

The oxidative ammonolysis of ethylene to acetonitrile over gamma-Al₂O₃ supported molybdenum catalysts

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Chapter 23

The Oxidative Ammonolysis of Ethylene to Acetonitrile over γ -Al₂O₃-Supported Molybdenum Catalysts

I. Peeters, J. van Grondelle, and R. A. van Santen

Schuit Institute of Catalysis, Eindhoven University of Technology,
P.O. Box 513, 5600 MB Eindhoven, Netherlands

The reaction of ethylene with ammonia, without gaseous oxygen, to acetonitrile over γ -Al₂O₃ supported molybdenum catalysts was studied. The effects of molybdenum loading and pretreatment on the catalytic activity were investigated. Experiments showed that the activity at the semi-steady-state is highly structure sensitive. Pretreated in oxygen, the catalyst is highly selective towards CH₃CN, with CO_x formed as side product. Pretreated in hydrogen, the catalyst is more active but less selective, with ethane formed as side product. Two mechanisms were deduced:

- 1) ammoxidation mechanism with consumption of lattice oxygen.
- 2) oxidative ammonolysis with coproduction of ethane, without lattice oxygen consumption.

The steady-state activity was independent of pretreatment and no oxygen containing products were observed, indicating that mechanism 1) can gradually change into 2) when removable lattice oxygen becomes depleted. The product distribution indicated that the mechanisms can be active simultaneously and separately. Mechanism 2 appeared to be operational on a MoO₂-like structure.

Acetonitrile is a well-known polar solvent. Although one of the more stable nitriles, it can be used as a reactant in a wide range of typical nitrile reactions, such as the synthesis of amides, amines and isocyanates.(1,2) A multitude of different processes are known to produce acetonitrile, such as the decomposition of alkyl amines(3,4) Also, reactions of ammonia with ethanol(5), acetic acid, acetic anhydride or thermal decomposition of several nitrogen containing compounds, and reactions of cyanogen, hydrocyanic acid or ammonia with hydrocarbons all yield acetonitrile(6,7). The most extensively studied system is the

formation of acetonitrile from CO, H₂ and NH₃, (6,8,9) For this reason, catalysts are most frequently based on molybdenum (10,11) or iron oxides (12,13) on silica or alumina supports. The addition of silver, copper, rhodium (10), manganese and alkali earths (8) is mentioned to improve the selectivity to acetonitrile considerably. HCN has been suggested as the principal intermediate for this reaction. (11) So basically, acetonitrile is produced by catalytic decomposition of higher molecules, or by substitution of oxygen with nitrogen. CH₃CN and HCN are the main side products of the propylene ammoxidation over Bi/Mo catalysts (Sohio process) and in some plants acetonitrile is recovered and purified. (1,2)

Much research has been done on allylic (amm)oxidation of olefins over molybdenum containing catalysts. [14] However, little is known about vinylic (amm)oxidation. Here we report the formation of CH₃CN from ammonia and ethylene as reactants over γ -Al₂O₃ supported molybdenum catalysts. To focus on the reactivity of lattice oxygen and to exclude surface reoxidation, oxidative ammonolysis experiments were done in the absence of gaseous oxygen. Two reaction mechanisms are proposed to explain the results. One is based on stoichiometric consumption of lattice oxygen and resembles the ammoxidation reaction mechanism, whereas the other is based on the hydrogenation of ethylene. Which mechanism is operative strongly depends on the catalyst pretreatment and the morphology created in time due to reaction.

