KINETICS OF CATALYTIC REDUCTION OF NITROGEN OXIDE BY CARBON MONOXIDE ON CuO/Al_2O_3 CATALYST

Zdeněk MUSIL and Vladimír POUR

Institute of Inorganic Chemistry,
Czechoslovak Academy of Sciences, 160 00 Prague 6

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The kinetics of the reduction of nitrogen oxide by carbon monoxide on CuO/Al_2O_3 catalyst (8·36 mass % CuO) were determined at temperatures between 413 and 473 K. The reaction was found to be first order in NO and zero order in CO. The observed kinetics are consistent with a rate equation derived from a mechanism proposed on the basis of IR spectroscopic measurements.

The catalytic reduction of nitrogen oxide by carbon monoxide to elemental nitrogen is one of the methods for removing nitrogen oxides from pollution emissions. The numerous studies on the kinetics of the process have been reviewed by Shelef[1,2]. The reaction was studied primarily on catalysts containing noble metals[3], but catalysts based on transition metal oxides have also received attention[4-6]. Among the most active of the latter group are copper-based catalysts supported on various carriers.

Rate equations describing the reaction kinetics differ considerably depending on both the type of catalyst and the method used to determine the kinetics. These differences are also reflected in a variety of mechanisms which have been proposed for the reaction. Divergent views centre around the mode of NO adsorption, and the formation of N_2O and its role in the reduction. It is generally assumed that the reduction proceeds by an oxidation-reduction mechanism with respect to the catalyst.

Apart from kinetic measurements, other methods have been used to support the proposed reaction mechanisms. These include simultaneous studies of the formation and changes in the surface complexes, and the rates of the elementary reaction steps. Ayen and Peters[7] correlated kinetic data for the reaction on a CuO/Al_2O_3 catalyst by an equation based on the Langmuir–Hinshelwood concepts, assuming the surface reaction of NO with CO adsorbed on active centres of the same type to be the rate-determining step. This equation does not, however, account for the formation of N_2O and its role in the reduction. The mechanism proposed by Rewick and Wise[5] on the basis of data for the adsorption on CuO and CuO/Al_2O_3 catalysts assumes dissociative adsorption of NO and subsequent reaction of the fragments with gaseous NO molecule to yield N_2 or N_2O. Echigoya and coworkers[8] determined the kinetics in a closed apparatus with recirculation; in addition, they used oxygen titration to establish the number of reduced catalyst centres on which the reaction occurred. The concept underlying their kinetic equation is that the reaction between NO and the reduced catalyst produces a complex which reacts with NO from the gas phase to form N_2O which, in turn, reacts with the reduced catalyst to yield elemental nitrogen. The oxidized centres are reduced by carbon monoxide.

London and Bell[9,10] have derived a kinetic equation for the reaction on a CuO/SiO_2 catalyst, based on kinetic measurements and IR spectroscopic evidence on the elementary reaction steps. The mechanism assumes that a chemisorbed NO molecule reacts with another centre to produce an adsorbed nitrogen fragment which undergoes a reaction with NO from the gas phase yielding N_2O which, in turn, reacts with a reduced Cu centre to form elemental nitrogen. This intricate reaction mechanism involving nine steps leads to a very complicated kinetic equation where only one rate constant can be attributed a physical meaning.

In previous papers[11,12] the adsorption and reaction of NO with CO on CuO/Al_2O_3 were studied by IR spectroscopy. The results indicate that the reaction mechanism may be represented by a sequence of four elementary steps: adsorption of NO on reduced centres leads to the formation of a surface complex undergoing subsequently a reaction with NO from the gas phase to form N_2O which, in turn, interacts with the reduced centres to yield elemental nitrogen.

The aim of this work was to determine the kinetics of the reduction over a temperature range 413–473 K on the same catalyst as used in the spectroscopic measurements, and to confront the data with kinetic consequences of the mechanism proposed on the basis of the spectroscopic evidence.

EXPERIMENTAL

Catalyst. A CuO/Al_2O_3 catalyst was prepared by saturating γ-alumina (Condea SC) with a $Cu(NO_3)_2$ solution, drying at 393 K for two hours, and calcinating in an oxygen atmosphere at 748 K for a period of four hours. The CuO content was 8·36 mass %, and the overall specific surface area $S = 148\ m^2\ g^{-1}$ (BET). X-ray diffraction analysis showed that the only other phase besides γ-Al_2O_3 was CuO.

Apparatus. The kinetics of the reaction between NO and CO were measured in an integral continuous plug-flow reactor, using catalyst weights of 0·5 or 1·0 g. The particle size ranged between 0·8 and 1·2 mm. To ensure isothermal conditions throughout the catalyst bed, the catalyst was diluted by crushed glass of the same particle size in a ratio of 1 : 10. The temperature, measured by a jacketed thermocouple located at the centre of the catalyst layer, was found to be constant along the length of the layer, the maximum deviation from an adjusted value being 0·5 K. Experiments with different catalyst weights and small particle sizes proved that the effects of external and internal diffusion were negligible.

