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A study of sodium promotion in Fischer–Tropsch synthesis: electrochemical control of a ruthenium model catalyst

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Sodium supplied to the surface of a ruthenium thin film catalyst by electro-pumping from a solid electrolyte (Na–β''-alumina) strongly alters the activity and selectivity of the latter in Fischer–Tropsch synthesis. Thus the range of utility of electrochemical promotion has been broadened, this being the first application to a C–C bond forming reaction. The methanation rate is strongly suppressed resulting in a marked increase in selectivity towards C_2–C_4 hydrocarbons, accompanied by an increase in the alkene : alkane ratio. The results obtained with this model system, including the "C_2 anomaly", are in close agreement with those found for classically promoted conventional dispersed catalysts. Alkali substantially increases the probability of chain growth and CO dissociation is not rate controlling; mechanistic implications are discussed.

Keywords: electrochemical promotion, Fischer–Tropsch synthesis, sodium

1. Introduction

Electrochemical promotion (EP) is a unique method for the *in situ* control of promoter concentration at the surface of a working metal catalyst [1]. As such, it may be used to investigate reaction mechanisms and to guide the development of classically promoted dispersed catalysts. Examples of the former are provided by our earlier studies on the EP of NO_x reduction over Pt and Cu [2–4], the selective hydrogenation of acetylene over Pt [5] and the triply-promoted epoxidation of ethylene over Ag [6]. Examples of the latter include effective alkali-promoted catalysts for NO_x reduction under realistic (simulated exhaust) conditions [7]. The EP technique entails electrochemical pumping of ions from a solid electrolyte to the surface of a porous, catalytically active metal film with which it is in contact. The catalyst is at the same time the working electrode of a solid state electrochemical cell. With Na–β''-alumina (a Na^+ conductor) as the solid electrolyte, controlling the catalyst potential measured with respect to a reference electrode (V_{WR}) controls the sodium coverage (θ_{Na}), work function and consequently the reactive behaviour of the catalyst surface [8].

The present investigation of Fischer–Tropsch synthesis (FTS) was undertaken with three principal objectives. First, to broaden the applicability of EP in the study of heterogeneous catalysis. With one exception [5], all the earlier work in this field has involved oxidation reactions; *none* of it has involved C–C bond forming reactions. Second, to investigate the effects of Na promotion on FTS with a view to contributing to our understanding of the mechanism. Third, to establish whether such EP data are of relevance to the behaviour and understanding of classical dispersed FTS catalysts.

The effective FTS catalysts are Ru, Fe, Co and Rh. Ruthenium was chosen for this exploratory study at atmospheric pressure because it exhibits high intrinsic activity for linear α-olefins production and because alkali promotion of conventional Ru FTS catalysts has already been studied [9–13].

There is broad agreement with respect to the consequences of alkali promotion, although the explanation of these effects remains controversial. Ensemble effects [10], electronic effects [11,12] and a decrease in the surface coverage and in the mobility of H adatoms [13,14] have been variously invoked, whereas Lahtinen and Somorjai [15] proposed that the principal effect of K is to inhibit graphite formation.

We conclude that CO dissociation is not rate limiting, that alkali promotion increases the probability of chain growth, and that electronic effects must play a significant role in the promoted reaction.

2. Experimental

The Ru catalyst (working electrode, W) consisted of a porous continuous thin film deposited by thermal decomposition of a solution of $Ru_3(CO)_{12}$ in acetone at 573 K in a nitrogen atmosphere on one face of a 45 mm × 15 mm × 1 mm wafer of a Na–β''-alumina solid electrolyte. Au reference (R) and counter (C) electrodes were deposited on the other face by Au sputtering in argon. The sample was suspended in a quartz, atmospheric pressure well-mixed reactor with all electrodes exposed to the reactant gas mixture. The

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system behaved as a single pellet, well-mixed reactor as described and discussed elsewhere [16].