Experimental

Catalysts were prepared by incipient wetness impregnation of a commercial γ -Al₂O₃ (Akzo, Ketjen CK-300, 200 m² g⁻¹, 0.6 ml g⁻¹, 250-500 μ m) with aqueous solutions of ammonium heptamolybdate ((NH₄)₆Mo₇O₂₄), followed by drying overnight in air at 110 °C and heating in a flow of artificial air to 550 °C for 1h. Before cooling to reaction temperature, the catalyst was heated in a 5 vol% O₂ in helium flow to 550 °C for 24 h and, when reductive pretreatment was desired, subsequently heated in a 10 vol% H₂ in helium flow from room temperature to 650 °C for 24 h. The temperature ramp was set at 5 °C/min for all cases and the total flow was kept at 20 Nml/min. No indications were found of the formation of bronzes (H_xMoO₃) after a hydrogen treatment. Bronzes are known for their colour changes while forming, and the formation is reversible, so a heat treatment in an inert atmosphere will reform the corresponding oxide. After testing no bronzes were observed. Reactions were performed in a fixed bed plug flow reactor, containing 1.0 g of catalyst. The temperature window applied was 350 to 550 °C and incremental molybdenum loadings were tested (3, 5, 10 and 15 wt%, based on atomic Mo). To a helium flow of 20 Nml/min containing 0.75 vol% of ethylene, pulses of ammonia were added, yielding 1.1 vol%. In this way flow conditions were mimicked. The reactor effluent was monitored on-line by a quadrupole mass spectrometer (Balzers QMG-420) which operated at ionisation potential of 70 eV and inlet pressure of 5.0·10⁻⁶ mBar. The Balzers software program "Quadstar 420 v3.05" was used in the multiple ion detection mode, where 16 different masses could be adjusted. The masses m/e= 2, 17, 18, 27, 30, 40 and 44 were used for identifying hydrogen, ammonia, water, ethylene, ethane, acetonitrile and carbon dioxide, respectively. Organic compounds

were quantified by introducing a sample into a Hewlett Packard 5890 A gas liquid chromatograph equipped with a Poraplot Q column, 10 m * 0.32 mm i.d., and flame ionisation detector (FID). Besides on-line sampling, off-line analysis could be performed by storing 15 samples in a 16 loop valve. Inorganic compounds, such as CO_x, were quantified by introducing a sample into a Porapak N column, 6 ft * 3x2mm (e.d. x i.d.) 80/100 mesh equipped with a thermal conductivity detector (TCD). The GLC was connected to a Nelson interface and a computer for spectra assimilation.

While collecting data, three important regions of the reaction could be distinguished, which are schematically shown in Figure 1:

- 1) the first 2 hours of a semi-steady-state, which was reached within 10 minutes after starting the reaction. Although the acetonitrile production was constant over this 2 hour period, the selectivity to other products was changing.
- 2) a transition period where strong changes in conversion and selectivity occurred, dependent on the catalyst.
- 3) after at least 20 hours of reaction when a *real* steady-state was reached.

A quasi turnover frequency (qTOF) was defined as moles acetonitrile produced per mole molybdenum per hour.

At various reaction times, samples for XPS analysis were taken. This was done by shutting the reactor after cooling the catalyst in helium. Subsequently the reactor was introduced into a nitrogen-filled glove box, where the XPS sample was prepared. The catalyst was crushed and mounted on an iron stub carrying an indium film. The sample was placed in a vessel in a nitrogen atmosphere for transport to the spectrometer. XPS spectra were measured on a VG-ESCALAB equipped with a standard dual X-ray source, of which the Al-K α part was used. Spectra were fitted with the VG analysis software.[15] Charging was corrected for by using the C 1s peak at 284.5 eV. The peak areas of the Mo 3d_{5/2} signals were used for calculating the percentage of Mo(IV) and Mo(VI). The ratio of Mo 3d and Al 2p areas was used as a tracer for changes in the dispersion of the molybdenum phase on the alumina surface.

Results and Discussion

Characteristic regions of the activity profile. Activity measurements were performed on catalysts with various molybdenum loading after an oxidative or a reductive pretreatment. Monitoring more than 20 hours time on stream, an unusual profile of acetonitrile formation was observed which is schematically shown in Figure 1. Three regions of interest are distinguished: a semi-steady-state, a transition and a steady-state period.

