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The nature of the carbonaceous layer formed on a MoO_3 model catalyst during propylene metathesis

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The carbonaceous layer formed on the surface of a MoO_3 model catalyst during propylene metathesis is examined using Auger electron spectroscopy and ex situ laser Raman spectroscopy. Auger spectroscopy confirms the formation of a carbonaceous layer similar to that found after catalysis performed by Mo metal and MoO_2. Raman spectroscopy indicates that the carbonaceous layer is primarily composed of surface-bound hydrocarbon fragments and small graphitic particles.

Keywords: olefin metathesis, molybdenum oxide, propylene, model catalyst

1. Introduction

The olefin metathesis reaction was first discovered in 1931 by Schneider and Frölich when it was observed that ethylene and butene were formed during pyrolysis of propylene [1]. It was over 30 years later that Banks and Bailey discovered that the reaction could be catalyzed in the heterogeneous phase with alumina-supported molybdenum oxide [2]. Shortly thereafter the reaction was found also to be catalyzed in the homogeneous phase [3], where the reaction is proposed to proceed by the initial formation of a carbene which further reacts with another olefin to form a metallacycle. This metallacycle may then thermally decompose to yield metathesis products [4–20]. Activation energies reported for heterogeneous systems, which are also thought to catalyze metathesis by the carbene-metallacycle mechanism, range from 6–9 kcal/mol [21,22].

A significant amount of work has been done recently to examine the use of thin films deposited on metal substrates as model catalysts to better understand the chemistry of supported metal oxides. It has been shown that below 650 K a molybdenum oxide film catalyzes olefin metathesis with an activity similar to that observed with supported molybdenum oxides. However, above 650 K the reaction proceeds with an activation energy of 60 kcal/mol, a value significantly higher than that seen for supported metathesis catalysts [23]. It has been suggested that metathesis at high temperature proceeds by carbene polymerization on the surface of the catalyst rather than metallacycle decomposition [24,25]. Also, it has been observed that the reaction proceeds in the presence of a thick carbonaceous layer in this high temperature regime. Based on the carbene recombination mechanism proposed for metathesis under these conditions, the carbonaceous layer is expected to be composed of a heterogeneous layer of hydrocarbon species, tightly bound to the catalysts surface. Ex situ Raman analysis is used to examine the nature of the carbonaceous layer deposited on the surface of a MoO_3 model catalyst after metathesis catalyzed in the high temperature regime.

2. Experimental

The apparatus used for these experiments is described in detail elsewhere [26,27]. Briefly, however, it consists of a bakeable, stainless steel, ultrahigh vacuum chamber which operates at a base pressure of 2×10^{-10} Torr after bakeout. The chamber is equipped with a 3 kV electron gun and a rotable hemispherical analyzer which are used for Auger spectroscopy by collecting $n(E)$ spectra. $\mathrm{d}n(E)/\mathrm{d}(E)$ spectra are obtained by differentiation using a Savitzky–Golay algorithm. The chamber is also equipped with a residual gas analyzer used for thermal desorption spectroscopy and leak testing.

The molybdenum foil sample is mounted to the end of a sample manipulator. The foil is cleaned using a standard procedure which consists of repeated cycles of heating to 1450 K in 2×10^{-7} Torr of oxygen followed by annealing to 2000 K to remove the oxygen from the surface. Cleanliness is verified by Auger spectroscopy.

A coaxial, high-pressure reactor contained within the chamber may be closed and filled to 1 atm while maintaining ultrahigh vacuum in the rest of the apparatus. Pressure in the reactor is monitored using a capacitance manometer and small samples of gas may be

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diverted directly to an in-line GC to monitor product accumulation.

Raman spectra were collected using a spectrometer consisting of a Spex double monochromator and a Peltier-effect-cooled photomultiplyer. Spectra were excited using the 514.5 and 488.0 nm lines of an argon ion laser. The laser was steered to the sample using two turning prisms and passed through an iris to eliminate plasma lines. Because of low signal intensity, plasma lines were still observable, so an appropriate laser line was chosen for each range to prevent interference between Raman and plasma lines. Spectra were taken from light back-scattered from the sample.

