JOURNAL OF CATALYSIS 132, 92-99 (1991)

Oxygen Surface Species on Lithium Nickelate Methane Coupling Catalysts and Their Interaction with Carbon Oxides

G. D. MOGGRIDGE, J. P. S. BADYAL,[1] AND R. M. LAMBERT[2]

Department of Chemistry, University of Cambridge, Cambridge CB2 1EW, United Kingdom

Received January 4, 1991; revised May 20, 1991

The surface chemistry of a $LiNiO_2$ methane coupling catalyst has been studied with respect to adsorption/desorption behaviour and interaction with carbon oxides. The results indicate that anion vacancies induced at the surface at high temperature are readily replenished by interaction with both O_2 and N_2O. The O^{2-} lattice oxygen species (α) so formed are thought to be responsible for methane coupling. A chemisorbed dioxygen species (β) appears to be formed at defect sites by adsorption of O_2; it is *not* formed by N_2O adsorption. Experiments with $^{18}O_2$ indicate that this chemisorbed β-O_2 desorbs by a dissociative recombination mechanism. These findings are in agreement with catalytic and electron spectroscopic studies. On the clean surface, CO_2 interacts strongly with O^{2-}, destroying sites for β-O_2 adsorption; it also removes preadsorbed β-O_2. CO, however, does not adsorb at all on the clean surface; it *does* react with β-O_2 to form a species (probably CO_3^{2-}) that evolves CO_2 on subsequent heating. This strongly supports the conclusion that the β species is a form of dioxygen.

INTRODUCTION

Following the pioneering work of Keller and Bhasin (*1*) many metal oxides have been screened as potential methane coupling catalysts (see for example Refs. (*2–5*) and references therein). Alkali-doped magnesium oxide catalysts have been extensively investigated, and in this area the work of Lunsford *et al.* has been particularly influential in regard to identification of catalytically active surface oxygen species and overall reaction mechanism (*6–11*). In such catalysts the metal ions exhibit fixed valency; another useful class of materials includes transition metal oxides in which the metal ions are capable of exhibiting variable valency. It is possible that in such systems the catalytic chemistry is significantly different from that which characterises nontransition metal oxide catalysts (*12–15*). A promising example of this type of material is Li-promoted NiO. Lithium oxide forms a continuous range of solid solutions in NiO, the end member of this series being the stoichiometric oxide, lithium nickelate ($LiNiO_2$).

Ungar *et al.* (*16*) investigated the methane coupling activity and selectivity of a series of structurally related mixed oxides, including lithium nickelate. It was found that $LiNiO_2$ and $LiYO_2$ were particularly active and selective catalysts with only the former apparently operating via a redox mechanism involving the depletion and replenishment of lattice oxygen: with $LiNiO_2$, catalytic activity continued for several hours in the absence of gaseous oxygen. The authors also found that pretreating $LiNiO_2$ with N_2O enhanced the activity for C_2 production (*17*).

Hatano and Otsuka (*18*) have carried out kinetic measurements on $LiNiO_2$, including isotope labelling studies, in an attempt to elucidate the reaction mechanism. They suggest that two distinct oxygen species exist at the catalyst surface, namely lattice oxide ions and adsorbed oxygen; it was proposed that these are responsible for oxidative coupling and deep oxidation, respectively. Most recently, Badyal *et al.* (*19*) have

---

[1] Present address: Department of Chemistry, University of Durham, Science Laboratories, South Road, Durham DH1 3LE, UK.

[2] To whom correspondence should be addressed.

0021-9517/91 $3.00

used a planar model system in order to characterise the oxygen species present at the surface of lithium-doped nickel oxide; a combination of Auger, XP, and UP spectroscopies was employed. It was found that in addition to O^{2-}, O^- is present at the undoped NiO surface; furthermore, Li doping led to the appearance of O_2^{2-}. The O^- and O_2^{2-} entities are of particular interest because both have been suggested as the active species in other catalyst systems (*6, 20*). Under the very low oxygen partial pressures used in the model study (*19*), both these species were found to be unstable at the temperatures required for oxidative methane coupling over $LiNiO_2$; these observations appear to be consistent with the present findings for practical $LiNiO_2$ catalysts.

