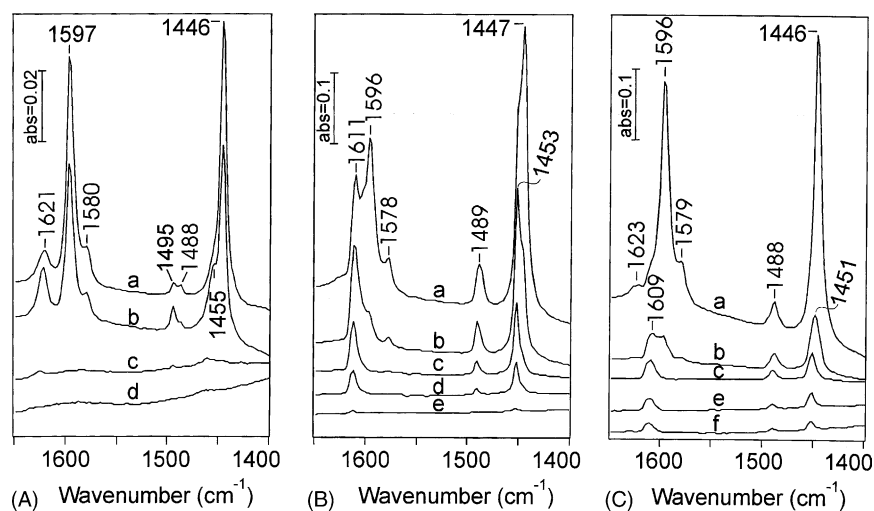


Fig. 4. FTIR spectra of pyridine adsorbed on (A) SiO₂; (B) 2% MoO₃/SiO₂ and (C) carburized 2% MoO₃/SiO₂. (a) In the presence of 0.1 Torr of pyridine and after evacuation at (b) 300 K; (c) 373 K; (d) 423 K; (e) 473 K and (f) 523 K. The spectra recorded before pyridine adsorption and that of the gas phase were subtracted.

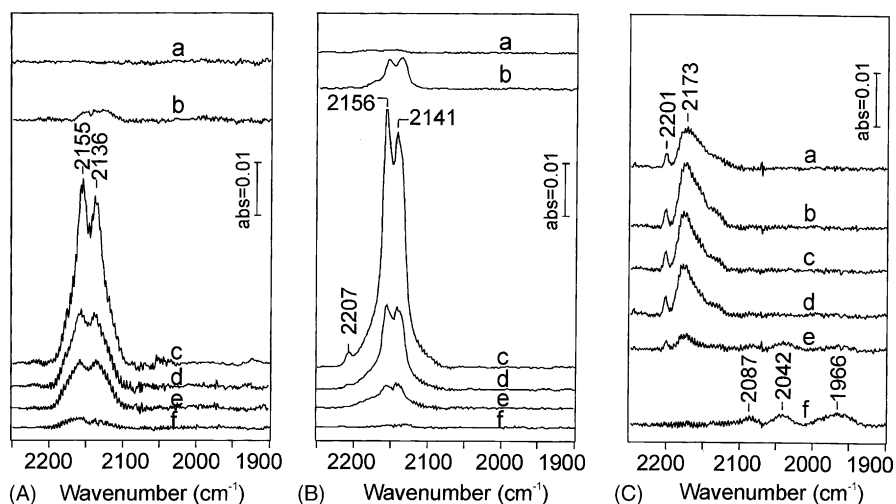


Fig. 5. FTIR spectra of CO adsorbed on (A) SiO_2 ; (B) 2% $\text{MoO}_3/\text{SiO}_2$ and (C) carburized 2% $\text{MoO}_3/\text{SiO}_2$. For (A) and (B) at 153 K in (a) 0.1 Torr; (b) 1 Torr; (c) 10 Torr of CO and heating the sample in 10 Torr of CO to (d) 173 K; (e) 193 K and (f) 213 K. For (C) at 153 K in (a) 0.02 Torr; (b) 1 Torr of CO and heating the sample in 1 Torr of CO to (c) 173 K; (d) 193 K; (e) 233 K and (f) 263 K. The spectrum recorded before CO adsorption and that of the gas phase were subtracted.

shifted to lower frequencies (Fig. 4B). They were detectable even at 423 K suggesting the increased strength of these centers. When the MoO_3 content has been increased the bands 1453 and 1612 cm^{-1} became more intense. Carburization of MoO_3 at 973 K led to an attenuation of these bands, but at the same time their stability further increased, as indicated by their presence even at 523–573 K (Fig. 4C). We note that neither the deposition of MoO_3 on SiO_2 nor the transformation of MoO_3 into Mo_2C induced the appearance of absorption band at 1540 cm^{-1} due to Brønsted acidic centers present on ZSM-5 samples.