Propylene used for these experiments was Linde CP grade. The propylene was further purified by bulb-to-bulb distillation and purity was verified using mass spectroscopy and a gas chromatograph. Gas Tech pre-purified grade nitrogen was used as supplied to ballast the high-pressure reactor 1 atm.

3. Results

The MoO_3 used for these experiments is synthesized by oxidation in the high-pressure cell with 200 Torr of oxygen at 550 K for 4 h. Figure 1 shows a Raman spectrum of the resulting film which exhibits features at 670, 822, and 1002 cm^{-1}. Shown for comparison is the Raman spectrum of MoO_3 powder (Mallinckrodt, 99.9% purity) obtained with the same equipment. These spectra agree well, and are also in agreement with previously published results for MoO_3 [28,29].

There is an additional feature clearly present in the spectrum of the film at $\sim$ 950 cm^{-1}. A mode of this frequency in the Raman spectrum has been assigned to the stretching mode of a terminal Mo=O species of an octahedrally coordinated polymolybdate [30–33]. This phase of MoO_3 is also expected to have a peak at $\sim$ 860 cm^{-1} and a weak peak at $\sim$ 700 cm^{-1}. The 860 cm^{-1} mode can be seen as a shoulder on the 822 cm^{-1} crystalline MoO_3 peak, but the 700 cm^{-1} peak is too weak to resolve.

Shown in figure 2 is a typical accumulation curve for the appearance of metathesis products catalyzed by the MoO_3 at 880 K with 450 Torr of propylene. The conversion in this experiment is less than 1%, so the accumulation curve is expected to be linear. This accumulation curve is typical for metathesis catalyzed by model oxides in that it exhibits an induction period in which the accumulation rate accelerates to a steady-state value [23]. Induction periods in olefin metathesis have been noted previously [34,35]. In addition to metathesis products, higher hydrocarbon products (C_5 and greater), and hydrogenolysis (CH_4 and C_2H_4) products are also evident. These have been observed previously for metathesis catalyzed by metallic molybdenum at similar temperatures [24,36].

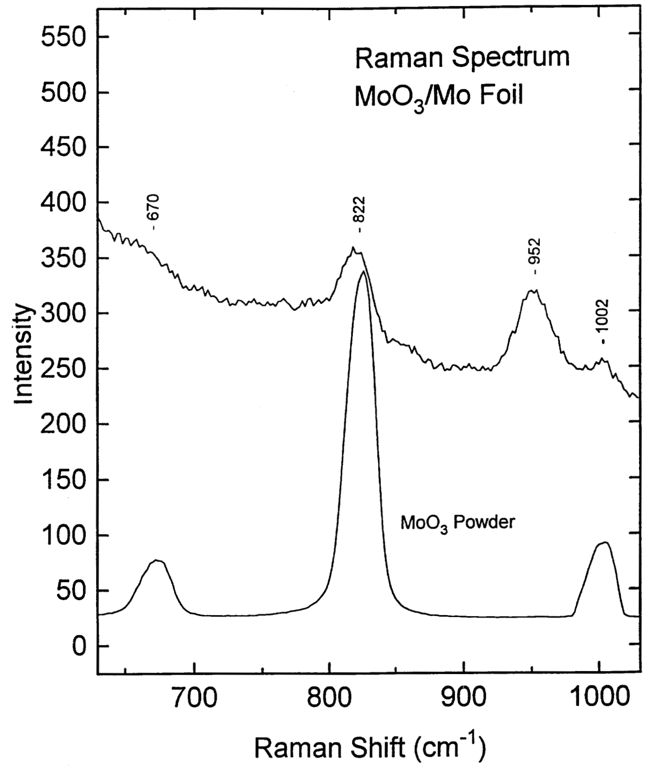

Figure 1. Raman spectrum in the range of 630 to 1030 cm^{-1} of the MoO_3 film formed by oxidation of Mo foil in 200 Torr oxygen at 550 K for 4 h. Shown for comparison is the spectrum of MoO_3 powder.