The major undesirable by-products of methane oxidative coupling are the carbon oxides that are present in significant concentration under reaction conditions. A study of their interaction with the active sites on the catalyst surface is therefore of interest. The present work is an attempt to characterise directly the active oxygen species at the surface of a practical $LiNiO_2$ catalyst and to investigate their reaction with carbon oxides. The interaction of N_2O with the catalyst has also been studied.

EXPERIMENTAL

Experiments were carried out in a somewhat unconventional high-vacuum apparatus incorporating mass spectrometric sampling; this has been described in detail elsewhere (*21*). The arrangement is designed for relatively high-pressure gas dosing of small catalyst samples located just outside the ioniser volume of a quadrupole mass spectrometer. Gas dosing was achieved by means of a set of three capillary tubes that terminated within 1 mm of the sample surface. By this means, dosing with active gases (N_2O, O_2, CO_2, CO) could be carried out at an effective pressure of $\sim 10^{-2}$ Torr at the sample surface, the background pressure remaining below 10^{-5} Torr; the system base pressure was 10^{-8} Torr.

$LiNiO_2$ was prepared by decomposition and reaction of Li_2CO_3 intimately ground together with NiO. This reactant mixture was heated as follows: 700 K for 1 h, 1000 K for 1 h, 1100 K for 15 h, 1200 K for 2 h. The formation of pure, stoichiometric $LiNiO_2$ was confirmed by powder X-ray diffraction measurements. For adsorption/desorption experiments the powdered sample was pressed into a wafer ($\sim 2 \times 2 \times 8$ mm) and mounted in a coil of platinum wire, which was used to provide resistive heating of the specimen. Appropriate blank experiments were carried out to ensure that the Pt wire was not itself responsible for any of the observed chemistry (*21*).

The catalyst sample was cleaned *in situ* by heating in a flow of oxygen (10^{-2} Torr at the sample surface) at 950 K and then 750 K for 5 min each, this cycle being repeated until a thermal desorption spectrum showed no evidence for evolution of CO_2 or H_2O. This cleaning procedure was repeated between every experiment. Thermal desorption spectra were taken using a constant heating current of 3.2 A, which resulted in a temperature sweep up to ~900 K; temperature measurement was carried out remotely by means of an Ircon 300LC infrared thermometer. A standard dosing procedure of 2 min at $\sim 10^{-2}$ Torr at the sample surface was used for all the adsorbates examined in this work because these conditions were found to produce saturation uptake in every case: this gas dosing procedure is referred to as "standard conditions" hereafter. The quadrupole mass spectrometer was operated in multiplexed mode allowing simultaneous monitoring of 16 mass numbers as a function of sample temperature. All experiments were performed at least twice.

RESULTS

Experiments fell into two categories: those to determine the nature of the oxygen surface species on $LiNiO_2$ and those to investigate reactions of CO_x with these oxygen species.

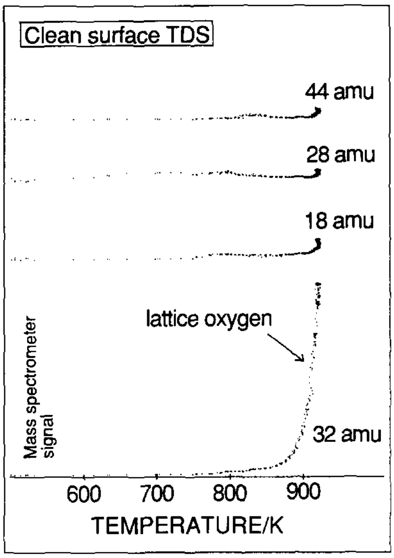


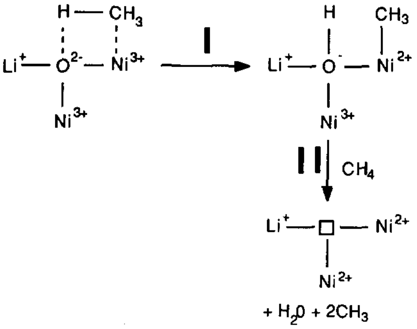
FIG. 1. Thermal desorption spectra for clean surface.