The Semi-Steady-State Period. The semi-steady-state is characterized by the constant formation of acetonitrile, while the selectivity to side products is changing. Considering the yield of acetonitrile versus reaction temperature a temperature (T_{opt}) was found where a maximum yield of acetonitrile was obtained. This T_{opt} shifted to a lower value at increasing Mo content for both pretreatments

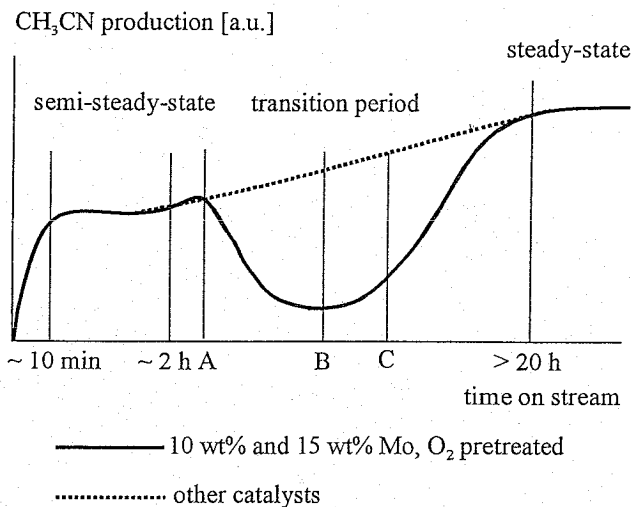


Figure 1: A schematic profile of the acetonitrile formation versus time on stream for various catalysts.

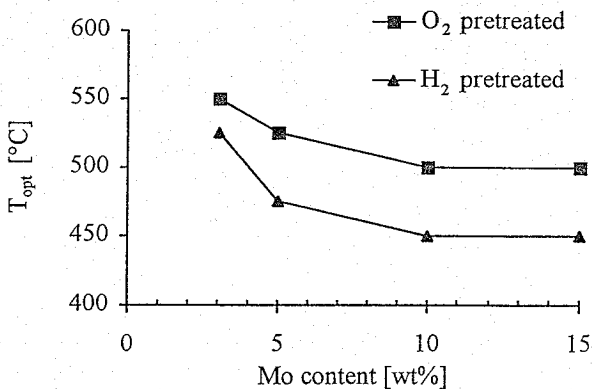


Figure 2: The temperature where maximum yield of acetonitrile is obtained versus molybdenum content for different pretreated catalysts at semi-steady-state condition (after 2 h time on stream).

(Figure 2). At temperatures exceeding T_{opt} , the complete dissociation of ammonia started to dominate, resulting in the desorption of nitrogen and thereby suppressing the desired reaction.

Figure 3 shows the ratio of the intensity of the XPS signals of Mo $3d$ and Al $2p$ for fresh catalysts and those which have been at various time on stream at 450 °C. Obviously, this ratio for the fresh catalysts increases with increasing molybdenum content (Figure 3; solid lines). Overall, this ratio of the oxygen pretreated catalysts is higher than the ones after a reductive treatment. Up to 5 wt% molybdenum, a similar increase is observed independent of the pretreatment applied. At higher molybdenum contents, however, the ratio for oxygen pretreated catalysts increased sharply compared to that of the hydrogen pretreated ones, which showed an almost linear behaviour. This observation is confirmed in the literature which states that molybdenum particles are better dispersed after calcination than after treating in hydrogen.[16]

So, with increasing molybdenum content the dispersion decreases, while hydrogen pretreatment induces an even stronger decrease. Considering that larger molybdenum particles are expected to be more active towards complete ammonia dissociation, it is explicable that this reaction starts to dominate at lower temperatures, shifting T_{opt} to a lower value with increasing molybdenum loading. It also follows that, for hydrogen pretreated catalysts T_{opt} is lower for the whole range considered (Figure 2; solid triangles).

Considering the optimal quasi turnover frequency ($qTOF_{opt}$) versus molybdenum content, the oxygen pretreated catalysts were less strongly affected by variation of the molybdenum content, and decreased slightly at molybdenum contents exceeding 10 wt% (Figure 4; solid squares). This indicates that the molybdenum added is well-spread on the alumina surface and accessible for reaction. Seemingly, the influence of dispersion effects starts to dominate at higher molybdenum content. This trend is also illustrated earlier in Figure 3.