Low temperature adsorption of CO also revealed differences among the samples. Previous studies [36] showed that the adsorption of CO on pure silica at 83 K leads to the attenuation of the 3744 cm^{-1} band and to the development of a new band at 3645 cm^{-1} . This was attributed to the interaction of CO with the terminal OH-group of silica. This phenomenon was observed for our SiO_2 and 2% $\text{MoO}_3/\text{SiO}_2$ samples. In addition, the adsorption of CO on SiO_2 produced peaks at 2136 and 2155 cm^{-1} (Fig. 5A). These features are ascribed to the physisorbed CO and to the CO interacted with OH groups of silica [36]. On $\text{MoO}_3/\text{SiO}_2$, another weak band appeared at 2207 cm^{-1} at 10 Torr of CO (Fig. 5B). This latter band was also detected on silica–alumina and was attributed to CO bonded to Lewis center [37]. Raising the temperature in the presence of CO, the 2207 cm^{-1} band disappeared at 193 K, and the other two around 213 K. Adsorption of CO on carburized $\text{MoO}_3/\text{SiO}_2$ produced absorption bands at 2201 and 2173 cm^{-1} even at CO pressure of 0.02 Torr (Fig. 5C). The intensity of the latter considerably increased with the pressure of CO. Both bands were quite stable: they were detectable in the presence of CO up to 263 K. Note that the carburization did not induced any new bands in the OH stretching region (not shown).

Summing up, FTIR spectroscopic measurements do not indicate the formation of Brønsted sites during calcination and carburization of $\text{MoO}_3/\text{SiO}_2$ catalyst. However, the adsorption of both pyridine and CO provides strong evidences for the higher strength of Lewis acidic centers for the carburized Mo sample on silica. Moreover, the appearance of the CO band at 2173 cm^{-1} on the $\text{Mo}_2\text{C}/\text{SiO}_2$ suggests the formation of a second type of Lewis sites.

There is an apparent discrepancy between pyridine and CO adsorption measurements, as the absorption bands of pyridine attached to Lewis sites decrease upon carburization, while a small increase in the $\sim 2200\text{ cm}^{-1}$ band due to CO occurred with the appearance of a new type of Lewis centers. This behavior can be explained by the different basicity of the two probe molecules. Pyridine is much more basic and covers all acid centers geometrically available. CO being a soft base adsorbs only on one part of the acid centers depending on their strength and CO pressure. It can be seen that the 2207 cm^{-1} band did not reach a saturation for the 2% $\text{MoO}_3/\text{SiO}_2$ sample even in 10 Torr of CO. Carburization led to Lewis sites that can adsorb CO more strongly which resulted in an intensity of the 2201 cm^{-1} band almost independent of CO pressure. In this case we can assume that all Lewis centers of this type are covered by CO. As regards the exact nature of these acid sites we cannot draw a definitive conclusion, but we assume they are probably Mo containing surface sites.

4. Conclusions

1. A decrease of all the OH stretching bands of $\text{MoO}_3/\text{ZSM-5}$ was observed during calcination. Both pyridine and CO adsorption measurements showed the decrease in the number of Brønsted acidic centers due to deposition of

Mo on ZSM-5. Carburization did not lead to regeneration of Brønsted acidic OH groups.

2. Mo deposited on SiO₂ reacts with the OH groups of the support during calcination and induces Lewis acidity. Carburization resulted in further OH consumption and the appearance of stronger Lewis acid sites. The generation of Brønsted sites was not observed either by pyridine or by CO adsorption. In the aromatization of CH₄ on Mo₂C/SiO₂, the activation of CH₄ probably occurs on the carbide phase, while oligomerization and aromatization of the C_xH_y forms may proceed on Lewis acidic sites.

Acknowledgements

This work was supported by the OTKA D38489 and TSO40877.