Quantitative analysis of the reaction products was carried out by on-line gas chromatography (Shimadzu-14B, Porapak-N, flame ionisation detector) and the detector was calibrated using standards of known concentration. Reactants were pure CO (Distillers MG) and pure H_2 (Distillers MG) and were fed to the reactor by mass flow controllers (Brooks 5850 TR). A galvanostat–potentiostat (Ionic Systems) was used to maintain a difference potential between the working and reference electrodes (potentiostatic mode). All experiments were carried out in potentiostatic mode by following the effect of catalyst potential (V_{WR}, measured with respect to the reference electrode) on the reaction rates. Decreasing the catalyst potential below the value corresponding to the electrochemically clean surface (400 mV) resulted in electro-pumping of Na to the Ru surface, thereby increasing θ_{Na}. Our previous work showed that θ_{Na} increased linearly with decreasing V_{WR} from zero to a maximum of $\sim$0.06 monolayers over the range of catalyst potential used here [8].

3. Results

CO was hydrogenated to hydrocarbons over the Ru EP model catalyst at 473 K and 1 bar total pressure. Linear alkenes and alkanes of carbon number up to 4 were the only products. Figure 1 shows steady-state (potentiostatic) rate data for hydrocarbon production as a function of catalyst potential (V_{WR}) for inlet gas composition $P_0(CO) = 25.33$ kPa, $P_0(H_2) = 76$ kPa ($H_2 : CO = 3$). Reaction rates are expressed as molecules of product per second. It is apparent that all rates decrease with increasing θ_{Na} (decreasing V_{WR}). Figure 2 shows the dependence of product selectivity on catalyst potential, where selectivity is defined as

$$S_i = \frac{r_i}{\sum_j r_j}, \qquad (1)$$

where r_i is the rate of formation of the product i. Figure 2 shows that the selectivity towards ethene, propene and 1-butene production increases while the selectivity towards methane and ethane formation decreases with increasing θ_{Na} (decreasing V_{WR}). The catalytic response of the system was reproducible and reversible with respect to the catalyst potential, i.e., returning V_{WR} to its original value restored the original values of the reaction rates.

It is apparent from figures 1 and 2 that while the effect of alkali is to reduce the rates of all catalytic reactions, the rates of formation of the higher alkenes are reduced less than the rates of formation of methane and ethane. *The result is an increase in selectivity towards the higher alkenes.* These results are presented numerically in table 1 which shows the relative changes in reaction rates and in selectivity for methane, ethene, ethane, propene and 1-butene as one proceeds from the alkali-free ruthenium catalyst to the optimally promoted ruthenium catalyst. It

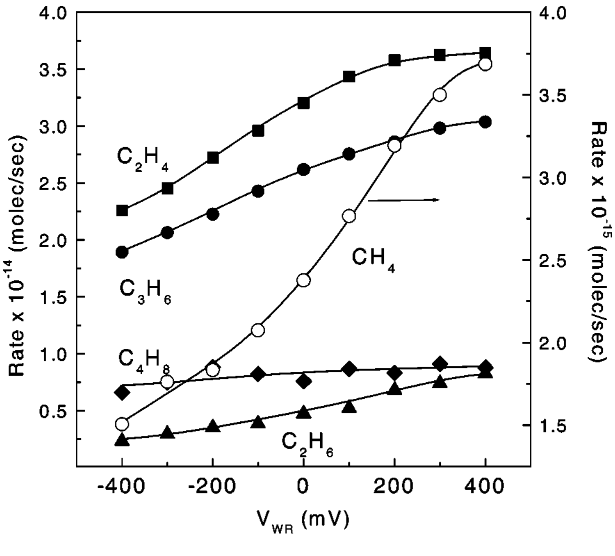

Figure 1. Effect of catalyst potential (V_{WR}) on the reaction rates of the formation of products. Note that the CH_4 production rate is represented on the right axes. Conditions: $P(CO) = 25.33$ kPa, $P(H_2) = 76$ kPa, $T = 473$ K.