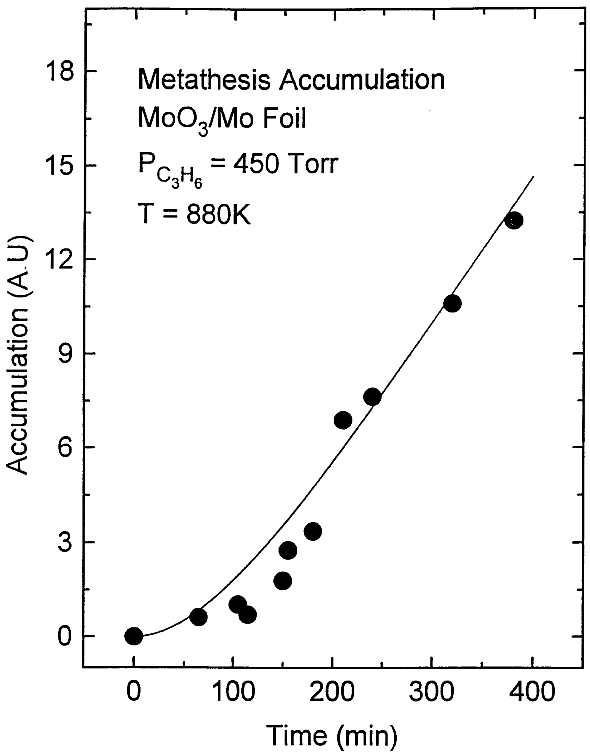

Figure 2. Metathesis product accumulation curve for reaction using a model MoO_3 catalyst with 450 Torr propylene at 880 K.

Auger electron spectroscopy is used to estimate the relative thickness of the carbonaceous layer on the surface of the catalyst after reaction from the relative C/Mo Auger peak ratios. The KLL transition near 270 eV is characteristic for carbon, and the molybdenum MNN transition near 160 eV was chosen because the peaks near 188 and 220 eV were often difficult to resolve because of the size of the carbon peak. The Auger spectra used to collect this data were taken well after any induction period was completed. The results of this experiment are shown in histogram form as figure 3, and indicate that the thickness of the carbonaceous layer decreases with increasing oxidation state. Nevertheless, the C Auger signal on MoO_3 still corresponds to the formation of several monolayers of carbon deposited on the catalyst surface. Shown as an inset in figure 3 is a typical carbon Auger spectrum taken of MoO_3 after reaction.

Several features not present in the Raman spectrum prior to reaction were observed after catalysis. Note that all Raman spectra were collected after removing the sample from the high-pressure reactor. As shown in figure 1, no carbonaceous species are introduced on to the surface by this procedure. This is confirmed by examining the spectral region between 2700 and 3300 cm^{-1} for the catalyst prior to reaction (figure 5) which is completely featureless. Figure 4 shows the Raman spectrum from 900 to 1800 cm^{-1} and figure 5 shows the features for the region between 2700 and 3300 cm^{-1} taken ex situ for the MoO_3 sample surface after reaction in 200 Torr of propylene at 880 K for 4 h.