The hydrogen pretreated catalysts with low molybdenum content initially had the best performance among all catalysts tested. At higher molybdenum content the $qTOF_{opt}$ decreased sharply (Figure 4; solid triangles), due to the lower dispersion of the hydrogen pretreated catalysts.

In summary, the semi-steady-state activity is highly structure sensitive. When oxygen pretreated, a higher yield of acetonitrile is obtained at higher molybdenum content (lower dispersion), whereas for hydrogen pretreated catalysts this concerns a low molybdenum content (high dispersion). This causes in Figure 4 the point of intersection at approximately 7 wt% molybdenum loading. Apparently the complete dissociation of ammonia, resulting in the desorption of nitrogen, is favoured on reduced larger molybdenum particles.

Transition Period. During the transition period strong fluctuations were observed in both activity and selectivity. All hydrogen pretreated catalysts and the oxygen pretreated catalysts with 5 wt% Mo or less showed a gradual increase in the formation of acetonitrile, until an upper limit was reached (Figure 1; dotted line). During this increase, the formation of ethane and hydrogen increased, while the

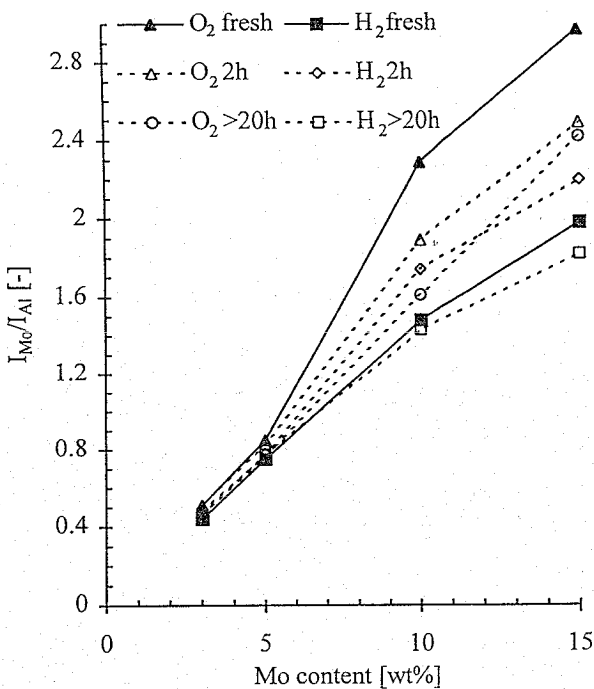


Figure 3: Ratios of the intensity of the XPS signals of Mo 3d and Al 2p of different catalysts at various time on stream.

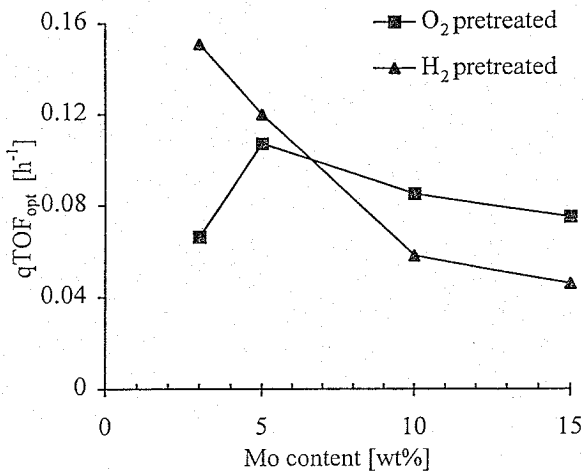


Figure 4: The maximum quasi turnover frequency versus molybdenum content for different pretreated catalysts in the semi-steady-state (after 2 h time on stream).

formation of CO_x and water decreased, resulting in an overall increase of the activity.

