J.C.S. СНЕМ. СОММ., 1981

Zeolite-catalysed Oxidation of Carbon Monoxide at Unusually Low Temperatures

By HORST FÖRSTER,* WOLFGANG FREDE, GUNTER PETERS, MONIKA SCHUMANN, and ULRICH WITTEN (Institute of Physical Chemistry, University of Hamburg, Laufgraben 24, D-2000 Hamburg 13, Federal Republic of Germany)

Summary Catalytic activity for oxidation of carbon monoxide at temperatures as low as 150 K has been found with zeolites of type A.

OWING to its poisonous properties the removal of carbon monoxide has gained great industrial importance and has focused research on catalysts which would enable the combustion of CO to proceed in a temperature range considerably lower than those of flames or explosions. As a result a number of solid catalysts, mainly oxides, have been explored, on which oxidation occurs from elevated temperatures down to 250 K.¹ From another point of view, the oxidation of carbon monoxide is frequently used as a test reaction for the development of oxidation catalysts.

Zeolites are active catalysts for many types of reaction. However, only a few investigations have been performed on carbon monoxide oxidation; these used faujasites and mordenites.²⁻⁴ These studies showed that the catalytic activity can be greatly increased by introduction of transition-metal ions, resulting in a drastic decrease in activation energy as indicated by the fact that reaction commences at lower temperatures. For example, these zeolites can be applied to the cleaning of automotive exhaust gases.⁵ Catalytic activity of the sodium forms, only found at higher temperatures, was ascribed to transition-metal impurities.²

Until now there has been only one report on CO oxidation using zeolites of type A, as far as we know, although they are suitable catalysts, especially for small molecules.⁶ In addition, zeolites of type A have advantages for fundamental studies, as they have a simple chemical composition, consisting of a primitive cubic arrangement of sodalite units, and the cations can be localized more definitely than in other zeolites.

We report for the first time a detailed study of CO oxidation by zeolites of type A, using $Na_{12}A$, Li_9Na_3A , Ca_4Na_4A , Ca_5Na_2A , Co_4Na_4A , Zn_4Na_4A , and Mg_4Na_4A (A = Al₁₂Si₁₂O₄₈), prepared by cation exchange from $Na_{12}A$. Adsorption of CO and subsequent oxidation to CO₂ were followed by i.r. spectroscopy between 150 and 300 K.

J.C.S. CHEM. COMM., 1981

Intense main bands with cation-dependent frequency shifts, generally to higher wavenumbers compared with the gas phase were observed for CO adsorbed at room temperature. The positions of these bands (Na⁺: 2160, Li⁺: 2185, Ca²⁺: 2190, Co²⁺: 2195, Zn²⁺: 2195, and Mg²⁺: 2197 cm⁻¹) can be correlated with the charge/radius ratio of the cations, as has been found with X- and Y-type zeolites.7 Therefore, the CO molecules are assumed to be located near the cations. The appearance of the main bands is generally accompanied by appearance of weaker sidebands to lower or higher frequencies.

Upon addition of oxygen at room temperature the oxidation reaction proceeds, as indicated by the appearance of the CO₂ asymmetric stretching band in the range 2330-2370 cm⁻¹. Simultaneously surface carbonate bands appear in the 1200—1800 $\rm cm^{-1}$ region.* The catalytic activity decreases in the series $Ca_5Na_2A > Li_9Na_3A > Mg_4Na_4A >$ Co₄Na₄A, while Na₁₂A is completely inactive.

I.r. investigation of CO adsorption on zeolites Na₁₂A and Ca_4Na_4A down to 150 K showed additional bands at 2350 cm⁻¹, which must be assigned to physisorbed CO₂.^{8,9} Upon addition of oxygen these bands were greatly enhanced.

It is the first time that oxidation of CO has been observed at these unusually low temperatures and catalysts become active which are inactive at higher temperatures. These surprising results require a more detailed examination.

For the present we conclude the following. (i) Adsorption of CO is the basic requirement for the reaction to proceed. (ii) Addition of gaseous oxygen greatly enhances the oxidation reaction, but participation of the lattice oxygen cannot be excluded. (iii) Catalytic activity is optimum for medium strength of adsorption of CO.

This work was supported in part by the Deutsche Forschungsgemeinschaft, and one of us (M. S.) is grateful for a studentship from the Max-Buchner Forschungsstiftung.

(Received, 10th July 1981; Com. 808.)

- ² T. A. Bregadze, V. A. Seleznev, A. A. Kadushin, and O. V. Krylov, Izv. Akad. Nauk SSSR, Ser. Khim., 1973, 2701.
- ³ F. B. Benn, J. Dwyer, A. Esfahani, N. P. Evmerides, and A. K. Szczepura, J. Catal. 1977, 48, 60.
- ⁶ F. B. Benn, J. Dwyer, A. Estanani, N. P. Evinerides, and A. Szczepura, J. Catal. F.
 ⁶ H. Pätow and L. Riekert, *Ber. Bunsenges. Phys. Chem.*, 1979, **83**, 807.
 ⁶ C.-M. Fu, M. Deeba, and W. K. Hall, *Ind. Eng. Chem.*, *Prod. Res. Dev.*, 1980, **19**, 299.
 ⁶ N. Y. Chen and P. B. Weisz, *Chem. Eng. Progr., Symp. Ser.*, 1967, **63**, 86.
 ⁷ C.-L. Angell and P. C. Schaffer, *J. Phys. Chem.*, 1966, **70**, 1413.
 ⁸ H. Förster, M. Schuldt, and R. Seelemann, *Z. Phys. Chem. (Neue Folge)*, 1975, **97**, 329.
 ⁹ Y. Delaval and E. Cohen de Lara, *J. Chem. Soc., Faraday Trans.* 1, 1981, 869.

¹ M. Katz, Adv. Catal., 1953, 5, 177.