4. Discussion

The formation of a carbonaceous layer on the surface of the metal or oxide is a common feature in heterogeneous catalysis [26,36]. In the case of reactions catalyzed both by metallic molybdenum and MoO_2, where the data of figure 3 demonstrates the presence of large amounts of carbon on the surface of the catalyst, restart reactions have shown that the catalytic reaction proceeds in the presence of the carbonaceous layer [23,36]. In the case of MoO_3, the carbonaceous layer is sufficiently thick to be seen using Raman spectroscopy and

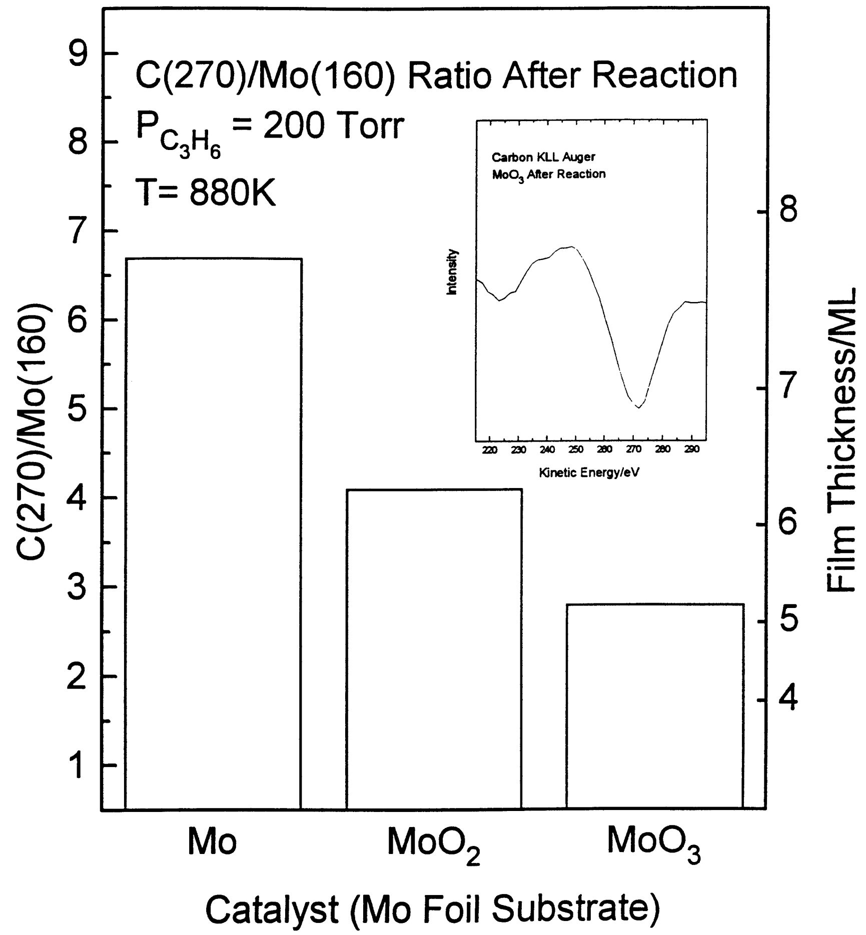

Figure 3. Histogram comparing relative thickness of carbonaceous deposits on model molybdenum and molybdenum oxide catalysts after reaction in 200 Torr propylene at 880 K. Shown as an inset is the carbon KLL Auger peak for a model MoO_3 catalyst after reaction under the same conditions.