Only with the 10 wt% and 15 wt% Mo catalysts pretreated in oxygen, the yield of acetonitrile passed through a minimum (Figure 1; solid line). Although a strong increase in activity is observed, the selectivity to acetonitrile drops sharply, resulting initially in an overall slight increase of the yield (Figure 1; A). During the period of low acetonitrile production the conversion of ethylene and ammonia increased to almost 100%, while products were methane, ethane, nitrogen, hydrogen and carbon monoxide (Figure 1; B). Despite the fact that the conversion slowly decreased, the formation of acetonitrile slowly increased. This was due to the reduction of methane, nitrogen and carbon monoxide formation (Figure 1; C).

XPS analysis of different stages of reaction of the 10 wt% Mo catalyst showed clearly an increase of the Mo(IV) fraction (Figure 5; black bars). A fresh catalyst, containing 100% Mo(VI), was not very active, but highly selective to acetonitrile (Figure 5; after ~ 1.3 h). Before the yield started to decrease, little reduction of molybdenum was observed with XPS (after ~ 2.5 h). Evidently, due to the higher molybdenum content, the presence of a large amount of still removable surface oxygen in a partly reduced catalyst (due to reaction) leads to a very high activity, but only towards the side reactions. These side reactions are terminated at depletion of removable lattice oxygen. Apart from the fact that the start of the decrease of the yield of acetonitrile occurred several hours later, the oxygen pretreated 15 wt% Mo catalyst reacted similar to its 10 wt% analogue: A, B and C in Figure 5 represent 6, 8.5 and 11.5 hours of reaction respectively.

Due to the lower Mo content and to the poor reducibility of smaller particles, these catalysts contain less removable lattice oxygen. Apparently, the reductive treatment of the 10 wt% and 15 wt% Mo catalysts has removed enough lattice oxygen to suppress a larger part of the side reactions, resulting in also a gradual increase of the formation of acetonitrile, similar to the catalysts with lower molybdenum content.

Steady-State Period. Compared to the semi-steady-state, significant increases in catalytic activity were observed over at least 20 hours time on stream at 450 °C. No oxygen containing products were detected in the reaction stream and the product distribution was constant, so a *real* steady-state was reached. This is different from the ammoxidation of propylene. Aykan [17] observed a fast decline in catalytic activity with increasing reduction of the catalyst in the absence of gaseous oxygen. When using different ratios of bismuth and molybdenum, the 30% MoO_3 on silica appeared to be a very poor catalyst. Experiments where acrylonitrile was introduced to the catalyst showed that a low activity to decomposition of this desired product gave a high selectivity to acrylonitrile. Amorphous SiO_2 and MoO_3 were found to be inert with respect to acrylonitrile. Only after complete reduction to MoO_2 the catalyst showed initially a high activity towards conversion of acrylonitrile to CO_2 , acetonitrile and propionitrile which decreased very rapidly due to large amounts of carbon deposition.

The point where steady-state was reached coincided with the absence of oxygen containing components in the product stream. Comparing the qTOF of the semi-

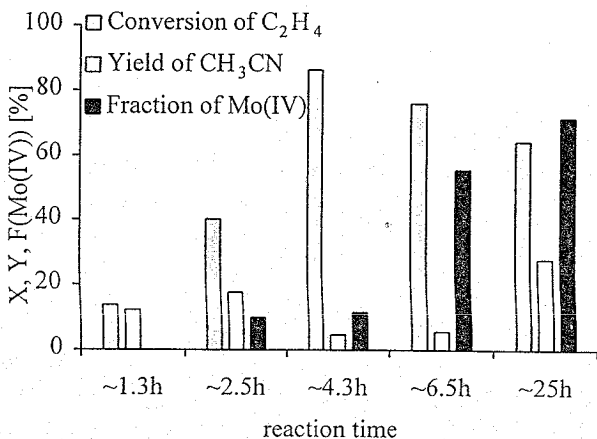


Figure 5: Reactivity profile of the oxygen pretreated 10 wt% Mo catalyst with corresponding percentage Mo(IV) obtained by XPS.

