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Long distance hydrogen spillover found by a radioactive assay for the Ru_5Pt/MCM-41 catalytic system

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Hydrogen transfer (spillover effect) from the bimetallic catalyst Ru_5Pt onto the mesoporous material MCM-41 over a distance of ~10 cm from the catalyst has been established from tracer experiments.

The 'spillover' effect has been under intensive investigation since it was postulated by Boudart in 1969.[1] There are several reviews[2–7] and numerous publications on this phenomenon especially on its application to catalytic processes.[8–17] More recent investigations also have been concerned with its application to hydrogen storage.[18–22] Although spillover, especially that of hydrogen, has been continually studied in the last three decades, several questions remained unanswered. In particular, both the nature of the activated species and the way in which they interact with the support remain unsolved.

Nanoparticles of Ru_5Pt[23–25] anchored within the channels of mesoporous silicate MCM-41 were the subject of this research. In our detail examinations of the hydrogen spillover effect, we have used tritium beta-radioactivity to monitor the H_2 absorption. Glass ampoules containing samples MCM, MCM + 1% Ru_5Pt and MCM + 10% Ru_5Pt (from 1.5 to 3 mg) were installed into the glass tube reactor (Figure 1), and then heated to 470 K under reduced pressure for 150 min. In control experiments, samples were installed separately one by one. A protium-tritium mixture (46% tritium) was used for the investigation of hydrogen adsorption. The amount of gas was controlled by pressure in an anti-vessel with a constant volume. The initial gas pressure was ~10 mTorr. The pressure in the system was observed to decrease as hydrogen was absorbed by the mesoporous material. As the pressure decreased, the residual gas was evacuated and a new portion of tritium gas was introduced. The experiment was carried out until constant pressure was achieved (~20 min). The total time necessary for saturation of samples by hydrogen was 100–320 min. After reaching equilibrium, the residual gas was pumped out and the samples cooled to room temperature. The pressure in the system remained unchanged, indicating that no gas was lost from the catalyst. The ampoules were taken out of the reactor and distilled water (4 ml) was added. In preliminary experiments, it had been shown that tritium anchored in mesoporous silica MCM-41 exchanges rapidly with water protons (several minutes). An aliquot of the solution [10 μl for low radioactivity samples or 10 μl of a diluted (200 times) solution for high radioactivity samples] were trasfered into 5 ml scintillation cocktail OptiPhase HiSafe 3 (Perkin Elmer, UK) and radioactivity was measured by a RackBeta 1215 liquid scintillation spectrometer (LKB Wallac, Finland). From three to five parallel measurements of each solution were conducted. The accuracy of measurements is 3%. The observed values are presented in Figure 2.

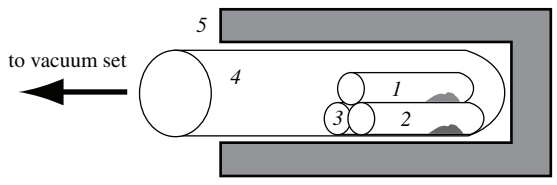

Figure 1 Reaction ampoules with samples (*1*)–(*3*) in the reaction vessel (*4*) and oven (*5*).

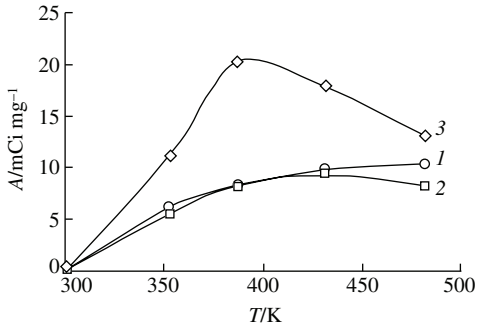

Figure 2 Dependence of radioactivity of tritium in the test mesoporous materials on temperature of the experiment at different catalyst contents: (*1*) 0%, (*2*) 1% and (*3*) 10%.