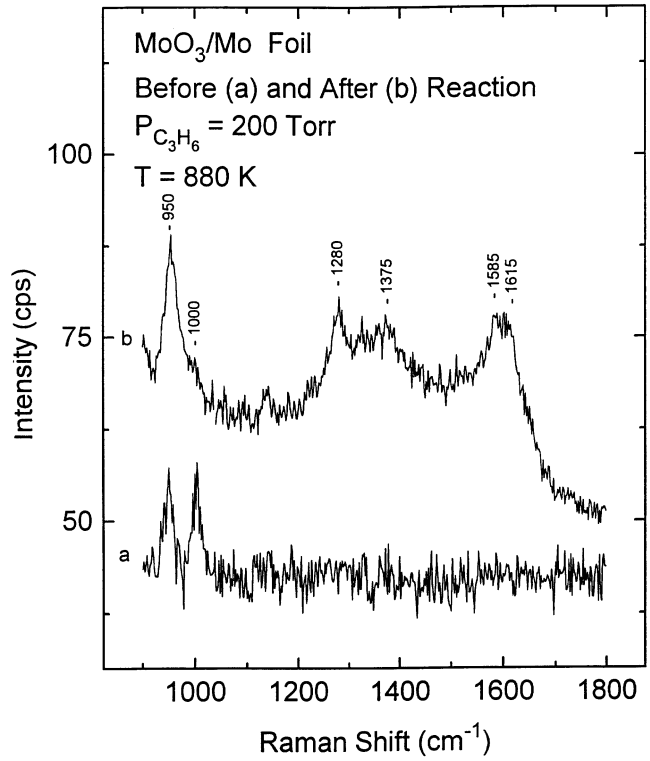

Figure 4. Raman spectrum in the region between 900 and 1800 cm^{-1} showing a model MoO_3 catalyst before (a) and after (b) reaction in 200 Torr propylene at 880 K for 30 min.

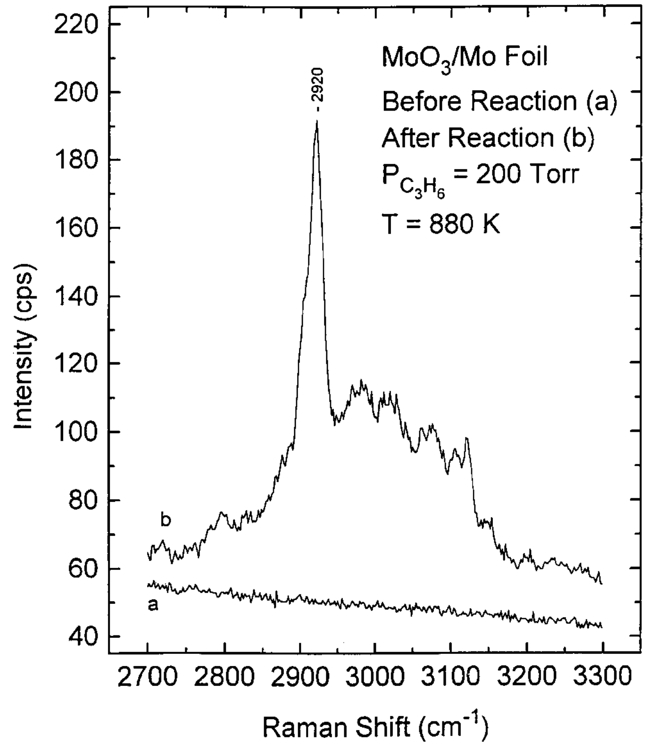

Figure 5. Raman spectrum in the region between 2700 and 3300 cm^{-1} showing a model MoO_3 catalyst before (a) and after (b) reaction in 200 Torr propylene at 880 K for 30 min.

the substrate is sufficiently unreactive that no contamination forms due to contact with air. Figure 5 shows features in the range between 2800 and 3100 cm^{-1} at 2797, 2923, 2983, 3019, 3076, and 3116 cm^{-1} which correspond to C–H stretching modes [37], indicating that the carbonaceous layer is at least in part composed of hydrocarbon fragments. The most obvious feature is at 2920 cm^{-1} which may be assigned to a $-CH_2-$ asymmetric stretch, indicating that the surface hydrocarbon is predominantly saturated, although the features evident above 3000 cm^{-1} suggest the presence of some olefinic species [38–41]. The corresponding $-CH_2-$ symmetric stretch should appear around 2870 cm^{-1} and the shoulder on the low-frequency side of the main 2920 cm^{-1} feature