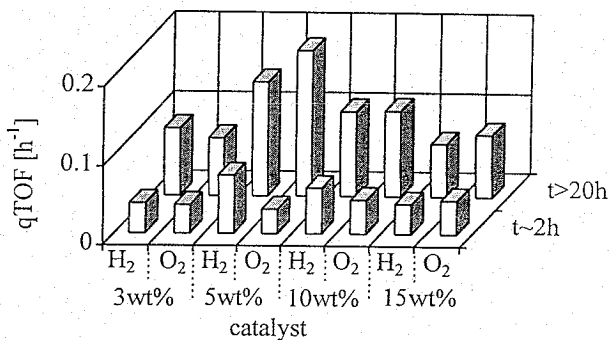


Figure 6a: The quasi turnover frequency at semi-steady-state and steady-state conditions at 450 °C of various catalysts.

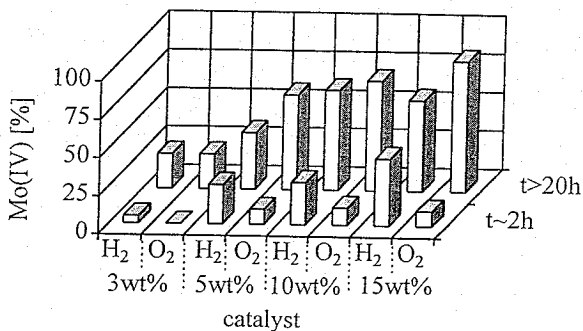


Figure 6b: The area percentage of the $3d_{5/2}$ XPS signal of Mo(IV) at ~228.5-229.5 eV at semi-steady-state and steady-state conditions at 450 °C of various catalysts.

steady-state and the steady-state, the largest increase is observed when the catalysts were pretreated with oxygen (Figure 6a). Overall, when reaching the steady-state, the oxygen pretreated catalysts reacted similarly to the hydrogen pretreated ones, considering the qTOF and product distribution.

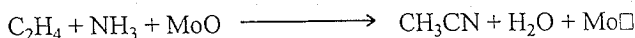
Samples taken at various time on stream showed different ratios of Mo(IV)/Mo(VI) in XPS. Figure 6b depicts the percentage of Mo(IV) in the period of semi-steady-state and in the steady-state of the reaction for the different pretreated catalysts with various molybdenum content. Again, it can be seen that large molybdenum particles are easier to reduce, because the amount of Mo(IV) increased with increasing loading. But it appeared that the hydrogen pretreatment did not remove all reactive oxygen, since in all cases the amount of Mo(IV) had increased after steady-state was reached. The increase of the yield of acetonitrile can not be attributed only to the increase of the amount of Mo(IV). Although the oxygen pretreated 5 wt% Mo catalyst yielded the highest qTOF, the largest amount of Mo(IV) was observed on the oxygen pretreated 15 wt% Mo catalyst. Evidently, a well-dispersed calcined precursor is needed to obtain the best performance in the steady-state, where both Mo(IV) and Mo(VI) species are present. At higher molybdenum loading the activity in the steady-state becomes independent of the pretreatment. This suggests the formation of a stable molybdenum structure during reaction. Fresh, hydrogen pretreated, catalysts with higher loading showed the Mo $3d_{5/2}$ peak at 228.5 eV. After a reaction period until steady-state was reached this peak shifted to 229.5 eV. Catalysts with lower loading showed already this Mo $3d_{5/2}$ peak at 229.5 eV after hydrogen pretreatment, suggesting a MoO₂-like structure.⁽¹⁵⁾ An XRD spectrum of the hydrogen pretreated 15 wt% Mo catalyst which had reached the steady-state showed clearly the presence of crystalline MoO₂. This in contrast with the fresh hydrogen pretreated catalyst, which showed no crystalline phase.

When submitted to reaction, an increase of the C $1s$ peak was observed suggesting that coke formation occurred. Since the catalytic activity showed no indications of deactivation, this carbon could be removed by the reaction stream, or even act as a reaction intermediate.