Characterisation of Oxygen Surface Species

(*i*) *Clean surface.* Having obtained a clean surface by the above procedure, and in the absence of subsequent oxygen chemisorption, a thermal desorption sweep reproducibly resulted in the type of spectrum shown in Fig. 1. This provides a reference clean surface spectrum and also gives an indication of the temperature at which lattice oxygen is lost from the catalyst. It can be seen that a continuous rise in the signal at 32 atomic mass units (amu) occurs at ~900 K and this may be attributed to the evaporation of oxide oxygen with concomitant decomposition of the surface region of the solid (see Scheme 1)

$$4LiNiO_2 \rightarrow 2Li_2O + 4NiO + O_2(g).$$

The mobility of lattice oxygen and its depletion under oxidative coupling conditions in the absence of gaseous oxygen have led to a number of suggestions that this lattice oxygen is the catalytically active species (*17, 18, 22*).



SCHEME 1. Oxygen depletion.

(*ii*) *Catalyst pretreatment with N_2O.* Given the earlier observation that N_2O can lead to oxidative coupling at significantly reduced temperatures, it is of interest to examine the possibly different efects of oxygenating the clean catalyst with N_2O and with O_2. Accordingly, the cleaned catalyst was heated at various temperatures (300 to 900 K) while dosing with N_2O (standard conditions), followed by cooling *in vacuo,* after which thermal desorption sweeps were carried out. The results are illustrated in Fig. 2, from which it is clear that N_2O dosing in the temperature interval 750–850 K leads to subsequent evolution of lattice oxygen into

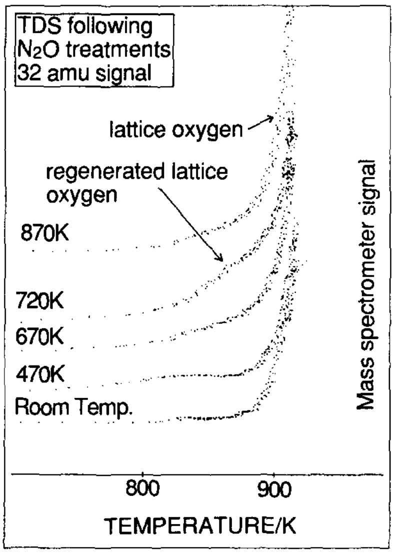


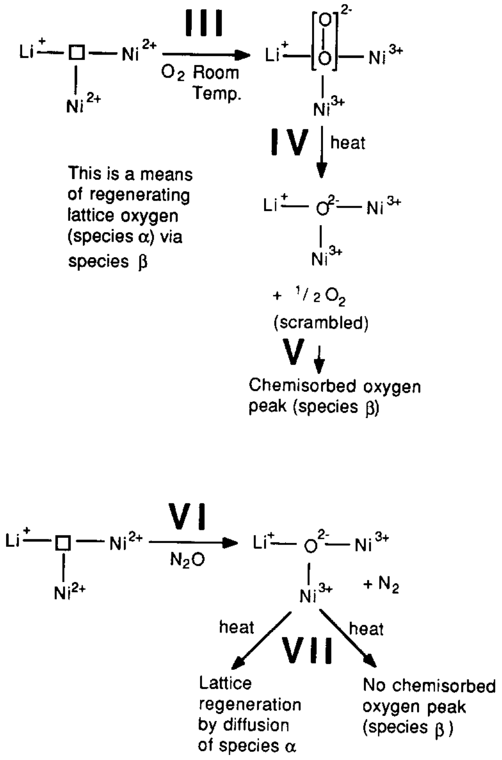
FIG. 2. Desorption spectra following N_2O treatments at various catalyst temperatures.

the gas phase at a substantially reduced temperature: a shoulder at ~830 K appears compared to the ~900 K onset of desorption for the untreated catalyst. Justification for the assignment of species α as lattice oxide oxygen (O^{2-}) comes principally from the quantity of O_2 evolved. The desorption feature persists for several hours in the absence of gaseous O_2, which corresponds to the depletion of many layers of oxide. This is demonstrated by comparison with the integrated intensity of the β peak, which has been quantified.