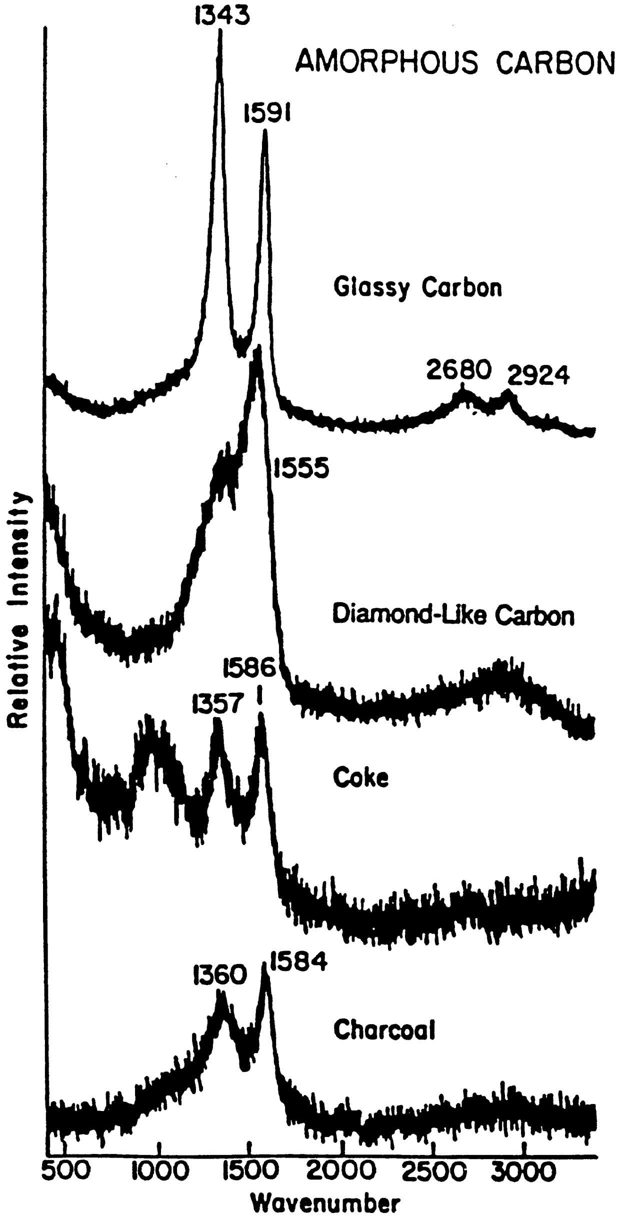

Figure 6. Raman spectra of various amorphous carbonaceous deposits (from ref. [44]).

may be from this mode. The corresponding $-CH_2-$ bending modes should appear at ~ 1380 and 1460 cm^{-1} and this spectral region is shown in figure 4. There is certainly Raman intensity in this region and a feature that appears at ~ 1370 cm^{-1}. The peak at ~ 950 cm^{-1} (assigned above to terminal Mo=O species) is still present although the ~ 1000 cm^{-1} MoO_3 feature is less well resolved. Examination of the lower frequency region between 600 and 1000 cm^{-1} shows that MoO_3 has reduced to primarily MoO_2. This is in accord with what has been observed by other workers [28,29,42,43]. Shown in figure 6 are Raman spectra of various carbonaceous samples [44]. Clearly the features at ~ 1360 and 1585 cm^{-1} in figure 4 may correspond to the presence of carbonaceous materials characterized as "coke" or "charcoal". Coke is further characterized by a peak at ~ 1000 cm^{-1} which is rather small in the data shown in figure 4 suggesting that the material on the surface may be characterized as charcoal. Note that the carbonaceous band does not extend above ~ 1600 cm^{-1} so that intensity above this region may be due to –CH– bends. In addition, features below 1375 cm^{-1}, which peak at ~ 1280 cm^{-1} are likely due to CH modes. Note that methylene groups have characteristic bands at ~ 1450 cm^{-1} so this likely contributes to the intensity in this region in figure 4. Intensity at ~ 1300 cm^{-1} and above ~ 1600 cm^{-1} may indicate the presence of some unsaturation and account for the 1280 and 1615 cm^{-1} features. In this case, the ~ 1300 cm^{-1} features are generally weaker than the ~ 1600 cm^{-1} peaks. Note that the layer is likely to be rather heterogeneous so that detailed assignments become difficult.

