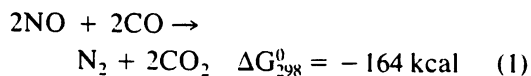


NOTES

Reduction at 300 K of NO by CO over Supported Platinum Catalysts

The reduction of NO by CO has been the subject of extensive research in recent years because of its fundamental importance in pollution control (1-3). The catalysts used have been mostly supported noble metal catalysts (Rh, Pt, Pd, Ru) (4-13), their single crystals (14-17), or polycrystalline metals (18, 19). The mechanism and pathway of this reaction have not been unambiguously determined. For example, controversy persists regarding whether N₂O or isocyanate (or both) is formed as an intermediate. Nitrous oxide is often obtained as the main product when supported metals are used (4, 8, 13), whereas most studies on single crystals give N₂ as the dominant product (14, 16, 17).

Reactions (1) and (2) are both thermodynamically favored at 298 K:



However, seldom are these kinetically facile at low temperatures (20, 21). We report here the catalytic reduction of NO by CO on platinum-supported catalysts at quite low temperatures, 300 K, and examine the influence of the support and water.

TiO₂ (Degussa P-25), Nb₂O₅ (Aldrich), SrTiO₃ (Alfa Products), Al₂O₃ (Degussa), and SiO₂ (Cab-o-sil) were used as supports. Pt (1 wt%)/oxide catalysts were prepared by impregnation as follows: the oxide powder was suspended in aqueous H₂PtCl₆ solution, dried at 100°C, and subsequently calcined at 650 K in air for 1 h.

The reactions were carried out in a closed gas circulation system. The catalyst was placed on a flat fused silica window at the

bottom of a reaction cell and reduced *in situ* with H₂ (100 Torr, 1 Torr = 133.3 N m⁻²) at 500 or 750 K for 1 h. The hydrogen was evacuated at the reduction temperature for 10 min. Mixtures of NO and CO, 50 Torr (ca. 600 μmol) each, were dosed after cooling to room temperature. The reactions were carried out at room temperature, if not otherwise specified. To provide a saturated constant partial pressure (ca. 20 Torr), degassed water was introduced into a Liebig condenser which formed part of the closed gas circulation system prior to introducing the CO and NO. CO, NO, N₂, H₂, N₂O, and CO₂ were determined by gas chromatography (Varian 90-P), using either He or Ar carrier gas. The column materials were molecular sieve 5A for CO, NO, N₂, and H₂, and Porapak Q for N₂O and CO₂.

Table I summarizes the effects of the support, of reduction temperature of the catalyst, and of water. The main products were CO₂ and N₂O for all catalysts suggesting that reaction (2) dominates. The most active catalyst, both in the absence and presence of water, is Pt/TiO₂. The other oxide supports show lower activity, particularly Pt/SiO₂, which is not active at all. Metal dispersion, generally central, is not the only factor here: the activity does not correlate directly with the surface area and it changes drastically by high-temperature reduction and addition of water even when the dispersion does not change. We suppose electronic effects of the support are important.

For Pt/TiO₂, reduced at 750 K, the primary products, when no H₂O was added, were initially CO₂ and N₂O. After 2 h, the N₂O rate began to decrease and N₂ formed, while the amount of CO₂ increased monotonically. A significant amount of N₂ was formed after 20 h with an equivalent N₂O

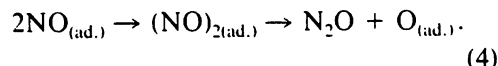
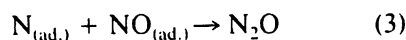
TABLE 1

Reduction of NO by CO over Pt(1 wt%)/Oxide Catalysts at Room Temperature

Catalyst ^a	Reduction temp (K)	Condition	Products (μmol)	
			CO ₂	N ₂ O
Pt/TiO ₂	500	CO-NO	76	78
	750	CO-NO	247	242
	750	CO-NO-H ₂ O	516	250
Pt/Nb ₂ O ₅	500	CO-NO	0	0
	750	CO-NO	41	22
	750	CO-NO-H ₂ O	252	143
Pt/SrTiO ₃	750	CO-NO	27	10
	750	CO-NO-H ₂ O	181	167
Pt/Al ₂ O ₃	750	CO-NO	17	19
	750	CO-NO-H ₂ O	30	41
Pt/SiO ₂	750	CO-NO	0	0
	750	CO-NO-H ₂ O	3	3