One might expect the immediate subsurface layers of the solid to release oxide oxygen at temperatures somewhat lower than those required for evaporation of oxygen diffusing from deeper down in the lattice. Hence it is plausible to assign the 830 K shoulder to regenerated lattice oxide; furthermore the high temperature required for its production and the effectiveness of both N_2O and O_2 in its formation are consistent with this view (see (iii) below and Scheme 2).

It thus appears that N_2O is capable of repopulating vacant lattice oxygen sites at these temperatures. Note, however, that no other oxygen surface species are formed (cf. (iii) below).

(*iii*) *Catalyst pretreatment with oxygen.* Experiments identical to those described in (ii) were performed, but with oxygen dosing instead of N_2O dosing. For catalyst temperatures ≳500 K dosing with O_2 produced results very similar to those obtained with N_2O. Once again, for gas exposures at temperatures between 750 and 850 K subsequent desorption measurements showed the onset of O_2 desorption at lower temperatures, although in this case the effect was somewhat less marked than it was with N_2O dosing. The desorption data very closely resemble those obtained using N_2O and are therefore not reproduced here. It thus appears that O_2 can also regenerate the lattice oxygen species under these conditions (see Schemes 1 and 2), albeit somewhat less effectively than N_2O.



SCHEME 2. Lattice regeneration with O_2 and N_2O.

When oxygen pretreatment was carried out at lower temperatures (i.e., below 500 K) a new desorption feature appeared, namely a distinct peak at around 800 K (Fig. 3). This behaviour does not occur with N_2O dosing under any conditions. We note in passing that the data in Fig. 3 were actually obtained with a particular $^{16}O_2$/$^{18}O_2$ gas mixture; the reasons for this emerge below. For present purposes, our interest focusses on the 32-amu trace in Fig. 3(a). It seems likely that the new feature at ~800 K is associated with a form of chemisorbed oxygen (species β), although the state of aggregation (atomic oxygen versus dioxygen) remains to be established. By means of appropriate sensitivity calibration experiments, we calculate that the area of the peak due to chemisorbed oxygen corresponds to $\sim 10^{-8}$ mol. BET surface area measurements showed the catalyst area to be $\sim 4.5\ m^2\ g^{-1}$, so that for the sample used to obtain these

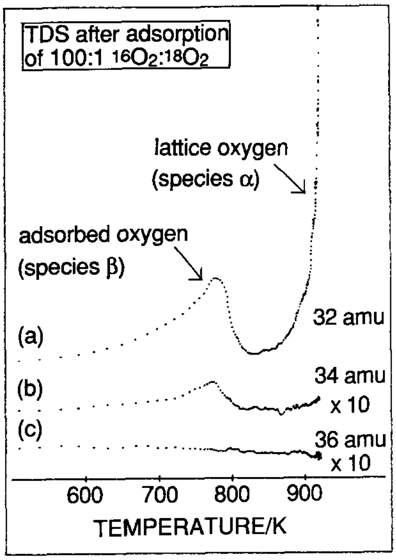


FIG. 3. Desorption spectra following catalyst treatment with 100 : 1 $^{16}O_2$: $^{18}O_2$ at room temperature.

particular data (0.131 g), taking the area per surface unit cell to be 1.25 × 10^{-20} m^2, we calculate ~4 × 10^{-5} mol of oxygen chemisorption sites on the catalyst surface. Hence, roughly 1 in 250 surface sites are occupied by chemisorbed oxygen, assuming the latter to be a dioxygen species (see below).