The carbon Auger spectrum lineshape (shown as an inset in figure 3) indicates that the composition of the carbonaceous layer is consistent with what has been observed previously for adsorbed hydrocarbon species on molybdenum [47,48]. The presence of the graphitic carbon species observed in the Raman spectrum cannot be resolved.

As noted above, restart reactions show that metathesis proceeds in the presence of such a carbonaceous layer. It has been shown using ethylene as the reactant that olefin metathesis proceeds via the formation of C_1 species which recombine forming products [25]. Surface science experiments also reveal the dissociation of ethylene and the formation of CH_2 species which react to form methane on oxidized Mo(100) [45]. The C_1 species can also polymerize to produce higher hydrocarbons where the yield at various masses is described by a Schulz–Flory distribution [25]. It has been shown that C_1 species in the form of adsorbed methyl groups can react on platinum to form ethylidyne initiating the formation of a strongly bound carbonaceous layer [46]. The carbonaceous layer may form by a similar route on this surface. The observation that the reaction proceeds at the same rate in the presence of such a layer after on average several thousand catalytic reactions have taken place per site implies that the average film thickness is some equilibrium value. The removal of the surface carbonaceous species presumably then results in the formation of gas phase species alluded to above. If, as suggested previously, this involves reaction with hydrogen, this postulate would predict that the rate of higher hydrocarbon formation should increase with the addition of hydrogen and the amount of surface carbon should correspondingly decrease. This effect is currently under investigation.

5. Conclusions

The thick carbonaceous layer formed on the surface of MoO_3 during metathesis catalysis is determined to consist of surface bound hydrocarbon fragments and graphitic carbon particles using Raman spectroscopy. Examination of the carbonaceous layer with Auger spectroscopy and performance of a restart reaction indicate that the layer rapidly reaches an equilibrium thickness and that the reaction precedes in the presence of this layer.

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References

[1] V. Schneider and P.K. Frölich, Ind. Eng. Chem. 23 (1931) 1045.
[2] R.L. Banks and G.C. Bailey, Ind. Eng. Chem. Prod. Res. Dev. 3 (1964) 170.
[3] N. Calderon, H.Y. Chen and K.W. Scott, Tetrahedron Lett. 8 (1967) 3327.
[4] J.L. Hérisson and Y. Chauvin, Makromol. Chem. 141 (1970) 161.
[5] J.P. Soufflet, D. Commercue and Y. Chauvin, C.R. Hebd. Séances Acad. Sci., Ser. C 276 (1973) 169 .
[6] R.J. Haines and G.J. Leigh, Chem. Soc. Rev. 4 (1975) 155.
[7] C.P. Casey and J. Burkhardt, J. Am. Chem. Soc. 96 (1974) 7808.
[8] E.O. Fischer and K.H. Dotz, Chem. Ber. 105 (1972) 3966.
[9] R.R. Schrock, J. Am. Chem. Soc. 96 (1974) 6976.
[10] R.R. Schrock, J. Am. Chem. Soc. 98 (1976) 5399.
[11] B.A. Dolgoplosk, Dokl. Chem. 216 (1974) 380.
[12] R.H. Grubbs, P.C. Burk and D.D. Carr, J. Am. Chem. Soc. 97 (1975) 3265.
[13] R.H. Grubbs, D.D. Carr, C. Hoppin and P.C. Burk, J. Am. Chem. Soc. 98 (1976) 3478.
[14] T.J. Katz and J. Rothschild, J. Am. Chem. Soc. 98 (1976) 2519.
[15] T.J. Katz and W.H. Hersch, Tetrahedron Lett. (1977) 585.
[16] C.P. Casey, H.E. Hunstra and M.C. Searnan, J. Am. Chem. Soc. 98 (1976) 608.
[17] F.N. Tebbe, G.W. Parshall and D.W. Overnall, J. Am. Chem. Soc. 101 (1979) 5074.
[18] J. Wengorius, R.R. Schrock, M.R. Churchill, J.R. Mussert and W.J. Young, J. Am. Chem. Soc. 102 (1980) 4515.