^a In each case, 1 g of catalyst was used, the reaction time was 4 h, and the initial amounts of NO and CO were 50 Torr (600 μmol) each.

decrease. Thus, N₂ is a secondary product and involves N₂O as an intermediate, as has been suggested earlier (13). Nitrous oxide can form by the reaction of NO with N dissociated from NO (Eq. (3)) or by decomposition of an NO dimer, (NO)₂ (Eq. (4)):

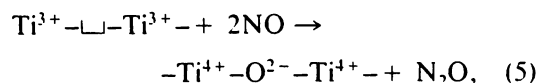


The reduction temperature also affects the activity. Catalysts reduced at high temperature (750 K) give greater reaction rates than those reduced at lower temperatures (500 K). In this case, SMSI (22) enhances the rate. We suppose that nitrogen-oxygen bonds dissociate more readily on the Pt/TiO₂ and Pt/Nb₂O₅ catalysts reduced at high temperature because of electron donation (i.e., an electronic effect) from reduced TiO₂ and Nb₂O₅ (Ti³⁺ or Nb⁴⁺) to an NO molecule or an NO dimer adsorbed on the Pt surface.

In the presence of water vapor, which

may condense on the surface of the catalyst, the activity was enhanced and no N₂ was formed. The effect is most significant for the *n*-type semiconductor supports (TiO₂, Nb₂O₅, and SrTiO₃). Presumably N₂O adsorption sites are blocked by adsorbed water.

In view of its particularly high activity at room temperature, Pt/TiO₂ was examined in more detail (Table 2). When the reaction was carried out at 365 K, lower than that used in earlier work (10, 11), the activity was considerably higher and the conversion of NO was completed during 1 h. When only CO was dosed, no products were detected, implying that, in the absence of NO, there are no reactive surface oxygen species for CO oxidation to CO₂. Upon addition of NO, the CO-NO reaction commenced. On the other hand, if only NO was dosed, a small amount of N₂O was formed (Table 2), probably by reaction with reduced TiO₂. This would involve Ti³⁺ (or electrons) and oxygen vacancies, as follows,



where \square denotes an oxygen vacancy.

TABLE 2

Reduction of NO by CO over Pt(1 wt%)/TiO₂ and TiO₂ Catalysts at Room Temperature

Catalyst ^a	Condition	Products (μmol)	
		CO ₂	N ₂ O
Pt/TiO ₂	CO-NO	181	225
	CO-NO ^b	298	282
	CO	0	0
	NO	0	26
TiO ₂	CO-NO	0	10
	CO-NO-H ₂ O	0	3

^a In each case, 1 g of catalyst was used, the reduction temperature was 750 K, the reaction time was 1 h, and the initial pressure of CO and NO was 50 Torr (600 μmol) each.

^b The reaction was carried out at 365 K.

Neat TiO₂ (without Pt) shows no sustainable activity. Only a tiny amount of N₂O was formed during the first hour, as suggested in Eq. (5). In the absence of Pt, there was no enhancement by water. These results establish that either the platinum surface or the boundary between platinum and the reduced TiO₂ contains active sites for the CO–NO reaction.

The catalytic character on the Pt/TiO₂ catalyst at room temperature was established by repeating the CO–NO reaction with no intervening pretreatment. In the series, 1800 μmol (600 μmol × 3) of NO reacted easily when 51 μmol of Pt was present. Thus, the reaction is catalytic with respect to Pt. In contrast, on the Pt/Al₂O₃ catalyst, the reaction stopped short of the extent required for catalytic activity.

In conclusion, the catalytic reduction of NO by CO to form N₂O and CO₂ proceeds at quite low temperatures (300 K) over platinum supported on TiO₂, Nb₂O₅, and SrTiO₃. The activity depends strongly on the support and on the reduction pretreatment temperature. Among the materials tested, Pt/TiO₂ reduced at 750 K was the most active, while Pt/SiO₂ was least active. In the absence of water, N₂ is formed as a secondary product. Adding water suppresses N₂ formation. The effect of water was most pronounced on the *n*-type semiconductors, TiO₂, Nb₂O₅, and SrTiO₃.

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