(*iv*) *Interaction with N_2O and dioxygen.* In order to investigate the relationship between the two oxygen species identified by the above experiments, the catalyst was predosed with N_2O at 750 K, cooled in vacuum, and then dosed with O_2 at 300 K, standard conditions being used for both gases. The desorption spectra obtained after this procedure showed that the chemisorbed oxygen species (species β) can still be generated by O_2 dosing following oxidation with N_2O, i.e., after lattice oxide regeneration, as shown in Scheme 2, VI and VII. However, the intensity of the corresponding β desorption peak is much reduced relative to that shown in Fig. 3a. Thus, reoxidation of the lattice by N_2O treatment reduces, but does not eliminate, the subsequent adsorption of O_2 to form species β. This strongly suggests that the chemisorbed species (β) is formed at surface sites that have been reduced.

(*v*) *Experiment with $^{18}O_2$.* In order to determine whether the chemisorbed oxygen species (β) was monatomic or diatomic, an isotope labelling experiment was carried out. Due to the relatively large volumes and pressures involved, it was not practical to dose the sample with a ~1 : 1 mixture of $^{18}O_2$ and $^{16}O_2$. Therefore a mixture with proportions of ~1 : 100 was dosed onto the clean catalyst at 300 K under standard conditions; mass spectrometric monitoring showed peaks at only 32 and 36 amu during this procedure, confirming that the apparatus itself was not responsible for any isotopic scrambling subsequently observed.

The desorption spectra monitored at 32, 34, and 36 amu after such a dosing procedure are illustrated in Fig. 3a–c. If the chemisorbed oxygen species (β) is diatomic then dosing with the 1 : 100 $^{18}O_2$: $^{16}O_2$ mixture should lead to 36 : 34 : 32 intensity ratios of 1 : 0 : 100 in the desorption spectra exhibited by the ~800 K peak. If this species is monatomic then the corresponding ratios would

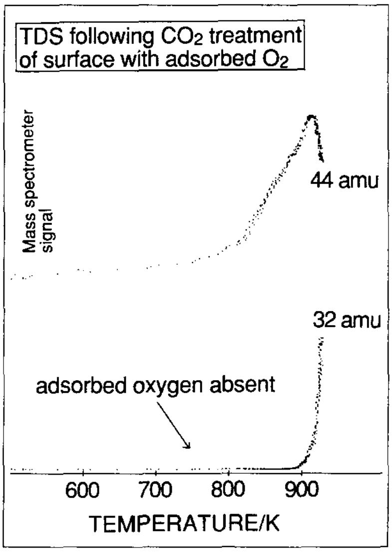


FIG. 4. O_2 and CO_2 desorption spectra following CO_2 treatment of surface predosed with oxygen at room temperature.

be 1 : 100 : 10000. Figure 3 is clearly indicative of this latter situation, thus demonstrating that the chemisorbed oxygen (species β) undergoes dissociation either during adsorption or at some stage before desorption (see Schemes 1 and 2).

CO_x Surface Species and Their Interaction with Oxygen Sites

(*i*) *Pretreatment with carbon dioxide.* For these measurements the catalyst was dosed at 300 K for 2 min with CO_2 under standard conditions. In order to avoid the possibility of introducing substantial amounts of carbonate into the bulk of the catalyst, higher adsorption temperatures were not investigated. The desorption spectra obtained after such treatments resembled the 44-amu trace in Fig. 4, indicating that a large amount of CO_2 is easily adsorbed on the catalyst surface. This could well be due to formation of a surface carbonate, for example

$$2LiNiO_2 + CO_2 \rightarrow Li_2CO_3 + Ni_2O_3.$$

The high-desorption temperature of CO_2 from the catalyst is consistent with the decomposition of such a surface carbonate.

