Activating Effect of Metallic Palladium on the Reduction Rate of Ni^{2+} Ions in an X Type Zeolite

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Summary The presence of metallic palladium in the vicinity of Ni^{2+} ions dispersed in an X type zeolite greatly increases the reduction rate of these ions; these results can be explained by a spill-over mechanism.

ATTEMPTS to obtain highly dispersed metal particles, which can exhibit outstanding catalytic properties, are currently of great interest, and for this reason the reduction by hydrogen of Ni^{2+} ions introduced in an X type zeolite[1,2] with the composition $Na_{24}Ni_{31}(SiO_2)_{106}(AlO_2)_{86}$ has been studied. We now report the influence on this reduction process of metallic palladium. The ratios $Pd^{2+}:Ni^{2+}$ of the two samples studied were 0·012 (sample A) and 0·43 (sample B), respectively.

Before being reduced, the samples were pretreated at 773 K first *in vacuo*, and then under an oxygen pressure of 13 kN m^{-2}. This oxygen treatment prevents the reduction of Pd^{2+} ions and therefore, the migration of the Pd^0 atoms

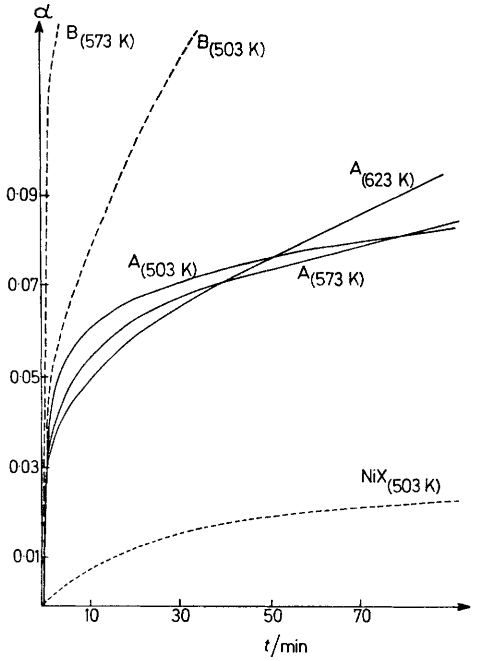

Figure. α(*t*) Reduction curves at different temperatures for Pd and Ni samples. Sample A, $Pd^{2+}:Ni^{2+} = 0{\cdot}012$; sample B $Pd^{2+}:Ni^{2+} = 0{\cdot}43$.

produced towards the external surface of the zeolite.[3] Subsequently, the Pd^{2+} ions stabilized in the cationic sites near the Ni_2^+ ions were reduced by hydrogen at 373 K. At this temperature, the migration of Pd^0 atoms did not occur.

The reduction of Ni^{2+} ions was studied at a hydrogen pressure of 6·6 kN m^{-2} in the temperature range 423—673 K

Below 623 K, the reduction rate was greatly increased in the presence of metallic palladium particularly when the Pd^0 concentration was high. The $\alpha(t)$ curves (Figure) which express the extent of the reduction in terms of time are not superimposable, which implies a complex mechanism. The activation energy varies with time and temperature; however for $\alpha < 0{\cdot}15$, the experimental activation energy (*ca.* 42 kJ mol^{-1}) is considerably lower than that measured for the NiX sample (117 kJ mol^{-1}).

Recent magnetic studies seem to indicate that, in this temperature range, there is no formation of Ni–Pd alloys and the average particle size is *ca.* 20 Å.

Above 623 K, the $\alpha(t)$ curves for A and B samples are the same as for Ni samples without Pd. In this temperature range, Pd^0 atoms migrate towards the external surface of the zeolite and thus no longer activate the reduction process of Ni^{2+} ions.

These results indicate that the reduction of Ni^{2+} ions is greatly increased in the presence of metallic palladium: the greater the Pd^0 concentration, the greater the activation effect. This effect can be interpreted in terms of a 'spill-over' mechanism[4] where the metallic palladium dissociatively adsorbs the hydrogen molecules. The hydrogen atoms formed migrate towards the Ni^{2+} ions and activate the reduction process. However, these results show that this mechanism requires the activating metal particle and the reduction site to be in close proximity.

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