Interaction of NO with the H_2-promoted Surfaces of MgO and Metal Ion-modified MgO

Geng Zhang, Tsunehiro Tanaka, Tsutomu Yamaguchi, Hideshi Hattori,* and Kozo Tanabe
Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060, Japan

H_2 preadsorption greatly enhanced the formation of NO_2^{2-} on MgO and metal-ion modified MgO, and promoted the formation of N_2O on Na^+-modified MgO by inductive interaction between adsorbed H and NO *via* the substrate.

Hydrogen molecules dissociate heterolytically on MgO[1–4] and metal-ion-modified MgO.[5] However, the changes in the electron configuration and electronic state of the surface resulting from H_2 adsorption have not been reported probably because the changes are too small to be detected by usual methods. An e.s.r. technique using an appropriate probe molecule has a high sensitivity and is useful for studying even small changes on the surface. Nitric oxide has been used as a probe to characterize the base site on metal ion-modified MgO[6] and CaO[7] by e.s.r. spectroscopy. We now report that the changes in surface properties resulting from H_2 adsorption may be detected by using NO as a probe molecule.

Catalysts were prepared by impregnating MgO separately with aqueous solutions of sodium hydroxide and aluminium nitrate followed by drying at 120 °C. Samples prepared were evacuated at 800 °C before use. E.s.r. spectra were measured at room temperature and spin concentrations were determined by using 4-hydroxy-TEMPOL (4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl) solution as a standard. Temperature programmed desorption (TPD) of adsorbed NO was carried out in a vacuum apparatus at a heating rate of 10 °C/min, and the gases evolved were monitored by mass spectrometry. ^{15}NO instead of ^{14}NO was used as an adsorbate to distinguish N_2O and N_2 from CO_2 and CO which are present as background gases.

The formation of NO_2^{2-} ($g_\parallel$ 2.0028, $A_\parallel$ 39.4 G, $g_\perp$ 2.0053; G = 10^{-4} T) was detected by e.s.r. when NO was adsorbed on MgO and modified MgO. The same spectrum has been reported on CaO[7] and MgO.[8] Iizuka *et al.*[7] suggested that the NO_2^{2-} was formed only on strongly basic sites. Table 1

Table 1. Effect of hydrogen preadsorption on the spin concentration of NO_2^{2-} species on modified MgO.

Catalyst	MgO	MgO–Na^{+} [a]	MgO–Al^{3+} [a]
	Spin conc. × 10^{16}/g		
No preads.	0.6	3.1	1.6
H_2 preads.[b]	1.8	4.2	4.7
	Surface area[c]/m^2 g^{-1}		
	150	70	70

[a] Content of the guest ion 0.43 mmol/g. [b] H_2 or D_2 was preadsorbed. [c] Specific surface area by the Brunauer–Emmett–Teller method using N_2 as adsorbate at −196 °C.

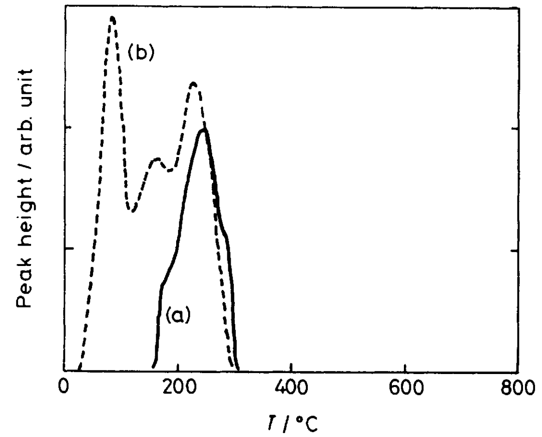

Figure 1. TPD profiles of N_2O desorbed from (a) Na^+ (0.43 mmol/g)–MgO and (b) the corresponding H_2-preadsorbed catalyst.

summarizes the spin concentrations of NO_2^{2-} formed on MgO and metal ion-modified MgO. Preadsorption of hydrogen enhances the number of NO_2^{2-} radicals for all catalysts. Preadsorption of hydrogen did not change the magnetic parameters of the signal of NO_2^{2-}; no hyperfine structure was observed. This strongly indicates that there is no direct interaction between NO_2^{2-} and adsorbed hydrogen. Consequently, it is postulated that the hydrogen preadsorption enhances the electron donating ability, namely the basic strength and concentration of basic sites, on the surfaces of pure MgO and metal ion-modified MgO in such a way that the adsorbed hydrogen changes the electronic state of the oxide surface itself rather than interacts directly with NO. Electron transfer from a ($Mg\text{–}H^- \cdots O\text{–}H^+$) pair to a neighbouring O^{2-} may enhance its basic strength. No significant differences in the concentration of NO_2^{2-} or in the magnetic parameters were observed if D_2 rather than H_2 was used.

The TPD profiles of the evolution of N_2O when NO was adsorbed on Na^+–MgO and H_2 preadsorbed Na^+–MgO are shown in Figure 1. The threshold temperature for the evolution of N_2O was lowered from 150 to 40 °C upon H_2 preadsorption. Preadsorption of hydrogen enhanced the formation of N_2O. The enhancement of the NO decomposition to N_2O possibly results from an increase in the number of NO molecules adsorbed adjacently.

A recent report of *ab initio* MO calculations based on Mg_4O_4 and $Mg_4O_4H_2$ clusters suggested the presence of inductive interactions in the H_2–H_2 system.[9] According to these calculations, dissociative adsorption of the second H_2 was greatly promoted by the first H_2 adsorption. Our results provide the first experimental evidence for H_2-induced interaction on an insulator.

The present experiment results indicating enhancement of base sites are consistent with the *ab initio* MO calculations. It is highly plausible that interaction between adsorbates through substrate (IBATS) is operating in the H_2–MgO system.

Received, 15th May 1989; Com. 9/02017I

References

1 T. Ito, T. Sekino, N. Moriai, and T. Tokuda, *J. Chem. Soc., Faraday Trans. 1*, 1981, **77**, 2181.
2 S. Coluccia, F. Boccuzzi, G. Ghiotti, and C. Morterra, *J. Chem. Soc., Faraday Trans. 1*, 1982, **78**, 2111.
3 S. Coluccia, F. Boccuzzi, G. Ghiotti, and C. Mirra, *Z. Phys. Chem., N. F.*, 1980, **121**, 141.
4 Y. Tanaka, Y. Imizu, and K. Tanabe, Proc. 7th Int. Congr. Catal., Tokyo, 1980, Kodansha, Tokyo and Elsevier, Amsterdam, 1981, part B, p. 1254.
5 K. Tanabe, G. Zhang, and H. Hattori, *Appl. Catal.*, 1989, **48**, 63.
6 G. Zhang, T. Tanaka, T. Yamaguchi, H. Hattori, and K. Tanabe, to be published.
7 T. Iizuka, Y. Endo, H. Hattori, and K. Tanabe, *Chem. Lett.*, 1976, 803.
8 J. H. Lunsford, *J. Chem. Phys.*, 1967, **46**, 4347.
9 H. Kobayashi, M. Yamaguchi, and T. Ito, *Shokubai (Catalyst)*, 1989, **31**, 68.