Catalysis Letters 34 (1995) 365–374

Aniline hydrogenolysis on nickel: effects of surface hydrogen and surface structure

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Received 7 July 1994; accepted 24 June 1995

Fluorescence yield near-edge spectroscopy (FYNES) above the carbon K edge and temperature programmed reaction spectroscopy (TPRS) have been used as the methods for characterizing the reactivity and structure of adsorbed aniline and aniline derived species on the Ni(100) and Ni(111) surfaces over an extended range of temperatures and hydrogen pressures. The Ni(100) surface shows appreciably higher hydrogenolysis activity towards adsorbed aniline than the Ni(111) surface. Hydrogenolysis of aniline on the Ni(100) surface results in benzene formation at 470 K, both in reactive hydrogen atmospheres and in vacuum. External hydrogen significantly enhances the hydrogenolysis activity for aniline on the Ni(100) surface. Based on spectroscopic evidence, we believe that the dominant aniline hydrogenolysis reaction is preceded by partial hydrogenation of the aromatic ring of aniline in the presence of 0.001 Torr of external hydrogen on the (100) surface. In contrast, very little adsorbed aniline undergoes hydrogen induced C–N bond activation on the Ni(111) surface for hydrogen pressures as high as 10^{-7} Torr below 500 K. Thermal dehydrogenation of aniline dominates with increasing temperature on the Ni(111) surface, resulting in the formation of a previously observed polymeric layer which is stable up to 820 K. Aniline is adsorbed at a smaller angle relative to the Ni(111) surface than the Ni(100) surface at temperatures below the hydrogenolysis temperature. We believe that the proximity and strong π-interaction between the aromatic ring of the aniline and the surface is one major factor which controls the competition between dehydrogenation and hydrogen addition. In this case the result is a substantial enhancement of aniline dehydrogenation relative to hydrogenation on the Ni(111) surface.

Keywords: aniline hydrogenation; aniline hydrogenolysis; nickel surface; temperature programmed reaction; near-edge X-ray absorption fine structure

1. Introduction

Hydrogenolysis of organonitrogen compounds on transition metal surfaces plays an important role in a wide range of catalytic processes. A series of aniline hydrogenolysis experiments in reactive hydrogen atmospheres are reported here

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and are compared with reactivities observed in the absence of external hydrogen. Spectroscopic studies have been used to establish correlations between the structure of the primary adsorbed species and their reactivity on two nickel single crystal surfaces.

Recent studies on the Pt(111) surface indicated that C–N bond activation in adsorbed aniline is substantially enhanced in the presence of external hydrogen [1,2]. The enhanced hydrogenolysis rate is associated with an increased supply of hydrogen at reaction temperature and a parallel adsorption geometry for the reactive intermediate. In contrast to the results for nickel discussed here, on platinum the primary aniline derived surface intermediate retains its aromatic character until it reaches hydrogenolysis temperature in the presence of hydrogen. In the absence of hydrogen, the adsorbed intermediate tilts away from the surface because of partial aniline dehydrogenation below the C–N bond cleavage temperature.

Adsorption of aniline has previously been studied on evaporated nickel films [3]. Aniline was found to adsorb both molecularly via the π-electrons and dissociatively via an anion formed by the release of a proton from the amino group. On well-defined nickel single crystal surfaces under ultrahigh vacuum (UHV) conditions, adsorbed aniline is thought to form polyaniline, an unreactive aromatic surface polymer which is stable to above 600 K [4,5]. Polymerization is believed to occur when surface activated ring carbon atoms lose their hydrogen and react with the amino groups on adjacent aniline groups. We find that aniline hydrogenolysis competes with dehydrogenation and polymerization in the presence of hydrogen atmospheres. The extent of aniline hydrogenolysis is larger on the open Ni(100) than on the close-packed Ni(111) surface, and increases with the pressure of surface hydrogen available during reaction. Both the surface structure and hydrogen availability play a key role in modifying the structure of reaction intermediates and the dominant surface reaction pathways.