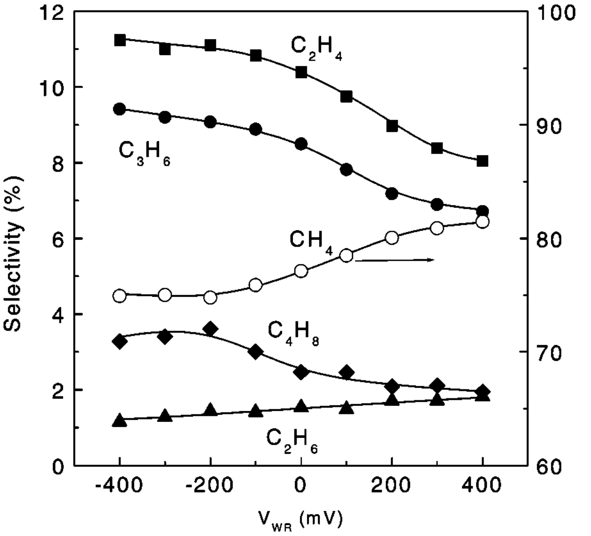

Figure 2. Effect of catalyst potential (V_{WR}) on the product selectivity. Note that the selectivity towards methane production is represented on the right axes. Conditions: $P(CO) = 25.33$ kPa, $P(H_2) = 76$ kPa, $T = 473$ K.

Table 1
Changes in rate Δr and selectivity (ΔS) between clean and optimally promoted catalyst divided by the unpromoted rate (r_0) and unpromoted selectivity (S_0), respectively.

	$\Delta r/r_0$ (%)	$\Delta S/S_0$ (%)
Methane	−59	−8
Ethene	−38	40
Ethane	−72	−33
Propene	−38	40
1-butene	−25	70

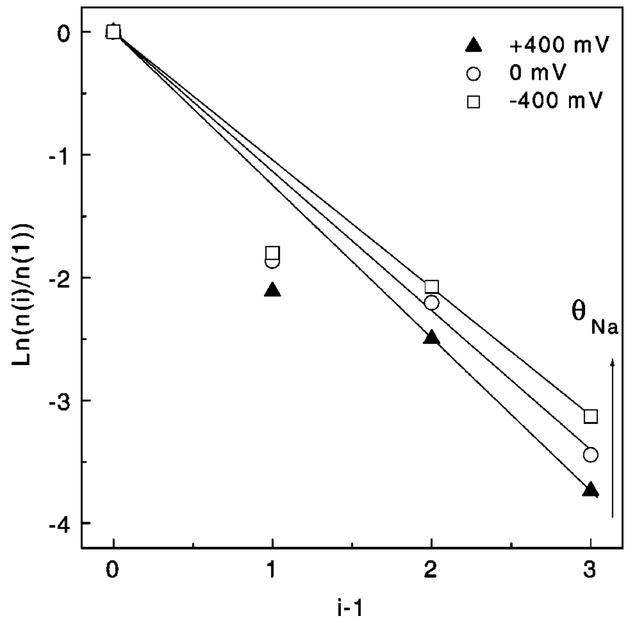

Figure 3. Experimental molecular distribution of the reaction products obtained at different catalyst potential. The solid lines represent the (theoretical) Anderson–Flory–Schulz distribution for a stepwise polymerisation of methylenes. $n(i)$ is the molar fraction of molecules having carbon number i.

is clear that the formation of higher alkenes is favoured by sodium promotion, a result that will be discussed below.

The Anderson–Flory–Schulz distribution for the FTS reaction yield [17] is given by

$$n(i) = n(1)\alpha^{i-1}, \qquad (2)$$

where i indicates the carbon number, α the chain growth probability and $n(i)$ the molar fraction of linear products with carbon number i (i.e., $n(1)$ is the molar fraction of C_1 product). This relation implies a polymerisation reaction that proceeds via addition of a single carbon monomer with α independent of the carbon number of the growing species. Equation (2) predicts a linear relationship between $\ln[n(i)/n(1)]$ and $i-1$, whence α can be obtained from the slope.