(*ii*) *CO_2/O_2 coadsorption.* Coadsorption experiments were carried out in which standard doses of CO_2 and O_2 were applied in succession, with the catalyst at 300 K. Measurements were carried out with CO_2 first, followed by O_2, and also in the reverse order. Similar desorption spectra were obtained in the two cases (Fig. 4). From these results we may conclude that preadsorbed CO_2 inhibits the uptake of chemisorbed oxygen (species β) and that preadsorbed chemisorbed oxygen (species β) is destroyed by subsequent exposure to CO_2. Hence it is clear that there is more than a simple site-blocking effect occurring here: CO_2 dosing actually removes preadsorbed oxygen, in addition to inhibiting oxygen adsorption from the gas phase. It is therefore reasonable to suggest that a substantial reorganisation of the surface occurs on CO_2 adsorption, the most likely effect being formation of a surface carbonate.

(*iii*) *CO_2/N_2O coadsorption.* These measurements were similar to those described under (ii) above but with N_2O dosing at 750 K substituted for O_2 dosing at 300 K. The results showed that although CO_2 dosing prevents N_2O from replenishing depleted lattice oxygen (species α), it does not lead to depletion of lattice oxygen (species α) already replenished by N_2O. Again, these observations are consistent with a change in surface structure upon CO_2 adsorption: such a change could inhibit surface to bulk diffusion of oxygen generated by dissociation of N_2O. It is also possible that CO_2 adsorption resulting in formation of surface carbonate could inhibit uptake of lattice oxygen simply by preventing dissociative adsorption of N_2O in the first place.

(*iv*) *CO/O_2 coadsorption.* No CO adsorption occurred on the freshly cleaned surface. However, the results for O_2 pretreatment under standard conditions with the catalyst at 300 K, followed by CO dosing (standard conditions) indicate that chemisorbed oxygen (species β) is active for the oxidation of CO to CO_2 (Fig. 5 and Scheme 3). CO is inactive with respect to the catalyst surface in the absence of chemisorbed oxygen; i.e., there is no detectable interaction with lattice oxygen sites (species α) at the surface.

DISCUSSION

Three principal points emerge from the results presented above.

1. Two distinct oxygen surface species are present on $LiNiO_2$: a chemisorbed species (β) and lattice oxide oxygen (α). The lattice oxygen surface species can be regenerated at high temperature by interaction with both gaseous O_2 and N_2O. The chemisorbed species (β) is only formed by O_2 uptake at low temperature; N_2O uptake does not give rise to this species. This very strongly suggests that the chemisorbed species (β) is diatomic while the lattice oxide oxygen (species α), as expected, is a monoatomic species. Ungar *et al.* (*17*) found that $LiNiO_2$ catalysts pretreated with N_2O above 700 K showed enhanced activity for C_2 pro-

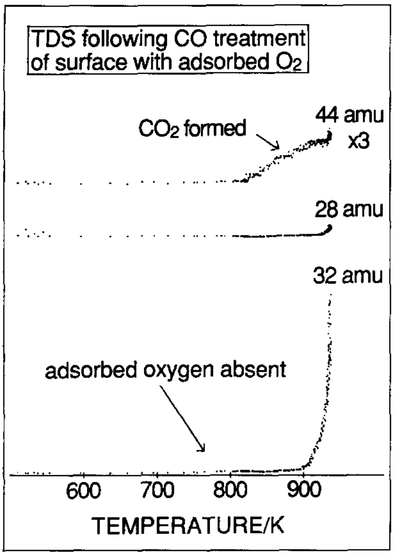


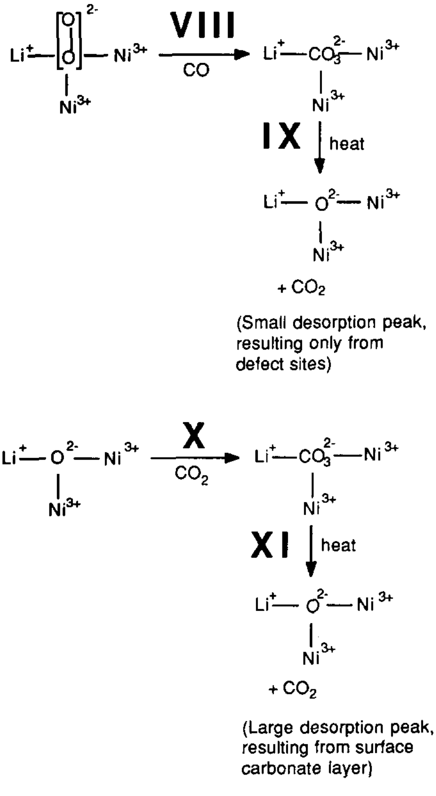
FIG. 5. O_2, CO, and CO_2 desorption spectra following CO treatment of surface predosed with oxygen at room temperature.