2. Experimental

The structure and reactivity of chemisorbed aniline has been studied both under UHV conditions ($\sim 10^{-10}$ Torr range) and in hydrogen pressures up to 0.01 Torr. Gas phase surface reaction products were monitored with a multiplexed mass spectrometer for temperature programmed reaction spectroscopy (TPRS) performed in an ultrahigh vacuum (UHV) system. Spectroscopic X-ray absorption measurements were performed to characterize the surface structure of aniline derived surface species using continuously tunable ultrasoft X-ray (270–330 eV) from a synchrotron radiation source. These X-ray absorption experiments, as described elsewhere [2], were performed as general users on Exxon's U-1 beamline at the National Synchrotron Light Source. The electronic structure and orientation of adsorbed surface intermediates were characterized using near-edge X-ray absorption fine structure (NEXAFS) detected using fluorescence yield (FY). The

FY detection technique makes it possible to study the surface species and reaction kinetics in the presence of reactive hydrogen. The nickel surfaces were cleaned by cycles of sputtering, oxygen treatment and annealing. The cleanliness of the surfaces was verified using Auger electron spectroscopy (AES). Aniline monolayers were formed by adsorbing aniline at 100 K and heating to 210 K to sublime multilayers formed during adsorption. The sample was resistively heated with a linear rate for all the temperature programmed measurements.

3. Results and discussion

Following adsorption at ~ 100 K, aniline is molecularly adsorbed on both nickel surfaces up to 250 K. Annealing the aniline adlayer causes multilayer desorption at 190 K, and physisorbed aniline desorbs in the 200–250 K range on both nickel surfaces studied (figs. 1 and 2). Further temperature increases induce significant

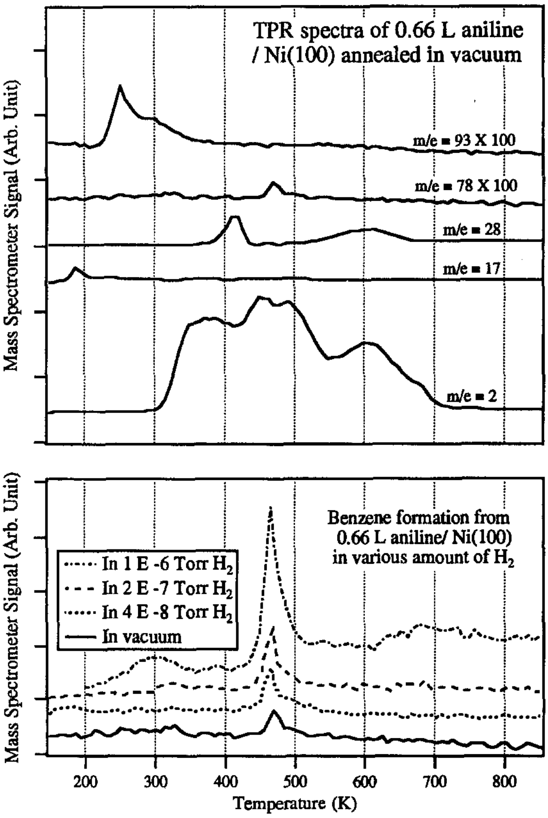

Fig. 1. Temperature programmed reaction spectra of 0.66 L of aniline adsorbed on the Ni(100) surface at 100 K. The heating rate during the TPRS is 5 K/s. The upper panel presents the major TP reaction products in the absence of hydrogen. The lower panel shows the increase in benzene production with increasing hydrogen pressures.

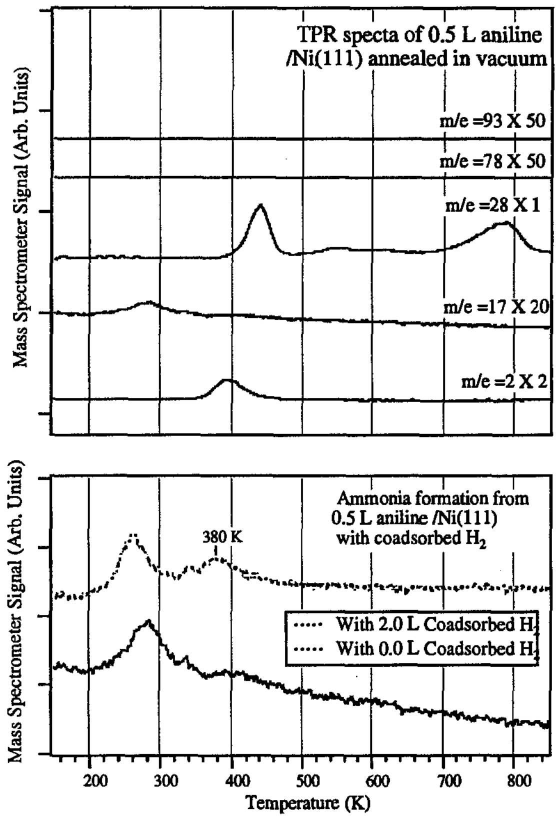

Fig. 2. Temperature programmed reaction spectra of the surface reaction products for a monolayer aniline on the Ni(111) surface. The dashed lines correspond to the same amount of aniline preadsorbed with half a monolayer of hydrogen. The heating rate during the TPRS is 2 K/s. In the presence of hydrogen, ammonia is produced during aniline hydrogenolysis at 380 K.