Our data have been plotted according to this relationship (figure 3). It can be seen that (i) the experimental distribution deviates from the Anderson–Flory–Schulz distribution at C_2 and (ii) the calculated chain growth probability increases with θ_{Na} (decreasing V_{WR}). Significant deviations from the Anderson–Flory–Schulz distribution are reported in the literature [18]. The C_2 anomaly found here is in very good agreement with the results of Quyoum et al. [19] who reported exactly the same effect for FTS over Ru supported on SiO_2. The C_2 anomaly has been rationalised in terms of secondary reactions, including (i) incorporation of ethene in growing chains [20], (ii) rapid readsorption of ethene [21] and (iii) hydrogenolysis of ethene [21].

As noted above, figure 3 shows that the slope of the distribution increases with increasing θ_{Na} (decreasing V_{WR}). The implications of this are made apparent in figure 4 where the chain growth probability is plotted against catalyst potential. It is evident that α increases with θ_{Na} (decreasing V_{WR}): the chain growth probability for the optimally promoted catalyst is much greater than that for the unpromoted catalyst (−400 versus 400 mV). Figure 5 shows the effect of catalyst potential on the alkene to alkane ratio for C_2 products. Decreasing the catalyst potential, i.e., increasing θ_{Na} causes an increase in the rate of production of ethene relative to ethane, with a maximum increase of 122%.

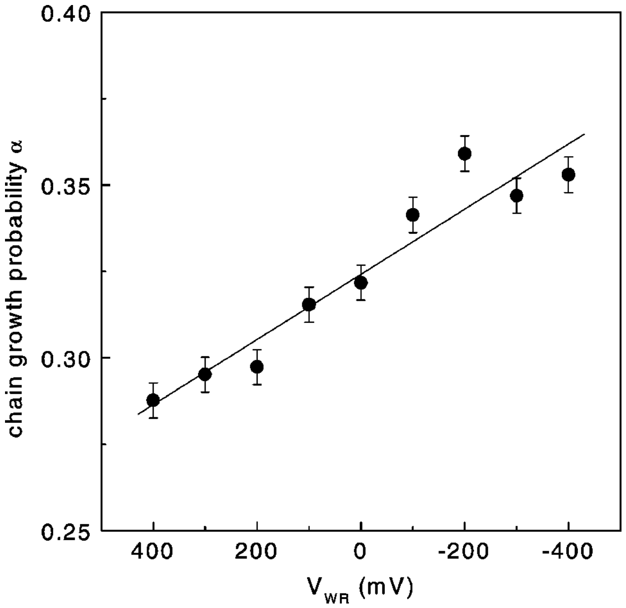

Figure 4. Effect of catalyst potential (V_{WR}) on the probability of chain growth. The error was calculated from the error in the linear regression shown in figure 3.

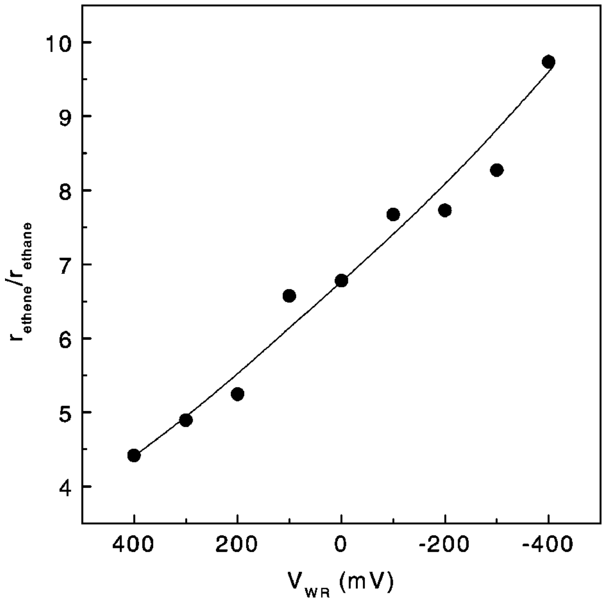

Figure 5. Effect of catalyst potential (V_{WR}) on the olefin to paraffin ratio for C_2 products.