The reaction mixture entering the reactor consisted of 4 vol % of the reactants (NO and CO), with molar ratios, n_{NO}^0/n_{CO}^0, equal to 0·5, 1·0, and 2·0, in argon as carrier gas. The reaction kinetics were measured over a space time interval $W/F = 0{\cdot}2 - 0{\cdot}4\ g\ h\ mol^{-1}$ at temperatures within the range 413–473 K.

The reaction mixture was analyzed at the inlet and outlet of the reactor by using a CHROM 4 gas chromatograph with double column arrangement (Laboratorní přístroje, Prague). The determination of N_2O and CO was made using a column packed with PORAPAC Q 80/120 mesh (Carlo Erba). The 5A 80/100 mesh molecular sieve used for the determination of Ar, N_2, NO and CO was first treated as described by Dietz[13] to prevent NO tailing. Hydrogen was used as the carrier gas.

Gases. Nitrogen oxide was evolved by adding a $NaNO_2$ solution dropwise to a solution of H_2SO_4 and $FeSO_4$. Other gases were used direct from pressure cylinders. Argon was purified in a tower packed with reduced BTS catalyst (Merck) to eliminate possible traces of oxygen. Carbon monoxide was freed from carbonyls by passing through a tower heated at 473 K, and then through another tower packed with glass wool. Hydrogen for gas chromatography was freed from oxygen traces, which interfere with NO determination, by passing through the reduced BTS catalyst and a tower packed with Pd/Al_2O_3, and then dried by $Mg(ClO_4)_2$ (Merck).

RESULTS AND DISCUSSION

The results of the kinetic measurements were treated in the form of a dependence of the conversion of NO defined as

$$y(\mathrm{NO}) = 1 - x_{\mathrm{NO}}/x^0_{\mathrm{NO}} , \qquad (1)$$

where x^0_{NO} and x_{NO} are the mole fractions of NO in the mixture at the reactor inlet and outlet, respectively, on the space time W/F at constant temperature. The obtained reaction isotherms $y(\mathrm{NO})$ *vs* $(W/T)_T$ were approximated by the empirical function

$$f(y) = 1 - \mathrm{Pn}(y) \exp(Ay) , \qquad (2)$$

where Pn is a second-degree polynomial. The reaction rate was calculated from the analytical derivative of this empirical function by substituting values of y.

First, the rate data were fitted to the power law rate expression

$$r_{\mathrm{NO}} = k_3 x^{\alpha}_{\mathrm{NO}} x^{\beta}_{\mathrm{CO}} . \qquad (3)$$

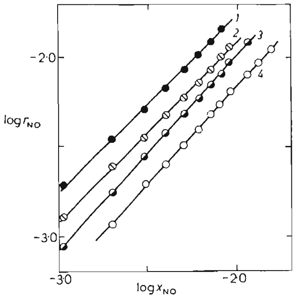

FIG. 1

Plot of log r_{NO} *vs* x_{NO}. $x^0_{\mathrm{CO}}/x^0_{\mathrm{NO}} = 2{\cdot}0$. *1* 473 K, *2* 453 K, *3* 433 K, *4* 413 K

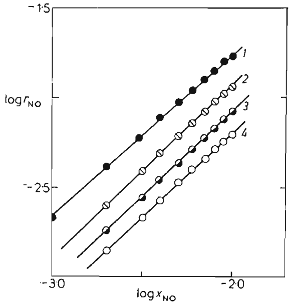

FIG. 2

Plot of log r_{NO} *vs* x_{NO}. $x^0_{\mathrm{CO}}/x^0_{\mathrm{NO}} = 1{\cdot}0$. *1* 473 K, *2* 453 K, *3* 433 K, *4* 413 K

A linear regression analysis of the whole set of data for various compositions resulted in the values $\alpha = 0.9737$ and $\beta = -0{\cdot}0253$. It is seen that the value of α is close to 1, and the value of β to zero. Thus, Eq. (*3*) can be simplified to the form

$$r_{NO} = k_4 x_{NO} , \qquad (4)$$

indicating that the reduction of NO is first order in NO and zero order in CO. The same dependence is shown by plots of $\log r_{NO}$ against $\log x_{NO}$ in Figs 1 to 3, which give straight lines of slope 1. The values of the rate constants of Eqs (*3*) and (*4*) for the individual experimental temperatures are listed in Table I.