dehydrogenation of adsorbed aniline between 300 and 700 K (see for instance mass 2 in both fig. 1 and 2). The massive dehydrogenation process is thought to affect all the aniline molecules that are chemisorbed on the nickel surface, since no peaks from molecular aniline are observed above the dehydrogenation temperature. The desorption of surface hydrogen may be the key factor that limits aniline hydrogenolysis under UHV conditions.

Since surface hydrogen coverages are expected to be important in modifying aniline hydrogenation and dehydrogenation on nickel surfaces, the experimental results below are presented to facilitate comparisons of the aniline reactions in vacuum with those in hydrogen atmospheres. In these experiments, the concentration of surface hydrogen is increased either by coadsorbing hydrogen with aniline or by characterizing the reaction in the presence of hydrogen atmospheres. In the discussion below, we will focus on changes in the reaction products, and the structure of reaction intermediates in response to increased hydrogen concentration.

In the aniline TPR experiments on the Ni(100) surface (illustrated in fig. 1), the hydrogenolysis of aniline occurs at 470 K, producing benzene as a gas phase product. Increased surface hydrogen availability during reaction greatly enhances the production of benzene. In the absence of external hydrogen, dehydrogenated aniline derived species remain on the surface above the hydrogenolysis temperature. Those surface species decompose at 600 K and produce hydrocarbon fragments (mass 16, 27, 28) from the Ni(100) surface. With a relatively small amount of hydrogen ($\sim 10^{-6}$ Torr), all the chemisorbed aniline from a 0.66 L exposure undergoes hydrogenolysis to form benzene at 470 K, so that no hydrocarbon species remain at higher temperature. The dehydrogenated amino group evolves into HCN during direct decomposition at 600 K or surface nitrogen at 900 K and above as indicated by Auger studies (spectra not shown) of the surface composition after annealing aniline under UHV conditions.

No detectable aniline hydrogenolysis is observed under UHV reaction conditions on the Ni(111) surface (fig. 2). With preadsorbed hydrogen, small amounts of ammonia are evolved from the Ni(111) surface at 380 K as indicated in the lower panel of fig. 2. The ammonia production remains quite small even in $\sim 10^{-7}$ Torr hydrogen pressures [6]. Even for hydrogen pressures in the 0.001 Torr range, only 20% of the aniline derived surface species are removed at $\sim$400 K. The remaining aniline derived surface species remain on the surface and decompose with increasing temperature [6]. This observation will be discussed more extensively in terms of precursor structure later in this paper. Thus with increased availability of hydrogen, hydrogenolysis becomes increasingly competitive with surface reaction pathways involving dehydrogenation. However, the extent of aniline hydrogenolysis observed on the Ni(111) surface is clearly smaller than the extent of hydrogenolysis observed on the Ni(100) surface.

The loss of hydrogen around 400 K is an important factor that limits aniline hydrogenolysis on the Ni(111) surface in low pressure environments [6], since hydrogen addition to the C–N bond is generally the slowest step. External hydrogen apparently stabilizes molecular aniline toward dehydrogenation and subsequent polymerization. The polymer formed during aniline dehydrogenation is stable up into the 600 K range. With further heating, thermal dehydrogenation of the surface aniline derived polymer produces a carbonaceous overlayer which contains carbon–nitrogen multiple bonds which are difficult to activate. This carbonaceous layer is stable up to 820 K when it fragments and produces N_2, HCN, C_2H_4. Both the extraordinary stability and eventual decomposition of this aniline derived surface species are enhanced by strong interactions with the Ni(111) surface as demonstrated by the NEXAFS results discussed below.