4. Discussion

The effects of increased alkali loading on the reaction may be summarised as follows:

(i) a decrease in all reaction rates;

(ii) an increase in the selectivity towards longer hydrocarbons;

(iii) an increase in the chain growth probability;

(iv) an increase in the alkene to alkane ratio.

We may rationalise these observations in terms of a model based on that proposed by Kellner and Bell [22,23], modified to account for water formation via a sequence of Langmuir–Hinshelwood steps rather than a single concerted Eley–Rideal step. Complexities introduced by possible alkene reincorporation [24] and chain branching do not affect the overall validity of the argument.

The surface-catalysed polymerisation uses CH_2 monomers, formed by hydrogenation of adsorbed CO in order to produce hydrocarbons. Chain growth occurs by addition of surface methylene species to adsorbed alkyl groups. These alkyl groups can undergo β-hydrogen abstraction to form α-olefins or hydrogen addition to form n-paraffins [25].

Figure 6 depicts the initiation, growth and termination of chains according to this mechanism. CO adsorbs (step 1) and dissociates (step 2) whereas H_2 is assumed to adsorb dissociatively (step 3). Adsorbed oxygen and hydrogen react to form water (steps 4 and 5). Chain initiation occurs when carbon adatoms react with hydrogen adatoms (steps 6, 7 and 8) to form CH, CH_2 (monomer) and CH_3 (chain initiator). Methane formation takes place when CH_3 is hydrogenated (step 9). Chain growth occurs by insertion of the monomer in a growing alkyl species (steps 10 and 11). Termination occurs by β-hydrogen elimination yielding an α-olefin (step 12) or by addition of hydrogen to form an n-alkane (step 13).

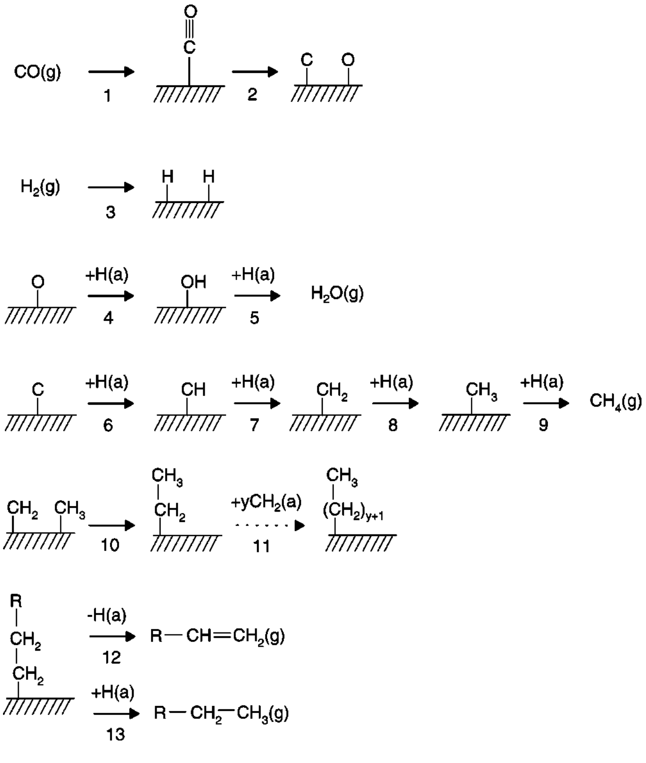

Figure 6. Proposed mechanism of hydrocarbon synthesis modified from [22,23].

It is generally accepted that the rate-limiting step is C hydrogenation rather than CO dissociation [22,26]. This view is consistent with the fact that whereas alkali metals facilitate the dissociation of adsorbed CO, alkali promotion nevertheless decreases all rates in FTS. Therefore alkali promotion data, such as those presented here, provide additional evidence that *the rate-limiting step cannot be CO dissociation*.