From a comparison with the control experiments, it has been found that the value of the radioactivity for the samples with MCM + 10% Ru_5Pt and consequently the ratio of tritium atoms to one Ru_5Pt group were approximately the same in experiments when all three samples were placed in the reactor simultaneously. However, the values observed for MCM + 1% Ru_5Pt and MCM alone were significantly lower (> 10 times). This dramatic decrease in hydrogen absorption for MCM samples with little or no catalyst for the three sample scenario is consistent with tritium spillover. It would appear that the sample of MCM + 10% Ru_5Pt acts as both tritium 'absorber' and 'activator', and permits transfer to the two adjacent samples with little or no catalyst. Furthermore, the distance of > 10 cm is no obstacle to transfer.

In Table 1, values calculated for the absorbed tritium atoms on one nanoparticle catalyst group are shown. Taking into account that in MCM-41 + 10% Ru_5Pt all the tritium is absorbed on the catalyst nanoparticles, we may conclude that, under the

Table 1 Calculations of tritium atoms absorbed by one Ru_5Pt group.

Temperature/K	MCM + 1% Ru_5Pt	MCM + 10% Ru_5Pt
301	0.38	0.08
353	13.2	2.7
387	20.2	4.9
432	22.3	4.3
434[a]	1.3	3.7

[a]Experiment was carried out with each sample separately.

optimum conditions (387 K), each nanoparticle [Ru_5Pt] takes up to five atoms of H to produce [H_5Ru_5Pt]. However, for MCM-41 + 1% Ru_5Pt and MCM-41 without catalyst, hydrogen adsorption is also observed. We consider that under these experimental conditions, [H_3Ru_5Pt] is formed and the other hydrogen impregnated into the MCM-41. The amount of the absorbed hydrogen reached 2.5×10^{20} atoms per gram of mesoporous material. Note that this value has been obtained under the reduced pressure of gas saturation. It may be reasonably supposed that pressure increase will bring about additional hydrogen adsorption by MCM-41.

From the rate of change of gas pressure during the initial stage of the experiment, it was possible to determine the activation energy of hydrogen adsorption on MCM-41 + 10% Ru_5Pt (Figure 3) of 25 kJ mol^{-1}. The rate of reaction at this stage presumably was determined by transfer of hydrogen from the catalyst to MCM-41. This value is slightly greater than the value found for the activation energy of H atoms diffusion on the surface of the quartz plate.[26,27]

The observation that hydrogen adsorption occurs on MCM-41 when the initiator (MCM-41 + 10% Ru_5Pt) is situated in a neighbourhood ampoule is of considerable significance. Although the hydrogen diffusion coefficient on the different surfaces may vary depending on experimental conditions[4] even the highest values do not provide an explanation to the effect observed here. Usually, hydrogen spillover is concerned with systems in which hydrogen migration occurs over small distances. The view has been held that the limiting stage in any spillover effect is the transition from catalyst to the surface of the support or from one support to another, but not hydrogen surface diffusion. There are reports that hydrogen transfer by the spillover effect may occur over distances of about 1 cm[28] or more.[29] We may suppose that in our case (gas pressure of 10 mTorr) the transition

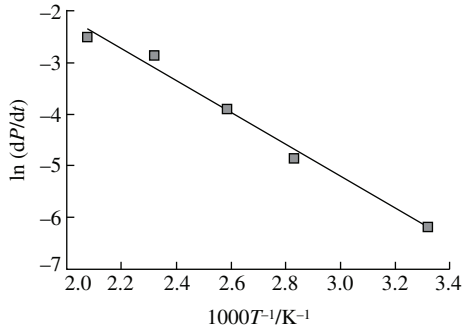

Figure 3 Temperature dependence of the initial rate for pressure alterations in the system.

of active hydrogen atoms occurs through the gas phase in the form of a jumpover rather than by surface diffusion.

Thus, we have been able to establish and efficiently investigate the effect of hydrogen spillover by tritium beta-radioactivity and that movement occurs through the gas phase by atom jumpover. The active catalyst serves to bring about the dissociation of the H_2 molecule.

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