

region 1300–1100 cm^{-1} , being superimposed to other absorptions in this region.

Thus, the IR spectra of the adsorbed species arising from urea show that actually reaction (3) occurs in the 300–423 K range on the catalyst surface.

The other main bands observed are certainly due to species that still contain free NH_2 groups, giving rise to N–H stretchings in the region 3450–3200 cm^{-1} . Accordingly, the prominent peak at 1642 cm^{-1} can be associated to the deformation mode of a nearly free amine group. However, this species is characterized by another strong band at 1562–1552 cm^{-1} , not present in the bulk urea spectrum; this band falls in the region of the asymmetric OCN stretching mode of amide anions, such as those formed by adsorption of acetamide on alumina [13] and on iron oxide [14].

This suggests that an adsorbed urea species is formed where one of the NH_2 groups is almost unperturbed, the carbonyl function and the other amine group being instead involved in the adsorption mechanism. It seems likely that urea adsorbs through the formation of an anionic species like that depicted in Scheme 1.

We also tried to adsorb urea over the catalyst from the gas-phase, under vacuum. In fact, it is reported [15] that urea can sublime in these conditions, without change. The IR analysis of the gas produced, however, only showed the presence of ammonia and CO_2 , possibly arising from reaction with moisture present in the solid itself. In particular we could not find the intense band at 2274 cm^{-1} of gas-phase isocyanic acid. Accordingly, the spectrum obtained after contacting this gas with the catalyst is dominated by the absorptions of ammonia and ammonium ions (Fig. 5a). However, if this spectrum is compared with that arising from adsorption of pure ammonia (Fig. 5b), it is evident (Fig. 5c) that additional features are present. In particular, bands at 3450, 3350 and 1660 cm^{-1} are certainly present, which show that the adsorbed species discussed above and identified as an adsorbed anionic form is certainly present. This means that undecomposed urea come to the catalyst surface. In these conditions we could not find the band near 2200 cm^{-1} due to isocyanate anions. This further confirms that the isocyanate species we find in our urea adsorption experiments from the solid state did not come from gas-phase isocyanate but from the surface transformation of urea.

4. Conclusions

The interaction of urea with a $\text{V}_2\text{O}_5\text{--MoO}_3\text{--TiO}_2$ catalyst has been studied from the solid state and from the gas phase. The adsorption of ammonia has also been studied for comparison. We could identify an urea decomposition mechanism giving rise first to an adsorbed anionic urea species, later evolving to adsorbed ammonia and ammonium species and to (iso)cyanate anions. The last species could evolve further to ammonia and CO_2 by reacting with water.

This supports the idea that the actual reducing agent in the urea/De NO_x reaction is ammonia, either formed in the gas-phase before reaching the catalyst surface or formed at the catalyst surface. On the other hand, if this process is applied to dirty waste gases also containing volatile organic compounds, the potential reactivity of the anionic form of urea and of isocyanate anions with these compounds possibly giving rise to polluting compounds must be taken into account.

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