In the absence of hydrogen on both the Ni(100) and Ni(111) surfaces, the aromatic ring in the aniline derived surface adsorbates remains intact in the temperature range 300–400 K as shown in the upper panels of figs. 3 and 4. The lower panels of these two figures indicate that in the presence of external hydrogen, hydrogenation of the adsorbed intermediate dominates on the Ni(100) surface, but not on the Ni(111) surface. The sections which follow describe the bonding and

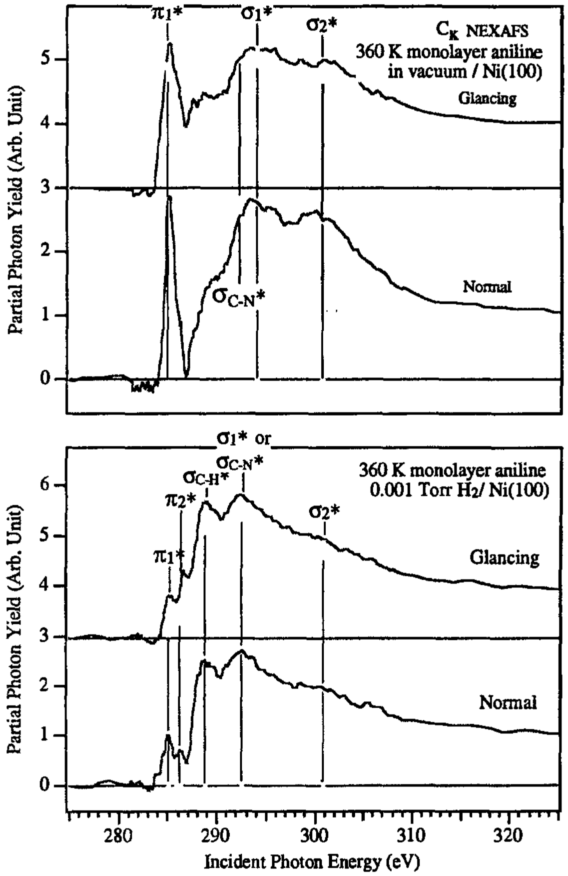

Fig. 3. Carbon K-edge NEXAFS spectra for monolayer aniline on Ni(100) annealed to 360 K. The upper panel presents spectra taken in vacuum, and the lower in hydrogen. The hydrogen spectra were taken after the adlayer is heated in 0.001 Torr hydrogen, followed by subsequent quenching and evacuating of the reactive gases. External hydrogen causes reduced aromaticity and partial hydrogenation of the carbon species.

orientation of the primary adsorbed species on both surfaces for temperatures just below the dominant surface reactions both in vacuum and in hydrogen. NEXAFS intensities and their angular dependence have been used here to characterize the structure of adsorbed aniline derived species and their orientation in the presence and absence of external hydrogen pressures [7].

The orientational dependence of the resonant transitions indicates that, for the aniline derived species, the aromatic rings are tilted on the Ni(100) surface at 360 K in vacuum (shown in the upper panel in fig. 3) [8]. The polar angle (the angle between the surface and the plane of the phenyl ring) is estimated to be 60°, from the ratio of π^* resonance intensity at two incidence angles ($I_{90^\circ}/I_{30^\circ}$), assuming the X-ray polarization factor to be 0.85. This relatively large tilt angle indicates that aniline interacts with the Ni(100) surface primarily through the amine nitrogen. On

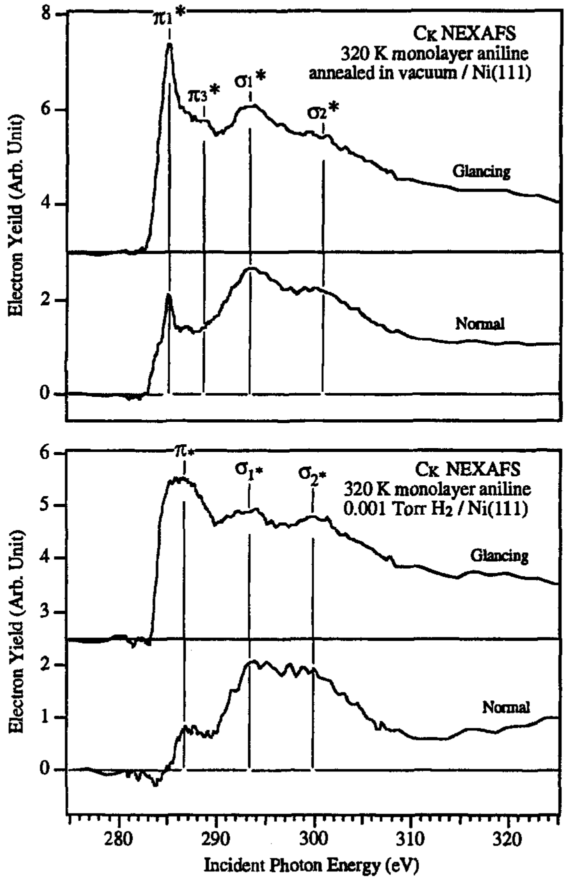

Fig. 4. Carbon K-edge NEXAFS spectra for monolayer aniline on Ni(111) annealed to 320 K. The upper panel presents spectra taken in vacuum, and the lower in hydrogen. The hydrogen spectra were taken after the adlayer is heated in 0.001 Torr hydrogen, followed by subsequent quenching and evacuating of the reactive gases. External hydrogen is instrumental in enhancing the interaction between the substrate and the carbon ring.