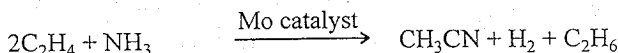
Proposed reaction mechanisms. It is expected that the formation of the main side-products is a strong function of the pretreatment. Water and CO_x were dominant on oxygen pretreated catalysts. Because of the formation of water, the formation of acetonitrile on an oxidic catalyst surface is favoured thermodynamically. Hydrogen pretreated catalysts formed mainly ethane and hydrogen. It should be remembered that the formation of acetonitrile and hydrogen directly from ethylene and ammonia is thermodynamically unfavourable ($\Delta G^0(427\text{ }^\circ\text{C}) \sim 10\text{ kJ/mol}$). This in contrast with the hydrogenation of ethylene: $\Delta G^0(427\text{ }^\circ\text{C}) \sim -50\text{ kJ/mol}$. Since ethane is always the main side product for hydrogen pretreated catalysts and catalysts in the steady-state period ($\sim 50\%$ selectivity), this exothermic reaction probably delivers the energy needed to drive the reaction. The following two mechanisms are proposed (Scheme 1):

It is obvious that deactivation occurs in mechanism (1), because the catalyst acts as a reactant. Apart from the fact that lattice oxygen is not replenished, this mechanism is

O₂ pretreated (1)



H₂ pretreated (2)



Scheme 1

similar to the ammoxidation mechanism proposed by Grasselli *et al.*(14). In mechanism (2) no deactivation is expected due to the fact that the catalyst is not altered by reaction. It is therefore suggested that the two mechanisms occur on different sites formed by different molybdenum structures.

Since conditions were found where besides acetonitrile, both oxygen containing products (water, CO_x) and non-oxygen containing products (ethane, hydrogen) were formed, it is concluded that the two mechanisms can occur simultaneously. The semi-steady-state condition where this happened showed a strong structure sensitivity.

In summary, it appears that during reaction a calcined catalyst, where mechanism (1) is dominant, changes into a catalyst where mechanism (2) dominates after removal of lattice oxygen. This transition proceeds gradually for molybdenum contents of 5 wt% or less. At higher molybdenum contents only after reductive treatment a gradual transition is observed. When calcined, the transition proceeds via a minimum in the formation of acetonitrile, due to a highly active period where side reactions dominate. Surface oxygen is removed by reaction until depletion, reaching a steady-state. This way the molybdenum phase is converted into a particular stable structure, acting as a real catalyst. The exact nature of this structure is suggested to be MoO₂-like, and is independent of the pretreatment applied at higher molybdenum content.

Conclusions

The oxygen pretreated catalysts have initially a high selectivity to acetonitrile and water with total combustion as side reaction. At higher molybdenum content, the yield of acetonitrile passes through a minimum, while the activity goes through a maximum. A hydrogen pretreated catalyst exhibits a gradual increase in activity and is less selective. The major products, besides acetonitrile, are hydrogen and ethane.

Two mechanisms are suggested:

- 1) one based on the ammoxidation mechanism with the consumption of lattice oxygen.
- 2) the other is based on oxidative ammonolysis, i.e. without consumption of lattice oxygen. For thermodynamic considerations a synergetic formation of ethane and acetonitrile is suggested.

The mechanisms can occur separately or simultaneously, depending on the amount of removable lattice oxygen. XPS showed only Mo(IV) and Mo(VI) species. The fraction of Mo(IV) increases with increasing Mo content for both pretreatments, due to the reducibility of larger Mo particles. Freshly calcined catalysts are highly selective, attributed to Mo(VI) sites present on a MoO₃-like structure. Catalysts in

the steady-state, containing reduced molybdenum, are highly active, but less selective. This is due to Mo(IV) sites, which enhance more effective N-H and C-H activation. For this reason the selectivity is also a strong function of the dispersion. Large, reduced molybdenum particles are too active towards complete ammonia dissociation, resulting in termination of the selective reaction. Although, due to the reaction the catalyst becomes more reduced, a large amount of removable lattice oxygen still present at higher molybdenum loading is very active, resulting in formation of methane, ethane, nitrogen, hydrogen and CO_x.

Finally, in the steady-state a reduced molybdenum structure is obtained which is not altered by reaction anymore, and acts as a real catalyst. This MoO₂-like structure can only be formed by the removal of lattice oxygen under reaction conditions.

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