duction. This observation coupled with the present results provides rather strong evidence that surface lattice oxygen (species α) is the active species for methane coupling. Furthermore, the observed low saturation coverage that characterises the chemisorbed oxygen species (β) suggests that this latter may occur at some type of defect site. The effect of preoxidising the surface on the subsequent uptake of chemisorbed oxygen (species β) indicates that the defect site in question is a reduced site.

2. Desorption of labelled chemisorbed oxygen (species β) results in essentially complete isotopic scrambling.

3. Chemisorbed oxygen (species β) interacts with CO to produce a surface species that evolves CO_2 upon subsequent heating. CO_2 on the other hand interacts very strongly with lattice oxygen at the surface (species α), probably forming a surface carbonate, resulting in the destruction of oxygen chemisorption sites. Both these effects involve direct chemical reaction of an oxygen surface species with a carbon oxide. In contrast with this, CO_2 seems to affect β-O_2 in an identical manner, regardless of the order of dosing. This implies that an effect involving adsorption sites rather than adsorbed species is involved. Since there is no evidence for the direct chemical reaction of chemisorbed oxygen (β) with CO_2, the behaviour here must involve β-O_2 adsorption site destruction by CO_2 uptake.

The electron spectroscopic work of Badyal *et al.* (*19*) on a model system indicated the existence of O_2^{2-} species on the surface of oxygenated $LiNiO_2$. Furthermore, it was shown that O^- present on NiO undergoes conversion to O_2^{2-} on Li dosing; this O_2^{2-} appears to be more stable at the $LiNiO_2$ surface than the O^- precursor. These observations are also consistent with Schemes 1 and 2. The identification of O_2^{2-} as the oxygen species β also satisfactorily explains the very different behaviour exhibited by N_2O and O_2 chemisorption (Schemes 1 and 2) and the selective



SCHEME 3. Interaction with carbon oxides.

reaction of CO with β oxygen but not with the α species (Scheme 3). These species were found to be unstable at high temperatures, as indeed is the chemisorbed oxygen species found in this work. The electron spectroscopic results (*19*) also showed O^-, a species widely regarded as being the active site on Li/MgO catalysts (*6–8*), to be absent on $LiNiO_2$ at high temperatures. On the other hand the prolonged methane coupling activity of $LiNiO_2$ in the absence of gaseous oxygen (*16, 17*) demonstrates the ability of this catalyst to generate active oxygen species from lattice oxide oxygen, thus indicating that in this case O^{2-} is the crucial agent.

The available evidence is consistent with the scheme given below for aspects of the surface chemistry of $LiNiO_2$ that are likely to be relevant to methane coupling. The activation of methane by lattice oxygen shown in Scheme 1 Steps I and II has already been proposed by Hatano and Otsuka (*18*). As noted above, this view is supported by the continued activity of $LiNiO_2$ as a coupling catalyst in the absence of gaseous oxygen, an observation that has been confirmed by Ungar *et al.* (*16, 17*). It is also consistent with the model studies (*19*) that show that O^{2-} is the dominant oxygen species on the surface of Li/Ni/O systems at elevated temperatures. Step III of Scheme 2 rationalises the formation of chemisorbed oxygen (species β) by uptake of O_2 (but not by uptake of N_2O) at anion vacancy sites. The subsequent evolution of $O_2(g)$ in desorption experiments may be ascribed to dissociation of the O_2^{2-} species to regenerate O^{2-} and $O_2(g)$; this accounts for replenishment of lattice oxygen (species α) and the evolution of isotoptically scrambled chemisorbed O_2 in the labelling experiments (Scheme 2, Steps IV and V). It is also consistent with the spectroscopic results (*19*) that show that the O_2^{2-} species decomposes into O^{2-} at temperatures $\gtrsim 573$ K. In the present work, this chemisorbed oxygen (species β) desorbs at ~800 K; the difference in temperature may be ascribed to thermally activated diffusion and recombination of oxygen atoms, which could occur at temperatures somewhat higher than that of the initial dissociation of O_2^{2-}. N_2O can of course also fill anion vacancy sites at the surface of oxygen deficient $LiNiO_2$, generating lattice oxide oxygen (species α) directly without the intervening chemisorbed species (Scheme 2, Steps VI and VII).