the active Ni(100) surface, disproportionation of aniline results in C–N bond activation even in the absence of externally added hydrogen. The aromatic ring system is relatively undisturbed so that gas phase benzene is the primary product resulting from aniline hydrogenolysis on the surface.

In contrast, aniline on the Ni(111) surface is adsorbed with the aromatic rings nearly parallel ($<20°$) to the surface below 250 K. This configuration is not stable when the temperature is raised to 320 K (fig. 4). As dehydrogenation begins, the carbon rings begin to reorient away from the surface, resulting in a polar angle of $\sim 40°$ at 320 K. This reorientation, coupled with hydrogen loss, contributes to the relatively low hydrogenolysis activity of aniline in the absence of hydrogen. Dehydrogenation may result in increased carbon–nitrogen bond order relative to molecular aniline [6], producing surface species which are extremely hard to activate.

Massive dehydrogenation and polymerization start to produce an extensively dehydrogenated layer which is π-bonded to the surface, as illustrated by the slight broadening of the π* resonances with respect to those observed for molecular aniline. A recent UPS study [6] suggests that full π-bonding with the substrate is not established until 400 K. The NEXAFS spectrum of aniline/Ni(111) annealed to 500 K (not shown due to limited space) is dominated by one very broad (~3 eV) π* resonance, indicating that the π* system is extensively delocalized either in the polymer overlayer or with the surface at elevated temperature. Strong adsorbate–substrate interaction eventually results in the cleavage of both C–C and C–N bonds at 800 K.

Hydrogen treatment at temperatures in the 300–400 K range causes dramatic changes in the NEXAFS spectra relative to adsorbed aniline heated in vacuum as illustrated by comparing the upper and lower panels of figs. 3 and 4. On the Ni(100) surface (fig. 3 lower panel), the intensities of the π* resonance are uniformly reduced at all X-ray incidence angles, about 70% lower than those observed for the vacuum annealed case. The reduction in π* intensity, together with the increased intensity of the $\sigma^*_{\text{C-H}}$ resonances, indicates that the carbon ring undergoes partial hydrogenation in H_2. In 0.001 Torr of hydrogen on the Ni(100) surface, the hydrogenation is so significant that the NEXAFS peak attributed to C–H bonds is the dominant peak in the aniline spectrum. The spectrum obtained for the aniline derived species at 360 K is surprisingly similar to the spectrum observed for molecular cyclohexylamine [9]. Both aniline and cyclohexylamine hydrogenolysis result in the formation of benzene. Thus hydrogenated and/or partially hydrogenated surface intermediate common to aniline and cyclohexylamine appears to be a common precursor for hydrogenolysis on the Ni(100) surface. Benzene desorption from the Ni(100) surface in the (400–500 K) temperature range has been observed previously during cyclohexene dehydrogenation [10] lending further support to the feasibility of hydrogenolysis mechanism involving hydrogenation and dehydrogenation. We have observed no cyclohexane or cyclohexene formation during hydrogenolysis of aniline or cyclohexylamine on the Ni(100) surface. Initially the aromatic ring is hydrogenated and the C–N bond activation process occurs, then the adsorbed cyclic hydrocarbon is dehydrogenated to form benzene at 470 K.

Aniline's aromatic ring is aligned more nearly parallel to the Ni(111) surface in the presence of hydrogen relative to the vacuum case after heating to 320 K (lower panel, fig. 4). At 320 K, the polar tilt angle is estimated to be less than 30° based on the angular dependence of the π* intensity. The small tilt angle contributes to the broadening of π* resonances because of enhanced interactions with the surface. At 320 K, the FWHM of the π* resonance of aniline increases to 3–4 eV in 0.001 Torr of hydrogen. This increased broadening suggests that delocalization of aromatic π-electrons through polymerization and/or interaction with the surface is enhanced in hydrogen. Strong interaction between aniline and the surface might be expected to enhance rates of either dehydrogenation or hydrogenation reactions.

Dehydrogenation of aniline appears to be enhanced on the Ni(111) surface with the conditions used here.