[19] T.R. Howard, J.B. Lee and R.H. Grubbs, J. Am. Chem. Soc. 102 (1980) 6878.

[20] R.H. Grubbs and T.K. Brunck, J. Am. Chem. Soc. 94 (1972) 25.

[21] E.S. Davie, D.A. Whan and C. Kemball, J. Catal. 24 (1972) 272.

[22] A.J. Moffat and A. Clark, J. Catal. 17 (1970) 264.

[23] B. Bartlett and W.T. Tysoe, J. Catal., in press.

[24] B. Bartlett, V. Shneerson and W.T. Tysoe, Catal. Lett. 32 (1995) 1.

[25] B. Bartlett and W.T. Tysoe, Catal. Lett. 44 (1997) 37.

[26] L.P. Wang and W.T. Tysoe, J. Catal. 28 (1991) 320 .

[27] L.A. Huezo, P.V. Kotvis, C. Crumer, C. Soto and W.T. Tysoe, Appl. Surf. Sci. 78 (1994) 113.

[28] P.A. Spevack and N.S. McIntyre, J. Phys. Chem. 96 (1992) 9029.

[29] P.A. Spevack and N.S. McIntyre, J. Phys. Chem. 97 (1993) 11020.

[30] K. Ajito, L.A. Nagahara, D.A. Tryk, K. Hashimoto and A. Fujiahima, J. Phys. Chem. 99 (1995) 16385.

[31] H. Hu and I.E. Wachs, J. Phys. Chem. 99 (1995) 10897.

[32] E. Payen, S.J. Kasztelan, J. Grimblot and J.P. Bonelle, J. Raman Spectros. 17 (1986) 233.

[33] L. Sequin, M. Figlarz, R. Cavagnat and J.C. Lasseques, Spectrochim. Acta A 51 (1995) 1323.

[34] R.C. Luckner and G.B. Wills, J. Catal. 28 (1973) 83.

[35] G.B. Wills, J. Fathikalajahi, S.K. Gangwal and S. Tang, Rec. Trav. Chim. 96 (1977) M110.

[36] L.P. Wang, C. Soto and W.T. Tysoe, J. Catal. 143 (1993) 92.

[37] L.J. Bellamy, *The Infrared Spectra of Complex Molecules* (Wiley, New York, 1960) p. 273.

[38] N.B. Colthup, L.H. Daly and S.E. Wiberly, *Introduction to Infrared and Raman Spectroscopy* (Harper and Row, New York, 1964).

[39] P. Laszlo and P.J. Stang, *Organic Spectroscopy* (Harper and Row, New York, 1971).

[40] J. Loader, *Basic Laser Raman Spectroscopy* (Heyden, London, 1970).

[41] R.L. Shriner, R.C. Fuson and D.Y. Crutin, *The Systematic Identification of Organic Compounds* (Wiley, New York, 1958).

[42] M. Yamada, J. Yasumaru, M. Houalla and D.M. Hercules, J. Phys. Chem. 95 (1991) 7037.

[43] W. Grünert, A.Y. Stakheev, R. Feldhaus, K. Anders, E.S. Shapiro and K.M. Minachev, J. Phys. Chem. 95 (1991) 1323.

[44] D.S. Knight and W.B. White, J. Mater. Res. 4 (1989) 385.

[45] G. Wu, B. Bartlett and W.T. Tysoe, Surf. Sci., submitted.

[46] D.H. Fairbrother, X.D. Peng and P.C. Stair, J. Chem. Soc. Faraday Trans. 91 (1995) 3619.

[47] L. Wang and W.T. Tysoe, Surf. Sci. 236 (1990) 325.

[48] L. Wang and W.T. Tysoe, Surf. Sci. 245 (1991) 320.