All the effects of sodium promotion ((i)–(iv) above) may be understood by postulating that the effect of alkali is to inhibit the hydrogenation steps. If hydrogenation is rate limiting, this would decrease all reaction rates (observation (i)). Because methanation is more hydrogen demanding than the FTS, the CH_4 rate is more strongly suppressed than those of the higher hydrocarbons. This results in increased selectivity towards higher hydrocarbons, implying increased chain growth probability (observations (ii) and (iii)). Finally, since termination to form alkanes involves consumption of hydrogen adatoms (H_a), whereas β-hydrogen elimination to form alkenes generates H_a, alkali-induced decrease in the hydrogenation rate should result in an increase of the alkene/alkane ratio, as found (observation (iv)).

How does Na decrease the rate of the hydrogenation steps? Broadly speaking, there are two possibilities. Alkali may act to (i) reduce the availability of H_a, or (ii) modify the intrinsic rate at which hydrogen adds to C adatoms. The first of these could reflect an ensemble effect due to blocking of adsorption sites; it could also reflect an electronic effect [27]. Both effects would act to decrease θ_H and their relative importance cannot be decided on the basis of available results, both here and in the literature [10,13,14]. The second possibility implies a change in metal–C bonding, as suggested by McClory et al. [10,12]. There is no direct experimental evidence nor any theoretical support for this (plausible) suggestion. Indirect evidence is provided by vibrational spectroscopy data which show that on metal surfaces electropositive and electronegative co-adsorbates decrease [28] and increase [11], respectively, the strength of the C–O bond, implying a corresponding increase or decrease, respectively, in the metal–C bond strength. This would be at least consistent with an alkali-induced reduction in the intrinsic hydrogenation rate.

In this connection the work of Okuhara et al. [11] is of interest. They studied the effect of K and P on FTS over alumina-supported ruthenium catalysts and found, in agreement with our work and earlier reports, that K increased the chain growth probability, decreased the reaction rate and increased the olefin to paraffin ratio. They also showed that P induced the opposite changes, i.e., decreased the chain growth probability, increased rate and decreased the alkene to alkane ratio.

This argues against ensemble effects being the sole cause of alkali-increased chain growth in FTS. *The strong implication is that there are also significant electronic effects.* We propose that such alkali-induced electronic effects could very well include another contribution, considered also by Okuhara et al., though overlooked by others. As noted above, co-adsorbed alkalis increase the metal–C bond strength in chemisorbed CO. This is well established experimentally [28] and well understood theoretically [29]. Thus under any given conditions of temperature and pressure, alkalis should increase θ_{CO} at the expense of θ_{H}, thus providing another factor favouring both chain growth and alkene production.

As noted above, in addition to increasing θ_{CO} alkali also promotes CO dissociation, thus increasing θ_{O} and θ_{C}. This effect should act to decrease θ_{H} even more. In this connection it is interesting to note that calculations by Baetzold show that although hydrogenation is rate limiting in FTS, the rate constant for CO dissociation determines hydrocarbon chain length: longer chains form if CO dissociation is accelerated [30].

In summary, it seems likely that alkali promotion of selectivity in FTS is the result of more than a single effect. The availability of hydrogen adatoms and the strength of the metal–C bond could both be affected, though we have no direct evidence for the latter. In addition, alkali-induced changes in θ_{CO} and its degree of dissociation, both well-documented effects, would also operate in the direction necessary to cause the observed behaviour.

There is a close correspondence between our results and those obtained with classically promoted dispersed Ru catalysts. We conclude that the effects of alkali promotion in FTS synthesis over Ru may be ascribed to modification of the metal surface chemistry, as discussed above. To first approximation, alkali-induced modification of the support or of the metal/support interaction appears not to be an important issue. Having demonstrated the utility of EP in the study of promoter effects in FTS carried out at 1 bar, future work will be carried out at ∼100 bar and complemented by post-reaction electron spectroscopic studies of surface species.

5. Conclusions

(1) Electrochemical promotion can be applied to C–C bond forming reactions and is a useful mechanistic probe in such systems.

(2) The EP behaviour of thin film Ru model catalysts in FTS under Na promotion closely parallels that of classically promoted dispersed catalysts. Activity, selectivity and the C_2 anomaly are all reproduced. Support effects are therefore not of prime importance.