Finally, Steps VIII, IX, X, and XI in Scheme 3 account for the difference in behaviour between CO and CO_2.

REFERENCES

1. Keller, G. E., and Bhasin, M. M., *J. Catal.* **73,** 9 (1982).
2. Sofranko, J. A., Leonard, J. J., and Jones, C. A., *J. Catal.* **103,** 302 (1987).
3. Ito, T., Wang, J.-X., Lin, C.-H., and Lunsford, J. H., *J. Am. Chem. Soc.* **107,** 506L (1985).
4. Otsuka, K., and Jinno, K., *J. Catal.* **100,** 353 (1986).
5. Burch, R., Squire, G. D., and Tsang, S. C., *Appl. Catal.* **43,** 105 (1988).
6. Driscoll, D. J., Martir, W., Wang, J.-X., and Lunsford, J. H., *J. Am. Chem. Soc.* **107,** 58 (1985).
7. Lin, C.-H., Wang, J.-X., and Lunsford, J. H. *J. Am. Chem. Soc.* **109,** 4808 (1987).
8. Ito, T., and Lunsford, J. H., *Nature* **314,** 721 (1985).
9. Hutchings, G. J., Scurrell, M. S., and Woodhouse, J. R., *J. Chem. Soc., Chem. Commun.,* 1862 (1987).
10. Hutchings, G. J., Scurrell, M. S., and Woodhouse, J. R., *J. Chem. Soc., Chem. Commun.,* 1388 (1987).
11. Hutchings, G. J., Scurrell, M. S., and Woodhouse, J. R., *in* "Proceedings, 9th International Congress on Catalysis, Calgary, 1988" (M. J. Phillips and M. Ternan, Eds.), Vol. 2, p. 923. Chem. Institute of Canada, Ottawa, 1988.
12. Otsuka, K., Liu, Q., and Morikawa, A., *Inorg. Chim. Acta* **118,** L24 (1986).
13. Jones, C. A., Leonard, J. J., and Sofranko, J. A., *J. Catal.* **103,** 311 (1987).
14. Hinsen, W., and Baerns, M., *Chem.-Ztg.* **107** (1983).
15. Burch, R., Squire, G. D., and Tsang, S. C., *Appl. Catal.* **46,** 69 (1989).
16. Ungar, R. K., Zhang, X., and Lambert, R. M., *Appl. Catal.* **42,** L1 (1988).
17. Ungar, R. K., Zhang, X., and Lambert, R. M., *J. Chem. Soc., Chem. Commun.* **8,** 473 (1989).
18. Hatano, M., and Otsuka, K., *J. Chem. Soc., Faraday Trans. 1* **85(2),** 199 (1989).
19. Badyal, J. P. S., Zhang, X., and Lambert, R. M., *Surf. Sci.* **225,** L15 (1990).
20. Otsuka, K., and Jinno, K., *Inorg. Chim. Acta.* **121,** 237 (1986).
21. Moggridge, G. D., Badyal, J. P. S., and Lambert, R. M., *J. Vac. Sci. Technol. A* **8**(5), 3874 (1990).
22. Otsuka, K., and Hatano, M., *Shokubai* **29,** 46 (1987).