Zeolite-catalysed Oxidation of Carbon Monoxide at Unusually Low Temperatures

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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 ($A = Al_{12}Si_{12}O_{48}$), prepared by cation exchange from $Na_{12}A$. Adsorption of CO and subsequent oxidation to CO_2 were followed by i.r. spectroscopy between 150 and 300 K.

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, Ca^{2+}: 2190, Co^{2+}: 2195, Zn^{2+}: 2195, and Mg^{2+}: 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 CO_2 asymmetric stretching band in the range 2330—2370 cm^{-1}. Simultaneously surface carbonate bands appear in the 1200—1800 cm^{-1} region.[8] The catalytic activity decreases in the series $Ca_5Na_2A > Li_9Na_3A > Mg_4Na_4A > Co_4Na_4A$, while $Na_{12}A$ is completely inactive.

I.r. investigation of CO adsorption on zeolites $Na_{12}A$ and Ca_4Na_4A down to 150 K showed additional bands at 2350 cm^{-1}, which must be assigned to physisorbed CO_2.[8,9] Upon addition of oxygen these bands were greatly enhanced.

In the case of zeolite $Na_{12}A$ the reaction was studied between 180 and 220 K. From preliminary experiments the reaction can be assumed to be of first-order in CO coverage but of zeroth-order in oxygen pressure. An activation energy as low as about 12 kJ/mol has been estimated.

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.

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