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A Synergistic Effect on Supported Bimetallic Metal–Technetium Catalysts

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A non-additive enhancement in activity has been observed for dehydrogenation of cyclohexane for bimetallic M–Tc catalysts compared with monometallic ones, probably owing to formation of the compounds Pt–Tc, Pd–Tc and Ni–Tc on the support.

The modification of deposited metallic catalysts by a second metal sometimes leads to an non-additive enhancement in activity.[1–3] We have now observed this phenomenon for new bimetallic catalysts containing technetium as one of their active components. The catalysts had the composition M–Tc/carrier, where M = Pt, Pd or Ni, and γ-Al_2O_3, MgO, SiO_2, Y_2O_3 and TiO_2 were used as carriers. The content of the deposited metals was 0.1–1%. In the dehydrogenation of cyclic hydrocarbons (cyclohexane, cyclohexene, methyl- and ethyl-cyclohexane) and dehydrocyclization of n-hexane a synergistic effect was observed: the activity of the bimetallic catalysts showed a non-additive enhancement compared with the monometallic ones, and the temperature at which the reaction began to take place by 80–100 °C. Results for the dehydrogenation of cyclohexane on mono- and bi-metallic catalysts are listed in Table 1. As is shown, the introduction of the second metal into the catalysts increases the yield of benzene several fold. Thus, on the platinum–technetium catalyst the amount of the aromatic product is 10 times greater than that on the monometallic catalysts. The difference in the yields of benzene for the Pd–Tc catalysts and the monometallic system is also very great. The magnitude of the effect depends on the ratio of the metals. For the platinum- and palladium–technetium catalysts a 1:1 ratio of metal to technetium proved to be optimum. For the nickel–technetium systems the catalysts are most active at an atomic ratio of Ni to Tc of 11:1. The nature of the carrier has a marked effect on the activity of the bimetallic catalysts. A comparison between Pt–Tc catalysts showed a decrease in activity depending on the substrate in the following order: γ-Al_2O_3 > MgO > TiO_2 > Y_2O_3 > SiO_2.

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Table 1 Dehydrogenation of cyclohexane on Tc–M/γ-Al_2O_3

Metal content (%)		Yield of benzene (%)
Tc	M	
Pt–Tc (593 K)		
—	0.05	8
0.05	—	—
0.05	0.05	70
Pd–Tc (593 K)		
0.10	—	2
—	0.10	2
0.10	0.10	33
Ni–Tc (693 K)		
—	2.0	25
0.10	—	3
0.10	2.0	55

The 'non-additive' behaviour of bimetallic catalysts was also evident from studies on adsorption properties. On bimetallic systems only half as much CO and H_2 is chemisorbed (at 295 K; 266 Pa) as on the monometallic catalysts. For example, the amount of H_2 chemisorbed on 0.5% Pt/Al_2O_3, 0.5% Tc/Al_2O_3 and 0.5% Pt–0.5% Tc/Al_2O_3 is equal to 1.1, 1.0 and 0.5 mmol g^{-1}, respectively. Similar results were observed for all the systems studied.

Thermodesorption measurements (at 0.1 MPa) showed that both hydrogen and carbon monoxide are adsorbed in two or three forms, which differ in bond strength. On bimetallic catalysts compared with monometallic ones the desorption temperature of strongly bonded hydrogen forms increases. Thus, for the catalyst 0.1% Pt/Al_2O_3 this desorption temperature is 733 K, for 0.1% Tc/Al_2O_3 the temperatures are 637 and 775 K, and for the system 0.05% Pt–0.05% Tc/Al_2O_3 they are 755 and 813 K. The thermodesorption measurements show that bimetallic catalysts have adsorption centres with bonding characteristics which are different from those of monometallic catalysts, pointing to a different chemical composition.

From the catalytic and adsorption data reported here it may be concluded that bimetallic catalysts are not just a mixture of monometallic catalysts but a basically different system, in which the two metals interact in some way. This assumption was confirmed by studies of optical properties and the phase composition of the surface.

Diffuse reflectance spectra showed that all the catalysts contain the ionic forms of the deposited metals. The spectra of bimetallic catalysts show some differences from the spectra of monometallic systems; they include additional bands. For example, the Ni–Tc catalysts show an additional adsorption band at 325–345 nm. It is noteworthy that the catalytic activity was at a maximum when this band appeared in the spectrum.

IR spectra of CO adsorbed on the surface of the catalysts were recorded to characterize the electronic state of the deposited metals. The spectra show two CO adsorption bands in the 2090–2050 and 1950–1800 cm^{-1} regions, which may be assigned to linear and bridging forms of CO adsorption. On bimetallic catalysts the position of the adsorption band of the M–CO bond is intermediate between its positions in the monometallic catalysts; its position depends on the ratio of metal (Pt or Pd) to Tc on the surface of the samples. For example, a change in the atomic ratio of Pt to Tc from 2:1 to 1:2 causes a shift of 11 cm^{-1}. The intensity of the above band for bimetallic catalysts is lower than that for monometallic samples. These data indicate that on the carrier surface formation of a continuum of compounds, including the two metals and the carrier, takes place, which leads to a gradual change in adsorption and catalytic properties of the bimetallic sample.

Phase analysis using electron diffraction showed that all the catalysts studied, except the metallic phase, contain a small amount of intact starting compounds, metal oxides, and, in some cases, spinels (*e.g.* $NiAl_2O_4$). In bimetallic catalysts the compounds M_xTc_y (M = Pt, Pd, Ni) were found. It is probable that formation of these compounds causes the changes in catalytic adsorption and optical properties of the catalysts. These compounds form additional highly active centres for the dehydrogenation of cyclic hydrocarbons and dehydrocyclization of n-hexane, which results in the non-additive enhancement in activity of bimetallic catalysts.

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References

1 M. Nodo, S. Shinoda and Y. Saito, *Bull. Chem. Soc. Jpn.*, 1988, **61**, 2541.
2 A. N. Startsev, *Kinet. Katal.*, 1990, **31**, 869.
3 V. A. Golodov, 5th All-Union Conference on Mechanism of Catalytic Reactions, Moscow, 1990 (in Russian), p. 12.