(3) Na causes a substantial increase in chain growth probability reflected by increased selectivity toward higher hydrocarbons. It also increases the alkene : alkane ratio.

(4) The effects of alkali promotion demonstrate that CO dissociation is not rate limiting and that effects in addition to purely geometrical ones must be taken into account. Such electronic effects may in part reflect alkali enhancement of CO chemisorption at the expense of hydrogen chemisorption.

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References

[1] C.G. Vayenas, S. Bebelis, I.V. Yentekakis and H.G. Lintz, Catal. Today 11 (1992) 303.

[2] I.V. Yentekakis, A. Palermo, N.C. Filkin, M.S. Tikhov and R.M. Lambert, J. Phys. Chem. B 101 (1997) 3759.

[3] R.M. Lambert, F.J. Williams, A. Palermo and M.S. Tikhov, Topics Catal. 13 (2000) 91, and references therein.

[4] R.M. Lambert, A. Palermo, F.J. Williams and M.S. Tikhov, Solid State Ionics, and references therein, in press.

[5] S. Tracey, A. Palermo, J.P. Holgado Vazquez and R.M. Lambert, J. Catal. 179 (1998) 231.

[6] A. Palermo, A. Husain and R.M. Lambert, Catal. Lett. 69 (2000) 175.

[7] M. Konsolakis, N. Macleod, J. Isaac, V. Yentekakis and R.M. Lambert, J. Catal. 193 (2000) 330.

[8] F.J. Williams, A. Palermo, M.S. Tikhov and R.M. Lambert, J. Phys. Chem. B 104 (2000) 615.

[9] R.D. Gonzalez and H. Miura, J. Catal. 77 (1982) 338.

[10] M.M. McClory and R.D. Gonzalez, J. Catal. 89 (1984) 392.

[11] T. Okuhara, H. Tamura and M. Misono, J. Catal. 95 (1985) 41.

[12] T.E. Hoost and J.G. Goodwin, Jr., J. Catal. 137 (1992) 22.

[13] T. Komaya, A.T. Bell, Z. Weng-Sieh, R. Gronsky, F. Engelke, T.S. King and M. Pruski, J. Catal. 152 (1995) 350.

[14] D.O. Uner, M. Pruski, B.C. Gerstein and T.S. King, J. Catal. 146 (1994) 530.

[15] J. Lahtinen and G.A. Somorjai, J. Mol. Catal. A 130 (1998) 255.

[16] I.V. Yentekakis and S. Bebelis, J. Catal. 137 (1992) 278.

[17] H. Schulz and M. Claeys, Appl. Catal. A 186 (1999) 91.

[18] G.P. van der Laan and A.A.C.M. Beenackers, Catal. Rev. Sci. Eng. 41 (1999) 255.

[19] R. Quyoum, V. Berdini, M.L. Turner, H.C. Long and P.M. Maitlis, J. Catal. 173 (1998) 355.

[20] S. Novak, R.J. Madon and H. Suhl, J. Catal. 77 (1982) 141.

[21] T. Komaya and A.T. Bell, J. Catal. 146 (1994) 237.

[22] C.S. Kellner and A.T. Bell, J. Catal. 70 (1981) 418.

[23] A.T. Bell, Catal. Rev. Sci. Eng. 23 (1981) 203.

[24] E. Iglesia, S.L. Soled and R.A. Fiato, J. Catal. 137 (1992) 212.

[25] E. Iglesia, Appl. Catal. A 161 (1997) 59.
[26] Y. Kobori, Y. Hirofumi, N. Shuichi, T. Onishi and K. Tamaru, J. Chem. Soc. Faraday Trans. I 78 (1982) 1473.
[27] S.C. Gebhard and B.E. Koel, J. Phys. Chem. 96 (1992) 7056.
[28] R.A. dePaola, J. Hrbek and F.M. Hoffmann, J. Chem. Phys. 82 (1985) 2484.
[29] N.D. Lang, S. Holloway and J.K. Nørskov, Surf. Sci. 150 (1985) 24.
[30] R.C. Baetzold, J. Phys. Chem. 88 (1984) 5583.