The contrasting carbon K-edge NEXAFS spectra of adsorbed aniline on both the Ni(111) and Ni(100) surfaces after heating with and without external hydrogen pressure (figs. 3 and 4) clearly indicate that hydrogen modifies the bonding and structure of the aniline derived species on the surfaces. When annealed *in the absence of hydrogen* into the 300–400 K range, the aniline derived species remains strongly aromatic on both surfaces, with its electronic structure relatively undisturbed from that of molecular aniline. In contrast, when annealed *in hydrogen*, on the Ni(100) surface the increased intensity of the C–H resonances and decreased intensity of the π^* resonances indicate that the dominant surface species is partially hydrogenated. On the Ni(111) surface the substantial intensity of the π^* resonances coupled with significant broadening clearly indicate that surface hydrogen significantly enhances the interaction of the aromatic group with the surface which results in dehydrogenation and massive polymerization.

To summarize, aniline hydrogenolysis on nickel model catalysts is a structure-sensitive reaction. Though C–N bond activation is enhanced by external hydrogen on both nickel surfaces studied, the structure sensitivity of the reaction results in marked contrast in the reaction temperature, products, and hydrogen pressure. The relatively open Ni(100) surface shows substantially higher aniline hydrogenolysis reactivity than the close-packed Ni(111) surface. On the Ni(100) surface, much less external hydrogen is required in order to achieve the same degree of aniline hydrogenolysis. On the Ni(100) surface, low temperature adsorption results in adsorption with the aromatic ring remote from the Ni surface. With increasing temperature and hydrogen pressure, a partially hydrogenated surface intermediate is formed which results in extensive C–N bond activation and benzene formation in the 470 K range. Aniline NEXAFS spectra on the Ni(111) surface are marked by adsorption at smaller angles with respect to the surface. The π^* resonances for adsorbed aniline on the Ni(111) surface are broader than those on the Ni(100) surface, indicating more extensive delocalization of the aromatic π-electrons. This configuration promotes the dehydrogenation of aniline which leads to the formation of the tenacious carbonaceous layer. Activation of the C–N bond in the resulting dehydrogenated species is apparently quite difficult, especially for hydrogen pressures below 10^{-7} Torr.

4. Conclusion

A combination of TPRS and NEXAFS measurements both in reactive hydrogen atmospheres and in vacuum was utilized to probe the structure of reactive species, reaction mechanisms and reactivity of aniline on the Ni(100) and Ni(111) surfaces. Aniline hydrogenolysis on nickel is a structure sensitive reaction. The Ni(100) surface exhibits appreciably higher hydrogenolysis activity towards adsorbed aniline than the close-packed Ni(111) surface. Though C–N bond activation is enhanced by external hydrogen on both nickel surfaces, much less external hydrogen is required for the Ni(100) surface in order to achieve the same degree of aniline hydrogenolysis. The relatively facile C–N bond cleavage on the Ni(100) surface is believed to be facilitated by the prior saturation of the aromatic rings. This proposal is consistent with observations from classical hydrodenitrogenation (HDN) catalysis which suggest that aromatic compounds are generally saturated prior to the nitrogen removal step.

Acknowledgement

Acknowledgement is made to the Office of Basic Energy Sciences, the Department of Energy (Grant No. DE-FGO2-91ER14-190), for the support of this research.

References

[1] S.X. Huang, D.A. Fischer and J.L. Gland, Preprints ACS Petroleum Chemistry Division 38 (1993) 692.
[2] S.X. Huang, D.A. Fischer and J.L. Gland, J. Vac. Sci. Technol. A 12 (1994) 2164.
[3] K. Kishi, K. Chinomi, Y. Inoue and S. Ikeda, J. Catal. 60 (1979) 228.
[4] A.K. Myers and J.B. Benziger, Langmuir 5 (1989) 1270.
[5] G.R. Schoofs and J.B. Benziger, J. Phys. Chem. 92 (1988) 741.
[6] S.X. Huang, D.A. Fischer, C. Muryn, G. Thornton and J.L. Gland, J. Phys. Chem., in preparation.
[7] J. Stöhr, *NEXAFS Spectroscopy* (Springer, Berlin, 1992).
[8] S.X. Huang, D.A. Fischer and J.L. Gland, Surf. Sci., in preparation.
[9] S.X. Huang, PhD Dissertation, University of Michigan, USA (1995).
[10] K.-A. Son, M. Mavrikakis and J.L. Gland, J. Phys. Chem., in press.