References

- [1] D. Wang, J.H. Lunsford, M.P. Rosynek, *Top. Catal.* 3 (1996) 299.
- [2] F. Solymosi, A. Szóke, *Catal. Lett.* 39 (1996) 157.
- [3] F. Solymosi, J. Cserényi, A. Szóke, T. Bánsági, A. Oszkó, *J. Catal.* 165 (1997) 150.
- [4] D. Wang, J.H. Lunsford, M.P. Rosynek, *J. Catal.* 169 (1997) 347.
- [5] L. Wang, L. Tao, M. Xie, G. Xu, *Catal. Lett.* 21 (1993) 35.
- [6] F. Solymosi, A. Erdőhelyi, A. Szóke, *Catal. Lett.* 32 (1995) 43.
- [7] R.W. Borry III, B.C. Lu, K. Young-ho, E. Iglesia, *Stud. Surf. Sci. Catal.* 119 (1998) 403.
- [8] W. Ding, G.D. Meitzner, D.O. Marler, B. Iglesia, *J. Phys. Chem. B* 105 (2001) 3928.
- [9] S. Liu, Q. Dong, R. Ohnishi, M. Ichikawa, *J. C. S. Chem. Commun.* 1445 (1997).
- [10] S. Liu, L. Wang, Q. Dong, R. Ohnishi, M. Ichikawa, *Stud. Surf. Sci. Catal.* 119 (1997) 241.
- [11] C.L. Zhang, S. Li, Y. Yuan, W. Zhang, T. Wu, L.W. Lin, *Catal. Lett.* 56 (1998) 207.
- [12] J.-Z. Zhang, M.A. Long, R.F. Howe, *Catal. Today* 44 (1998) 293.
- [13] D. Wang, J.H. Lunsford, M.P. Rosynek, *Top. Catal.* 3 (1996) 289.
- [14] L. Chen, L. Lin, Z. Xu, X. Li, T. Zhang, *J. Catal.* 157 (1995) 190.
- [15] F. Solymosi, A. Oszkó, P. Tolmascov, *J. Phys. Chem. B* 106 (2002) 9613.
- [16] Z.A. Liu, M. Nutt, B. Iglesia, *Catal. Lett.* 3–4 (2002) 271.
- [17] F. Solymosi, L. Bugyi, A. Oszkó, I. Horváth, *J. Catal.* 185 (1999) 160.
- [18] F. Solymosi, L. Bugyi, A. Oszkó, *Catal. Lett.* 57 (1999) 103.
- [19] L. Bugyi, A. Oszkó, F. Solymosi, *Surf. Sci.* 516 (2002) 74.
- [20] L. Bugyi, A. Oszkó, F. Solymosi, *Surf. Sci.* 519 (2002) 139.
- [21] D. Wang, H.J. Lunsford, M. Rosynek, *Stud. Surf. Sci. Catal.* 107 (1997) 257.
- [22] F. Solymosi, A. Szóke, *Stud. Surf. Sci. Catal.* 119 (1998) 355.
- [23] R. Németh, F. Solymosi, submitted for publication.
- [24] R.W. Borry, Y.H. Kim, A. Huffsmith, J.A. Reimer, B. Iglesia, *J. Phys. Chem. B* 103 (1999) 5787.
- [25] Y.H. Kim, R.W. Borry, E. Iglesia, *Micropor. Mesopr. Mater.* 35–36 (2000) 495.
- [26] W. Ding, S. Li, G.D. Meitzner, E. Iglesia, *J. Phys. Chem. B* 105 (2001) 506.
- [27] L. Su, Y. Xu, X. Bao, *J. Nat. Gas Chem.* 11 (2002) 18.
- [28] S. Liu, L. Wang, R. Ohnishi, M. Ichikawa, *J. Catal.* 181 (1999) 175.
- [29] T.T. Vu Ha, V. Le Tiep, P. Meriaudeau, C. Naccache, *J. Mol. Catal. A: Chem.* 181 (2002) 283.
- [30] J.S. Lee, S.T. Oyama, M. Boudart, *J. Catal.* 106 (1987) 125.
- [31] J.C. Vedrine, A. Auroux, V. Balis, P. Dejaifve, C. Naccache, P. Wierzchowski, E.G. Derouane, B.J. Nagy, J. Gilson, J. van Hooff, J.P. van den Berg, J. Wolthuizen, *J. Catal.* 59 (1979) 248.
- [32] N. Topsøe, K. Pedersen, E.G. Derouane, *J. Catal.* 70 (1981) 41.
- [33] M.R. Basila, T.R. Kantner, H.K. Rhee, *J. Phys. Chem.* 71 (1967) 2192.
- [34] J. Szanyi, M.T. Paffett, *Micropor. Mater.* 7 (1996) 201.
- [35] S. Rajagopal, J.A. Marzari, R. Miranda, *J. Catal.* 151 (1995) 192.
- [36] T.P. Beebe, P. Gelin, J.T. Yates, *Surf. Sci.* 148 (1991) 526.
- [37] A.A. Tsyganenko, O.V. Manailova, K.M. Bulanin, P.Yu. Storozhev, S. Haukka, A. Palukka, M. Lindblad, *Stud. Surf. Sci. Catal.* 130 (2000) 3149.