Next, the experimental kinetic data were fitted to a rate equation following from the mechanism derived from IR spectroscopic measurements. As indicated by these measurements, the first step is the adsorption of NO on reduced Cu active centres. The adsorbed NO then reacts with a gas-phase NO molecule to form N_2O, leaving an oxidized centre. A small fraction of N_2O molecules, depending on the temperature, are released to the gas phase, while the major portion react with the reduced centres to produce nitrogen gas. The oxidized centres are reduced by carbon monoxide.

These results are consistent with the following reaction scheme:

$$\mathrm{NO(g)} + \mathrm{RC} \rightarrow \mathrm{NO(ads)} \qquad (5)$$

$$\mathrm{NO(ads)} + \mathrm{NO(g)} \rightarrow \mathrm{N_2O(s)} + \mathrm{OC} \qquad (6)$$

$$\mathrm{N_2O(s)} + \mathrm{RC} \rightarrow \mathrm{N_2(g)} + \mathrm{OC} \qquad (7)$$

$$\mathrm{OC} + \mathrm{CO(g)} \rightarrow \mathrm{RC} + \mathrm{CO_2(g)} \qquad (8)$$

$$\mathrm{N_2O(s)} \rightarrow \mathrm{N_2O(g)} + * \qquad (9)$$

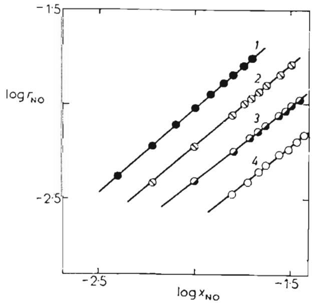

FIG. 3

Plot of $\log r_{NO}$ *vs* x_{NO}. $x^0_{CO}/x^0_{NO} = 0{\cdot}5$. *1* 473 K, *2* 453 K, *3* 433 K, *4* 413 K where RC represents the Cu^+ cation of the partially reduced CuO surface, OC denotes the oxidized CuO surface, $N_2O(s)$ is the weakly and non-specifically bound form of N_2O, and * denotes the centre of N_2O adsorption.

The rates of the elementary reaction steps may be expressed by the following relations:

$$r_5 = k_5 x_{NO} [RC] \tag{10}$$

$$r_6 = k_6 x_{NO} [NO] (ads) \tag{11}$$

$$r_7 = k_7 [N_2O] (s) [RC] \tag{12}$$

$$r_8 = k_8 x_{NO} [OC] \tag{13}$$

$$r_9 = k_9 [N_2O] (s) \tag{14}$$

TABLE I

Rate constants of Eqs (*3*) and (*4*)

Temperature K	Eq. (*3*) $\alpha = 0{\cdot}9737$ $\beta = 0{\cdot}025$	Eq. (*4*) $\alpha = 1{\cdot}0$ $\beta = 0$
413	0·600	0·623
433	0·826	0·846
453	1·167	1·183
473	1·711	1·773

TABLE II

Constants of Eq. (*16*)

Temperature K	Constants	
	a	*b*
413	0·605	0·003
433	0·790	−0·006
453	1·188	−0·019
473	1·704	0·097

where the brackets designate the surface concentrations of the species. On the assumptions that N_2O is non-specifically bound, the reaction yielding gaseous N_2O is negligible, and none of the reactions is rate-determining, the overall rate of NO reduction may be expressed as

$$r_{NO} = \frac{k_5k_6Lx_{NO}x_{CO}/(k_5 + k_6)}{x_{CO} + k_5k_6x_{NO}/(k_5 + k_6)\,k_8}, \qquad (15)$$

where L denotes the total number of active centres,

$$L = [RC] + [OC] + [NO]\,(\text{ads})\,.$$

Introducing $a = k_5k_6L/(k_5 + k_6)$ and $b = k_5k_6/(k_5 + k_6)\,k_8$ simplifies Eq. (*15*) to

$$r_{NO} = ax_{NO}x_{CO}/(x_{CO} + bx_{NO})\,. \qquad (16)$$

The values of the constants a and b for the individual temperatures and compositions, obtained by linear regression analysis, are summarized in Table II.

The values of the constant b are very small, and the product (bx_{NO}) is negligible compared with x_{CO}. Hence, Eq. (*16*) may be reduced to

$$r_{NO} = bx_{NO}\,. \qquad (17)$$

Thus, the rate equation derived from IR spectroscopic measurements gives an adequate description of the reaction kinetics even at elevated temperatures. Eq. (*15*) is identical with the relation derived by Echigoya and coworkers[8] from measurements of the reaction rates and the determination of the number of surface centres.

The apparent activation energy evaluated from the temperature dependence of the rate constant is equal to 28·8 ± 2 kJ mol^{-1}. This relatively low value compares with values found by other authors; Gasan-Zade[14], for example, found $E = 25{\cdot}1$ kJ mol^{-1}. In line with these results is also the lowest E value found by Alkhazov and coworkers[15] for CuO as one of a series of oxide catalysts.

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